A Short Synthesis of Tetraalkoxydiborane(4) Reagents

Natia R. Anastasi, Karen M. Waltz, Wimali L. Weerakoon, and John F. Hartwig*

Contribution from the Department of Chemistry, Yale University, P.O. Box 208107,
New Haven, Connecticut 06520-8107

Received September 26, 2002

The synthesis of a series of bis(catecholato)diborane(4) compounds, $B_2(1,2\text{-}O_2C_6H_4)_2$, $B_2(1,2\text{-}O_2C_6H_3Me\text{-}4)_2$, $B_2(1,2\text{-}O_2C_6H_2Me_2\text{-}3,5)_2$, $B_2[1,2\text{-}O_2C_6H_3Bu^t\text{-}4)]_2$, and $B_2[1,2\text{-}O_2C_6H_2Bu^t{}_2\text{-}3,5]_2$, is reported. The compounds have been synthesized by reaction of 1% sodium/mercury amalgam with the corresponding halocatecholboranes, which are cleanly formed from the reaction of BCl_3 or BBr_3 and catechol. Combining these two steps in one pot, $B_2[1,2\text{-}O_2C_6H_3Bu^t\text{-}4)]_2$ was prepared from BCl_3 and 4-*tert*-butylcatechol, and $B_2[1,2\text{-}O_2C_6H_2Bu^t{}_2\text{-}3,5]_2$ was prepared from 3,5-di-*tert*-butylcatechol and BBr_3 on a multigram scale. Bis(pinacolato)diborane(4) was not formed from reaction of chloropinacolborane and Na/Hg, but it was formed by in situ addition of pinacol to either $B_2[1,2\text{-}O_2C_6H_3Bu^t\text{-}4)]_2$ or $B_2[1,2\text{-}O_2C_6H_2Bu^t{}_2\text{-}3,5]_2$. Cyclic voltammetry indicated that the reduction potentials of the chlorocatecholborane reactant and of the bis(catecholato)diborane(4) product are similar. These similar potentials make selective reduction of haloborane difficult and thus far unique to sodium−mercury amalgam.

Introduction

Diborane reagents of the general formula $B_2(OR)_4$ have been utilized recently as reagents for a series of transition metal-catalyzed reactions. The first example of a reaction employing these reagents was reported in the early 1990s by Miyaura and co-workers, who described the diboration of alkynes catalyzed by $Pt(PPh_3)_4$.[1,2] Metal-catalyzed diboration has since been extended to a useful methodology. The addition of diborane(4) reagents to alkenes,[3,4] dienes,[5] allenes,[6] α,β-unsaturated ketones,[7] imines,[8] diazoalkanes,[9] thiocarbonyls,[10] and vinyl sulfides[10] has been reported. Diborane(4) reagents have also been used by Ishiyama and Miyaura[11] to prepare, from aryl and vinyl halides and triflates, aryl and vinyl boronic esters[12−16] that are useful in palladium-catalyzed Suzuki couplings.[17]

Diborane(4) reagents also have been used to prepare metal−boryl complexes. For example, oxidative addition of the boron−boron bond of bis(pinacolato)diborane(4) to triphenylphosphine-ligated Pt(0) produced $Pt(PPh_3)_2(Bpin)_2$,[18] which is an intermediate in the catalytic diboration of alkynes.[19] Oxidative addition of the boron−boron bond to many other metal centers has been reported both before[20] and after[21−25] the isolation of this platinum bis-boryl complex. Reaction of a diborane(4) reagent with a metal carborane cluster formed an unusual dimeric boron cage.[26]

Recently our group has used diborane(4) compounds as reagents for the catalytic borylation of low molecular weight and polymeric hydrocarbons under both photochemical[27] and thermal conditions to form terminal alkylboronates.[28,29] In collaboration with Ishiyama and Miyaura, we have also reported room-temperature

---

[1] Ishiyama, T.; Matsuda, N.; Miyaura, N.; Suzuki, A. *J. Am. Chem. Soc.* **1993**, *115*, 11018.

[2] Ishiyama, T.; Matsuda, N.; Murata, M.; Ozawa, F.; Suzuki, A.; Miyaura, N. *Organometallics* **1996**, *15*, 713.

[3] Ishiyama, T.; Yamamoto, M.; Miyaura, N. *Chem. Commun.* **1997**, *1997*, 689.

[4] Iverson, C. N.; Smith, M. R., III *Organometallics* **1997**, *16*, 2757.

[5] Ishiyama, T.; Yamamoto, M.; Miyaura, N. *Chem. Commun.* **1996**, *1996*, 2073.

