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Investigations of the Metal Halide Catalyzed Alkylation Reactions of Pentaborane(9)

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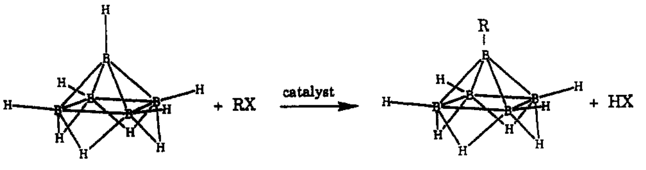
A high-yield route to 1-(isopropyl)pentaborane(9) (1-(i-C_3H_7)B_5H_8) has been developed with use of the early-transition-metal halides $HfCl_4$ and $ZrCl_4$ as alkylation catalysts. Comparison studies of the effect of various catalysts and reaction conditions on the catalyzed propylation reaction are discussed. The $ZrCl_4$-catalyzed alkylation of pentaborane(9) (B_5H_9) with n-ClC_3H_7, i-ClC_3H_7, n-ClC_4H_9, s-ClC_4H_9, and various butenes produces 1-(alkyl)pentaborane(9) compounds in which the secondary alkyl isomer is favored irrespective of the alkyl source. The effect of the $ZrCl_4$ catalyst and Lewis bases on the isomerization of 1-(i-C_3H_7)B_5H_8 and 1-(n-C_3H_7)B_5H_8 to the other 1-(propyl)pentaborane isomer, and to 2-(propyl)pentaboranes, was also investigated. In the n-propyl chloride alkylation the isomerization of the propyl group appears to occur prior to substitution onto pentaborane, while in the isopropyl chloride case, the isomerization may arise from catalyst interaction with 1-(i-C_3H_7)B_5H_8. The utility of $ZrCl_4$ and $HfCl_4$ catalysts for B_5H_9 alkylation with MeCl, EtCl, cyclopentyl chloride, cyclohexyl chloride, CH_2Cl_2, and 2,3-$Cl_2C_4H_8$ was also examined.

Introduction

The use of Friedel–Crafts catalysts in electrophilic substitution reactions on boron hydrides goes back more than 30 years. The majority of these reactions involve the use of pentaborane(9) (B_5H_9), alkyl halides or olefins, and traditional catalysts such as $AlCl_3$ or $FeCl_3$.[1-10] Alkylation of B_5H_9 occurs at the apex or B(1) site (eq 1), consistent with that theoretically predicted on the basis of charge separation studies.[11] The literature on Friedel–Crafts-catalyzed alkylation of B_5H_9, however, is far from complete. Many of the reports are very sketchy in their descriptions of the reaction conditions, product amounts and types, and side products. It is therefore often difficult to formulate generalizations vis-à-vis optimization of the alkylation reaction. What does emerge from the literature is that alkylations of B_5H_9 with $AlCl_3$ as the catalyst are often accompanied by side products that signify borane cage degradation to alkylboron dihalides, boron trihalides, and diborane.[7] In the $AlCl_3$-catalyzed alkylation of 2-MeB_5H_8 with MeCl to form 1,2-$Me_2B_5H_7$, the side products include alkylhalopentaborane(9) species as well as boron halides.[10]



B_5H_9 1-RB_5H_8 (1)

Our goal in this area of pentaborane(9) chemistry is to establish selective, high-yield routes to alkylpentaborane(9) compounds with use of metal halide catalysts. We report herein the results of our initial studies using isopropyl chloride (i-ClC_3H_7) and n-propyl chloride (n-ClC_3H_7). The optimized parameters in the synthesis of 1-(i-C_3H_7)B_5H_8 should be applicable to metal halide catalyzed alkylation reactions with other alkyl halides and possibly other boron hydrides. Reactions with the primary and secondary butyl halides n-ClC_4H_9 and s-ClC_4H_9 gave similar results with regard to the alkyl isomer of pentaborane(9) formed. The effect of various transition-metal halide catalysts on the isomerization of 1-(i-C_3H_7)B_5H_8 was also examined. The early-transition-metal halides that were found to be effective catalysts for the alkylation of B_5H_9 with secondary alkyl halides were $ZrCl_4$ and $HfCl_4$. The application of these catalysts in B_5H_9 alkylations with MeCl, EtCl, cyclopentyl chloride, and cyclohexyl chloride were also investigated in order to determine the range of utility of these early-transition-metal halides as borane alkylation catalysts. Metal halide catalyzed reactions of the alkyl dihalides CH_2Cl_2 and $C_4H_8Cl_2$ are also reported.

Results and Discussion

A. Metal Halide Catalyzed Reactions of Pentaborane(9) with Isopropyl Chloride. Previous reports on Friedel–Crafts alkylations of boron halides provide only a limited basis for comparison of catalysts and reaction conditions because there are inconsistencies in the reaction variables between experiments. In a number of reports the experimental procedures and the types and yields of products are incomplete. The yields of alkylated pentaborane(9) species are variously reported as actual yields,[4,6,8-10] and percent conversions[3,5,7] or are occasionally not specified.[1-4,9] Specific isomers of the alkylated pentaborane(9) compounds were often not determined.[2,3,5]

In the investigations reported below, internally consistent experimental procedures were used so that the catalytic activities of a variety of metal halide catalysts could be directly compared. In the first series of experiments equimolar quantities of B_5H_9 and isopropyl chloride were used, generally about 7 mmol of each. The catalyst ratio was 10 mol %, about 0.7 mmol, and the catalyst was loaded into a 100-mL reaction flask under nitrogen. The

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[1] Blay, N. J.; Dunstan, I.; Williams, R. L. *J. Chem. Soc.* **1960**, 430–433.

[2] Levy, A.; Weilmuenster, E. A. U.S. Patent 2,987,554, 1961.

[3] Neff, J. A.; Wandel, E. J. U.S. Patent 2,977,388, 1961.

[4] Altwicker, E. R.; Garrett, A. B.; Weilmuenster, E. A.; Harris, S. W. U.S. Patent 3,038,012, 1962.

[5] Altwicker, E. R.; Garrett, A. B.; Weilmuenster, E. A.; Harris, S. W. U.S. Patent 3,052,725, 1962.

[6] Onak, T. P.; Gerhart, F. J. *Inorg. Chem.* **1962**, *1*, 742–744.

[7] Ryschkewitsch, G. E.; Haris, S. W.; Mezey, E. J.; Sisler, H. H.; Weilmuenster, E. A.; Garrett, A. B. *Inorg. Chem.* **1963**, *2*, 890–893.

[8] Graefe, A. F. U.S. Patent 3,135,803, 1964.

[9] Onak, T.; Dunks, G. B.; Searcy, I. W.; Spielman, J. *Inorg. Chem.* **1967**, *6*, 1465–1471.

[10] Tucker, P. M.; Onak, T.; Leach, J. B. *Inorg. Chem.* **1970**, *9*, 1430–1441.

[11] Hoffman, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *37*, 2872–2883.

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Table I. Percentages of Borane Compounds Recovered in the Propylation of Pentaborane(9)[a] with Isopropyl Chloride as a Function of Catalyst[b]

	amt of borane compd, %				
catalyst	1-(i-C_3H_7)-B_5H_8	1-(n-C_3H_7)-B_5H_8	2-(C_3H_7)-B_5H_8	B_5H_9	1-EtB_5H_8
$AlCl_3$	12.2	16.8	4.3	64.8	1.9
$FeCl_3$	60.0	2.3	trace	37.7	
$NbCl_5$	41.3		trace	58.7	
$TaCl_5$	59.4	5.1	trace	35.5	
$ZrCl_4$	89.5	2.3		8.2	
$HfCl_4$	80.9	11.5	7.7		

[a] B_5H_9 and i-ClC_3H_7 were used in a 1:1 mole ratio. The amount of catalyst used in each case was 10 mol %. [b] No reaction occurs for the following catalysts: BF_3, Pd/charcoal, $TiCl_4$, $SnCl_4$, $ZnBr_2$, $(C_5H_5)_2ZrCl_2$, $(C_5H_5)_2Zr(H)Cl$, YCl_3.

B_5H_9 and the isopropyl chloride were condensed into the reaction flask on the vacuum line. The reaction flask was sealed and placed in a -78 °C bath and the mixture warmed to room temperature (ca. 23 °C) with stirring over 3 h and then stirred at room temperature for an additional 1 h. The reaction flask contents were then separated and analyzed. The various alkylated pentaborane(9) isomers were separated by gas chromatography, individually characterized by ^{11}B and ^{1}H NMR spectroscopy, and verified by mass spectrometry. Table I lists the percentages and types of borane products obtained with use of the surveyed catalyst, several of which bear further discussion. First it should be noted that when no catalyst is employed, no alkylation occurs. In addition, no reaction occurs when BF_3, Pd on charcoal, $TiCl_4$, $SnCl_4$, $ZnBr_2$, $(C_5H_5)_2ZrCl_2$, $(C_5H_5)_2Zr(H)Cl$, and YCl_3 are used as catalysts.

The first catalyst we examined was the traditional Friedel–Crafts catalyst $AlCl_3$. Earlier reports on the use of $AlCl_3$ catalyst in the alkylation of B_5H_9 indicated that this catalyst does not always result in clean, straightforward reactions. For example, Sisler and co-workers[7] examined the alkylation of B_5H_9 (49.9 mmol) with ethyl chloride (55.0 mmol) in the presence of $AlCl_3$ (3.9 mmol or 7.8% based on borane). The reagents were stirred together for 2 days at 25 °C. The products reported were 1-EtB_5H_8 (25 mmol, based on borane), HCl (2.1 mmol), C_2H_6 (16.2 mmol), H_2 (25 mmol), B_2H_6 (1.2 mmol), $EtBCl_2$, and BCl_3. There are several noteworthy aspects of these results. First, the yield of HCl is very low on the basis of the presumed reaction stoichiometry. Second, most of the alkyl halide not used in the alkylation reaction was reduced to ethane. The formation of significant quantities of hydrogen and the lower boranes B_2H_6, $EtBCl_2$, and BCl_3 indicate that borane cage degradation occurred. Similar side-product formation and borane cage degradation occurred during the synthesis of 1,2-dimethylpentaborane(9) with $AlCl_3$ as the catalyst.[10]

Our investigations with $AlCl_3$ revealed additional interesting side products. In addition to the desired product, 1-(i-C_3H_7)B_5H_8 (12.2%), two other isomers of propylpentaborane were formed, 1-(n-C_3H_7)B_5H_8 (16.8%) and 2-(C_3H_7)B_5H_8 (4.3%, both isomers). It is clear that $AlCl_3$ does not provide good selectivity in terms of either the propyl isomer (iso vs normal) or the borane isomer (1-substituted vs 2-substituted) formed. Another interesting aspect of the $AlCl_3$-catalyzed reaction was the carbon–carbon bond cleavage product 1-ethylpentaborane(9), which was not produced with use of other metal halide catalysts. The formation of 1-ethylpentaborane(9) must be involved at some point in the reaction. These results led to the conclusion that $AlCl_3$ is not a suitable catalyst for many B_5H_9 alkylations.

