

and stirred for 0.5 h at room temperature. Lithium bromide precipitated and was removed by centrifuging. The solid was extracted repeatedly (3×10 mL) with pentane. The combined pentane extract, on distillation, gave 9.80 g (81% of pure di-*tert*-butyl *n*-hexylboronate, bp 94–96 °C (6.5 mm).

Registry No. RB(OH)₂ (R = *n*-hexyl), 16343-08-1; RB(OH)₂ (R = 3-hexyl), 86595-36-0; RB(OH)₂ (R = cyclopentyl), 63076-51-7; RB(OH)₂ (R = (1*E*)-1-octenyl), 42599-16-6; RB(OH)₂ (R = (1*E*)-3,3-dimethyl-1-butenyl), 86595-37-1; RB(OR')₂ (R = *n*-hexyl, R' = methyl), 2344-23-2; RB(OR')₂ (R = *n*-hexyl, R' = ethyl), 86595-38-2; RB(OR')₂ (R = 3-hexyl, R' = methyl), 37981-92-3; RB(OR')₂ (R = (1*E*)-1-octenyl, R' = methyl), 86595-39-3; RB(OR')₂ (R = (1*E*)-1-octenyl, R' = isopropyl), 86595-40-6; RB(OR')₂ (R = *n*-hexyl, R' = (CH₂)₃), 86290-24-6; RB(OR')₂ (R = 3-hexyl, R' = (CH₂)₃), 86290-28-0; RB(OR')₂ (R = cyclopentyl, R' = C(CH₃)₂C(CH₃)₂), 66217-55-8; RB(OR')₂ (R = (1*E*)-1-octenyl, R' = (CH₂)₂), 86595-41-7; RB(OR')₂ (R = (1*E*)-3,3-dimethyl-1-butenyl, R' = (CH₂)₃), 86595-42-8; RB(OR')₂ (R = *n*-hexyl, R' = isopropyl), 86290-26-8; RB(OR')₂ (R = cyclopentyl, R' = methyl), 41156-60-9; RB(OR')₂ (R = cyclopentyl, R' = ethyl), 86595-43-9; RB(OR')₂

(R = cyclopentyl, R' = isopropyl), 86595-44-0; RB(OR')₂ (R = cyclohexyl, R' = ethyl), 86595-45-1; RB(OR')₂ (R = *cis*-4-octenyl, R' = methyl), 86595-46-2; RB(OR')₂ (R = (1*E*)-3,3-dimethyl-1-butenyl, R' = methyl), 86595-47-3; RB(OR')₂ (R = (1*E*)-1-hexenyl, R' = phenyl), 86595-48-4; RB(OR')₂ (R = *cis*-1-bromo-1-octenyl, R' = methyl), 86595-49-5; RB(OR')₂ (R = (1*E*)-1-hexenyl, R' = *tert*-butyl), 86595-50-8; RB(OR')₂ (R = *n*-hexyl, R' = *tert*-butyl), 86595-51-9; RB(OR')₂ (R = *n*-hexyl, R' = (CH₂)₂), 86290-25-7; RB(OR')₂ (R = *n*-hexyl, R' = C(CH₃)₂C(CH₃)₂), 86308-26-1; RB(OR')₂ (R = (1*E*)-1-octenyl, R' = (CH₂)₃), 86595-52-0; RB(OR')₂ (R = *cis*-4-octenyl, R' = (CH₂)₂), 86595-53-1; RB(OR')₂ (R = *cis*-4-octenyl, R' = (CH₂)₃), 86595-54-2; RBBBr₂SMe₂ (R = *n*-hexyl), 64770-04-3; RBBBr₂SMe₂ (R = 3-hexyl), 64770-06-5; RBBBr₂SMe₂ (R = cyclopentyl), 64770-10-1; RBBBr₂SMe₂ (R = (1*E*)-1-octenyl), 86687-40-3; RBBBr₂SMe₂ (R = (1*E*)-3,3-dimethyl-1-butenyl), 72228-60-5; RBBBr₂SMe₂ (R = *cis*-1-bromo-1-octenyl), 86610-17-5; RBBBr₂SMe₂ (R = *cis*-4-octenyl), 86610-18-6; RBBBr₂SMe₂ (R = (1*E*)-1-hexenyl), 72228-56-9; RBBBr₂SMe₂ (R = cyclohexyl), 86610-19-7; methanol, 67-56-1; trimethylene glycol, 504-63-2; *tert*-butyl alcohol, 75-65-0; ethanol, 64-17-5; 2-propanol, 67-63-0; pinacol, 76-09-5; ethylene glycol, 107-21-1; phenol, 108-95-2.