[6] Ishiyama, T.; Kitano, T.; Miyaura, N. *Tetrahedron Lett.* **1998**, *39*, 2357.

[7] Lawson, Y. G.; Lesley, M. J. G.; Norman, N. C.; Rice, C. R.; Marder, T. B. *Chem. Commun.* **1997**, *21*, 2051.

[8] Mann, G.; John, K. D.; Baker, R. T. *Org. Lett.* **2000**, *2*, 2105.

[9] Abu Ali, H.; Goldberg, I.; Kaufmann, D.; Burmeister, C.; Srebnik, M. *Organometallics* **2002**, *21*, 1870.

[10] Carter, C. A. G.; Vogels, C. M.; Harrison, D. J.; Gagnon, M. K. J.; Norman, D. W.; Langler, R. F.; Baker, R. T.; Westcott, S. A. *Organometallics* **2001**, *20*, 2130.

[11] Ishiyama, T.; Murata, M.; Miyaura, N. *J. Org. Chem.* **1995**, *60*, 7508.

[12] Weil, T.; Wiesler, U. M.; Herrman, A.; Bauer, R.; Hofkens, J.; De Schryver, F. C.; Mullen, K. *J. Am. Chem. Soc.* **2001**, *123*, 8101.

[13] Yu, S.; Saenz, J.; Srirangam, J. K. *J. Org. Chem.* **2002**, *67*, 1699.

[14] Lin, S.; Danishefsky, S. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 1967.

[15] Fuerstner, A.; Seidel, G. *Org. Lett.* **2002**, *4*, 541.

[16] Takagi, J.; Takahashi, K.; Ishiyama, T.; Miyaura, N. *J. Am. Chem. Soc.* **2002**, *124*, 8001.

[17] Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.

[18] Iverson, N.; Smith, M. R., III *J. Am. Chem. Soc.* **1995**, *117*, 4403−4404.

[19] Iverson, C. N.; Smith, M. R., III *Organometallics* **1996**, *15*, 5155−5165.

[20] Nguyen, P.; Lesley, G.; Taylor, N. J.; Marder, T. B.; Pickett, N. L.; Clegg, W.; Elsewood, M. R. J.; Norman, N. C. *Inorg. Chem.* **1994**, *33*, 4623.

[21] He, X.; Hartwig, J. F. *Organometallics* **1996**, *15*, 400.

[22] Hartwig, J. F.; He, X. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 315.

[23] Lesley, G.; Nguyen, P.; Taylor, N. J.; Marder, T. B.; Scott, A. J.; Clegg, W.; Norman, N. C. *Organometallics* **1996**, *15*, 5137.

[24] Dai, C.; Stringer, G.; Marder, T. B.; Baker, R. T.; Scott, A. J.; Clegg, W.; Norman, N. C. *Catal. Today* **1996**, *27*, 285.

[25] Rickard, C. E. F.; Roper, W. R.; Williamson, A.; Wright, L. J. *Organometallics* **2000**, *19*, 4344.

[26] Curtis, M. A.; Mueller.; Beez, V.; Pritzkow, H.; Siebert, W.; Grimes, R. N. *Inorg. Chem.* **1997**, *36*, 3602.

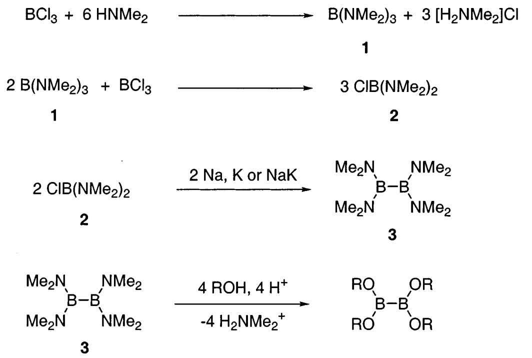
[27] Chen, H.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 3391.

[28] Chen, H.; Schlecht, S.; Semple, T. C.; Hartwig, J. F. *Science* **2000**, *287*, 1995.

[29] Kondo, Y.; Garcia-Cuadrado, D.; Hartwig, J. F.; Boaen, N. K.; Wagner, N. L.; Hillmayer, M. A. *J. Am. Chem. Soc.* **2002**, *124*, 1164.

