

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

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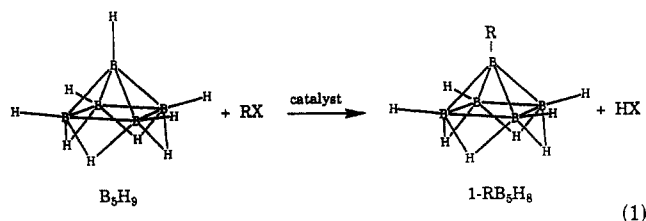
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A high-yield route to 1-(isopropyl)pentaborane(9) (1-(*i*-C₃H₇)B₅H₉) has been developed with use of the early-transition-metal halides HfCl₄ and ZrCl₄ as alkylation catalysts. Comparison studies of the effect of various catalysts and reaction conditions on the catalyzed propylation reaction are discussed. The ZrCl₄-catalyzed alkylation of pentaborane(9) (B₅H₉) with *n*-ClC₃H₇, *i*-ClC₃H₇, *n*-ClC₄H₉, *s*-ClC₄H₉, 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 ZrCl₄ catalyst and Lewis bases on the isomerization of 1-(*i*-C₃H₇)B₅H₉ and 1-(*n*-C₃H₇)B₅H₉ 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*-C₃H₇)B₅H₉. The utility of ZrCl₄ and HfCl₄ catalysts for B₅H₉ alkylation with MeCl, EtCl, cyclopentyl chloride, cyclohexyl chloride, CH₂Cl₂, and 2,3-Cl₂C₄H₈ 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) (B₅H₉), alkyl halides or olefins, and traditional catalysts such as AlCl₃ or FeCl₃.¹⁻¹⁰ Alkylation of B₅H₉ 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 B₅H₉, 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 B₅H₉ with AlCl₃ as the catalyst are often accompanied by side products that signify borane cage degradation to alkylboron dihalides, boron trihalides, and diborane.⁷ In the AlCl₃-catalyzed alkylation of 2-MeB₅H₉ with MeCl to form 1,2-Me₂B₅H₇, the side products include

alkylhalopentaborane(9) species as well as boron halides.¹⁰

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*-ClC₃H₇) and *n*-propyl chloride (*n*-ClC₃H₇). The optimized parameters in the synthesis of 1-(*i*-C₃H₇)B₅H₉ 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*-ClC₄H₉ and *s*-ClC₄H₉ 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*-C₃H₇)B₅H₉ was also examined. The early-transition-metal halides that were found to be effective catalysts for the alkylation of B₅H₉ with secondary alkyl halides were ZrCl₄ and HfCl₄. The application of these catalysts in B₅H₉ 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 CH₂Cl₂ and C₄H₈Cl₂ 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 B₅H₉ 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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Table I. Percentages of Borane Compounds Recovered in the Propylation of Pentaborane(9)^a with Isopropyl Chloride as a Function of Catalyst^b

catalyst	amt of borane compd, %				
	1-(<i>i</i> -C ₃ H ₇)-B ₅ H ₈	1-(<i>n</i> -C ₃ H ₇)-B ₅ H ₈	2-(C ₃ H ₇)-B ₅ H ₈	B ₅ H ₉	1-EtB ₅ H 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 B₅H₉ and *i*-C₃H₇Cl 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: BF₃, Pd/charcoal, TiCl₄, SnCl₄, ZnBr₂, (C₅H₅)₂ZrCl₂, (C₅H₅)₂Zr(H)Cl, YCl₃.

B₅H₉ 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 ¹¹B and ¹H 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 BF₃, Pd on charcoal, TiCl₄, SnCl₄, ZnBr₂, (C₅H₅)₂ZrCl₂, (C₅H₅)₂Zr(H)Cl, and YCl₃ are used as catalysts.

The first catalyst we examined was the traditional Friedel-Crafts catalyst AlCl₃. Earlier reports on the use of AlCl₃ catalyst in the alkylation of B₅H₉ indicated that this catalyst does not always result in clean, straightforward reactions. For example, Sisler and co-workers⁷ examined the alkylation of B₅H₉ (49.9 mmol) with ethyl chloride (55.0 mmol) in the presence of AlCl₃ (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-EtB₅H₈ (25 mmol, based on borane), HCl (2.1 mmol), C₂H₆ (16.2 mmol), H₂ (25 mmol), B₂H₆ (1.2 mmol), EtBCl₂, and BCl₃. 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 B₂H₆, EtBCl₂, and BCl₃ indicate that borane cage degradation occurred. Similar side-product formation and borane cage degradation occurred during the synthesis of 1,2-dimethylpentaborane(9) with AlCl₃ as the catalyst.¹⁰

Our investigations with AlCl₃ revealed additional interesting side products. In addition to the desired product, 1-(*i*-C₃H₇)B₅H₈ (12.2%), two other isomers of propylpentaborane were formed, 1-(*n*-C₃H₇)B₅H₈ (16.8%) and 2-(C₃H₇)B₅H₈ (4.3%, both isomers). It is clear that AlCl₃ 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 AlCl₃-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 AlCl₃ is not a suitable catalyst for many B₅H₉ alkylations.