Organoboranes. 31. A Simple Preparation of Boronic Esters from Organolithium Reagents and Selected Trialkoxyboranes

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The reaction of methyllithium with trimethoxyborane at -78 °C in ethyl ether yields a mixture of methylated boranes and their corresponding "ate" complexes. We have found that under the same conditions triisopropoxyborane reacts cleanly with methyllithium to form the lithium methyltriisopropoxyborate complex. Protonation of this complex with anhydrous hydrogen chloride quantitatively yields methyl diisopropoxyborane. This reaction of organolithium reagent with triisopropoxyborane appears to provide a general, valuable route to boronic esters. Other alkoxyboranes were examined for their selectivity for monomethylation by methyllithium. In addition to triisopropoxyborane, triisobutoxyborane and tri-*sec*-butoxyborane also give the methylboronic esters quantitatively. This development provides the first general preparation of boronic esters from organolithium reagents.

The utility of boronic esters and acids has largely been limited in the past to protecting groups in carbohydrate chemistry¹ and as derivatizing agents for difunctional compounds for GC and GC-MS analysis.² Recently the homologation of boronic esters has been demonstrated, and this promises to become an important application of boronic esters.³⁻⁵ A variety of methods have been used to prepare boronic esters. The addition of Grignard reagents to trialkoxyboranes at low temperatures followed by an aqueous hydrolysis yields the boronic acids.⁶⁻⁹ However, low yields are realized for the smaller alkyl groups, and subsequent esterification is necessary to obtain the ester. The redistribution of triorganylboranes with trialkoxyborane¹⁰ and trihaloboranes^{11,12} has been employed. Other less direct routes utilizing haloboranes,¹³ catecholborane,¹⁴ and thexylborane^{15,16} have been described. However, the alkyl groups employed are limited to those obtained via hydroboration. While alkylolithiums have been used, they tend to form the borinic ester preferentially.¹⁷ Having overcome these difficulties and limitations, we describe

here a simple and direct route for preparing boronic esters from organolithium reagents and selected trialkoxyboranes.

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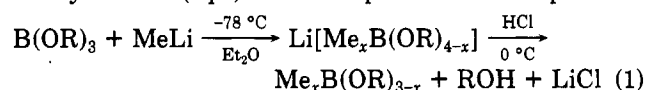
Table I. Methylation of Borane Derivatives with Methylolithium^a

borane derivative	methylboronic ester, %	methylborinic ester, %	Me ₂ B and Li(Me ₂ B), %	starting material, %
trichloroborane	<i>b</i>	3	32	65
fluorodimethoxyborane	10	<i>b</i>	28	62
chlorodimethoxyborane	43	6	16	35
trimethoxyboroxine	<i>b</i>	<i>b</i>	20	80
trimethoxyborane	8	3	14	75
triethoxyborane	65	10	7	17
triisopropoxyborane	98	1	<i>b</i>	1
tributoxyborane	82	9	<i>b</i>	9
tri- <i>sec</i> -butoxyborane	98	1	<i>b</i>	1
triisobutoxyborane	98	1	<i>b</i>	1
tri- <i>tert</i> -butoxyborane	2	<i>b</i>	22	76
tribenzyoxyborane	42	25	4	29

^a Accuracy estimated $\pm 5\%$. ^b No material, $< 1\%$.