10.1021/om0208016 CCC: $25.00
Publication on Web 12/20/2002

Scheme 1



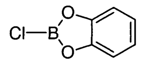
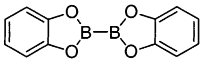
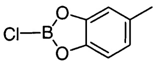
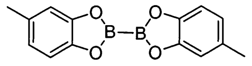
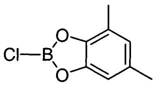
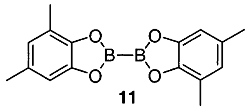
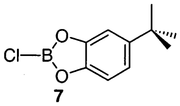
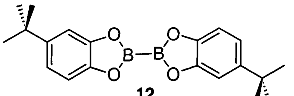
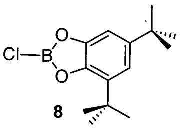
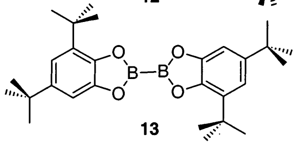
borylations of arenes catalyzed by iridium complexes.[30−32] Borylation of benzylic C−H bonds with bis(pinacolato)diborane(4) has also been reported.[33]

The current synthesis of bis(pinacolato) (B_2pin_2) or bis(catecholato) diborane(4) (B_2cat_2) reagents is multistep.[34] Some diborane(4) reagents are now commercially available, but the cost is high. The most commonly used synthetic route to diborane(4) compounds is shown in Scheme 1 and follows work from the 1960s reported by Brotherton.[35,36] Marder optimized this route,[20,37] and Srebnik and co-workers described some modifications.[38] In this synthetic scheme, boron trichloride is allowed to react with dimethylamine or pyrrolidine to form the corresponding tris(dialkylamino)borane, **1**. After this compound is isolated, reaction with 0.5 equiv of boron trichloride produces **2**, which is subsequently coupled in the presence of sodium, potassium, or sodium/potassium alloy to form tetrakis(dimethylamino)diborane(4), **3**. The desired alkoxydiborane(4) reagents are then generated by reaction of **3** with an alcohol, a diol, or a catechol under acidic conditions. The synthesis requires careful purification of all intermediates, and the overall yield is around 30%.

Although the reduction of chlorocatecholboranes by sodium or potassium in refluxing xylenes in the presence of triethylamine has been reported in the patent literature,[39] no subsequent publications citing this procedure have been reported. We have been unable to obtain acceptable yields by this method.

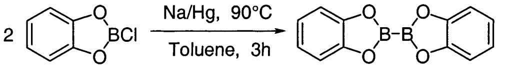
Instead, we report the convenient synthesis of a series of bis(catecholato)diborane(4) reagents from the homocoupling of halocatecholboranes in the presence of sodium/mercury amalgam. This conversion allows for a convenient, large-scale, one-pot synthesis of $B_2cat^*_2$ (cat* = 4-methylcatecholate, 4-*tert*-butylcatecholate, 3,5-dimethylcatecholate, or 3,5-di-*tert*-butylcatecholate) from BX_3 (X = Cl, Br) and the appropriate catechol. Although B_2pin_2 (pin = pinacolate) did not form by the direct reduction of the corresponding chloroborane, it was formed by reaction of pinacol with $B_2cat^*_2$.

Table 1. Reduction of Chlorocatecholboranes to Diborane(4) Compounds

Starting Material	Product	Yield
 **4**	 **9**	42%
 **5**	 **10**	52%
 **6**	 **11**	57%
 **7**	 **12**	96%
 **8**	 **13**	85%

Results and Discussion

In an attempt to synthesize a metal−boryl complex by Na/Hg reduction of a transition metal chloride and chlorocatecholborane (ClBcat), we observed that Na/Hg cleanly converted ClBcat to bis(catecholato)diborane(4) (B_2cat_2, eq 1). Considering the potential of this reaction as a convenient synthesis of diborane(4) compounds, we explored its scope with a series of substituted chlorocatecholboranes. The isolated yields from the coupling reactions are summarized in Table 1. The results in Table 1 indicate that the yields of the diborane(4) products depend on their solubility. When the catecholate group bears *tert*-butyl substituents, the diborane(4) reagents were produced in high yields.



(1)

In a typical coupling reaction, a toluene solution of chlorocatecholborane was added to a vial containing 2.5 equiv of 1% sodium mercury amalgam. The reaction mixture was heated at 90 °C with vigorous stirring for 3 h. After this time, the mercury layer was allowed to settle, and the toluene solution was decanted. The solution was then carefully filtered through a plug of Celite. In most cases, product was obtained simply by evaporation of the solvent. Recrystallization from toluene/pentane removed small amounts of impurities that possess three B−O bonds at boron, as determined by their resonance at δ 22 in the ^{11}B NMR spectrum,[40] and that were present after some preparations. The sodium/mercury amalgam was regenerated by filtering the used

---

(30) Ishiyama, T.; Takagi, J.; Ishida, K.; Miyaura, N.; Anastasi, N. R.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 390.