The other traditional Friedel-Crafts catalyst examined in the propylation reaction was FeCl₃. This catalyst gave a higher yield of 1-(*i*-C₃H₇)B₅H₈, 60.0% vs 12.2% for the AlCl₃-catalyzed reaction. The selectivity for formation of 1-(*i*-C₃H₇)B₅H₈ (60.0%) over 1-(*n*-C₃H₇)B₅H₈ (2.3%) was also much higher with FeCl₃.

The search for better catalysts for pentaborane(9) alkylations led to the investigation of early-transition-metal halides. Suga and co-workers¹² had studied the Lewis-acid-catalyzed alkylation of benzene with *sec*-butyl chloride and found AlCl₃ and AlBr₃ to be very active catalysts, while ZnCl₂ and SnCl₄ were inactive. Classified among the moderately active catalysts in Suga's results were FeCl₃ and NbCl₅ and, in the weak catalyst category, ZrCl₄ and TiCl₄.

Table I shows that several of the early-transition-metal halides work very well as alkylation catalysts for B₅H₉. TaCl₅ gives results (59.4% for 1-(*i*-C₃H₇)B₅H₈) similar to those for FeCl₃ under the standard reaction conditions. NbCl₅ gave a slightly lower yield (41.3% for 1-(*i*-C₃H₇)B₅H₈). The group IIIB metal halides gave the best results in terms of yield and 1-(*i*-C₃H₇)B₅H₈ selectivity. The highest yield (89.5%) was obtained with ZrCl₄ as the catalyst. HfCl₄ also gave a high yield of 1-(*i*-C₃H₇)B₅H₈ (80.9%). In the HfCl₄-catalyzed reaction all the B₅H₉ is used in the alkylation reaction to form alkylpentaborane(9) compounds. In fact, HfCl₄ was the only catalyst in the series that gave this result. TiCl₄ did not act as a catalyst for borane alkylations under the standard reaction conditions. NbCl₅, ZrCl₄, and HfCl₄ are all reusable as catalysts. The other zirconium compounds examined, (C₅H₅)₂ZrCl₂ and (C₅H₅)₂Zr(H)Cl, were not catalytically active under the conditions used. When Zr(BH₄)₄ was tried as a catalyst, the product 1-(*i*-C₃H₇)B₅H₈ was formed but the catalyst was consumed in the reaction, presumably forming ZrCl₄. Among the products that were obtained from the Zr(BH₄)₄ standard reaction were HCl, B₂H₆, unreacted isopropyl chloride, unreacted B₅H₉, 1-(*i*-C₃H₇)B₅H₈ (70.2%), and 1-(*n*-C₃H₇)B₅H₈ (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 HfCl₄ were not examined, as the standard reaction with HfCl₄ converted all of the B₅H₉ into alkylpentaborane(9) species, and only its selectivity can be potentially altered. Increased contact time for both the FeCl₃ and the NbCl₅ reactions show an increase not only in the amount of 1-(*i*-C₃H₇)B₅H₈ formed but also in the amount of 1-(*n*-C₃H₇)B₅H₈ formed, indicating some decrease in selectivity. Increased contact time in the ZrCl₄ case increases the minor isomer, 1-(*n*-C₃H₇)B₅H₈, from 2% under standard reaction conditions to 13% at the longer reaction time. This is consistent with the results from the FeCl₃ and NbCl₅ reactions.

With both the FeCl₃ and the ZrCl₄ catalysts, reactions at a lower temperature were examined in an attempt to increase the selectivity of the alkylation. In the FeCl₃ reaction, with a maximum temperature of -22 °C, the desired 1-(*i*-C₃H₇)B₅H₈ was formed exclusively but in only 13.7% yield. The maximum reaction temperature for the ZrCl₄ low-temperature reactions was 0 °C. Two different reactions were done at this lower temperature. The small

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>i</i> -C ₃ H ₇)B ₅ H ₈	1-(<i>n</i> -C ₃ H ₇)B ₅ H ₈	2-(C ₃ H ₇)B ₅ H ₈	B ₅ H 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 B₅H₉ starting material was recovered as (alkyl)pentaboranes or B₅H₉. ^b Reused catalyst.

Table III. Percentages of Borane Compounds Formed in the ZrCl₄-Catalyzed Propylation of Pentaborane(9) with Isopropyl Chloride under Various Reaction Conditions