Results and Discussion

The reaction of methylolithium with various trihaloboranes, trialkoxyboranes, and mixed haloalkoxyboranes was carried out by using conditions similar to those reported earlier.¹⁸ There is a rapid reaction of the boron compound with the equivalent of the methylolithium in diethyl ether at -78°C , forming a mixture of complexes. These anionic complexes can be destroyed by protonation¹⁹ with anhydrous hydrogen chloride at 0°C , liberating the methylboranes (eq 1). The composition of these products



can be readily estimated from the peak heights of the ¹¹B NMR spectrum for trialkoxyborane, methylboronate, dimethylboronate, and trimethylborane. Since tetramethylborate is protonated by hydrogen chloride to trimethylborane, a sample was analyzed prior to protonation for the presence of tetramethylborate. The results of the reaction of methylolithium with various boron compounds are summarized in Table I. It is apparent that a wide range of selectivities toward monomethylation exist in the reaction of methylolithium with various boron compounds. It is especially noteworthy that triisopropoxyborane, tri-*sec*-butoxyborane, and triisobutoxyborane give essentially quantitatively the monomethylated boronate esters.

The above results can be rationalized by examining the mechanism. A monoalkyltrialkoxylborate 1 is readily formed irreversibly by the attack of an alkylolithium reagent and trialkoxyborane (eq 2). This complex, 1, is in equilibrium with the boronic ester 2 and lithium alkoxide (eq 3). The boronic ester is susceptible to additional reaction with the alkylolithium reagent, yielding the dialkyldialkoxylborate complex 3 (eq 4), which is in equilibrium with the borinic ester 4 and lithium alkoxide (eq 5). Successive steps would give rise to the trialkylborane and lithium tetraalkylborate from the alkylation of the borinic ester and trialkylborane by the alkylolithium.

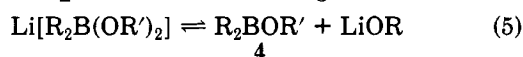
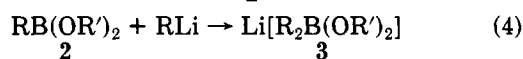
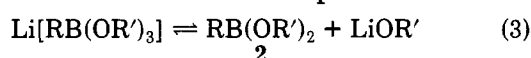


Table II. Alkylation of Triisopropoxyborane with Organolithium Reagents

organolithium reagent	boronic ester, %	borinic ester, %
methylolithium	98	1
<i>n</i> -butyllithium	96	<i>a</i>
<i>sec</i> -butyllithium	98	2
<i>tert</i> -butyllithium	65 (97) ^b	18 (2) ^b
phenyllithium	96	<i>a</i>

^a No material detected by ¹¹B NMR, $< 1\%$. ^b Reaction carried out at -98°C instead of -78°C .