(31) Ishiyama, T.; Takagi, J.; Hartwig, J. F.; Miyaura, N. *Angew. Chem., Int. Ed.* **2002**, *41*, 3056.

(32) Takagi, J.; Sato, K.; Hartwig, J. F.; Ishiyama, T.; Miyaura, N. *Tetrahedron Lett.* **2002**, *43*, 5649.

(33) Ishiyama, T.; Ishida, K.; Takagi, J.; Miyaura, N. *Chem. Lett.* **2001**, 1082.

(34) Ishiyama, T.; Murata, M.; Ahiko, T.-A.; Miyaura, N. *Org. Synth.* **2000**, *77*, 176.

(35) Brotherton, R. J.; McCloskey, A. L.; Petterson, L. L.; Steinberg, H. *J. Am. Chem. Soc.* **1960**, *82*, 6242.

(36) Brotherton, R. J.; McCloskey, A. L.; Boone, J. L.; Manasevit, H. M. *J. Am. Chem. Soc.* **1960**, *82*, 6245.

(37) Clegg, W.; Elsegood, M. R. J.; Lawlor, F. J.; Norman, N. C.; Pickett, N. L.; Robins, E. G.; Scott, A. J.; Nguyen, P.; Taylor, N. J.; Marder, T. B. *Inorg. Chem.* **1998**, *37*, 5289.

(38) Abu Ali, H.; Goldberg, I.; Srebnik, M. *Eur. J. Inorg. Chem.* **2002**, *1*, 73.

(39) Brotherton, R. J.; Fullerton; Woods, W. G. U.S. patent 3,009,-941, 1960; *Chem. Abstr.* **1960**, *55*, 18011.

mercury and adding the appropriate amount of sodium metal to the mercury layer.[41]

Unsubstituted chlorocatecholborane is commercially available, but the other halocatecholboranes are not. Nonetheless, halocatecholboranes are generated easily by the reaction of boron trichloride or boron tribromide with the corresponding catechol. In fact, simple evaporation of the solvent and HX (X = Cl or Br) product from the reaction between a catechol and BX_3, dilution with toluene, and addition of the sodium/mercury amalgam produced the desired diborane(4) compounds in yields similar to those of the reactions of isolated haloboranes. By this procedure we prepared bis(4-*tert*-butylcatecholato)diborane(4) (**12**) on a 7-g scale in one pot with a yield of 72% from BCl_3 and 4-*tert*-butylcatechol. Similarly, the one-pot synthesis of bis(3,5-di-*tert*-butylcatecholato)diborane(4) (**13**) starting from boron tribromide and 3,5-di-*tert*-butylcatechol gave the desired product in 83% yield.

To determine if other reducing reagents would similarly induce the coupling of chloroboranes, we allowed 4-*tert*-butyl chlorocatecholborane to react with metallic Na, K, Mg, Zn dust, metallic Na in conjunction with Pd/C, sodium naphthalide, sodium anthracenide, sodium benzophenone ketyl, magnesium anthracenide, potassium on graphite, potassium on alumina, and commercially available 20% sodium mercury amalgam. In no case did these reagents give the desired product. No reaction or decomposition of the chlorocatecholborane to compounds with ^{11}B NMR chemical shifts near δ 22 was detected.

Attempts to reproduce the patented[39] reduction of ClBcat with the combination of triethylamine and alkali metal reductant in refluxing xylenes resulted in similar decomposition products. Less than 10% of the diborane(4) compound was observed by ^1H NMR spectroscopy, and large amounts of decomposition products resonating at δ 22 in the ^{11}B NMR spectrum were observed. We were perplexed by this exclusive selectivity for reduction of the haloborane by 1% Na/Hg. Other reducing agents with reduction potential similar to Na/Hg, such as sodium anthracenide, resulted solely in these products with resonances near δ 22.[41]

Cyclic voltammetry demonstrated that the reduction potentials for the starting material of the product are similar. Figure 1 shows voltammograms of solutions containing 2.0 mM substrate and 0.1 M tetrabutylammonium hexafluorophosphate in methylene chloride. The reduction of both compounds is irreversible. This irreversible reduction of B_2cat_2 explains the difficulty in preparing B_2cat_2 by reduction of ClBcat. The lower potential at which B_2cat_2 is reduced, coupled with the irreversibility of this reduction, shows that the synthesis of B_2cat_2 relies on kinetic phenomena.

The scope of the borane that underwent coupling by Na/Hg was also evaluated. Chlorothiocatecholboranes and BrBBN did not form diborane(4) compounds in measurable yield from reduction with Na/Hg. Extended heating of BrBBN under the coupling conditions led predominantly to products containing a bridging oxygen, as judged by ^{11}B NMR spectroscopy.[40] Chloropinacolborane quickly formed products resonating at δ 22 in the ^{11}B NMR spectrum.