B ₅ H ₉ : <i>i</i> -ClC ₃ H ₇	amt of ZrCl ₄ , ^a mol %	reactn conditions	amt of borane compd, %		
			1-(<i>i</i> -C ₃ H ₇)B ₅ H ₈	1-(<i>n</i> -C ₃ H ₇)B ₅ H ₈	B ₅ H ₉
1:1 ^b	10	-78 °C → room temp/3 h	89.5	2.3	8.2
		room temp/1 h			
1:1	50	-78 °C → room temp/3 h	93.4	1.5	5.1
		room temp/1 h			
1:1	10	-78 °C → room temp/3 h	72.4	13.8	13.8
		room temp/45 h			
1:1 ^c	10	-78 °C → room temp/3 h	87.7	4.1	8.2
		room temp/1 h			
1:1	10	-78 °C → 0 °C/3 h	85.5	8.2	6.3
		0 °C/1 h			
1:1 ^d	50	-78 °C → room temp/3 h	77.7	12.8	9.5
1:1 ^e	50	-78 °C → room temp/3 h	88.3	3.8	7.9
		room temp/1 h			
1:2	50	-78 °C → room temp/3 h	64.4	26.1	5.6
		room temp/1 h			
2:1	15	-78 °C → room temp/3 h	96.5	1.5	<i>f</i>
		room temp/1 h			
1:1 ^g	10 (ZrCl ₄)	-78 °C → room temp/3 h	76.9	9.3	5.9
	10 (AlCl ₃)	room temp/1 h			
1:1	50 (ZrCl ₄)	-78 °C → room temp/3 h	84.0	5.3	10.7
	5 (H ₂ O)	room temp/1 h			
1:1	50 (ZrCl ₄)	-78 °C → room temp/3 h	78.0	8.9	13.1
	25 (Et ₂ O)	room temp/1 h			
1:1	50 (ZrCl ₄)	-78 °C → room temp/3 h	no reactn		
	excess (Et ₂ O)	room temp/1 h			
1:1	50	<i>h</i>	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 ZrCl₄. ^f Yield of 1-(*i*-C₃H₇)B₅H₈ based on amount of *i*-ClC₃H₇ used. ^g 79.9% 2-(C₃H₇)B₅H₈ also formed. ^h 2-ClC₃H₇ and ZrCl₄ were mixed together first for 1/2 h at room temperature; B₅H₉ 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 ZrCl₄ reactions is not as pronounced as in the FeCl₃ case.

Three of the catalysts, NbCl₅, HfCl₄, and ZrCl₄, were reused in standard reactions to confirm that they are not being consumed in the reaction. Both HfCl₄ and ZrCl₄ give comparable results whether the catalyst was fresh or used. NbCl₅ 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*-C₃H₇)B₅H₈.

The ratios of the reactants and catalysts were also varied during the optimization of the ZrCl₄-catalyzed alkylation reaction. When the catalyst was increased from 10 to 50 mol %, the yield of the desired product 1-(*i*-C₃H₇)B₅H₈ 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*-C₃H₇)B₅H₈ to 64.4% and in-

creasing the yield of 1-(*n*-C₃H₇)B₅H₉ to 26.1%. Conversely, using a 2-fold excess of B₅H₉ in the reaction resulted in a 96.5% yield of 1-(*i*-C₃H₇)B₅H₉ with significantly less of the minor isomer, 1-(*n*-C₃H₇)B₅H₉ (1.5%), formed. An excess of B₅H₉ in the reaction thus leads to the most selective, high-yield route to 1-(*i*-C₃H₇)B₅H₉. A possible explanation for this difference in alkyl selectivity involves the order in which the three components of the reaction (alkyl halide, B₅H₉, and ZrCl₄) interact. A route consistent with the results would involve the initial formation of a catalyst-alkyl halide complex followed by reaction with B₅H₉. 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 B₅H₉, 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 B₅H₉, 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*-C₃H₇)B₅H₉ obtained when a 2-fold excess of B₅H₉ to alkyl halide is used is very good, it is apparently a maximum yield, as the isopropyl chloride that did not react with the B₅H₉ was reduced to propane. In fact, it appears that all of the 1:1 reactions between B₅H₉ and isopropyl chloride with ZrCl₄ 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 ZrCl₄ catalyst by sublimation before use did not eliminate the propane formation, and yields of 1-(*i*-C₃H₇)B₅H₉ and 1-(*n*-C₃H₇)B₅H₉ remained virtually identical with those attained in the standard ZrCl₄-catalyzed reaction. Adding 5% H₂O to the ZrCl₄-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-ZrCl₄ slurry was stirred for 1/2 h at room temperature before the B₅H₉ was added. The reaction mixture was then treated in the standard reaction manner. The product yields were 79.4% of 1-(*i*-C₃H₇)B₅H₉, 10.8% of 1-(*n*-C₃H₇)B₅H₉, and 9.8% unreacted B₅H₉. 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 B₅H₉ and isopropyl chloride at room temperature for 3.5 h produced no propane. The ZrCl₄ catalyst was added, and the reaction was continued in the usual manner to produce 3.5% propane, 94.8% 1-(*i*-C₃H₇)B₅H₉, and 1.7% 1-(*n*-C₃H₇)B₅H₉. HCl was produced in 95.9% yield based on alkyl halide. This reaction procedure appears to rule out a primary role for B₅H₉ in propane formation.

To confirm that the ZrCl₄ is responsible for the propane formation, a mixture of 50 mol % ZrCl₄ 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

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

$\text{B}_5\text{H}_9 + 2\text{-XC}_3\text{H}_7 \xrightarrow[\text{room temp, 1 h}]{\text{ZrCl}_4 (50 \text{ mol } \%), -78^\circ\text{C} \rightarrow \text{room temp, 3 h}} \text{products}$				
X	amt of borane compd, %			
	1-(<i>i</i> -C ₃ H ₇)- B ₅ H ₉	1-(<i>n</i> -C ₃ H ₇)- B ₅ H ₉	2-(C ₃ H ₇)- B ₅ H ₉	B ₅ H 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 B₅H₉ and *i*-XC₃H₇ were used in a 1:1 ratio with 50 mol % ZrCl₄. The corresponding HX was also formed in these reactions.

isopropyl chloride was recovered. When isopropyl chloride and ZrCl₄ interact at room temperature for longer periods of time, propane continues to form at a slow rate over several weeks.