The other traditional Friedel–Crafts catalyst examined in the propylation reaction was $FeCl_3$. This catalyst gave a higher yield of 1-(i-C_3H_7)B_5H_8, 60.0% vs 12.2% for the $AlCl_3$-catalyzed reaction. The selectivity for formation of 1-(i-C_3H_7)B_5H_8 (60.0%) over 1-(n-C_3H_7)B_5H_8 (2.3%) was also much higher with $FeCl_3$.

The search for better catalysts for pentaborane(9) alkylations led to the investigation of early-transition-metal halides. Suga and co-workers[12] had studied the Lewis-acid-catalyzed alkylation of benzene with *sec*-butyl chloride and found $AlCl_3$ and $AlBr_3$ to be very active catalysts, while $ZnCl_2$ and $SnCl_4$ were inactive. Classified among the moderately active catalysts in Suga's results were $FeCl_3$ and $NbCl_5$ and, in the weak catalyst category, $ZrCl_4$ and $TiCl_4$.

Table I shows that several of the early-transition-metal halides work very well as alkylation catalysts for B_5H_9. $TaCl_5$ gives results (59.4% for 1-(i-C_3H_7)B_5H_8) similar to those for $FeCl_3$ under the standard reaction conditions. $NbCl_5$ gave a slightly lower yield (41.3% for 1-(i-C_3H_7)B_5H_8). The group IIIB metal halides gave the best results in terms of yield and 1-(i-C_3H_7)B_5H_8 selectivity. The highest yield (89.5%) was obtained with $ZrCl_4$ as the catalyst. $HfCl_4$ also gave a high yield of 1-(i-Cl_3H_7)B_5H_8 (80.9%). In the $HfCl_4$-catalyzed reaction all the B_5H_9 is used in the alkylation reaction to form alkylpentaborane(9) compounds. In fact, $HfCl_4$ was the only catalyst in the series that gave this result. $TiCl_4$ did not act as a catalyst for borane alkylations under the standard reaction conditions. $NbCl_5$, $ZrCl_4$, and $HfCl_4$ are all reusable as catalysts. The other zirconium compounds examined, $(C_5H_5)_2ZrCl_2$ and $(C_5H_5)_2Zr(H)Cl$, were not catalytically active under the conditions used. When $Zr(BH_4)_4$ was tried as a catalyst, the product 1-(i-C_3H_7)B_5H_8 was formed but the catalyst was consumed in the reaction, presumably forming $ZrCl_4$. Among the products that were obtained from the $Zr(BH_4)_4$ standard reaction were HCl, B_2H_6, unreacted isopropyl chloride, unreacted B_5H_9, 1-(i-C_3H_7)B_5H_8 (70.2%), and 1-(n-C_3H_7)B_5H_8 (13.2%). A white nonvolatile solid remained at the end of the reaction.

The better catalysts in Table I were studied in more depth in order to optimize the alkylation yield and selectivity. Tables II and III show the percentages of pentaborane(9) products of these reactions. Further reactions with $HfCl_4$ were not examined, as the standard reaction with $HfCl_4$ converted all of the B_5H_9 into alkylpentaborane(9) species, and only its selectivity can be potentially altered. Increased contact time for both the $FeCl_3$ and the $NbCl_5$ reactions show an increase not only in the amount of 1-(i-C_3H_7)B_5H_8 formed but also in the amount of 1-(n-C_3H_7)B_5H_8 formed, indicating some decrease in selectivity. Increased contact time in the $ZrCl_4$ case increases the minor isomer, 1-(n-C_3H_7)B_5H_8, from 2% under standard reaction conditions to 13% at the longer reaction time. This is consistent with the results from the $FeCl_3$ and $NbCl_5$ reactions.

With both the $FeCl_3$ and the $ZrCl_4$ catalysts, reactions at a lower temperature were examined in an attempt to increase the selectivity of the alkylation. In the $FeCl_3$ reaction, with a maximum temperature of -22 °C, the desired 1-(i-C_3H_7)B_5H_8 was formed exclusively but in only 13.7% yield. The maximum reaction temperature for the $ZrCl_4$ low-temperature reactions was 0 °C. Two different reactions were done at this lower temperature. The small

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(12) Suga, S.; Nakajima, T.; Segi, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1465–1466.

Table II. Percentages of Borane Compounds Formed in the Propylation of Pentaborane(9) with Isopropyl Chloride under Various Reaction Conditions[a]

		amt of borane compd, %			
amt of catalyst, mol %	reactn conditions	1-(i-C_3H_7)B_5H_8	1-(n-C_3H_7)B_5H_8	2-(C_3H_7)B_5H_8	B_5H_9
		Catalyst $FeCl_3$			
10	−78 °C → room temp/3 h room temp/1 h	60.0	2.3		37.7
10	−78 °C → room temp/3 h room temp/69 h	69.8	8.1		22.1
10	−78 °C → 22 °C/3 h −22 °C/1 h	13.7			86.3
		Catalyst $HfCl_4$			
10	−78 °C → room temp/3 h room temp/1 h	80.9	11.5	7.7	
10[b]	−78 °C → room temp/3 h room temp/1 h	78.4	12.8	8.8	trace
		Catalyst $NbCl_5$			
10	−78 °C → room temp/3 h room temp/1 h	41.3		trace	58.7
10	−78 °C → room temp/3 h room temp/45 h	53.1	5.5		41.4
10[b]	−78 °C → room temp/3 h room temp/1 h	27.3			72.7
50	−78 °C → room temp/3 h room temp/1 h	41.8	1.7		56.6

[a] In all cases, all of the B_5H_9 starting material was recovered as (alkyl)pentaboranes or B_5H_9 [b] Reused catalyst.

Table III. Percentages of Borane Compounds Formed in the $ZrCl_4$-Catalyzed Propylation of Pentaborane(9) with Isopropyl Chloride under Various Reaction Conditions

			amt of borane compd, %		
B_5H_9:i-ClC_3H_7	amt of $ZrCl_4$,[a] mol %	reactn conditions	1-(i-C_3H_7)B_5H_8	1-(n-C_3H_7)B_5H_8	B_5H_9
1:1[b]	10	−78 °C → room temp/3 h room temp/1 h	89.5	2.3	8.2
1:1	50	−78 °C → room temp/3 h room temp/1 h	93.4	1.5	5.1
1:1	10	−78 °C → room temp/3 h room temp/45 h	72.4	13.8	13.8
1:1[c]	10	−78 °C → room temp/3 h room temp/1 h	87.7	4.1	8.2
1:1	10	−78 °C → 0 °C/3 h 0 °C/1 h	85.5	8.2	6.3
1:1[d]	50	0 °C/1 h	77.7	12.8	9.5
1:1[e]	50	−78 °C → room temp/3 h room temp/1 h	88.3	3.8	7.9
1:2	50	−78 °C → room temp/3 h room temp/1 h	64.4	26.1	5.6
2:1	15	−78 °C → room temp/3 h room temp/1 h	96.5	1.5	*f*
1:1[g]	10 ($ZrCl_4$) 10 ($AlCl_3$)	−78 °C → room temp/3 h room temp/1 h	76.9	9.3	5.9
1:1	50 ($ZrCl_4$) 5 (H_2O)	−78 °C → room temp/3 h room temp/1 h	84.0	5.3	10.7
1:1	50 ($ZrCl_4$) 25 (Et_2O)	−78 °C → room temp/3 h room temp/1 h	78.0	8.9	13.1
1:1	50 ($ZrCl_4$) excess (Et_2O)	−78 °C → room temp/3 h room temp/1 h	no reactn		
1:1	50	*h*	79.4	10.8	9.8

[a] Mole percent of catalyst based on amount of pentaborane. [b] Standard reaction. [c] Reused catalyst. [d] No warm-up period. [e] Sublimed $ZrCl_4$. [f] Yield of 1-(i-C_3H_7)B_5H_8 based on amount of i-ClC_3H_7 used. [g] 79.9% 2-(C_3H_7)B_5H_8 also formed. [h] 2-ClC_3H_7 and $ZrCl_4$ were mixed together first for 1/2 h at room temperature; B_5H_9 was then added, and the reaction conditions followed the 3-h warm-up from −78 °C to room temperature followed by an additional 1 h of mixing at room temperature.

differences in the results, shown in Table III, are apparently due to the difference in the warm-up period. The selectivity of the propylpentaborane(9) compounds formed in the lower temperature $ZrCl_4$ reactions is not as pronounced as in the $FeCl_3$ case.

Three of the catalysts, $NbCl_5$, $HfCl_4$, and $ZrCl_4$, were reused in standard reactions to confirm that they are not being consumed in the reaction. Both $HfCl_4$ and $ZrCl_4$ give comparable results whether the catalyst was fresh or used. $NbCl_5$ undergoes a color change from bright yellow to a dull yellow-orange during the course of the reaction, and its reuse leads to a significant decrease in the yield of 1-(i-C_3H_7)B_5H_8.

The ratios of the reactants and catalysts were also varied during the optimization of the $ZrCl_4$-catalyzed alkylation reaction. When the catalyst was increased from 10 to 50 mol %, the yield of the desired product 1-(i-C_3H_7)B_5H_8 increased from 89.5% to 93.4%, respectively, a borderline increase in yield.

Using a 2-fold excess of isopropyl chloride resulted in a significant decrease in the selectivity of the alkyl isomer, decreasing the yield of 1-(i-C_3H_7)B_5H_8 to 64.4% and increasing the yield of 1-(n-C_3H_7)B_5H_8 to 26.1%. Conversely, using a 2-fold excess of B_5H_9 in the reaction resulted in a 96.5% yield of 1-(i-C_3H_7)B_5H_8 with significantly less of the minor isomer, 1-(n-C_3H_7)B_5H_8 (1.5%), formed. An excess of B_5H_9 in the reaction thus leads to the most selective, high-yield route to 1-(i-C_3H_7)B_5H_8. A possible explanation for this difference in alkyl selectivity involves the order in which the three components of the reaction (alkyl halide, B_5H_9, and $ZrCl_4$) interact. A route consistent with the results would involve the initial formation of a catalyst–alkyl halide complex followed by reaction with B_5H_9. If the formation of the (n-propyl)pentaborane(9) arises from the conversion of the isopropyl–zirconium complex to a n-propyl–zirconium complex prior to interaction with B_5H_9, then the longer lifetime of the propyl–zirconium complex can lead to less alkyl isomer selectivity in the propylpentaborane(9) products. This result should predominate in reactions with an excess of alkyl halide. The opposite result should be observed of reactions with an excess of B_5H_9, as the isopropyl halide–zirconium complex should have a shorter lifetime in which to rearrange to the n-propyl–zirconium complex.

Although the 96.5% yield of 1-(i-C_3H_7)B_5H_8 obtained when a 2-fold excess of B_5H_9 to alkyl halide is used is very good, it is apparently a maximum yield, as the isopropyl chloride that did not react with the B_5H_9 was reduced to propane. In fact, it appears that all of the 1:1 reactions between B_5H_9 and isopropyl chloride with $ZrCl_4$ as catalyst produce propane, with no unreacted alkyl halide remaining at the conclusion of the reaction. Only when a 2-fold excess of isopropyl chloride is used is any alkyl halide recovered, but even in this case, a small amount of propane is formed.