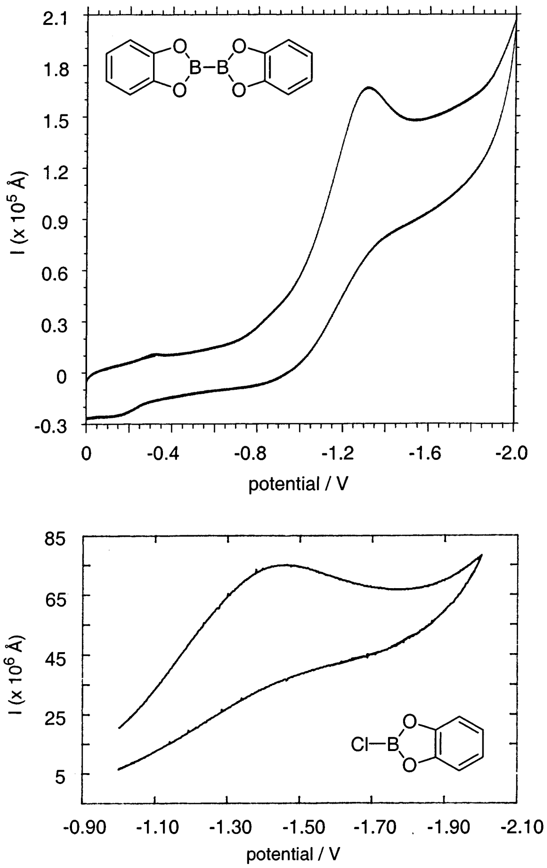


Figure 1. Cyclic voltamogram of bis(catecholato)diborane(4) (**9**) (top) and chlorocatecholborane (**4**) (bottom).

We were particularly interested in finding an alternative route to bis(pinacolato)diborane(4) (B_2pin_2) because it is often used in metal-catalyzed reactions. B_2pin_2 is the most effective reagent for the formation of arylboronic esters from aryl halides and for the borylation of hydrocarbons. Exchange of pinacol for catechol at three-coordinate boron has been reported.[43,44] Thus, we used a standard exchange process to access this material. Formation of di-*tert*-butylcatecholate **12** in one pot from BCl_3 and 4-*tert*-butylcatechol and addition of 2 equiv of pinacol, followed by stirring at room temperature for 1 h, gave complete conversion of **12** to B_2pin_2 by ^1H NMR spectroscopy.

Separation of the desired bis(pinacolato)diborane(4) from the free 4-*tert*-butylcatechol side product was not straightforward, but was accomplished by addition of a particular base to the final solution to deprotonate the catechol or by column chromatography. Unfortunately, crystallization and sublimation generated mixtures of the two compounds. Attempts to convert the catechol to a catecholate salt with most bases or to an acetal by

---

(40) Nöth, H.; Wrackmeyer, B. In *NMR Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: New York, 1978; Vol. 14, p 271.

(41) Since the beginning of these studies where we have used this method of recycling mercury, we have been using the same bottle of mercury, without substantial loss of mass.

(42) (a) Steckan, E. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 683. (b) *Lange's Handbook of Chemistry*, 13th ed.; McGraw-Hill: New York, 1985.

(43) Hoffmann, R. W.; Ditrich, K.; Froch, S. *Liebigs Ann. Chem.* **1987**, *1987*, 977.

(44) (a) Ohmura, T.; Yamamoto, Y.; Miyaura, N. *J. Am. Chem. Soc.* **2000**, *122*, 4990. (b) Feng, Z.; Hellberg, M. *Tetrahedron Lett.* **2000**, *41*, 5813.

addition of acetone with or without acid led to decomposition of the bis(pinacolato)diborane(4). However, addition of 2 equiv of $LiNMe_2$ to an ether solution of the mixture at low temperature, quick evaporation of solvent, extraction of the white solid with pentane, and crystallization after concentration of the pentane solution gave pure B_2pin_2 in 32% yield, relative to the free catechol, for the one-pot synthesis of B_2pin_2 starting with BBr_3 and 4-*tert*-butylcatechol. Elution of the mixture of B_2pin_2 and catechol through an alumina column with diethyl ether also gave pure B_2pin_2 in a slightly higher 46% overall yield for the same one-pot method.