If the monoalkyltrialkoxylborate 1 can be cleanly formed and if equilibrium (eq 3) favors this complex, the boronic ester would be formed selectively following the protonation of the alkyltrialkoxylborate complex 1. Thus, factors that affect the stability of 1, forming the boronic ester and lithium alkoxide, are the primary causes for the successive formation of alkylated boranes. As seen in Table I, the choice of the alkoxy group strongly influences the selectivity of alkylation by an organolithium reagent. Methoxy-, ethoxy-, and isopropoxylithium alkoxides in this order show increasing solubility in an ether solvent. The precipitation of the insoluble lithium alkoxide results in the shifting of the equilibrium (eq 3) toward the boronic ester 2 resulting in higher alkylated boranes. Similarly, an alkyltrialkoxylborate or alkylhalodialkoxylborate is not expected to be stable as it readily eliminates the lithium halide as a precipitate, yielding the alkylidihaloborane or boronic ester. While lithium *tert*-butoxide is very soluble in ether, the reaction of tri-*tert*-butoxyborane with methylolithium yields almost exclusively trimethylborane. Presumably this is due to larger steric interaction of the *tert*-butoxy groups, favoring the boronic ester 2 over the alkyltri-*tert*-butoxyborate complex 1. The effect of the steric interaction of the organolithium would also be expected to effect equilibrium (eq 3). The reaction of triisopropoxyborane with various organolithium reagents was investigated to determine whether the choice of the organolithium affects the selectivity of the boronic ester. The results are shown in Table II. Only in the reaction with *tert*-butyllithium was there any significant amount of dialkylborinic ester formed. However, the amount of dialkylation could be readily reduced by carrying the reaction out at a lower temperature, -98°C , cleanly forming the *tert*-butylboronic ester. The reaction of trimethoxyborane with methylolithium gives poorer selectivity in pentane, than in ether or tetrahydrofuran, in contrast to triisopropoxyborane, which selectively yields the boronic ester in pentane, ether, or tetrahydrofuran.

Diisopropoxyorganylboranes were isolated in good yields from the reaction of triisopropoxyborane with some readily available organolithiums. The results are summarized in

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Table III. Isolated Diisopropoxyorganylboranes

boronic ester	physical properties		
	yield, %	n_D^{20}	bp, °C (mmHg)
methyldiisopropoxyborane	71	1.3751	105–107 (751)
butyldiisopropoxyborane	85	1.3930	145–147 (746)
sec-butyldiisopropoxyborane	79	1.3896	138–140 (749)
tert-butyldiisopropoxyborane	68 ^a	1.3898	136–138 (754)
phenyldiisopropoxyborane	84	1.4620	98–101 (8)
dichloromethyldiisopropoxyborane	84	1.4180	66–68 (10)

^a Reaction carried out at –98 °C.

Table III. A ¹¹B NMR analysis of the reaction mixture indicated the clean formation of the boronic ester, detecting only trace quantities of the borinic ester and starting material. Importantly, there is no observable isomerization of the *tert*-butylboronic ester, as detected by oxidation to the alcohol or by ¹³C NMR, which has been observed by others.^{7,18,20,21}

Diisopropoxydichloromethylborane was isolated in excellent yield from the reaction of dichloromethylolithium with triisopropoxyborane. This boronic ester has been shown by Rathke to be a useful intermediate, reacting with organolithium and organomagnesium reagents via transfer reactions to give substituted boranes.²² While either trimethoxyborane or triisopropoxyborane cleanly gives the dichloromethylboronic ester, our procedure eliminates one step, the esterification of the dichloromethaneboronic acid with isopropyl alcohol.

Following the development of the organolithium reaction with trialkoxyboranes, we sought to extend this reaction to the more familiar Grignard reagents. There was little difference in selectivity using the various boron compounds as was seen in Table I. In all cases, a mixture of the boronic and borinic esters were observed.

Conclusion

We have shown the unusual selectivity of some trialkoxyboranes to react cleanly with organolithium reagents. This has been developed into a general method of preparing a variety of boronic esters which cannot be obtained via hydroboration. These compounds are now available for extending the versatility of organoboranes.

Experimental Section

General Comments. All glassware was dried at 140 °C for at least 3 h, assembled hot, and cooled under a stream of nitrogen. All reactions were carried out under a static pressure of nitrogen. Anhydrous ethyl ether (Mallinckrodt) was stored over 4-Å molecular sieves under nitrogen and was used without further purification. Tetrahydrofuran was distilled from sodium benzophenone ketal and stored under a nitrogen atmosphere. Technical grade pentane was purified by stirring over concentrated sulfuric acid, treated with solid potassium carbonate, distilled from lithium aluminum hydride, and stored under nitrogen.