Attempts to minimize or eliminate this propane formation were largely unsuccessful. Purification of the $ZrCl_4$ catalyst by sublimation before use did not eliminate the propane formation, and yields of 1-(i-C_3H_7)B_5H_8 and 1-(n-C_3H_7)B_5H_8 remained virtually identical with those attained in the standard $ZrCl_4$-catalyzed reaction. Adding 5% H_2O to the $ZrCl_4$-catalyzed reaction did not affect the yields or ratios of the pentaborane(9) products or the production of propane.

Other modifications were investigated in an attempt to determine what species were causing the propane formation. In one reaction the alkyl halide–$ZrCl_4$ slurry was stirred for 1/2 h at room temperature before the B_5H_9 was added. The reaction mixture was then treated in the standard reaction manner. The product yields were 79.4% of 1-(i-C_3H_7)B_5H_8, 10.8% of 1-(n-C_3H_7)B_5H_8, and 9.8% unreacted B_5H_9. All of the isopropyl chloride not used in the alkylation reaction was converted to propane. Thus, premixing does not increase the total amount of alkylpentaborane(9) or propane formed but does decrease the alkyl isomer selectivity of the propylpentaborane(9) species formed.

In another experiment, a 2:1 mixture of B_5H_9 and isopropyl chloride at room temperature for 3.5 h produced no propane. The $ZrCl_4$ catalyst was added, and the reaction was continued in the usual manner to produce 3.5% propane, 94.8% 1-(i-C_3H_7)B_5H_8, and 1.7% 1-(n-C_3H_7)B_5H_8. HCl was produced in 95.9% yield based on alkyl halide. This reaction procedure appears to rule out a primary role for B_5H_9 in propane formation.

To confirm that the $ZrCl_4$ is responsible for the propane formation, a mixture of 50 mol % $ZrCl_4$ and isopropyl chloride was stirred and warmed from −78 °C to room temperature over 3 h and then stirred at room temperature for an additional 1 h. At the end of this reaction 1.8% of propane was produced along with HCl, and the unreacted isopropyl chloride was recovered. When isopropyl chloride and $ZrCl_4$ interact at room temperature for longer periods of time, propane continues to form at a slow rate over several weeks.

Table IV. Percentages of Borane Compounds Formed in the Propylation of Pentaborane(9) with Various Isopropyl Halides[a]

$$B_5H_9 + 2\text{-}XC_3H_7 \xrightarrow[\substack{-78\ ^\circ\text{C} \to \text{room temp, 3 h} \\ \text{room temp, 1 h}}]{\text{ZrCl}_4\ (50\ \text{mol}\ \%)} \text{products}$$

	amt of borane compd, %			
X	1-(i-C_3H_7)-B_5H_8	1-(n-C_3H_7)-B_5H_8	2-(C_3H_7)-B_5H_8	B_5H_9
Cl	93.4	1.5		5.1
Br	64.1	25.7	trace	10.2
I	60.3	8.6	trace	31.1

[a] B_5H_9 and i-XC_3H_7 were used in a 1:1 ratio with 50 mol % $ZrCl_4$. The corresponding HX was also formed in these reactions.

The effects of various halogens on the alkyl halide used in the $ZrCl_4$-catalyzed propylation reaction are tabulated in Table IV. Isopropyl chloride is the clear choice for the $ZrCl_4$-catalyzed reaction with a yield of 93.4% for the desired product 1-(i-C_3H_7)B_5H_8, compared to 64.1% and 60.3% for isopropyl bromide and isopropyl iodide, respectively. The isopropyl bromide reaction exhibited poor alkyl isomer selectivity.

The addition of 10 mol % $AlCl_3$ (based on B_5H_9) to the standard $ZrCl_4$ reaction procedure did not increase the overall yields, as more of the minor isomer 1-(n-C_3H_7)B_5H_8 was formed. The addition of a weak base to the reaction mixture was also investigated. When 50 mol % $ZrCl_4$ and 25 mol % diethyl ether were used in the reaction between B_5H_9 and isopropyl chloride, there was a slight decrease in the overall yield of propylpentaborane(9) species and a more significant decrease in the alkyl isomer selectivity. When excess diethyl ether was used, no alkylation occurred, as expected.

B. Metal Halide Catalyzed Reactions of Pentaborane(9) with Propene. The metal halide catalyzed alkylation of B_5H_9 with olefins was also attempted on the basis of reports with ethylene as the olefin and $AlCl_3$ as the catalyst.[1,3,6,7] Our initial survey of reactions involving B_5H_9, propene (in equimolar amounts), and catalyst (17–50 mol %) did not produce alkylation when $ZrCl_4$, $NbCl_5$, $Zr(BH_4)_4$, and $(C_5H_5)_2Zr(H)Cl$ were used as catalysts.

The addition of a small amount of isopropyl chloride to the B_5H_9–propene reaction produced 40.8% of 1-(i-C_3H_7)B_5H_8 under standard reaction conditions. The use of hydrogen chloride substantially improved the $ZrCl_4$-catalyzed reaction, and with an excess of HCl the yields of 1-(i-C_3H_7)B_5H_8 are good, though about 10% lower than that obtained with isopropyl chloride.

A sealed-NMR-tube reaction of propene and B_5H_9 with $ZrCl_4$–HCl indicated that the reaction does not go to completion even after 3 weeks but reaches a steady state after about 12 h. The time to reach a steady state in the NMR-tube experiment may not be directly compared to that of the larger scale reactions, but it is interesting that the reaction appears not to go to completion. In all the $ZrCl_4$–HCl-catalyzed reactions in Table V small quantities of propane were also formed. Unreacted propene was also found after reactions in which less than 50% of the B_5H_9 was converted to 1-(i-C_3H_7)B_5H_8. Other catalysts that were active in the isopropyl chloride alkylations performed comparably with propene–HCl reactions.

C. Selectivity Studies. The Friedel–Crafts alkylation of benzene with a secondary alkyl halide produces the

Table V. Percentages of Borane Compounds Formed in the $ZrCl_4$-Catalyzed Propylation of Pentaborane(9) with Propene under Various Reaction Conditions

			amt of borane compd, %		
B_5H_9:propene[a]	additional reagents	reacn conditions	1-(i-C_3H_7)B_5H_8	1-(n-C_3H_7)B_5H_8	B_5H_9
1:1		−78 °C → room temp/3 h room temp/1 h	no reacn		
2:3	pentane solvent	−78 °C → room temp/4 h room temp/6 h	no reacn		
1:1[b]	15% i-ClC_3H_7	−78 °C → room temp/3 h room temp/1 h	40.8		59.2
1:1	50% HCl	−78 °C → room temp/3 h room temp/1 h	49.9	trace	50.1
1:1[c]	100% HCl	−78 °C → room temp/3 h room temp/1 h	72.3	2.7	25.0
1:1.3	130% HCl	−78 °C → room temp/3 h	78.7	4.7	16.6

[a] 50 mol % $ZrCl_4$ catalyst was used based on pentaborane. [b] A trace of 2-(C_3H_7)B_5H_8 was also formed. [c] 57 mol % of $ZrCl_4$ was used in this reaction.

Table VI. Percentages of Pentaborane Products Formed in the Metal Halide Catalyzed Reaction of Pentaborane(9) with *n*-Propyl Chloride

		amt of borane compd, %		
catalyst[a]	time at room temp,[b] h	1-(i-C_3H_7)-B_5H_8	1-(n-C_3H_7)-B_5H_8	B_5H_9
$AlCl_3$ (23)[c]	69	3	15	74
$FeCl_3$ (19)	69	27	1	72
$ZrCl_4$ (14)	1	17	1	82
$ZrCl_4$ (53)	1	20	1	79
$ZrCl_4$ (53)	45	68	13	19

[a] The mole percent of catalyst used is given in parentheses. B_5H_9 and n-ClC_3H_7 were used in a 1:1 mole ratio. [b] All reactions have a 3-h warm-up period from −78 °C to room temperature preceding the indicated reaction time of mixing at room temperature. [c] This $AlCl_3$-catalyzed reaction also produced 4% 2-(C_3H_7)B_5H_8 and 4% 1-EtB_5H_8.

secondary alkyl isomer. However, the reactions of aromatics with n-propyl halides produce both the n-propyl and isopropylarene products. This preference for the secondary alkyl isomer product also applies to alkylation reactions with other primary alkyl halides.[13]

The metal halide catalyzed propylation of B_5H_9 with n-ClC_3H_7 was examined by use of various catalysts and reaction times. The types and yields of the alkylated pentaborane(9) products formed in these reactions are listed in Table VI. In all the $ZrCl_4$- and $FeCl_3$-catalyzed reactions, the major alkylpentaborane(9) species formed is 1-(i-C_3H_7)B_5H_8. (Analogously, in the $AlCl_3$-catalyzed reaction of n-propyl bromide with benzene, the major product is isopropylbenzene.[13]) However, when a strong Friedel–Crafts catalyst such as $AlCl_3$ is used, the major isomer formed from n-ClC_3H_7 is 1-(n-C_3H_7)B_5H_8, in 15% yield, with a total alkylation yield of 26%. 1-EtB_5H_8 was also formed, as in the $AlCl_3$-catalyzed reaction of B_5H_9 and isopropyl chloride.

The $ZrCl_4$-catalyzed propylations of B_5H_9 with n-ClC_3H_7 produced 17% 1-(i-C_3H_7)B_5H_8 with less than 1% of 1-(n-C_3H_7)B_5H_8 under the standard reaction conditions. When the reaction time at room temperature is extended to 45 h, 68% 1-(i-C_3H_7)B_5H_8 and 13% 1-(n-C_3H_7)B_5H_8 formed. Extending the reaction time significantly increases the total amount of propylpentaborane(9) products produced, but an increase in the mole percent of $ZrCl_4$ used does not. In all the n-ClC_3H_7 reactions, some of the unused starting alkyl halide is converted to propane, as was observed with isopropyl chloride.

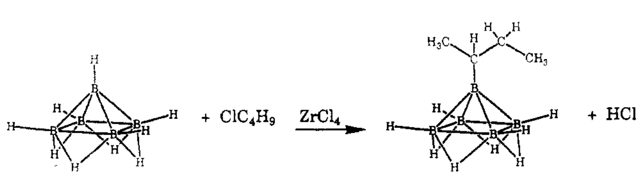
Table VII. Comparisons of Percentages of Pentaborane Products Produced When Isopropyl[a] and *n*-Propyl Chlorides Are Used

			amt of borane compd, %		
catalyst[b]	time at room temp,[c] h	alkyl halide	1-(i-C_3H_7)-B_5H_8	1-(n-C_3H_7)-B_5H_8	B_5H_9
$FeCl_3$ (19)	69	n-ClC_3H_7	27	1	72
$FeCl_3$ (10)	69	i-ClC_3H_7	70	8	22
$ZrCl_4$ (14)	1	n-ClC_3H_7	17	1	82
$ZrCl_4$ (10)	1	i-ClC_3H_7	90	2	8
$ZrCl_4$ (53)	1	n-ClC_3H_7	20	1	79
$ZrCl_4$ (50)	1	i-ClC_3H_7	93	2	5
$ZrCl_4$ (53)	45	n-ClC_3H_7	68	13	19
$ZrCl_4$ (10)	45	i-ClC_3H_7	72	14	14

[a] Data for the i-ClC_3H_7 reactions were previously discussed.[1] [b] The mole percent of the catalyst used in listed in parentheses. [c] All reactions have a 3-h warm-up period from −78 °C to room temperature preceding the indicated reaction time of mixing at room temperature.