The effects of various halogens on the alkyl halide used in the ZrCl₄-catalyzed propylation reaction are tabulated in Table IV. Isopropyl chloride is the clear choice for the ZrCl₄-catalyzed reaction with a yield of 93.4% for the desired product 1-(*i*-C₃H₇)B₅H₉, 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 % AlCl₃ (based on B₅H₉) to the standard ZrCl₄ reaction procedure did not increase the overall yields, as more of the minor isomer 1-(*n*-C₃H₇)B₅H₉ was formed. The addition of a weak base to the reaction mixture was also investigated. When 50 mol % ZrCl₄ and 25 mol % diethyl ether were used in the reaction between B₅H₉ 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 B₅H₉ with olefins was also attempted on the basis of reports with ethylene as the olefin and AlCl₃ as the catalyst.^{1,3,6,7} Our initial survey of reactions involving B₅H₉, propene (in equimolar amounts), and catalyst (17–50 mol %) did not produce alkylation when ZrCl₄, NbCl₅, Zr(BH₄)₄, and (C₅H₅)₂Zr(H)Cl were used as catalysts.

The addition of a small amount of isopropyl chloride to the B₅H₉-propene reaction produced 40.8% of 1-(*i*-C₃H₇)B₅H₉ under standard reaction conditions. The use of hydrogen chloride substantially improved the ZrCl₄-catalyzed reaction, and with an excess of HCl the yields of 1-(*i*-C₃H₇)B₅H₉ are good, though about 10% lower than that obtained with isopropyl chloride.

A sealed-NMR-tube reaction of propene and B₅H₉ with ZrCl₄-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 ZrCl₄-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 B₅H₉ was converted to 1-(*i*-C₃H₇)B₅H₉. 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

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

catalyst ^a	time at room temp, ^b h	amt of borane compd, %		
		1-(<i>i</i> - C_3H_7) B_5H_8	1-(<i>n</i> - 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-Et B_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-Et B_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

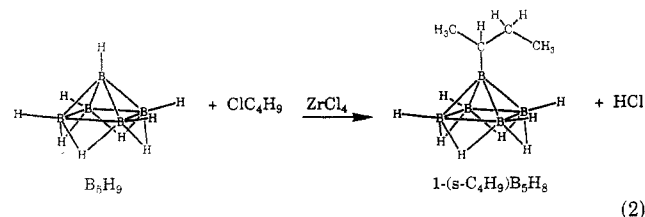
catalyst ^b	time at room temp, ^c h	alkyl halide	amt of borane compd, %		
			1-(<i>i</i> - C_3H_7) B_5H_8	1-(<i>n</i> - C_3H_7) B_5H_8	B_5H_9
FeCl_3 (19)	69	<i>n</i> - ClC_3H_7	27	1	72
FeCl_3 (10)	69	<i>i</i> - ClC_3H_7	70	8	22
ZrCl_4 (14)	1	<i>n</i> - ClC_3H_7	17	1	82
ZrCl_4 (10)	1	<i>i</i> - ClC_3H_7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



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_9) 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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Table VIII. Percentages of (Butyl)pentaboranes Formed with Various Butyl Chlorides and Reaction Conditions

BuX ^a	amt of ZrCl ₄ , mol %	reactn conditions	amt of borane compd, %		
			1-(s-C ₄ H ₉)B ₅ H ₈	other RB ₅ H ₈ ^b	B ₅ H ₉
<i>n</i> -ClC ₄ H ₉	50	-78 °C → room temp/3 h room temp/1 h	21	5 (1)	74
<i>s</i> -ClC ₄ H ₉	58	-78 °C → room temp/3 h room temp/1 h	57	11 (3) ^c	27
<i>s</i> -ClC ₄ H ₉	38	-78 °C → 50 °C/3 h -50 °C/1 h	69	3 (1)	28
<i>t</i> -ClC ₄ H ₉	58	-78 °C → room temp/3 h room temp/1 h			
<i>n</i> -ClC ₄ H ₉	50	90 °C/3 h	25	33 (4)	42
<i>n</i> -ClC ₄ H ₉ ^d	50	65 °C/3 h	52	25 (4)	23

^a B₅H₉ and the butyl chlorides were used in a 1:1 ratio. ^b The numbers of other types of 1-RB₅H₈ species formed are listed in parentheses.

^c Also 5% 2-RB₅H₈. ^d Excess B₅H₉ was used (10.5 mmol to 5.11 mmol of 1-ClC₄H₉). Mole percent of the catalyst for this reaction is based on the amount of butyl halide used. no reactn

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*-ClC₄H₉ as the alkyl halide under standard reaction conditions produced a 57% yield of 1-(s-C₄H₉)B₅H₈ 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 ZrCl₄-catalyzed alkylations with *n*-ClC₄H₉. Butylation with *n*-ClC₄H₉ was also surveyed at 65 and 90 °C. The 90 °C reaction produced 25% of 1-(s-C₄H₉)B₅H₈ and 33% of four other apically substituted pentaborane(9) compounds. The room-temperature reaction with *n*-ClC₄H₉ produced a comparable yield of 1-(s-C₄H₉)B₅H₈ and only 5% of another 1-(alkyl)pentaborane(9). The number of (alkyl)pentaborane(9) isomers increases with reaction temperature for both *n*-ClC₄H₉ and *s*-ClC₄H₉.