Preparation of the desired B_2pin_2 from the exchange of pinacol for bis(3,5-di-*tert*-butylcatecholato)diborane(4) **13** was also attempted to exploit differences in solubility. Diborane(4) **13** was synthesized in one pot starting with BCl_3 and the appropriate catechol. After addition of the catechol to the resulting diborane(4) compound, cooling of the mixture containing B_2pin_2 and 3,5-di-*tert*-butylcatechol at −35 °C precipitated the diborane(4) compound in 23% yield. The yield for this process was lower than for generation of B_2pin_2 from **12** because the exchange of pinacol for the substituted catechol occurred in lower yield with the more hindered diborane(4) **13**.

Summary

We have discovered a convenient method to prepare bis(catecholato)diborane(4) compounds and a method to convert these products to analogous bis(pinacolato)-diborane(4) compounds, both of which are useful materials for a variety of organometallic processes. The new method for preparation of these materials on a multigram scale is shorter than the previous method, which required several steps and produced the product in modest overall yield.

Experimental Section

Unless otherwise noted, all manipulations were performed in an inert atmosphere glovebox or by using standard Schlenk techniques. ^1H NMR spectra were recorded at 300, 400, or 500 MHz. Proton chemical shifts are reported in ppm relative to residual protiated solvent as internal standard. ^{13}C NMR spectra were recorded at 100.58 or 125.75 MHz. ^{11}B NMR spectra were recorded at 96.38 MHz. ^{11}B chemical shifts are reported in parts per million relative to $BF_3{\cdot}Et_2O$ as external standard. Resonances downfield of the standard are assigned positive chemical shifts. Cyclic voltammetry was performed with a $Ag/AgNO_3$ reference electrode in conjunction with a carbon working electrode and a platinum counter electrode. The measurements were made on 2.0 mM solutions of chlorocatecholborane or bis(catecholato)diborane(4) in a 0.1 M solution of tetrabutylammonium hexafluorophosphate in dichloromethane at a scan rate of 100 mV/s. Dichloromethane solvent was distilled from calcium hydride. Toluene solvent was distilled from sodium/benzophenone ketyl. 4-Methylchlorocatecholborane,[45] 3,5-dimethylchlorocatecholborane,[46] 4-*tert*-butyl chlorocatecholborane,[21] 3,5-di-*tert*-butyl chlorocatecholborane,[21] and chloropinacolborane[47] were prepared according to literature procedures. All other chemicals were used as received by commercial suppliers.

General Procedure for the Formation of Bis(catecholato)diborane(4) Compounds. Bis(4-di-*tert*-butylcatecholato)diborane(4) (12): 4-*tert*-Butyl chlorocatecholborane (107 mg, 0.508 mmol) was dissolved in toluene (1 mL) and transferred to a vial containing 1% Na/Hg amalgam (2.5 equiv of Na). The mixture was heated at 90 °C under nitrogen for 3 h with vigorous stirring. The progress of the reaction was monitored by ^{11}B NMR spectroscopy. The suspension was allowed to settle after complete conversion of the chloroborane. The solution was removed by pipet from the amalgam and filtered through Celite. Evaporation of solvent gave 96% yield (75.4 mg) of **12**. ^1H NMR (C_6D_6) δ 1.17 (s, 18H), 6.95 (d, $J = 8.4$ Hz, 2H), 7.08 (d, $J = 8.4$ Hz, 2H), 7.30 (s, 2H); ^{13}C NMR (C_6D_6) δ 32.09, 35.15, 110.90, 112.61, 120.73, 146.46, 146.69, 147.43; ^{11}B NMR (C_6D_6) δ 31.8.

Bis(catecholato)diborane(4) (9):[48] Chlorocatecholborane (102 mg, 0.662 mmol) was coupled by the general procedure to produce **9**. ^{11}B NMR showed the presence of decomposition products with three oxygen atoms on the boron in approximately 10% yield. Partial evaporation of solvent and layering of the concentrated solution with pentane gave B_2cat_2 (33.6 mg, 42% yield) that was judged to be pure by NMR spectroscopy. ^1H NMR (C_6D_6) δ 6.80 (q, $J = 3.0$ Hz), 7.06 (q, $J = 3.0$ Hz); ^{13}C NMR (THF-d_8) δ 113.03, 123.57, 148.42; ^{11}B NMR (C_6D_6) δ 31.9.

Bis(4-methylcatecholato)diborane(4) (10):[48] 4-Methylchlorocatecholborane (104 mg, 0.619 mmol) was coupled by the general procedure to produce 43.2 mg of **10** (52% yield). ^1H NMR (C_6D_6) δ 2.05 (s, 6H), 6.62 (d, $J = 8.1$ Hz, 2H), 6.94 (s, 2H), 6.99 (d, $J = 8.1$ Hz, 2H); ^{13}C NMR (C_6D_6) δ 9.81, 111.08, 112.34, 122.58, 131.88, 144.86, 146.99; ^{11}B NMR (C_6D_6) δ 31.6.

