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Synthesis of Mono- and Dihalogenated Derivatives of $(Me_2S)_2B_{12}H_{10}$ and Palladium-Catalyzed Boron–Carbon Cross-Coupling Reactions of the Iodides with Grignard Reagents

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Two series of compounds, 9-X-1,7-$(Me_2S)_2B_{12}H_9$ and 9,10-X_2-1,7-$(Me_2S)_2B_{12}H_8$ (X = Cl, Br, I), have been synthesized from reactions of 1,7-$(Me_2S)_2B_{12}H_{10}$ with various halogenating reagents. In addition, reactions of 1,7-$(Me_2S)_2B_{12}H_{10}$ with 2,4-$(NO_2)_2C_6H_3SCl$ and PhSeBr resulted in 9-(2′,4′-$(NO_2)_2C_6H_3S$)-1,7-$(Me_2S)_2B_{12}H_9$ and 9,10-$(PhSe)_2$-1,7-$(Me_2S)_2B_{12}H_8$, respectively. X-ray studies of the dibromo, monoiodo, and aryl thioether derivatives show that electrophilic substitution in 1,7-$(Me_2S)_2B_{12}H_{10}$ takes place at positions 9 and 10, as in the case of the *meta*-carborane 1,7-$C_2B_{10}H_{12}$. From 1,12-$(Me_2S)_2B_{12}H_{10}$ the halides 2-X-1,12-$(Me_2S)_2B_{12}H_9$ (X = Br, I) were prepared. For both 1,7- and 1,12-$(Me_2S)_2B_{12}H_{10}$ the best iodination results were obtained using iodine monochloride in refluxing acetonitrile. In the presence of 5 mol % $(PPh_3)_2PdCl_2$ the iodides 9-I-1,7-$(Me_2S)_2B_{12}H_9$, 2-I-1,12-$(Me_2S)_2B_{12}H_9$, and 9,10-I_2-1,7-$(Me_2S)_2B_{12}H_8$ react with RMgX (R = Me, Ph, Bn; X = Cl, Br) in THF to yield the corresponding *B*-alkyl- and *B*-aryl-substituted products in good yields without using CuI as a cocatalyst. The bromo derivative 9-Br-1,7-$(Me_2S)_2B_{12}H_9$ did not react under similar conditions. No interference from the nearby Me_2S substituent was observed in palladium-catalyzed substitution of iodide in 2-I-1,12-$(Me_2S)_2B_{12}H_9$. Presumably due to the intramolecular activation of an aryl C–H bond of the benzyl substituent in the inermediate palladium complex, the yield of 9,10-Bn_2-1,7-$(Me_2S)_2B_{12}H_8$ was significantly lower than those of the dimethyl and diphenyl derivatives. The molecular structures of 9-R-1,7-$(Me_2S)_2B_{12}H_9$ (R = Ph, Bn) and 2-Bn-1,12-$(Me_2S)_2B_{12}H_9$ were obtained by single-crystal X-ray analysis.

Introduction

Construction of carbon−carbon bonds via the palladium-catalyzed cross-coupling reactions of organic halides and triflates with organometallic reagents, in particular using Suzuki and Stille protocols, has become a routine synthetic tool of modern organic synthesis.[1] On the other hand, examples of substitution in carborane and borane clusters based on similar boron−carbon cross-coupling reactions are still scarce. Zakharkin and co-workers[2] were the first to apply this methodology to iodocarboranes in 1982. It was further developed by Jones[3] and Hawthorne.[4] Most recently Vinas et al.[5a] and Eriksson et al.[5b] reported on the substitution of iodine in 3-I-1,2-$C_2B_{10}H_{11}$ and 2-I-1,12-$C_2B_{10}H_{11}$, respectively, by various aryl groups. Palladium-catalyzed substitution has been also extended to monocarborane derivatives $[12\text{-}ICB_{11}H_{11}]^-$ and $[1\text{-R-}12\text{-}ICB_{11}H_{10}]^-$ (R = Me, Ph).[6] In the $[B_{12}H_{12}]^{2-}$ series Grüner and co-workers[7] successfully used $[(Bn_2NH)B_{12}H_{10}I]^-$ as a cross-coupling substrate, while

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Hawthorne and co-workers[8] replaced the iodine in $[B_{12}H_{11}I]^{2-}$ with methyl, *n*-octadecyl, and phenyl groups.