In an attempt to increase the yield of 1-(s-C₄H₉)B₅H₈ and decrease the number of other substituted pentaborane(9) compounds in the *n*-ClC₄H₉ alkylation reaction, an intermediate reaction temperature was chosen and the B₅H₉ to *n*-ClC₄H₉ ratio was increased to 2:1. The reaction mixture was heated to 65 °C for 3 h, and the yield of 1-(s-C₄H₉)B₅H₈ doubled to 52%, but the formation of four other alkylated pentaborane(9) species in 25% yield still occurred.

In the AlCl₃-catalyzed propylation of benzene with *n*-propyl halide, the yield of isopropylbenzene increased as the temperature of the reaction increased.¹⁴ In the AlCl₃-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 ZrCl₄-catalyzed butylation of B₅H₉ do not cause an analogous increase in 1-(s-C₄H₉)B₅H₈ produced but do result in the formation of more (alkyl)pentaborane(9) isomers. The doubling of the yield of 1-(s-C₄H₉)B₅H₈ in the 65 °C reaction of *n*-ClC₄H₉ with B₅H₉ 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

butene ^a	amt of ZrCl ₄ , mol %	amt of borane compd, %		
		1-(s-C ₄ H ₉)-B ₅ H ₈	other RB ₅ H ₈ ^b	B ₅ H ₉
1-butene	40	60	2 (3)	38
<i>cis</i> -2-butene	50	61	5 (4)	34
<i>trans</i> -2-butene	29	60	3 (4)	37

^a A 1:1:1 ratio of B₅H₉:butene:HCl was used. ^b The numbers of other types of 1-RB₅H₈ species are listed in parentheses.

Table X. Isomerization of (Propyl)pentaboranes in Contact with ZrCl₄ for 2 Days

starting isomer	distribn after 2 days, %		
	1-(<i>i</i> -C ₃ H ₇)-B ₅ H ₈	1-(<i>n</i> -C ₃ H ₇)-B ₅ H ₈	2-(C ₃ H ₇)-B ₅ H ₈
1-(<i>i</i> -C ₃ H ₇)B ₅ H ₈	75	19	6
1-(<i>n</i> -C ₃ H ₇)B ₅ H ₈	3	95	2

tert-Butyl chloride does not react with B₅H₉ 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 B₅H₉ with ZrCl₄ and 1-butene, *cis*-2-butene, or *trans*-2-butene in the presence of HCl all produce approximately 60% yields of 1-(s-C₄H₉)B₅H₈ along with small percentages of other alkylated pentaborane(9) products. These results suggest that HCl adds to the butene prior to its reaction with B₅H₉. An attempted butylation reaction with ZrCl₄ 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*-C₃H₇)B₅H₈ and 1-(*n*-C₃H₇)B₅H₈ were placed into separate reaction flasks containing ZrCl₄. 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*-C₃H₇)B₅H₈ isomerization had progressed further.

The extent of the isomerization of *n*-propyl bromide to isopropyl bromide in the presence of AlCl₃ 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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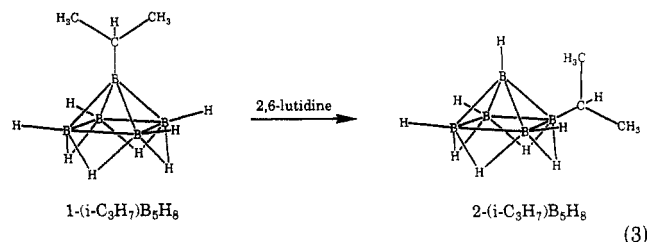
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propyl group occurs before substitution. However, both *n*-propylbenzene and isopropylbenzene will isomerize to the other isomer in the presence of $\text{AlCl}_3\text{-H}_2\text{O}$.^{17,18} Likewise, *n*-butylbenzene undergoes isomerization to *sec*-butylbenzene 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*- $\text{ClC}_3\text{H}_7\text{-ZrCl}_4$ (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).