Table VII lists the yields of 1-(i-C_3H_7)B_5H_8 and 1-(n-C_3H_7)B_5H_8 formed when isopropyl and n-propyl halides are used under similar reaction conditions. In all reactions, 1-(i-C_3H_7)B_5H_8 was the major product regardless of which alkyl halide was used. One point of interest in Table VII is the relatively small difference in alkyl isomer product distribution in the $ZrCl_4$-catalyzed n-ClC_3H_7 and i-ClC_3H_7 reactions at the longer reaction times. The amount of 1-(i-C_3H_7)B_5H_8 formed in the n-ClC_3H_7 reaction increases with extended reaction time.

Reactions involving n-ClC_4H_9 and s-ClC_4H_9 as the alkylating agents in the $ZrCl_4$-catalyzed alkylation of B_5H_9 were also examined. The major (butyl)pentaborane(9) isomer formed in all reactions was 1-(s-C_4H_9)B_5H_8 (eq 2).



B_5H_9 1-(s-C_4H_9)B_5H_8

(2)

The various reagents and reaction conditions used in the butylation of B_5H_9 are listed in Table VIII. The highest yield of 1-(s-C_4H_8)B_5H_8, 69%, was formed with s-ClC_4H_9 and a maximum reaction temperature of −50 °C. These conditions produced 3% of another apically substituted pentaborane(9), and 28.3% of the B_5H_9 was recovered. Only one other apically substituted pentaborane(9) is

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[13] Roberts, R. M.; Khalaf, A. A. *Friedel-Crafts Alkylation Chemistry-A Century of Discovery*; Marcel Dekker: New York, 1984.

Table VIII. Percentages of (Butyl)pentaboranes Formed with Various Butyl Chlorides and Reaction Conditions

			amt of borane compd, %		
BuX[a]	amt of $ZrCl_4$, mol %	reactn conditions	1-(s-C_4H_9)B_5H_8	other RB_5H_8[b]	B_5H_9
n-ClC_4H_9	50	−78 °C → room temp/3 h room temp/1 h	21	5 (1)	74
s-ClC_4H_9	58	−78 °C → room temp/3 h room temp/1 h	57	11 (3)[c]	27
s-ClC_4H_9	38	−78 °C → 50 °C/3 h −50 °C/1 h	69	3 (1)	28
t-ClC_4H_9	58	−78 °C → room temp/3 h room temp/1 h			
n-ClC_4H_9	50	90 °C/3 h	25	33 (4)	42
n-ClC_4H_9[d]	50	65 °C/3 '	52	25 (4)	23

[a] B_5H_9 and the butyl chlorides were used in a 1:1 ratio. [b] The numbers of other types of 1-RB_5H_8 species formed are listed in parentheses. [c] Also 5% 2-RB_5H_8. [d] Excess B_5H_9 was used (10.5 mmol to 5.11 mmol of 1-ClC_4H_9). Mole percent of the catalyst for this reaction is based on the amount of butyl halide used. no reacn

formed in this reaction, whereas in some other reactions the total number of substituted pentaboranes(9) products is as high as five. This decrease in the number of isomers formed is most likely due to the decrease in the reaction temperature.

Using s-ClC_4H_9 as the alkyl halide under standard reaction conditions produced a 57% yield of 1-(s-C_4H_9)B_5H_8 and four other alkylated pentaborane(9) compounds (11% yield total), of which three were apically substituted and one was basally substituted. This trend in the increase in the number of isomers formed under the standard conditions was also observed in the $ZrCl_4$-catalyzed alkylations with n-ClC_4H_9. Butylation with n-ClC_4H_9 was also surveyed at 65 and 90 °C. The 90 °C reaction produced 25% of 1-(s-C_4H_9)B_5H_8 and 33% of four other apically substituted pentaborane(9) compounds. The room-temperature reaction with n-ClC_4H_9 produced a comparable yield of 1-(s-C_4H_9)B_5H_8 and only 5% of another 1-(alkyl)pentaborane(9). The number of (alkyl)pentaborane(9) isomers increases with reaction temperature for both n-ClC_4H_9 and s-ClC_4H_9.

In an attempt to increase the yield of 1-(s-C_4H_9)B_5H_8 and decrease the number of other substituted pentaborane(9) compounds in the n-ClC_4H_9 alkylation reaction, an intermediate reaction temperature was chosen and the B_5H_9 to n-ClC_4H_9 ratio was increased to 2:1. The reaction mixture was heated to 65 °C for 3 h, and the yield of 1-(s-C_4H_9)B_5H_8 doubled to 52%, but the formation of four other alkylated pentaborane(9) species in 25% yield still occurred.

In the $AlCl_3$-catalyzed propylation of benzene with n-propyl halide, the yield of isopropylbenzene increased as the temperature of the reaction increased.[14] In the $AlCl_3$-catalyzed butylation of benzene with n-butyl chloride, however, an increase in the reaction temperature from 0 to 80 °C does not produce significantly more sec-butylbenzene but does produce an additional isomer.[15] The butylation of benzene at 0 °C forms 34% n-butylbenzene and 66% sec-butylbenzene, while the butylation at 80 °C affords 22% n-butylbenzene, 62% sec-butylbenzene, and 16% isopropylbenzene. The elevated temperatures in the $ZrCl_4$-catalyzed butylation of B_5H_9 do not cause an analogous increase in 1-(s-C_4H_9)B_5H_8 produced but do result in the formation of more (alkyl)pentaborane(9) isomers. The doubling of the yield of 1-(s-C_4H_9)B_5H_8 in the 65 °C reaction of n-ClC_4H_9 with B_5H_9 is most likely a result of the 2:1 ratio of pentaborane to butyl chloride.

Table IX. Percentages of (Butyl)pentaboranes Formed with Various Butenes

		amt of borane compd, %		
butene[a]	amt of $ZrCl_4$, mol %	1-(s-C_4H_9)-B_5H_8	other RB_5H_8[b]	B_5H_9
1-butene	40	60	2 (3)	38
cis-2-butene	50	61	5 (4)	34
trans-2-butene	29	60	3 (4)	37

[a] A 1:1:1 ratio of B_5H_9:butene:HCl was used. [b] The numbers of other types of 1-RB_5H_8 species are listed in parentheses.

Table X. Isomerization of (Propyl)pentaboranes in Contact with $ZrCl_4$ for 2 Days

	distribn after 2 days, %		
starting isomer	1-(i-C_3H_7)-B_5H_8	1-(n-C_3H_7)-B_5H_8	2-(C_3H_7)-B_5H_8
1-(i-C_3H_7)B_5H_8	75	19	6
1-(n-C_3H_7)B_5H_8	3	95	2

tert-Butyl chloride does not react with B_5H_9 under standard reaction conditions. In fact, we have found no references to tertiary alkyl derivatives of borane clusters that have been prepared by metal halide catalyzed reactions.

Table IX shows that butylations of B_5H_9 with $ZrCl_4$ and 1-butene, cis-2-butene, or trans-2-butene in the presence of HCl all produce approximately 60% yields of 1-(s-C_4H_9)B_5H_8 along with small percentages of other alkylated pentaborane(9) products. These results suggest that HCl adds to the butene prior to its reaction with B_5H_9. An attempted butylation reaction with $ZrCl_4$ catalyst at −50 °C produced no (alkyl)pentaborane(9) products.

To discern when the formation of the different alkyl isomers was occurring, the simpler (propyl)pentaborane(9) system was examined more closely. Pure 1-(i-C_3H_7)B_5H_8 and 1-(n-C_3H_7)B_5H_8 were placed into separate reaction flasks containing $ZrCl_4$. The flask contents were mixed for 2 days at room temperature. Table X shows that while both isomers had undergone rearrangement to the other isomer and to the basally substituted propylpentaborane(9) species, the 1-(i-C_3H_7)B_5H_8 isomerization had progressed further.

The extent of the isomerization of n-propyl bromide to isopropyl bromide in the presence of $AlCl_3$ is dependent on the amount and type of catalyst used and the reaction temperatures.[13,16] Most of the investigations on the formation of isopropylbenzene state that isomerization of the

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(14) Ipatieff, V. N.; Pines, H.; Schmerling, L. J. Org. Chem. 1940, 5, 253–263.

(15) Roberts, R. M.; Shiengthong, D. J. Am. Chem. Soc. 1960, 82, 132–135.

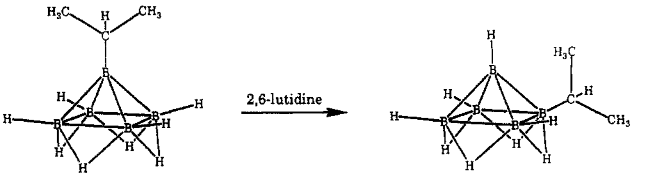
(16) (a) Cronwell, T. I.; Jones, G. L. J. Am. Chem. Soc. 1951, 73, 3506–3507. (b) Karabatsos, G. J.; Fry, J. I.; Meyerson, S. J. Am. Chem. Soc. 1970, 92, 614–620. (c) Lee, C. C.; Woodcock, D. J. J. Am. Chem. Soc. 1970, 92, 5992–5995.

propyl group occurs before substitution. However, both *n*-propylbenzene and isopropylbenzene will isomerize to the other isomer in the presence of $AlCl_3$–H_2O.[17,18] Likewise, *n*-butylbenzene undergoes isomerization to *sec*-butylbenzene in the presence of a Friedel–Crafts catalyst.[17] Halide rearrangement with use of $ZrCl_4$ has also been reported for the formation of 2-butylethylboron bromide from (α-bromoethyl)diethylboron.[19]

In the B_5H_9 system we found that isomerization of the propyl group can occur either before or after its substitution onto B_5H_9. In the isomerization of 1-(*n*-C_3H_7)B_5H_8, the extent of formation of 1-(*i*-C_3H_7)B_5H_8 and 2-(C_3H_7)B_5H_8 is much less than in the isomerization of 1-(*i*-C_3H_7)B_5H_8 to 1-(*n*-C_3H_7)B_5H_8 and 2-(C_3H_7)B_5H_8. From Table VI, the amount of 1-(*i*-C_3H_7)B_5H_8 formed after 2 days at room temperature when *n*-ClC_3H_7 is used as the alkylating agent is 68% compared to 3% formed in the reaction between pure 1-(*n*-C_3H_7)B_5H_8 and $ZrCl_4$. Also an NMR-tube experiment in which *n*-ClC_3H_7, $ZrCl_4$, and HCl were mixed together showed that over half of the *n*-ClC_3H_7 converted to isopropyl chloride and propane in less than 2 days. These results suggest that the majority of the *n*-propyl to isopropyl rearrangement must occur prior to substitution onto B_5H_9.