We are interested in the application of this methodology to halogenated derivatives of 1,2-, 1,7-, and 1,12-$(Me_2S)_2$-$B_{12}H_{10}$ (**1**−**3**).[9] In this paper we describe their synthesis and characterization as well as reactions of iodides with Grignard reagents leading to *B*-alkyl and -aryl derivatives that are difficult to obtain by other methods. While among the isomers of carborane 1,2-$C_2B_{10}H_{12}$ is the easiest and 1,12-$C_2B_{10}H_{12}$ is the most difficult isomer to prepare, in the $(Me_2S)_2B_{12}H_{10}$ series it is the 1,2-isomer that can only be obtained in very small quantities.[9b] For this reason halogenation of **2** and **3**, received most of our attention. Nevertheless, some preliminary information on the bromination and iodination of **1** was also obtained.

Results and Discussion

Bromination.[10] The distribution of charges among the boron atoms of **1**−**3** and, therefore, their behavior toward electrophilic substitution is expected to be similar to that of 1,2-, 1,7-, and 1,12-$C_2B_{10}H_{12}$ due to their similarities in structure and polarization of the *ipso*-boron atoms by formally positively charged sulfur atoms. To test the validity of this analogy we attempted the preparation, isolation, and characterization of mono- and dibrominated derivatives of **1**−**3**. Unlike the bromination of 1,7-$C_2B_{10}H_{12}$, which requires $AlCl_3$ as a catalyst,[11a] mono- and dibromination of **2** by Br_2 in CH_2Cl_2 take place at room temperature without $AlCl_3$. The ^{11}B NMR spectrum of the monobrominated product contains 8 signals. The two most downfield signals of intensities 1 and 2 are singlets. The ^{1}H NMR spectrum of the product (500 MHz, CD_3CN) revealed only one signal at 2.51 ppm suggesting that substitution occurred at either position 9(10) or 2(3). In CD_2Cl_2, the splitting of the methyl signal into a set of two closely spaced resonances is observed, in agreement with the expected diastereotopicity of two methyl groups attached to the same sulfur atom in either 9(10)- or 2(3)-brominated product. ^{11}B−^{11}B{^{1}H} COSY did not provide a definite answer due to some overlap of the singlets. A good quality crystal for X-ray diffraction study could not be obtained. However, addition of 2 equiv of bromine to a solution of **2** in dichloromethane produced mostly dibrominated product, although it required more time for completion. The ^{11}B NMR spectrum of the product displayed a high-symmetry 2:2:2:4:2 pattern. This is consistent with bromination of boron verticies related by a plane of symmetry, namely either 9 and 10 or 2 and 3. The X-ray structure of 9,10-Br_2-1,7-$(Me_2S)_2B_{12}H_8$ (**5**) (Figure 1, Table 1) revealed that substitution indeed occurred at positions 9 and 10, similar to the bromination of 1,7-$C_2B_{10}H_{12}$.[11b]

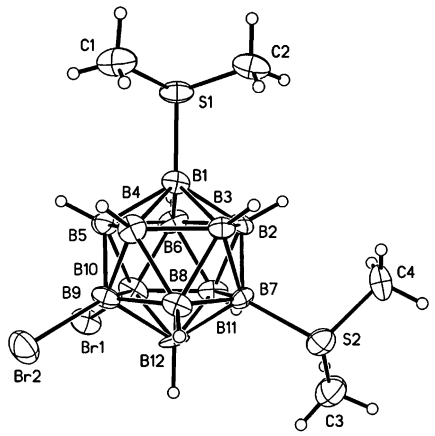

Figure 1. Molecular structure of 9,10-Br_2-1,7-$(Me_2S)_2B_{12}H_8$ (**5**).

Judging from the rate of disappearance of bromine color, reaction of **3** for which only one monohalogenated isomer is possible with 1 equiv of bromine in dichloromethane is much slower than that of **2**. This is expected on the basis of the behavior of 1,12-$C_2B_{10}H_{12}$ that is known to be less reactive toward electrophilic reagents than other isomers due to a lower negative charge on its 10 equiv boron atoms. The ^{11}B NMR of the product (160.5 MHz) displays only 6 signals instead of the expected 8 due to the accidental overlap of two signals due to nonequivalent *ipso*-boron atoms 1 and 12 and another overlap of two signals of intensity 2. Due to signal overlaps, ^{11}B−^{11}B{^{1}H} COSY was not helpful in signal assignment. The ^{1}H NMR spectrum of 2-Br-1,12-$(Me_2S)_2B_{12}H_9$ (**6**) has two methyl resonances at 2.58 and 2.49 ppm. The former probably belongs to the Me_2S group at B(1), which is in close proximity of the electron-withdrawing bromine substituent. The ^{13}C{^{1}H} NMR spectrum also reveals two different methyl signals. No attempt was made to synthesize the corresponding dibromo derivative because a mixture of several isomers, with no particular isomer predominating, was previously obtained from 1,12-$C_2B_{10}H_{12}$.[4b]