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) $_2\text{CH}_2$) 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) $_2\text{CH}_2$ (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) $_2\text{CH}_2$ was prepared by isomerization of (1- B_5H_8) $_2\text{CH}_2$ 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) $_2\text{CH}_2$), 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) $_2\text{CH}_2$. A similar reaction with HfCl_4 catalyst at 65 °C for 2 days also produced (1- B_5H_8) $_2\text{CH}_2$ (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- $\text{Cl}_2\text{C}_4\text{H}_8$ 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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Experimental Section

A. Instrumentation. Inert-atmosphere techniques²² employed throughout these investigations included the use of standard high-vacuum lines, nitrogen-filled glovebags, and a glovebox (Vacuum Atmospheres Model HE-493). ¹¹B (160.46 or 115.545 MHz) and ¹H (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. B₅H₉ and Zr(BH₄)₄ were obtained from 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, ZnBr₂, SnCl₄, FeCl₃, NbCl₅, ZrCl₄, HfCl₄, TaCl₅, and YCl₃ were purchased from Aldrich Chemical Co. and used as received, except where noted otherwise. TiCl₄ was purchased from Alfa Chemical Co., AlCl₃ and (C₅H₅)₂ZrCl₂ were obtained from Mallinckrodt, and Pd/charcoal was acquired from Matheson Coleman and Bell. The gaseous HCl (technical grade), BF₃ (CP grade), propene (CP grade), 1-butene, *cis*-2-butene, and *trans*-2-butene were purchased from Matheson Co. (C₅H₅)₂Zr(H)Cl²³ was prepared by a known literature route. Diethyl ether was purchased from Mallinckrodt (analytical grade) and dried and distilled over Na/benzophenone prior to use. The hydrocarbon solvents hexane (Worun 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 LiAlH₄ and stored over Na(s)/benzophenone. 2,6-Lutidine was also distilled and stored under vacuum. Dichloromethane (CH₂Cl₂) was obtained from VWR Scientific and distilled and stored over P₂O₅. 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 ZrCl₄, FeCl₃, HfCl₄, TaCl₅, NbCl₅, YCl₃), in a glovebag (for AlCl₃, (C₅H₅)₂ZrCl₂, (C₅H₅)₂Zr(H)Cl, Pd/charcoal, ZnBr₂, or SnCl₄), or by vacuum-line transfer techniques (for BF₃ or TiCl₄). 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*-ClC₃H₇) 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 B₅H₉ 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 noncondensable 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 ¹¹B 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 B₅H₉, 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 ¹¹B 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, ¹¹B NMR, ¹H 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 ¹¹B 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 ¹¹B NMR spectrum (in C₆D₆) for 1-(*i*-C₃H₇)B₅H₈ is as follows: B(1), –39.85 ppm (singlet); B(2–5), –14.00 ppm (doublet, *J* = 159.7 Hz). Upon broad-band ¹H decoupling, the doublet at –14.00 ppm becomes a singlet. The ¹H NMR spectrum (in C₆D₆) 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*-C₃H₇)B₅H₈ 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 ¹²C₃¹¹B₅¹H₁₅ 106.16).

The ¹¹B NMR spectrum (in C₆D₆) for the minor isomer 1-(*n*-C₃H₇)B₅H₈ 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 ¹H broad-band decoupling. The ¹H NMR spectrum (in C₆D₆) 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 ¹²C₃¹¹B₅¹H₁₅ 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.

(22) Shriver, D. F.; Drezdson, 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 B₅H₉

catalyst ^a	alkyl halide	reacn conditions	yield, %	
			1-(<i>i</i> -C ₃ H ₇)B ₅ H ₈	1-(<i>n</i> -C ₃ H ₇)B ₅ H ₈
AlCl ₃ (23) ^b	<i>n</i> -ClC ₃ H ₇	-78 °C → room temp/3 h		
rel ^c		room temp/69 h	2	24
absolute ^d			4	20
AlCl ₃ (10) ^b	<i>i</i> -ClC ₃ H ₇	-78 °C → room temp/3 h		
rel		room temp/1 h	16	22
absolute			18	20
FeCl ₃ (19)	<i>n</i> -ClC ₃ H ₇	-78 °C → room temp/3 h		
rel		room temp/69 h	27	1
absolute			28	1
FeCl ₃ (10)	<i>i</i> -ClC ₃ H ₇	-78 °C → room temp/3 h		
rel		room temp/72 h	75	7
absolute			71	8
FeCl ₃ (10)	<i>i</i> -ClC ₃ H ₇	-78 °C → room temp/3 h		
rel		room temp/1 h	64	4
absolute			67	3
ZrCl ₄ (10)	<i>i</i> -ClC ₃ H 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 AlCl₃-catalyzed reactions, the percentage of 1-(*n*-C₃H₇)B₅H₈ produced includes the amount of 1-EtB₅H₈ produced also, as the chemical shifts for the apical borons of these two species overlap in the ¹¹B NMR spectra. ^c Relative yields were obtained from integration of the ¹¹B 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 ZrCl₄-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 B₅H₉ to *i*-ClC₃H₇ (Table III), 14 mmol of B₅H₉ 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 AlCl₃ and the ZrCl₄ 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 ZrCl₄. B₅H₉ (5.22 mmol), isopropyl chloride (5.14 mmol), and H₂O (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*-C₃H₇)B₅H₈, 5.3% of 1-(*n*-C₃H₇)B₅H₈, and 10.7% of unreacted B₅H₉.

The diethyl ether used in the ZrCl₄-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 Et₂O, the amounts of reagents used were as follows: 3.5 mmol of ZrCl₄, 7.1 mmol of *i*-ClC₃H₇, 7.16 mmol of B₅H₉, and 9.23 mmol of Et₂O. No alkylation occurred in this reaction mixture containing excess diethyl ether.