In the 2-day reaction of B_5H_9 with *i*-ClC_3H_7–$ZrCl_4$ (Table VII), the ratio of 1-(*i*-C_3H_7)B_5H_8 to 1-(*n*-C_3H_7)B_5H_8 formed was about 5:1. In the isomerization of pure 1-(*i*-C_3H_7)B_5H_8 with $ZrCl_4$, the ratio of 1-(*i*-C_3H_7)B_5H_8 to 1-(*n*-C_3H_7)B_5H_8 formed was about 4:1. Thus, the loss of alkyl selectivity as the reaction time is increased may be attributed to the catalyst-induced rearrangement of 1-(*i*-C_3H_7)B_5H_8.

Other NMR-tube experiments of 1-(*i*-C_3H_7)B_5H_8 were also examined. A THF solution of pure 1-(*i*-C_3H_7)B_5H_8 forms only a trace of 2-(C_3H_7)B_5H_8 after 3 weeks, with no significant increase during the following 15 weeks. The stronger Lewis base 2,6-lutidine isomerized pure 1-(*i*-C_3H_7)B_5H_8 quantitatively to 2-(*i*-C_3H_7)B_5H_8 in less than 1 day (eq 3).



1-(i-C_3H_7)B_5H_8 2-(i-C_3H_7)B_5H_8

(3)

Preliminary NMR studies on the effect of various metal halide catalysts in the isomerization of 1-(*i*-C_3H_7)B_5H_8 were examined. The catalysts $FeCl_3$, $ZrCl_4$, and $HfCl_4$ caused isomerization of 1-(*i*-C_3H_7)B_5H_8 to 1-(*n*-C_3H_7)B_5H_8 and 2-(C_3H_7)B_5H_8 with rearrangement to 1-(*n*-C_3H_7)B_5H_8 occurring at a faster rate. The extent of isomerization for each catalyst varied greatly in terms of ratio of the isomers formed and time to reach a steady state. Processes more complicated than a simple equilibrium are apparently involved. These isomerizations are catalyst-induced, as pure samples of 1-(*i*-C_3H_7)B_5H_8 and 1-(*n*-C_3H_7)B_5H_8, stored under a vacuum, appear to be indefinitely stable and under no isomerization.

D. Other Metal Halide Catalyzed Reactions of B_5H_9. The formation of a 14.8% yield of 1-MeB_5H_8 was accomplished with a 1:1 ratio of methyl chloride and B_5H_9 with 50 mol % $ZrCl_4$ catalyst at 100 °C for 3 h. Under the standard reaction conditions, no methylation occurred, which indicates that more stringent reaction conditions may be generally necessary in order to achieve a good level of alkylation with primary alkyl halides.

Ethylation under standard reaction conditions produced a yield of 3% 1-EtB_5H_8, which increased to 71% 1-EtB_5H_8 and 4% 2-EtB_5H_8 at 100 °C for 3 h in a stainless steel bomb.

Cyclic alkyl halides were also found to alkylate B_5H_9 in the presence of a metal halide catalyst. Under standard reaction conditions, cyclopentyl chloride and B_5H_9 (1:1) produced 24% 1-(cyclopentyl)pentaborane (in addition to three other unidentified apically substituted pentaborane(9) products). The preparation of 1-(cyclohexyl)pentaborane(9) was accomplished with either cyclohexyl chloride or cyclohexene. The use of cyclohexyl chloride and 61 mol % $ZrCl_4$ (based on B_5H_9) produced 26% 1-(cyclohexyl)pentaborane(9) (1-(C_6H_{11})B_5H_8), along with small amounts of two other alkylated pentaborane(9) species. Using a 1:1:1 mixture of cyclohexene, HCl, and B_5H_9 with 38% $ZrCl_4$ also produced a 26% yield of 1-(C_6H_{11})B_5H_8 along with similar side products. This latter reaction most likely occurs via addition of HCl to the olefin and is therefore presumed to be equivalent to the reaction with cyclohexyl chloride.

The use of Friedel–Crafts catalysis to link two pentaborane(9) cages together via a methylene group has been previously reported.[20,21] Sisler and co-workers produced the apically substituted bis(1-pentaboryl)methane ((1-B_5H_8)$_2CH_2$) in 4.5% yield using $AlCl_3$ catalyst.[20] The side product (1-pentaboryl)(dichloroboryl)methane ((1-B_5H_8)CH_2BCl_2) was also formed in 1.1% yield. Subsequent investigations produced higher yields of (1-B_5H_8)$_2CH_2$ (27%) and (1-B_5H_8)CH_2BCl_2 (23%) with use of lower temperatures and a longer reaction period.[21] The basally substituted compound (2-B_5H_8)$_2CH_2$ was prepared by isomerization of (1-B_5H_8)$_2CH_2$ with use of hexamethylenetetramine.[21]

Initial attempts to link two B_5H_9 cages via a methylene group with $ZrCl_4$ as catalyst were unsuccessful under the standard reaction conditions, at 40 °C for 2.5 h and at 60 °C for 2 h. The use of $HfCl_4$ as the catalyst was somewhat more successful. When a reaction mixture with 10 mmol of B_5H_9 and 5 mmol of CH_2Cl_2 with 1.4 mmol of $HfCl_4$ catalyst was stirred at room temperature for 2 months in a reaction vessel smaller than that previously used in the standard reaction, 6% of the carbon-linked bis(pentaboryl)methane ((1-B_5H_8)$_2CH_2$), was produced, accompanied by 1-MeB_5H_8 rather than the side product (1-pentaboryl)(dichloroboryl)methane ((1-B_5H_8)CH_2BCl_2), which was produced in the reaction with $AlCl_3$ catalyst. 1-MeB_5H_8 is more readily separated than (1-B_5H_8)CH_2BCl_2 from (1-B_5H_8)$_2CH_2$. A similar reaction with $HfCl_4$ catalyst at 65 °C for 2 days also produced (1-B_5H_8)$_2CH_2$ (2%) and 1-MeB_5H_8 (1%).

2,3-Dichlorobutane does not produce the desired 2,3-bis(pentaboryl)butane product under standard reaction conditions, but an interesting alkylation does occur. When 2,3-$Cl_2C_4H_8$ and B_5H_9 are reacted in the presence of $ZrCl_4$ catalyst, 7% 1-(isobutyl)- and 1% 1-(*sec*-butyl)pentaborane formed. At 50 °C for 2 h 42% 1-(isobutyl)pentaborane(9) and 7% 1-(sec-butyl)pentaborane(9) were produced.

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(17) Nenitzescu, C. D.; Necsoiu, I.; Glatz, A.; Zalman, M. *Chem. Ber.* **1959**, *92*, 10–17.

(18) Roberts, R. M.; Bandenberger, S. G.; Panayides, S. G. *J. Am. Chem. Soc.* **1958**, *80*, 2507–2509.

(19) Brown, H. C.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1972**, 71–72.

(20) Altwicker, E. R.; Ryschkewitsch, G. E.; Garett, A. B.; Sisler, H. H. *Inorg. Chem.* **1964**, *3*, 454–455.

(21) Beard, W. R. Ph.D. Thesis, University of Wisconsin, Madison, WI.

Experimental Section

A. Instrumentation. Inert-atmosphere techniques[22] employed throughout these investigations included the use of standard high-vacuum lines, nitrogen-filled glovebags, and a glovebox (Vacuum Atmospheres Model HE-493). ^{11}B (160.46 or 115.545 MHz) and ^{1}H (500 MHz) NMR spectra were obtained with Bruker AM-500 and AM-360 spectrometers. Infrared spectra were acquired with a Beckman 4250 IR spectrophotometer. Mass spectral data were obtained at various electronvolt levels with either a Kratos MS-80RFA or a Kratos MS-25 spectrometer. Preparative gas chromatography was accomplished with a Varian Model 3700 gas chromatograph equipped with either a 20 ft × $^3/_8$ in. or 8 ft × $^3/_8$ in. column (solid support Chromasorb W, acid washed and treated with dimethylchlorosilane, 30/60 mesh; liquid phase 20% Apiezon L) or a 2 ft × $^1/_4$ in. column (20% Apiezon L–Chromasorb W 45/60).

B. Chemicals. B_5H_9 and $Zr(BH_4)_4$ were obtained form laboratory stock and their purities confirmed by infrared and NMR spectroscopy. Isopropyl chloride, 1-chloropropane, 2-chloro-2-methylpropane, *n*-butyl chloride, *sec*-butyl chloride, 2,6-lutidine, methyl chloride, ethyl chloride, cyclopentyl chloride, cyclohexyl chloride, cyclohexene, 2,3-dichlorobutane, $ZnBr_2$, $SnCl_4$, $FeCl_3$, $NbCl_5$, $ZrCl_4$, $HfCl_4$, $TaCl_5$, and YCl_3 were purchased from Aldrich Chemical Co. and used as received, except where noted otherwise. $TiCl_4$ was purchased from Alfa Chemical Co., $AlCl_3$ and $(C_5H_5)_2ZrCl_2$ were obtained from Mallinckrodt, and Pd/charcoal was acquired from Matheson Coleman and Bell. The gaseous HCl (technical grade), BF_3 (CP grade), propene (CP grade), 1-butene, *cis*-2-butene, and *trans*-2-butene were purchased from Matheson Co. $(C_5H_5)_2Zr(H)Cl$[23] was prepared by a known literature route. Diethyl ether was purchased from Mallinkrodt (analytical grade) and dried and distilled over Na/benzophenone prior to use. The hydrocarbon solvents hexane (Worum Chemical Co., solvent grade), heptane (Aldrich Chemical Co., spectrophotometric grade), and octane (Aldrich Chemical Co., reagent grade) were dried and distilled over Na. THF was distilled from $LiAlH_4$ and stored over Na(s)/benzophenone. 2,6-Lutidine was also distilled and stored under vacuum. Dichloromethane (CH_2Cl_2) was obtained from VWR Scientific and distilled and stored over P_2O_5. All chemical reagents were handled either in a vacuum line or under a dry nitrogen atmosphere in a glovebag or a drybox.

C. Standard Reaction Procedure for Isopropyl Chloride–Metal Halide Catalyzed Alkylation Reactions. All reactions were carried out in a 100-mL round-bottom reaction flask equipped with a 12-mm O-ring stopcock (Kontes or Ace) and containing a Teflon-coated magnetic stirring bar. The catalyst was transferred into the reaction flask in a glovebox (for $ZrCl_4$, $FeCl_3$, $HfCl_4$, $TaCl_5$, $NbCl_5$, YCl_3), in a glovebag (for $AlCl_3$, $(C_5H_5)_2ZrCl_2$, $(C_5H_5)_2Zr(H)Cl$, Pd/charcoal, $ZnBr_2$, or $SnCl_4$), or by vacuum-line transfer techniques (for BF_3 or $TiCl_4$). Typically 10 mol % (0.5–0.7 mmol) of catalyst was used for the initial comparison reactions, but catalyst amounts of up to 50 mol % were used in selected reactions.