The organolithium reagents are commercial materials (Aldrich or Alfa). The concentrations were standardized prior to use,²³ but not purified further. The trialkoxyboranes are available from commercial sources (Aldrich or Callery) or are prepared by the method of Brown and Krishnamurthy.²⁴ The monohalodimethoxyboranes were prepared by redistribution of the trihaloborane (Aldrich) with trimethoxyborane. The anhydrous hydrogen chloride in ether solutions (ca. 3 M) was prepared using

a Brown apparatus from hydrochloric acid and sulfuric acid.²⁵ The ether solution was standardized by titration with base.

The ¹H NMR spectra were recorded on a Varian T-60 (60 MHz) spectrometer, relative to tetramethylsilane. ¹¹B NMR were obtained on a Varian FT-80A spectrometer (25.517 MHz), relative to boron trifluoride etherate. Microanalysis was performed in house.

General Procedure Determining the Selectivity of Methylolithium Alkylations with Various Boron Compounds. To a 50-mL flask fitted with a magnetic stirring bar and adapter was added 10 mL of solvent and 5 mmol of the boron compound. The solution was cooled with a dry ice/acetone bath, and 5 mmol of methylolithium was slowly added dropwise via a syringe. The resulting mixture was stirred an additional 0.5 h, then allowed to warm to room temperature, and stirred 0.5 h further. A sample was removed to detect the presence of lithium tetramethylborate by ¹¹B NMR. The reaction mixture was cooled to 0 °C, and 5 mmol of anhydrous hydrogen chloride in ether was added. After the mixture was stirred 15 min and then warmed to room temperature, a second sample was analyzed by ¹¹B NMR for the various methylated boranes. The percentage of trimethylborane, starting boron compound, and borinic and boronic esters were estimated by using peak height. This procedure appears to give good mass balances, ±5%, for compounds with similar peak widths at half-height. The results are shown in Tables I and II.

General Procedure for the Isolation of Diisopropoxyorganylborane Esters. To a 500-mL flask fitted with a magnetic stirring bar and adapter was added 200 mL of anhydrous ether and 50 mmol (9.40 g, 11.45 mL) of triisopropoxyborane. The solution was cooled in a dry ice/acetone bath. A 50-mmol sample of the organolithium reagent was added slowly via a double-ended needle in 30–45 min, which gave rise to a white solid. The reaction mixture was stirred an additional hour, allowed to warm to room temperature, and then stirred an additional 3 h. The mixture was then cooled to 0 °C, and 53 mmol of anhydrous hydrogen chloride in ether was added by syringe and stirred for 0.5 h. The ether solution was decanted by a double-ended needle from the lithium chloride precipitate and combined with the ether washes of the solid. After the ether was removed by atmospheric distillation, the residual material was distilled at atmospheric or reduced pressure, with only a small amount of pot residue remaining after distillation.

Preparation of Diisopropoxymethylborane. The reaction was conducted as described above by using methylolithium (37.0 mL, 50 mmol). Distillation yielded 6.75 mL of material (71% yield): bp 105–107 °C (751 mmHg); n_D^{20} 1.3751; proton NMR (neat) δ 4.35 (septet, 2 H), 1.1 (d, 12 H), 0.13 (br s, 3 H); boron NMR (neat) +30.2 ppm (s). Anal. Calcd for C₇H₁₇BO₂: C, 58.44; H, 11.91; B, 7.51. Found: C, 58.34; H, 12.17; B, 7.37.

Preparation of Diisopropoxy-*n*-butylborane. Reacting (36.0 mL, 50 mmol) *n*-butyllithium with triisopropoxyborane gave an 85% yield of diisopropoxybutylborane: bp 145–147 °C (746 mmHg); n_D^{20} 1.3930; proton NMR (neat) δ 4.38 (septet, 2 H), 0.8–1.45 (br s, 9 H), 1.15 (d, 12 H); boron NMR (neat) +30.3 ppm (s). Anal. Calcd for C₁₀H₂₃BO₂: C, 64.54; H, 12.46; B, 5.80. Found: C, 64.44; H, 12.60; B, 5.93.