Bis(3,5-dimethylcatecholato)diborane(4) (11): 3,5-Dimethylchlorocatecholborane (122 mg, 0.669 mmol) was coupled as described in the general procedure to produce **11**. Approximately 5% of μ-O[B($O_2C_6H_2$-3,5-Me_2)]$_2$ was observed by ^{11}B NMR spectroscopy. Recrystallization by layering a concentrated toluene solution with pentane and cooling at −35° C afforded analytically pure **11** (56.0 mg, 57% yield). ^1H NMR (C_6D_6) δ 2.09 (s, 6H), 2.25 (s, 6H), 6.52 (s, 2H), 6.87 (s, 2H); ^{13}C NMR (C_6D_6) δ 15.00, 21.57, 111.03, 122.87, 125.55, 133.20, 144.57, 147.61; ^{11}B NMR δ 31.4. Anal. Calcd for $C_{16}H_{16}B_2O_4$: C, 65.38; H, 5.49. Found: C, 65.69; H, 5.52.

Bis(3,5-di-*tert*-butylcatecholato)diborane(4) (13):[20] 3,5-Di−*tert*-butylchlorocatechol−borane (133 mg, 0.499 mmol) was coupled by the general procedure to produce 98.2 mg (0.212 mmol) of **13**. ^1H NMR (C_6D_6) δ 1.35 (s, 18H), 1.50 (s, 18H), 7.13 (d, $J = 1.8$ Hz, 2H), 7.28 (d, $J = 1.8$ Hz, 2H); ^{13}C NMR (C_6D_6) δ 30.37, 32.25, 35.04, 35.44, 108,89, 117.44, 136.04, 144.51, 147.02, 149.01; ^{11}B NMR (C_6D_6) δ 32 (v br).

Small-Scale, One-Pot Synthesis of 9 Starting from BBr_3 and Catechol. Catechol (220 mg, 1.99 mmol) was suspended in toluene (8 mL), and the suspension was cooled to 0 °C. BBr_3 (200 μL, 2.12 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature, and the solvent was evaporated to dryness. The purity of the bromocatecholborane was checked by ^{11}B NMR spectroscopy. The compound was then dissolved in toluene, and, following the general procedure above, coupling of the resulting bromocatecholborane produced biscatecholatodiborane(4) in 38% isolated yield.

Small-Scale, One-Pot Synthesis of 12 from BBr_3 and 4-*tert*-Butylcatechol. Following the procedure described for **9**, 4-*tert*-butylcatechol (230 mg, 1.30 mmol) was allowed to react with BBr_3 (140 μL, 1.51 mmol) to produce BrBcat*, which

---

(45) Schulz, H.; Gabbert, G.; Pritzkow, H.; Sieber, W. *Chem. Ber.* **1993**, *126*, 1593.

(46) Waltz, K. M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2000**, *122*, 11358.

(47) Herberich, G. E.; Fischer, A. *Organometallics* **1996**, *15*, 58.

(48) Lawlor, F. J.; Norman, N. C.; Pickett, N. L.; Robins, E. G.; Nguyen, P.; Lesley, G.; Marder, T. B.; Asmore, J. A.; Green, J. C. *Inorg. Chem.* **1998**, *37*, 5282.

was subsequently coupled in the presence of sodium/mercury amalgam to produce 227 mg (87%) of **12**.

Large-Scale, One-Pot Synthesis of 12 from BCl_3 and 4-*tert*-Butylcatechol. 4-*tert*-Butylcatechol (8.95 g, 0.0505 mol) was dissolved in toluene (50 mL) and transferred to a Schlenk flask. The solution was cooled to 0 °C and a solution of BCl_3 in heptane (81 mL of a 1.0 M solution) was added dropwise. Strong evolution of HCl gas was observed immediately. The volume of the solution was reduced to approximately half, and Na/Hg was added (Na 3.10 g, 0.135 mol, 22.6 mL, 1.53 mol of Hg). The reaction mixture was heated at 90 °C and stirred with a mechanical stirrer for 5 h. The flask was brought inside a drybox where the solution was decanted from the amalgam layer. Filtration through Celite and evaporation of toluene gave 6.11 g (72.5%) of **12** that was judged pure by NMR spectroscopy.