Isopropyl chloride (2-chloropropane, *i*-ClC_3H_7) in amounts of 5–7 mmol was transferred into the reaction vessel either by syringe (syringe filled in the glovebag) while the reaction flask was kept on the vacuum line under nitrogen gas flow and at −196 °C or by the use of standard vacuum-line techniques. A stoichiometric amount (5–7 mmol) of B_5H_9 was then vacuum-transferred into the reaction flask. The flask was then closed, removed from the vacuum line, and immersed in a −78 °C dry ice–ethanol bath in a 1-L stirring Dewar and the mixture stirred magnetically. The bath temperature was raised from −78 °C to ambient temperature over 3 h and then maintained at room temperature for an additional 1 h.

The reaction flask was then reattached to the vacuum line, the contents were cooled to −196 °C, and any noncondensible gases produced were measured. The volatile components in the reaction vessel were transferred to the vacuum line and fractionated by vacuum distillation through a U-trap at −107 °C (2,2,4-trimethylpentane slush) into a −196 °C trap. Nonvolatiles were dissolved in hexane or benzene and examined by ^{11}B NMR spectroscopy to identify borane products not transferred into the vacuum line.

The volatile compounds distilling through the −107 °C U-trap and condensing in the −196 °C U-trap included HCl, unreacted alkyl halide, and propane. They were identified by gas-phase infrared spectroscopy. Isopropyl chloride was separated from propane an HCl by distillation through a −126 °C (methylcyclohexane slush) U-trap into a −196 °C U-trap. Propane and HCl distill through the −126 °C U-trap while isopropyl chloride condenses. If a mixture of HCl and propane was present, then it was chemically separated as follows. The mixed amount of HCl and propane gases were measured on the vacuum line and then condensed into a reaction flask containing a slight excess of pyridine. The flask contents were warmed to room temperature and then vacuum-distilled through a U-trap at −78 °C into a −196 °C trap. The propane distilled passed the −78 °C U-trap and was subsequently measured. The amount of HCl produced in the reaction is obtained by difference.

The reaction flask contents condensing in the −107 °C U-trap, consisting of (alkyl)pentaborane(9) products and unreacted B_5H_9, were condensed into a NMR tube with use of an O-ring vacuum pump-through attachment and their relative concentrations determined by integration of their ^{11}B NMR spectra.

Absolute yield data were obtained in the following manner. The contents of the NMR tube containing the pentaborane(9) compounds were transferred to a detachable storage flask equipped with a 4-mm Kontes O-ring stopcock on the vacuum line. An equivalent amount by volume of hydrocarbon solvent such as hexane, heptane, or octane was added to the borane mixture, and samples (no larger than 500 μL) of this solution were syringed onto a 20-ft gas chromatography column. The alkylated pentaborane(9) species were collected separately under a nitrogen–helium gas flow in a −196 °C trap as they came off the column. The separated alkylpentaborane(9) compounds obtained from the entire product mixture were transferred to separate traps on the vacuum line, and spectral data in the form of infrared, ^{11}B NMR, ^{1}H NMR, and mass spectra were obtained. Individual yields by weight were determined by transferring the pure compound into a detachable weighing pump-through flask equipped with two 4-mm O-ring stopcocks. (In a typical 7-mmol reaction the amount of the major isomer was in the 0.2–0.4-g weight range. The smaller amounts of minor product were obtained from the intensities of their ^{11}B NMR spectra relative to those of the major pentaborane(9) species present.) Table XI lists the relative and absolute yields obtained for some of the propylation reactions. The ^{11}B NMR spectrum (in C_6D_6) for 1-(*i*-C_3H_7)B_5H_8 is as follows: B(1), −39.85 ppm (singlet); B(2–5), −14.00 ppm (doublet, J = 159.7 Hz). Upon broad-band ^{1}H decoupling, the doublet at −14.00 ppm becomes a singlet. The ^{1}H NMR spectrum (in C_6D_6) contains the following resonances: −2.40 ppm (very broad, intensity 4); +1.02 ppm (broad, intensity 6); +1.23 ppm (broad, intensity 1); 2.39 ppm (quartet, J = 162.5 Hz, intensity 4). The infrared spectrum was obtained in the gas phase with use of 10 Torr of sample in a 10 cm long cell equipped with NaCl windows. 1-(*i*-C_3H_7)B_5H_8 has the following major absorbances: 2950 (s), 2880 (m, sh), 2605 (vs), and 1380 (m, br) cm^{-1}. The mass spectrum measured at 30 eV shows a parent ion peak at m/e 106.2 (calculated for $^{12}C_3{}^{11}B_5{}^{1}H_{15}$ 106.16).

The ^{11}B NMR spectrum (in C_6D_6) for the minor isomer 1-(*n*-C_3H_7)B_5H_8 is as follows: B(1), −43.34 ppm (singlet); B(2–5), −13.82 ppm (doublet, J = 158.4 Hz). The basal doublet becomes a singlet upon ^{1}H broad-band decoupling. The ^{1}H NMR spectrum (in C_6D_6) contains the following resonances: −2.51 ppm (broad, intensity 4); +0.95 ppm (broad, intensity 2); +1.09 ppm (triplet, J = 7.3 Hz, intensity 3); +1.53 ppm (broad, intensity 2); +2.40 ppm (quartet, J = 161.1 Hz, intensity 4). The mass spectrum measured at 30 eV showed a parent ion peak at m/e 106.3 (calculated for $^{12}C_3{}^{11}B_5{}^{1}H_{15}$ 106.16).

D. Reaction Variations in the Isopropyl Chloride Alkylation Reaction. When a longer reaction time was used, the experiment was first set up in the same manner as described in procedure C with the appropriate ratio of starting material and catalyst. The reaction mixture was warmed to room temperature as in part C and then stirred at room temperature for the appropriate amount of time as indicated in Tables II and III.

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[22] Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*; Wiley: New York, 1986.

[23] Buchwald, S. L.; LaMaire, S. J.; Nielson, R. B.; Watson, B. T.; King, S. W. *Tetrahedron Lett.* **1987**, *28*, 3895–3898.

Table XI. Relative and Absolute Yields Obtained in the Metal Halide Catalyzed Propylation of B_5H_9

catalyst[a]	alkyl halide	reacn conditions	yield, %	
			$1-(i-C_3H_7)B_5H_8$	$1-(n-C_3H_7)B_5H_8$
$AlCl_3$ (23)[b]	$n-ClC_3H_7$	−78 °C → room temp/3 h		
rel[c]		room temp/69 h	2	24
absolute[d]			4	20
$AlCl_3$ (10)[b]	$i-ClC_3H_7$	−78 °C → room temp/3 h		
rel		room temp/1 h	16	22
absolute			18	20
$FeCl_3$ (19)	$n-ClC_3H_7$	−78 °C → room temp/3 h		
rel		room temp/69 h	27	1
absolute			28	1
$FeCl_3$ (10)	$i-ClC_3H_7$	−78 °C → room temp/3 h		
rel		room temp/72 h	75	7
absolute			71	8
$FeCl_3$ (10)	$i-ClC_3H_7$	−78 °C → room temp/3 h		
rel		room temp/1 h	64	4
absolute			67	3
$ZrCl_4$ (10)	$i-ClC_3H_7$	−78 °C → room temp/3 h		
rel		room temp/1 h	88	4
absolute			89	3

[a] Mole percent of catalyst (in parentheses) based on amount of pentaborane. [b] In the $AlCl_3$-catalyzed reactions, the percentage of $1-(n-C_3H_7)B_5H_8$ produced includes the amount of $1-EtB_5H_8$ produced also, as the chemical shifts for the apical borons of these two species overlap in the ^{11}B NMR spectra. [c] Relative yields were obtained from integration of the ^{11}B NMR spectrum of the reaction mixture. [d] Absolute yields were obtained from weighing the individual (propyl)pentaboranes after separation on the gas chromatograph.

The experiments that have a maximum temperature lower than room temperature were also set up by following the standard reaction procedure. The reaction flask was then placed in a −78 °C ethanol–dry ice slush bath and warmed to the desired temperature over a 3-h period with stirring. The reaction temperature was maintained by addition of crushed dry ice as necessary. For the $ZrCl_4$-catalyzed experiment in which the ceiling temperature is 0 °C and there is no warm-up period, the flask containing the reagents was placed directly into a 0 °C ice bath.

In reactions that had a 2:1 ratio of B_5H_9 to $i-ClC_3H_7$ (Table III), 14 mmol of B_5H_9 was used for 7 mmol of isopropyl chloride and vice versa for the 1:2 reaction. In this sense, the scales of the reactions were kept the same.

E. Reactions with Additional Reagents. The $AlCl_3$ and the $ZrCl_4$ in the dual-catalyst reaction were loaded into the 100-mL reaction flask in the glovebox. The two catalysts were mixed together, the remaining reagents were added into the flask on the vacuum line, and the reaction was commenced as described in procedure C. The reaction in which a small amount of water was added with the catalyst was set up as in the standard reaction procedure by first loading the flask with 2.4 mmol of $ZrCl_4$. B_5H_9 (5.22 mmol), isopropyl chloride (5.14 mmol), and H_2O (0.25 mmol) were measured in the gas phase and condensed one at a time (in that order) into the reaction flask at −196 °C. The reaction followed the standard reaction procedure, and the products collected from this reaction were a trace of noncondensable gases 0.62 mmol (12.0%) of propane, 5.13 mmol (99.8%) of HCl, 84.0% of $1-(i-C_3H_7)B_5H_8$, 5.3% of $1-(n-C_3H_7)B_5H_8$, and 10.7% of unreacted B_5H_9.

The diethyl ether used in the $ZrCl_4$-catalyzed reactions was measured as a gas and condensed into the reaction flask at −196 °C on the vacuum line before the warm-up period in the standard reaction procedure. In the reaction with excess Et_2O, the amounts of reagents used were as follows: 3.5 mmol of $ZrCl_4$, 7.1 mmol of $i-ClC_3H_7$, 7.16 mmol of B_5H_9, and 9.23 mmol of Et_2O. No alkylation occurred in this reaction mixture containing excess diethyl ether.

F. Halogen Series. The results for the use of $i-BrC_3H_7$ and $i-IC_3H_7$ in place of $i-ClC_3H_7$ in the $ZrCl_4$-catalyzed reaction are listed in Table IV. The reactions were set up according to the standard reaction procedure for $i-ClC_3H_7$. $i-BrC_3H_7$ and $i-IC_3H_7$ were measured and transferred by syringe.

G. General Reaction Procedure for Propene–Metal Halide Catalyzed Alkylation Reactions. The catalyst was loaded under a nitrogen atmosphere (glovebox or glovebag) into a 250-mL round-bottom reaction flask equipped with a 12-mm O-ring stopcock and containing a Teflon-coated magnetic stirring bar. In the mixed-catalyst reaction with $ZrCl_4$ and $AlCl_3$, the solid catalysts were mixed together at this point. The mole percent of catalyst used was based on the amount of B_5H_9 used in each reaction. B_5H_9, typically 5–7 mmol, and the appropriate amount of propene (Tables V and VI) were condensed into the reaction flask. Any additional reagents (pentane (7 mL for 7 mmol of B_5H_9), isopropyl chloride, or HCl) were then condensed into the flask. The reaction mixtures were then subjected to the standard reaction and work-up procedures.