F. Halogen Series. The results for the use of *i*-BrC₃H₇ and *i*-IC₃H₇ in place of *i*-ClC₃H₇ in the ZrCl₄-catalyzed reaction are listed in Table IV. The reactions were set up according to the standard reaction procedure for *i*-ClC₃H₇. *i*-BrC₃H₇ and *i*-IC₃H₇ 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 ZrCl₄ and AlCl₃, the solid catalysts were mixed together at this point. The mole percent

of catalyst used was based on the amount of B₅H₉ used in each reaction. B₅H₉, 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 B₅H₉), 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 B₅H₉ was used with an equivalent amount of HCl and a 30% excess of propene and ZrCl₄ (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*-ClC₃H₇ 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 B₅H₉ in all cases except the reaction involving the heating of *n*-ClC₄H₉ to 65 °C (a 2:1 ratio of B₅H₉ to *n*-ClC₄H₉ 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 ¹¹B 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 ¹¹B NMR spectra.

The major isomer, 1-(*sec*-butyl)pentaborane (1-(*s*-C₄H₉)B₅H₈) was separated by using gas chromatography (8-ft column). The ¹¹B NMR spectrum of 1-(*s*-C₄H₉)B₅H₈ 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 (C₆D₆) 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 ^1H 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*-C₃H₇)B₅H₉ and 1-(*n*-C₃H₇)B₅H₉ are compared, coupling can be resolved only for protons on the γ -carbon in 1-(*n*-C₃H₇)B₅H₉. 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 ^1H spectrum. The carbon farthest away from the apical boron in 1-(*s*-C₄H₉)B₅H₉ is two carbons away and shows a triplet coupling pattern. The ^1H NMR spectrum for 1-(*n*-C₄H₉)B₅H₉ would have γ - and δ -carbons whose protons would both be expected to show coupling. The mass spectrum of 1-(*s*-C₄H₉)B₅H₉ shows a parent ion peak at m/e 120.1810 (calculated for $^{12}\text{C}_4^{11}\text{B}_5$ 120.1795).

The *n*-C₄H₉ reaction mixtures that were heated above room temperature were contained in a 30-mL stainless steel bomb. The ZrCl₄ catalyst was added to the bomb in the glovebox, the bomb was evacuated on the vacuum line, and B₅H₉ and *n*-C₄H₉ 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 B₅H₉, 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 ZrCl₄. Gas chromatographically purified 1-(*i*-C₃H₇)B₅H₉ (1.5 mmol) was vacuum-transferred into a standard 50-mL round-bottom reaction flask containing 0.8 mmol of ZrCl₄. The mixture was stirred magnetically for 2 days at room temperature. The isomerization of 1-(*n*-C₃H₇)B₅H₉ (0.7 mmol) with ZrCl₄ (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 ZrCl₄. ZrCl₄ 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 CD₂Cl₂ (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 ^1H NMR spectrum showed about 50% conversion to *i*-C₃H₇Cl, along with a small amount of C₃H₈. No further isomerization was evident after 117 h.

L. Isomerization Studies of 1-(*i*-C₃H₇)B₅H₉. 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*-C₃H₇)B₅H₉ 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 FeCl₃ 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: ZrCl₄, 86% 1-(*i*-C₃H₇)B₅H₉, 7% 1-(*n*-C₃H₇)B₅H₉, and 7% 2-(C₃H₇)B₅H₉ after 12 h with insignificant further changes over 6 weeks; FeCl₃, 59% 1-(*i*-C₃H₇)B₅H₉, 12% 1-(*n*-C₃H₇)B₅H₉, and 29% 2-(C₃H₇)B₅H₉ after 1 week with insignificant further changes over 4 weeks; HfCl₄, 73% 1-(*i*-C₃H₇)B₅H₉, 19% 1-(*n*-C₃H₇)B₅H₉, and 8% 2-(C₃H₇)B₅H₉ after 6 weeks with insignificant further changes over an additional 4 weeks; NbCl₅ and (C₅H₅)₂ZrCl₂, trace isomerization after 2–3 weeks.

Lewis base catalyzed isomerization of 1-(*i*-C₃H₇)B₅H₉ was also investigated by ^{11}B NMR spectroscopy. A THF solution of 1-(*i*-C₃H₇)B₅H₉ showed only trace isomerization to 2-(*i*-C₃H₇)B₅H₉

during 15 weeks at room temperature. A 2,6-lutidine solution of 1-(*i*-C₃H₇)B₅H₉ showed nearly quantitative conversion to 2-(*i*-C₃H₇)B₅H₉ after 17 h at room temperature. The ^{11}B NMR spectrum of 2-(*i*-C₃H₇)B₅H₉ 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 ^1H NMR spectrum is as follows: H_{bridge,1}, -2.06 ppm (broad, intensity 2); H_{bridge,2}, -2.71 ppm (broad, intensity 2); CH(CH₃)₂, +1.12 (broad, intensity 1); CH(CH₃)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 ppm (quartet, $J = 170.0$ Hz, intensity 1).