Iodination. Iodine slowly reacts with **2** upon prolonged reflux in acetonitrile. However, addition of a stoichiometric amount of $AlCl_3$ to a solution of **2** and iodine (1:1) in CH_2Cl_2 at room temperature results in quick fading of iodine color. The ^{11}B NMR spectrum of the isolated iododerivative displays a pattern of 8 signals, similar to that of 9-Br-1,7-$(Me_2S)_2B_{12}H_9$ (**4**), except for the chemical shift of the iodine-substituted boron, which moves upfield drastically (−24.8 ppm compared to −8.7 ppm for the bromoderivative). Similar upfield signals were observed for the iodine-substituted boron atoms in other iodinated boranes and carboranes.[12] As in the case of **4**, the ^{1}H NMR spectrum of the iododerivative in CD_2Cl_2 has two closely spaced methyl resonances. The molecular structure of 9-I-1,7-$(Me_2S)_2B_{12}H_9$ (**7**) determined by single-crystal X-ray diffraction established that substitution took place at the 9(10) position (Figure 2,

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Table 1. Crystallographic Data for 9,10-Br_2-1,7-$(Me_2S)_2B_{12}H_8$ (**5**), 9-I-1,7-$(Me_2S)_2B_{12}H_9$ (**7**), and 9-(2′,4′-$(NO_2)_2C_6H_3S$)-1,7-$(Me_2S)_2B_{12}H_9$ (**12**)

	5	**7**	**12**
chem formula	$C_4H_{20}B_{12}Br_2S_2$	$C_4H_{21}B_{12}IS_2$	$C_{10}H_{24}B_{12}N_2O_4S_3$
fw	421.86	389.95	462.21
space group	$P2_12_12_1$	$P2_1/n$	$P2_1/c$
a, Å	9.599(3)	9.6936(10)	7.9282(16)
b, Å	9.699(2)	13.8905(10)	23.867(5)
c, Å	19.070(6)	13.0341(10)	12.364(3)
β, deg	90	108.923(10)	91.080(10)
V, Å^3	1775.5(8)	1660.2(2)	2288.3(8)
Z	4	4	4
ρ(calcd), g cm^{-3}	1.578	1.560	1.342
cryst size, mm	0.3 × 0.3 × 0.4	0.42 × 0.38 × 0.31	0.38 × 0.12 × 0.08
temp, °C	−60	−73	−73
radiatn (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
μ, mm^{-1}	4.776	2.152	0.345
R_1[a] [$I > 2\sigma(I)$]	0.0629	0.0175	0.0599
wR_2[b] (all data)	0.1669	0.0441	0.1855

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

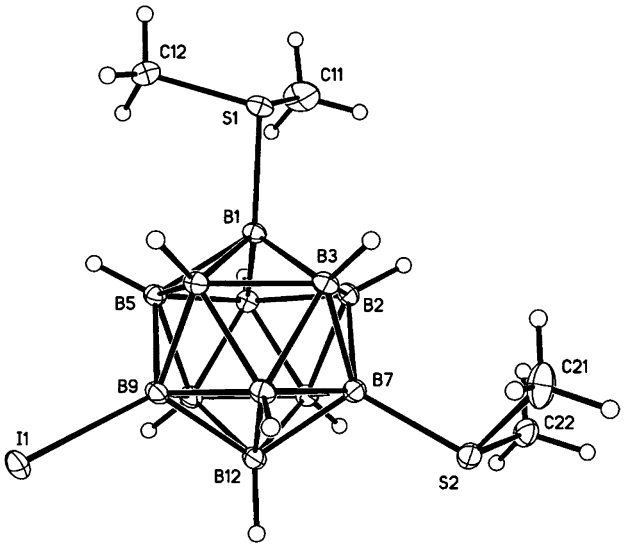


Figure 2. Molecular structure of 9-I-1,7-$(Me_2S)_2B_{12}H_9$ (**7**).