In the sealed-NMR-tube propene reactions 0.055 mmol of B_5H_9 was used with an equivalent amount of HCl and a 30% excess of propene and $ZrCl_4$ (0.086 mmol). The reagents were not allowed to mix until all were in the NMR tube. The NMR tube was sealed under vacuum. The solvent used was Skelly B (hexane).

H. Procedure for *n*-Propyl Chloride– and Various Butyl Halide—Metal Halide Catalyzed Alkylation Reactions. These reactions were set up and worked up in the same manner as indicated in part C with catalyst amounts ranging from 14 to 53 mol % (based on pentaborane) and the reaction conditions (time and temperature) noted in Table VI. Comparisons with $i-ClC_3H_7$ are in Table VII. Table XI lists the relative and absolute yields obtained for some of these reactions.

The butyl chloride reactions were run on a 5-mmol scale with use of a 1:1 ratio of B_5H_9 in all cases except the reaction involving the heating of $n-ClC_4H_9$ to 65 °C (a 2:1 ratio of B_5H_9 to $n-ClC_4H_9$ was used here). Reactions that had a maximum reaction temperature of 25 °C or less underwent a 3-h warm-up period with stirring from −78 °C to the maximum reaction temperature (either −50 °C or room temperature) followed by an additional 1 h of stirring at the ceiling temperature.

At the end of the reaction period noncondensable gases produced in the reaction were measured on the vacuum line and the volatile components were transferred to the vacuum line. The nonvolatiles soluble in benzene or hexane were examined by ^{11}B NMR spectroscopy to confirm that all the borane products were accounted for.

The volatiles were fractionated by vacuum distillation through a U-trap at −107 °C into a −196 °C trap. the contents of the −196 °C trap were HCl and butane formed in the reaction. HCl and butane were chemically separated by using pyridine as described previously in part C. The −107 °C U-trap contained unreacted starting materials and alkylated pentaborane(9) species. The (butyl)pentaborane(9) yield was determined by integration of the ^{11}B NMR spectra.

The major isomer, 1-(*sec*-butyl)pentaborane ($1-(s-C_4H_9)B_5H_8$) was separated by using gas chromatography (8-ft column). The ^{11}B NMR spectrum of $1-(s-C_4H_9)B_5H_8$ is as follows: B(1), −40.66 ppm (singlet); B(2–5), −14.1 ppm (doublet, J = 159.1 Hz). The basal boron doublet becomes a singlet upon ^1H broad-band decoupling. The ^1H NMR spectrum (C_6D_6) shows the following resonances: −2.53 ppm (very broad, intensity 4); +1.05 ppm (triplet, J = 7.35 Hz, intensity 3); +1.12 ppm (slightly broadened, intensity 3); +1.44 ppm (broad, intensity 2); +1.52 ppm (broad, intensity 1); +2.38 ppm (quartet, J = 161.6 Hz, intensity 4). Another feature of the ^{1}H NMR spectrum indicative of the *sec*-butyl isomer is the loss of coupling of the butyl protons. When the couplings of the propyl group protons in 1-(i-C_3H_7)B_5H_8 and 1-(n-C_3H_7)B_5H_8 are compared, coupling can be resolved only for protons on the γ-carbon in 1-(n-C_3H_7)B_5H_8. The protons on the α- and β-carbons (or the carbons that are attached to boron B(1) or are next to a carbon attached to a boron) show broad peaks in the ^{1}H spectrum. The carbon farthest away from the apical boron in 1-(s-C_4H_9)B_5H_8 is two carbons away and shows a triplet coupling pattern. The ^{1}H NMR spectrum for 1-(n-C_4H_9)B_5H_8 would have γ- and δ-carbons whose protons would both be expected to show coupling. The mass spectrum of 1-(s-C_4H_9)B_5H_8 shows a parent ion peak at m/e 120.1810 (calculated for $^{12}C_4{}^1H_{17}{}^{11}B_5$ 120.1795).

The n-ClC_4H_9 reaction mixtures that were heated above room temperature were contained in a 30-mL stainless steel bomb. The $ZrCl_4$ catalyst was added to the bomb in the glovebox, the bomb was evacuated on the vacuum line, and B_5H_9 and n-ClC_4H_9 were transferred into the bomb. The bomb was closed and placed in a preheated oven for 3 h at the specified temperature (either 65 or 90 °C). The reaction mixture was worked up in the same manner as described above.

I. Reaction Procedure for Butene Reactions. The butene reactions were carried out in 200-mL round-bottom reaction flasks equipped with a 12-mm Teflon O-ring stopcock and a Teflon-coated magnetic stirring bar. The indicated amount (Table IX) of catalyst was transferred to the flask in the glovebox. Approximately 5 mmol each of B_5H_9, the butene, and HCl were vacuum-transferred into the flask. The reaction vessel was placed in a −78 °C bath and warmed to room temperature over 3 h followed by an additional 1 h of stirring at room temperature. The reaction mixture was worked up in the same manner as for the butyl chloride reactions.

J. Isomerizations of Propylpentaboranes with $ZrCl_4$. Gas chromatographically purified 1-(i-C_3H_7)B_5H_8 (1.5 mmol) was vacuum-transferred into a standard 50-mL round-bottom reaction flask containing 0.8 mmol of $ZrCl_4$. The mixture was stirred magnetically for 2 days at room temperature. The isomerization of 1-(n-C_3H_7)B_5H_8 (0.7 mmol) with $ZrCl_4$ (0.8 mmol) was set up similarly. Isomer ratios were analyzed by ^{11}B NMR spectroscopy (Table X).

K. Isomerization of *n*-Propyl Chloride with $ZrCl_4$. $ZrCl_4$ was added (0.5 cm in height) to an NMR-tube apparatus (medium-wall NMR tube equipped with a 4-mm O-ring stopcock) in the glovebox. n-Propyl chloride and CD_2Cl_2 (0.3 mL each) were transferred into the NMR tube under a nitrogen atmosphere via syringe. A 0.055-mmol amount of HCl was added to the NMR tube under vacuum. After 43 h at room temperature the ^{1}H NMR spectrum showed about 50% conversion to i-ClC_3H_7 along with a small amount of C_3H_8. No further isomerization was evident after 117 h.

L. Isomerization Studies of 1-(*i*-C_3H_7)B_5H_8. For metal halide investigations the catalyst (about 0.4 cm in height) was added to the NMR-tube apparatus in the glovebox. Approximately 1 mmol of pure 1-(i-C_3H_7)B_5H_8 was condensed into the NMR tube along with enough hexane so that the total solution height was 5 cm. The NMR tubes were shaken to mix the contents, and the extent of isomerization was monitored by ^{11}B NMR spectroscopy. (The presence of $FeCl_3$ shifted and broadened the ^{11}B resonances, so after 4 weeks the tube contents were separated from the catalyst on the vacuum line.) The results for the various catalysts are as follows: $ZrCl_4$, 86% 1-(i-C_3H_7)B_5H_8, 7% 1-(n-C_3H_7)B_5H_8, and 7% 2-(C_3H_7)B_5H_8 after 12 h with insignificant further changes over 6 weeks; $FeCl_3$, 59% 1-(i-C_3H_7)B_5H_8, 12% 1-(n-C_3H_7)B_5H_8, and 29% 2-(C_3H_7)B_5H_8 after 1 week with insignificant further changes over 4 weeks; $HfCl_4$, 73% 1-(i-C_3H_7)B_5H_8, 19% 1-(n-C_3H_7)B_5H_8, and 8% 2-(C_3H_7)B_5H_8 after 6 weeks with insignificant further changes over an additional 4 weeks; $NbCl_5$ and $(C_5H_5)_2ZrCl_2$, trace isomerization after 2–3 weeks.

Lewis base catalyzed isomerization of 1-(i-C_3H_7)B_5H_8 was also investigated by ^{11}B NMR spectroscopy. A THF solution of 1-(i-C_3H_7)B_5H_8 showed only trace isomerization to 2-(i-C_3H_7)B_5H_8 during 15 weeks at room temperature. A 2,6-lutidine solution of 1-(i-C_3H_7)B_5H_8 showed nearly quantitative conversion to 2-(i-C_3H_7)B_5H_8 after 17 h at room temperature. The ^{11}B NMR spectrum of 2-(i-C_3H_7)B_5H_8 is as follows: B(1), −52.91 ppm (doublet, J = 170.2 Hz); B(2), +4.92 ppm (singlet); B(3,5), −14.55 ppm (doublet, J = 158.2 Hz); B(4), −19.03 ppm (doublet, J = 165.8 Hz). The ^{1}H NMR spectrum is as follows: $H_{bridge,1}$, −2.06 ppm (broad, intensity 2); $H_{bridge,2}$, −2.71 ppm (broad, intensity 2); $CH(CH_3)_2$, +1.12 (broad, intensity 1); $CH(CH_3)_2$, +0.94 ppm (doublet, J = 6.81 Hz, intensity 6); $H_{B(3-5)}$, +2.41 ppm (quartet, J = 160.0 Hz, intensity 3); $H_{B(1)}$, +0.92 pm (quartet, J = 170.0 Hz, intensity 1).

M. Reaction of Methyl Chloride and B_5H_9 at 100 °C. A stainless steel bomb was charged with 2.5 mmol of $ZrCl_4$ in the drybox. Methyl chloride (5.12 mmol) and B_5H_9 (5.01 mmol) were transferred into the bomb under vacuum. The bomb was closed and heated in a 100 °C oven for 3 h. The reaction converted 14.8% of the B_5H_9 to 1-MeB_5H_8. HCl (1.37 mmol, 27%) was produced along with 0.21 mmol of noncondensables, and 2.66 mmol of MeCl was recovered.

N. Reaction of Ethyl Chloride and B_5H_9 at 100 °C. A stainless steel bomb was charged with 2.5 mmol of $ZrCl_4$ in the drybox. Ethyl chloride (5.10 mmol) and B_5H_9 (5.00 mmol) were transferred into the bomb under vacuum. The bomb was closed and heated in a 100 °C oven for 3 h. The boranes present at the end of the reaction were 70.6% of 1-EtB_5H_8, 4.3% of 2-EtB_5H_8, and 25.1% of B_5H_9.

O. 1-(Cyclopentyl)pentaborane. $ZrCl_4$ (2.7 mmol), cyclopentyl chloride (5.0 mmol), and B_5H_9 (5.03 mmol) were reacted as noted in procedure C. The catalyst appeared to be soluble in this reaction. The volatile components of the reaction were separated on the vacuum line by distillation through a U-trap at −107 °C into a U-trap at −196 °C. HCl (1.59 mmol) passed the −107 °C U-trap. The major product, 1-(c-C_5H_9)B_5H_8, was separated by gas chromatography with the 8-ft column. Its ^{11}B NMR spectrum is as follows: B(1), −43.18 ppm (singlet); B(2–5), −13.88 ppm (doublet, J = 159.1 Hz). The ^{1}H NMR spectrum shows the following resonances: +2.41 ppm (quartet, J = 162.3 Hz, intensity 4); +1.49 ppm (broad, intensity 1); +1.46–1.35 ppm (multiplet, intensity 4); +0.98–0.92 ppm (multiplet, intensity 4); −2.48 ppm (broad, intensity 4). As with other (alkyl)pentaboranes, the coupling on the carbon near the boron to which the alkyl group is attached is unresolved.