Large-Scale, One-Pot Synthesis of 13 from BBr_3 and 3,5-Di-*tert*-butyl chlorocatecholborane. 3,5-Di-*tert*-butyl chlorocatechol (5.01 g, 0.0224 mol) was loaded into a two-neck flask. Freshly distilled toluene (35 mL) was added under a constant stream of nitrogen gas. The solution was cooled to 0 °C. BBr_3 (3.4 mL, 0.036 mol) was then added dropwise to the cooled solution. The reaction mixture was allowed to stir at 0 °C for 0.5 h and then allowed to warm to room temperature. The solvent was then evaporated, and the reaction mixture was checked by ^{11}B NMR spectroscopy to verify the complete evaporation of the excess BBr_3 and assess the purity of the bromocatecholborane produced. Na/Hg (Na 1.26 g, 0.055 mol; Hg 9.2 mL, 0.62 mol) was added, and the reaction mixture was heated at 90 °C and stirred vigorously with a mechanical stirrer for 5 h. The solution was subsequently filtered through a bed of Celite. Evaporation of toluene gave a white solid. ^1H and ^{11}B NMR spectroscopy showed this material to contain impurities with three oxygens on the boron atom in approximately 5% yield. Recrystallization from toluene/pentane at −35 °C generated 3.19 g (83%) of pure **13**.

Synthesis of B_2pin_2 from 4-*tert*-Butylcatechol, Boron Trichloride, and Pinacol. Boron trichloride (47 mL of a 1.0 M solution in heptane) was loaded into a 250-mL Schlenk flask, and the solution was cooled to 0 °C. 4-*tert*-Butylcatechol (4.02 g, 0.023 mol) was dissolved in pentane (40 mL), and the solution was added to the boron trichloride. The reaction mixture was stirred at 0 °C for 0.5 h, and was then slowly allowed to warm to room temperature. The reaction mixture was then stirred at room temperature for an additional 1 h. The solvent was evaporated under vacuum, and the flask was brought inside the glovebox. Toluene (60 mL) was added to the flask, along with previously made Na/Hg (2.5 equiv of Na, Na 2.02 g, 0.088 mol; Hg 14.5 mL, 0.99 mol), and the reaction mixture was heated at 90 °C for 6 h with vigorous stirring. The solution was filtered through Celite, and pinacol (545 mg, 4.62 mmol) was added to the filtrate. The resulting solution was stirred at room temperature for 1 h. The solvent was evaporated, and diethyl ether (5 mL) was added. The solution was cooled at 0 °C, and a suspension of $LiNMe_2$ (240 mg, 4.62 mmol) in 50 mL of diethyl ether was added slowly. The solvent was subsequently evaporated, and the white residue was extracted with pentane (50−60 mL). Concentration of the solution and crystallization at −35 °C afforded B_2pin_2 (187 mg, 32% yield) that was judged pure by NMR spectroscopy and matched the spectra of commercial material.[49] Alternatively, elution of the mixture of B_2pin_2 and 4-*tert*-butylcatechol through a short column of neutral alumina (Brockman activity I) afforded clean B_2pin_2 that was collected in the first few fractions in yields up to 46%. ^1H NMR (C_6D_6) δ 1.01 (s); ^{13}C NMR (C_6D_6) δ 23.63, 81.62.

One Pot-Synthesis of B_2pin_2 from BCl_3 and 3,5-Di-*tert*-butylcatechol. Boron trichloride (4 mL of a 1.0 M solution) in heptane (5 mL) was loaded into a 100-mL Schlenk flask, and the solution was cooled to 0 °C. 3,5-Di-*tert*-butylcatechol (3.54 g, 0.016 mol) was dissolved in pentane (40 mL), and this solution was added slowly by syringe to the solution of boron trichloride. The reaction mixture was stirred at 0 °C for 0.5 h. After this time, it was allowed to warm to room temperature and was stirred at room temperature for an additional 1 h. The solvent was evaporated, and the flask was brought inside a glovebox. Toluene (60 mL) was added to the flask, along with previously made Na/Hg (2.5 equiv of Na, Na 0.91 g, 0.040 mol; Hg 6.5 mL, 0.45 mol), and the reaction mixture was heated at 90 °C for 6 h with vigorous stirring. The solution was filtered through Celite, and pinacol (545 mg, 4.62 mmol) was added to the filtrate. The solution was stirred at room temperature for 1 h. The solvent volume was reduced to less than 3 mL, and the concentrated solution was layered with pentane and cooled at −35 °C. Pure B_2pin_2 was obtained in 23% yield (93.7 mg, 0.037 mmol).

Acknowledgment. We thank the NSF (CHE-9986236) for support of this work. We also thank Prof. Albert J. Fry for help with cyclic voltammetry and Prof. John Ellis for useful discussions on reduction potentials.

OM0208016

---

[49] This compound is currently commercially available from 10 different sources.