Preparation of Diisopropoxy-sec-butylborane. A 50-mmol (38.0-mL) sample of *sec*-butyllithium was used to prepare 7.90 g (79%), bp 138–140 °C (749 mmHg), of diisopropoxy-sec-butylborane: n_D^{20} 1.3896; proton NMR (neat) δ 4.40 (septet, 2 H), 1.10 (d, 12 H), 0.9 (br m, 9 H); boron NMR (neat) +30.7 ppm (s).

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Anal. Calcd for $C_{10}H_{23}BO_2$: C, 64.54; H, 12.46; B, 5.80. Found: C, 64.55; H, 12.58; B, 5.88.

Preparation of Diisopropoxy-*tert*-butylborane. The reaction was conducted as described in the general procedure, except that 50 mmol (38.5 mL) of *tert*-butyllithium was added to triisopropoxyborane at -98°C in a methanol/liquid nitrogen cold bath. Distillation yielded 6.33 g (68%), bp $136\text{--}138^\circ\text{C}$ (754 mmHg), of the *tert*-butylboronic ester: n_D^{20} 1.3898; proton NMR (neat) δ 4.50 (septet, 2 H), 1.15 (d, 12 H), 0.98 (s, 9 H); boron NMR (neat) +29.5 ppm (s). Anal. Calcd for $C_{10}H_{23}BO_2$: C, 64.54; H, 12.46; B, 5.80. Found: C, 64.63; H, 12.74; B, 5.94.

Preparation of Diisopropoxyphenylborane. The reaction was carried out as described in the general procedure by using 50 mmol (22.8 mL) of phenyllithium. Distillation of the residue, bp $98\text{--}101^\circ\text{C}$ (9 mmHg), gave an 8.85-g (84% overall) yield of the phenylboronic ester: n_D^{20} 1.4630; proton NMR (neat) δ 7.4 (m, 5 H), 4.6 (septet, 2 H), 1.10 (d, 12 H); boron NMR (neat) +27.7 ppm (s). Anal. Calcd for $C_{12}H_{19}BO_2$: C, 69.94; H, 9.29; B, 5.24. Found: C, 69.91; H, 9.31; B, 5.32.

Preparation of Diisopropoxy(dichloromethyl)borane. The procedure according to Rathke²² was used in the preparation of dichloromethylithium and was reacted with 50 mmol of triisopropoxyborane at -98°C . Distillation of the residue, bp $66\text{--}68^\circ\text{C}$ (10 mmHg), gave an 8.91 g (84%) overall yield of the dichloromethylboronic ester: n_D^{20} 1.4180; proton NMR (neat) δ 5.25

(s, 1 H); 4.7 (septet, 2 H), 1.15 (d, 12 H); boron NMR (neat) +23.5 ppm (s). Anal. Calcd for $C_7H_{15}BCl_2O_2$: C, 39.49; H, 7.10; Cl, 33.30; B, 5.08. Found: C, 39.67; H, 7.26; Cl, 33.10; B, 4.90.