P. 1-(Cyclohexyl)pentaborane. This reaction was run as noted in procedure O with $ZrCl_4$ (4.3 mmol), cyclohexyl chloride (7.0 mmol), and B_5H_9 (7.03 mmol). The volatile components of the reaction were separated on the vacuum line by distillation through a U-trap at −126 °C into a U-trap at −196 °C. HCl (1.22 mmol) passed the −126 °C trap. The major product, 1-(C_6H_{11})B_5H_8 (26% yield), was separated by gas chromatography with the 8-ft column. The ^{11}B NMR spectrum of 1-(C_6H_{11})B_5H_8 is as follows: B(1), −40.6 ppm (singlet); B(2–5), −14.1 ppm (doublet, J = 151.48 Hz). The ^{1}H NMR spectrum shows the following resonances: −2.58 ppm (broad, intensity 4); +1.11 ppm (broad, intensity 1); +1.20–1.90 ppm (multiplets, intensity 10); +2.39 ppm (quartet, J = 159.74 Hz, intensity 4). The mass spectrum shows a parent ion peak at m/e 145.2 (calculated for $^{12}C_6H_{19}{}^{10}B^{11}B_4$ 145.20).

The reaction of cyclohexene and B_5H_9 was run as above with 1.9 mmol of $ZrCl_4$, 5.0 mmol of cyclohexene, 5.01 mmol of B_5H_9, and 5.0 mmol of HCl. The catalyst appeared to be soluble in the reaction mixture. The volatile components of the reaction were separated on the vacuum line by distillation through a U-trap at −107 °C into a U-trap at −196 °C. HCl produced in the reaction passed the −107 °C trap. The major product, 1-(C_6H_{11})B_5H_8 (26% yield), was separated by gas chromatography with the 8-ft column.

Q. Bis(pentaboryl)methane. In a typical reaction in a 30-mL glass reaction tube equipped with a 4-mm Kontes O-ring stopcock and containing a Teflon-coated magnetic stirring bar, 1.4 mmol of $HfCl_4$, 10.19 mmol of B_5H_9, and 4.97 mmol of CH_2Cl_2 were stirred and warmed from −78 °C to room temperature over a 3-h period and then stirred at room temperature for 16 h. After the 16-h period no significant amount of HCl was produced, so the stirring at room temperature was continued for a total reaction time of 2 months. The yield of $(1\text{-}B_5H_8)_2CH_2$ was 6% along with less than 1% of 1-MeB_5H_8, which was separated from (1-B_5-

$H_8)_2CH_2$ by fractional distillation through a −22 °C U-trap, through which 1-MeB_5H_8 passed. The ^{11}B NMR spectrum for $(1\text{-}B_5H_8)_2CH_2$ is as follows: B(1), −41.18 ppm (singlet); B(2–5), −13.85 ppm (doublet, J = 160.7 Hz). The ^1H NMR spectrum shows the following resonances: −2.38 ppm (very broad, intensity 8); +0.24 ppm (broad, intensity 2); +2.48 ppm (quartet, J = 161.6 Hz, intensity 8).

A 2-day 65 °C reaction in a 30-mL stainless steel bomb containing $HfCl_4$ (2.5 mmol), CH_2Cl_2 (5.09 mmol), and B_5H_9 (10.68 mmol) produced a 2% yield of $(1\text{-}B_5H_8)_2CH_2$ and 1% of 1-MeB_5H_8.

R. Reactions between 2,3-$Cl_2C_4H_8$ and B_5H_9. A typical reaction, run as noted in procedure C, contained 0.82 mmol of $ZrCl_4$, 3.5 mmol of 2,3-dichlorobutane (2,3-$Cl_2C_4H_8$), and 7 mmol of B_5H_9. The (butyl)pentaborane product, separated by gas chromatography with the 8-ft column, was primarily 1-(i-C_4H_9)B_5H_8, in 7% yield, whose ^{11}B NMR spectrum is as follows: B(1), −44.22 ppm (singlet); B(2–5), −13.87 ppm (J = 159.4 Hz). The ^1H NMR spectrum exhibits the following resonances: −2.47 ppm (very broad, intensity 4); +0.90 ppm (broad multiplet, intensity 2); +1.04 ppm (doublet, J = 6.40 Hz, intensity 6); +1.71 ppm (broad multiplet, intensity 1); +2.40 ppm (quartet, J = 162.5 Hz, intensity 4). The mass spectrum of 1-(i-C_4H_9)B_5H_8 has a parent ion peak at m/e 119.2 (calculated for $^{12}C_4H_{17}{}^{10}B^{11}B_4$ 119.235).

In another reaction between 2,3-$Cl_2C_4H_8$ (3.5 mmol), B_5H_9 (7 mmol), and $ZrCl_4$ (0.7 mmol) in a 100-mL reaction flask at 50 °C for 2 h, the (butyl)pentaborane products, separated by gas chromatography with the 8-ft column, consisted of 1-(i-C_4H_9)B_5H_8 (42%) and 1-(s-C_4H_9)B_5H_8 (7%).

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Registry No. B_5H_9, 19624-22-7; $AlCl_3$, 7446-70-0; $FeCl_3$, 7705-08-0; $NbCl_5$, 10026-12-7; $TaCl_5$, 7721-01-9; $ZrCl_4$, 10026-11-6; $HfCl_4$, 13499-05-3; BF_3, 7637-07-2; Pd, 7440-05-3; $TiCl_4$, 7550-45-0; $SnCl_4$, 7646-78-8; $ZnBr_2$, 7699-45-8; $(C_5H_5)_2ZrCl_2$, 1291-32-3; $(C_5H_5)_2Zr(H)Cl$, 37342-97-5; YCl_3, 10361-92-9; 1-(i-C_3H_7)B_5H_8, 37838-05-4; 1-(n-C_3H_7)B_5H_8, 34692-67-6; 2-(n-C_3H_7)B_5H_8, 126724-90-1; 1-EtB_5H_8, 23753-61-9; 2-ClC_3H_7, 75-29-6; 2-BrC_3H_7, 75-26-3; 2-IC_3H_7, 75-30-9; n-ClC_3H_7, 540-54-5; n-ClC_4H_9, 109-69-3; s-ClC_4H_9, 78-86-4; t-ClC_4H_9, 507-20-0; 1-(s-C_4H_9)B_5H_8, 92276-87-4; CH_2Cl_2, 75-09-2; 2,3-$Cl_2C_4H_8$, 7581-97-7; 1-(c-C_5H_9)B_5H_8, 126724-91-2; 1-(C_6H_{11})B_5H_8, 126724-92-3; $(1\text{-}B_5H_8)_2CH_2$, 93659-46-2; 1-(i-C_4H_9)B_5H_8, 126724-93-4; 2-(i-C_3H_7)B_5H_8, 126724-94-5; 1-butene, 106-98-9; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; ethyl chloride, 75-00-3; cyclopentyl chloride, 930-28-9; cyclohexyl chloride, 542-18-7; methyl chloride, 74-87-3.

Supplementary Material Available: Spectra for 1-(i-C_3H_7)B_5H_8 (^{11}B NMR, ^1H NMR, and mass spectra), 1-(n-C_3H_7)B_5H_8 (^1H NMR and mass spectra), and 1-(s-C_4H_9)B_5H_8 and 1-(i-C_4H_9)B_5H_8 (^1H NMR spectra) (7 pages). Ordering information is given on any current masthead page.

Quantitative Analysis of Ligand Effects (QALE). Systematic Study of Iron–Phosphorus Bond Lengths and Their Relationship to Steric Thresholds

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Systematic determination of Fe–P bond lengths for the set of complexes (η-Cp)(CO)(L)FeCOMe containing "sterically unencumbered" σ-donor phosphorus(III) ligands shows that the Fe–P bond lengths vary over a narrow range (2.195 ± 0.015 Å) and are only slightly dependent on the σ-donicity and size of the ligand. π-Acid ligands (i.e. $P(OR)_3$) exhibit significantly shorter Fe–P bond lengths around 2.10 Å. In light of this virtual constancy of σ bond length for a family of complexes, it is reasonable to expect steric thresholds to be manifest. We report on five systems that can be analyzed in terms of sharp thresholds.

Introduction

Although ligand effects have been employed in organometallic chemistry for nearly 20 years, only recently have there been attempts to extract information about the stereoelectronic factors that influence the thermodynamics and kinetics of reactions by quantitative analysis of ligand effects (for which we use the acronym QALE).[1-13] QALE is based on the premise that certain thermodynamic, kinetic, and structural properties of a complex and its reactions can be expressed in terms of steric and electronic parameters assigned to the ligands involved. This leads to a correlation method, often made linear in the stereoelectronic parameters, from which insights about structure or reactivity may be drawn. A complicating feature is the type of bonding (σ or π) that exists between the ligand and the metal fragment. Dose the bond type range smoothly, with no abrupt transition, from one end

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(1) Golovin, M. N.; Rahman, M. M.; Belmonte, J. E.; Giering, W. P. *Organometallics* **1985**, *4*, 1981–91.

(2) Rahman, M. M.; Liu, H.-Y.; Prock, A.; Giering, W. P. *Organometallics* **1987**, *6*, 650–8.

(3) Rahman, M. M.; Liu, H.-Y.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1989**, *8*, 1–7.

(4) Liu, H. Y.; Eriks, K.; Giering, W. P.; Prock, A. *Inorg. Chem.* **1989**, *28*, 1759–63.

(5) Dahlinger, K.; Falcone, F.; Poe, A. J. *Inorg. Chem.* **1986**, *25*, 2654–8.

(6) Poe, A. J. *Pure Appl. Chem.* **1988**, *60*, 1209–16.

(7) Brodie, N. M.; Chen, L.; Poe, A. J. *Int. Nat. J. Kinetics*, **1988**, *20*, 467–91.

(8) Gao, Y.-C.; Shi, Q.-Z; Kershner, D. L.; Basolo, F. *Inorg. Chem.* **1988**, *27*, 188–91.

(9) Zizelman, P. M.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3771–84.

(10) Baker, R. T.; Calabrese, J. C.; Krusic, P. J.; Therien, M. J.; Trogler, W. C. *J. Am. Chem. Soc.* **1988**, *110*, 8392–412.

(11) Nolan, S. P.; Hoff, C. D. *J. Organomet. Chem.* **1985**, *290*, 365.

(12) Ching, S.; Shriver, D. F. *J. Am. Chem. Soc.* **1989**, *111*, 3228.

(13) Lee, K.-W.; Brown, T. L. *Inorg. Chem.* **1987**, *26*, 1852–6.

0276-7333/90/2309-1758$02.50/0