M. Reaction of Methyl Chloride and B₅H₉ at 100 °C. A stainless steel bomb was charged with 2.5 mmol of ZrCl₄ in the drybox. Methyl chloride (5.12 mmol) and B₅H₉ (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 B₅H₉ to 1-MeB₅H₈. 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 B₅H₉ at 100 °C. A stainless steel bomb was charged with 2.5 mmol of ZrCl₄ in the drybox. Ethyl chloride (5.10 mmol) and B₅H₉ (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-EtB₅H₈, 4.3% of 2-EtB₅H₈, and 25.1% of B₅H₉.

O. 1-(Cyclopentyl)pentaborane. ZrCl₄ (2.7 mmol), cyclopentyl chloride (5.0 mmol), and B₅H₉ (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*-C₅H₉)B₅H₈, 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 ^1H 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 ZrCl₄ (4.3 mmol), cyclohexyl chloride (7.0 mmol), and B₅H₉ (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-(C₆H₁₁)B₅H₈ (26% yield), was separated by gas chromatography with the 8-ft column. The ^{11}B NMR spectrum of 1-(C₆H₁₁)B₅H₈ is as follows: B(1), -40.6 ppm (singlet); B(2–5), -14.1 ppm (doublet, $J = 151.48$ Hz). The ^1H 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 $^{12}\text{C}_6\text{H}_{19}^{10}\text{B}^{11}\text{B}_4$ 145.20).

The reaction of cyclohexene and B₅H₉ was run as above with 1.9 mmol of ZrCl₄, 5.0 mmol of cyclohexene, 5.01 mmol of B₅H₉, 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-(C₆H₁₁)B₅H₈ (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 HfCl₄, 10.19 mmol of B₅H₉, and 4.97 mmol of CH₂Cl₂ 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-B₅H₈)₂CH₂ was 6% along with less than 1% of 1-MeB₅H₈, which was separated from (1-B₅-

$\text{H}_8)_2\text{CH}_2$ by fractional distillation through a -22°C U-trap, through which 1- MeB_5H_8 passed. The ^{11}B NMR spectrum for $(1-\text{B}_5\text{H}_8)_2\text{CH}_2$ 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 $(1-\text{B}_5\text{H}_8)_2\text{CH}_2$ and 1% of 1- MeB_5H_8 .

R. Reactions between 2,3- $\text{Cl}_2\text{C}_4\text{H}_8$ 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- $\text{Cl}_2\text{C}_4\text{H}_8$), and 7 mmol of B_5H_9 . The (butyl)pentaborane product, separated by gas chromatography with the 8-ft column, was primarily 1-($i\text{-C}_4\text{H}_9$) 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-($i\text{-C}_4\text{H}_9$) B_5H_8 has a parent ion peak at m/e 119.2 (calculated for $^{12}\text{C}_4\text{H}_{17}^{10}\text{B}^{11}\text{B}_4$ 119.235).

In another reaction between 2,3- $\text{Cl}_2\text{C}_4\text{H}_8$ (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-($i\text{-C}_4\text{H}_9$) B_5H_8 (42%) and 1-($s\text{-C}_4\text{H}_9$) 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; $(\text{C}_6\text{H}_5)_2\text{ZrCl}_2$, 1291-32-3; $(\text{C}_6\text{H}_5)_2\text{Zr}(\text{H})\text{Cl}$, 37342-97-5; YCl_3 , 10361-92-9; 1-($i\text{-C}_3\text{H}_7$) B_5H_8 , 37838-05-4; 1-($n\text{-C}_3\text{H}_7$) B_5H_8 , 34692-67-6; 2-($n\text{-C}_3\text{H}_7$) B_5H_8 , 126724-90-1; 1-Et B_5H_8 , 23753-61-9; 2- ClC_3H_7 , 75-29-6; 2-Br C_3H_7 , 75-26-3; 2- IC_3H_7 , 75-30-9; $n\text{-ClC}_3\text{H}_7$, 540-54-5; $n\text{-ClC}_4\text{H}_9$, 109-69-3; $s\text{-ClC}_4\text{H}_9$, 78-86-4; $t\text{-ClC}_4\text{H}_9$, 507-20-0; 1-($s\text{-C}_4\text{H}_9$) B_5H_8 , 92276-87-4; CH_2Cl_2 , 75-09-2; 2,3- $\text{Cl}_2\text{C}_4\text{H}_8$, 7581-97-7; 1-($c\text{-C}_5\text{H}_9$) B_5H_8 , 126724-91-2; 1-(C_6H_{11}) B_5H_8 , 126724-92-3; $(1-\text{B}_5\text{H}_8)_2\text{CH}_2$, 93659-46-2; 1-($i\text{-C}_4\text{H}_9$) B_5H_8 , 126724-93-4; 2-($i\text{-C}_3\text{H}_7$) 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-($i\text{-C}_3\text{H}_7$) B_5H_8 (^{11}B NMR, ^1H NMR, and mass spectra), 1-($n\text{-C}_3\text{H}_7$) B_5H_8 (^1H NMR and mass spectra), and 1-($s\text{-C}_4\text{H}_9$) B_5H_8 and 1-($i\text{-C}_4\text{H}_9$) 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 $(\eta\text{-Cp})(\text{CO})(\text{L})\text{FeCOMe}$ 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. $\text{P}(\text{OR})_3$) 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. Does the bond type range smoothly, with no abrupt transition, from one end

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