Registry No. 2 (R = methyl, R' = methyl), 7318-81-2; 2 (R = methyl, R' = *tert*-butyl), 819-38-5; 2 (R = methyl, R' = ethyl), 86595-26-8; 2 (R = methyl, R' = isopropyl), 86595-27-9; 2 (R = methyl, R' = butyl), 86595-28-0; 2 (R = methyl, R' = *sec*-butyl), 86595-29-1; 2 (R = methyl, R' = isobutyl), 86595-30-4; 2 (R = methyl, R' = phenyl), 51901-79-2; 2 (R = butyl, R' = isopropyl), 86595-32-6; 2 (R = *sec*-butyl, R' = isopropyl), 86595-33-7; 2 (R = *tert*-butyl, R' = isopropyl), 86595-34-8; 2 (R = phenyl, R' = isopropyl), 1692-26-8; 2 (R = dichloromethyl, R' = isopropyl), 62260-99-5; 4 (R = methyl, R' = methyl), 4443-43-0; 4 (R = methyl, R' = ethyl), 86610-16-4; 4 (R = methyl, R' = phenyl), 86595-31-5; 4 (R = *tert*-butyl, R' = isopropyl), 86595-35-9; Me_3B , 593-90-8; $Li(Me_4B)$, 2169-38-2; trichloroborane, 10294-34-5; fluorodimethoxyborane, 367-46-4; chlorodimethoxyborane, 868-81-5; trimethoxyboroxine, 102-24-9; trimethoxyborane, 121-43-7; triethoxyborane, 150-46-9; triisopropoxyborane, 5419-55-6; tributoxyborane, 688-74-4; tri-*sec*-butoxyborane, 22238-17-1; triisobutoxyborane, 13195-76-1; tri-*tert*-butoxyborane, 7397-43-5; tribenzoxymethoxyborane, 1095-03-0; methylithium, 917-54-4; *n*-butyllithium, 109-72-8; *sec*-butyllithium, 598-30-1; *tert*-butyllithium, 594-19-4; phenyllithium, 591-51-5.

Molecular Orbital Study of Bonding, Structure, and Substitution Reactions of Bis(borabenzene)iron

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We carried out nonparametrized molecular orbital calculations on borabenzene anion ($C_6H_6B^-$, designated BBz^-) and on its "sandwich" complexes $(BBz)_2Fe$ and $(BBz)_2Co$. The π electrons in BBz^- are delocalized. The main bonding interactions between the transition-metal atom and the BBz^- ring are similar to those in metallocenes and bis(arene) complexes, namely, π donation from the ring to the metal atom and δ back-donation from the metal atom to the ring. Transition-metal 4p orbitals seem to contribute significantly to the metal-ring bonding. The sequence of the predominantly 3d molecular orbitals in both complexes is the following: $d_\delta(x^2 - y^2, xy) < d_\sigma(z^2) \ll d_\pi(xz, yz)$. Crystallographic studies have shown that transition-metal atom in borabenzene complexes is closer to the *p*-C atom than to the B atom in the ring. This slippage seems to maximize the important π and δ overlaps between metal and ring orbitals and also to minimize summed energy of those occupied molecular orbitals that are significantly delocalized over the metal atom and the rings. The predicted degree of slippage in $(BBz)_2Fe$ agrees well with the observed slippage in two $(BBz)_2Co$ complexes. Although borabenzene orbitals are polarized, the important Fe- BBz overlaps are practically insensitive to rotation of the rings because iron d_π and d_δ orbitals are not tilted. We cannot predict the optimal conformation of $(BBz)_2Fe$ on the basis of overlaps. But comparison of orbital energies in three conformations points at a small preference for the conformation in which the B atoms are trans to each other. This apparent discrepancy between the criteria of maximum overlap and minimum orbital energy indicates that noncovalent intramolecular interactions can affect conformations. Electrophilic substitution at the α -C atoms of the BBz^- ligands appears to be charge controlled. Nucleophilic substitution at the B atoms appears to be frontier controlled and assisted by slippage of the BBz^- rings.

Introduction

Various carbocycles form a myriad of π complexes with transition metals, but few heterocycles form such compounds.¹ Several cyclic molecules or ions containing heteroatoms are isoelectronic with cyclopentadiene anion and benzene, and they also form "half-sandwich" and "sandwich" complexes with metals. One such ligand is the borabenzene (or borine) anion $C_6R_5Br^-$, drawn schemat-

ically in 1. Regardless of the nature of groups R and R', which in our study are H atoms ($C_6H_6B^-$), we will designate this ligand BBz^- . Borabenzene complexes with transition metals have been known for 12 years, and this knowledge has recently been reviewed.²⁻⁴ Among the most studied such complexes are the $(BBz)_2M$ "sandwiches" (shown in

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