Scheme 1

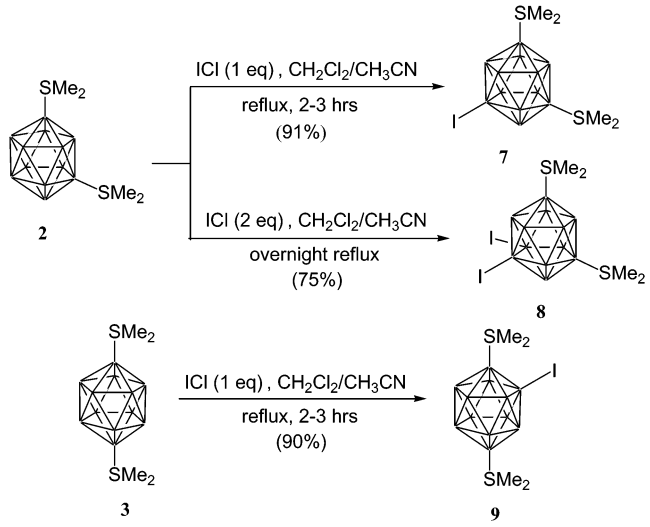


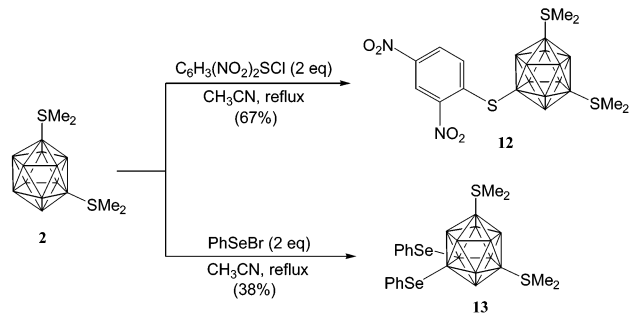
Table 1).

Iodination of **2** by 2 equiv of I_2-AlCl_3 results in 9,10-I_2-1,7-$(Me_2S)_2B_{12}H_8$ (**8**). The ^{11}B NMR spectrum of **8** is very similar to that of the bromine analogue except for the upfield chemical shift of the iodine-substituted boron atoms. A $^{11}B-^{11}B\{^1H\}$ COSY experiment assisted in unambiguous assignment of all signals and indirectly supported the substitution at positions 9 and 10 as no cross-coupling could be seen between the signal of B(1,7) and that of the iodine-substituted boron atoms (see the Supporting Information). Both mono- and diiodinated derivatives of **2** obtained via the I_2-AlCl_3 route were contaminated by an unknown impurity. Although double recrystallization of **7** from ethyl acetate considerably reduced the amount of impurity, it only led to 30% recovery of the product. We encountered the same problem upon attempted purification of **8**. It seems that impurities form upon reaction of the iododerivatives with aluminum trichloride, as the ^{11}B NMR spectrum of **7** changed upon stirring with $AlCl_3$ in CH_2Cl_2. Obviously, a much cleaner synthesis of **7** and **8** was in demand. Fortunately, iodination of **2** by 1 or 2 equiv of iodine monochloride in acetonitrile upon reflux provided the above derivatives essentially free of side products (Scheme 1). Contrary to the iodination of 1,7-$C_2B_{10}H_{12}$,[4a] no catalyst is necessary.

Similarly, 2-I-1,12-$(Me_2S)_2B_{12}H_9$ (**9**) can be obtained either from the reaction of **3** with I_2-AlCl_3 in CH_2Cl_2 at room temperature or with ICl in CH_3CN upon reflux. As in the case of **2**, the former reagent produces side products, which cannot be easily removed, and ICl is a better choice for the synthesis of **9**. Its ^{11}B NMR spectrum has fewer signals than expected due to the accidental overlap of two signals of intensity 2. The iodine-substituted boron atom appears at −24.9 ppm, almost 15 ppm upfield from the corresponding signal of the bromine-substituted compound. The remainder of the signals was assigned using $^{11}B-^{11}B\{^1H\}$ COSY (see the Supporting Information). There are two methyl resonances in the ^1H NMR and $^{13}C\{^1H\}$ NMR spectra of **9** due to the presence of two nonequivalent dimethyl sulfide groups. The synthesis of diiodo derivatives was not attempted for the same reason as in the case of bromination.

Bromination and Iodination of 1. Attempted synthesis of the mono- and dihalogenated derivatives of **1** using Br_2 and I_2-AlCl_3 resulted in mixtures of isomers. It seems that these isomers are 9- and 8-X-1,2-$(Me_2S)_2B_{12}H_9$ in the former case and 9,12- and 8,10-X_2-1,2-$(Me_2S)_2B_{12}H_8$ in the latter

Scheme 2



case. The isomers formed in approximately equal amounts. This is contrary to the halogenation of 1,2-$C_2B_{10}H_{12}$, which results in preferential substitution at boron atoms 9 and 12. Such behavior might be due to a smaller difference in negative charge between positions 9,12 and 8,10 in **1** compared to that in 1,2-$C_2B_{10}H_{12}$. All attempts to separate the isomers failed.

Chlorination of 2. The synthesis of analogous chlorinated derivatives of **1**−**3** was not planned initially due to the expected lack of reactivity of resulting B−Cl bonds toward substitution. However, serendipitous chlorination of **2** was observed upon stirring with methanesulfonyl chloride (2 equiv) in dichloromethane in the presence of $AlCl_3$ (no reaction occurs without $AlCl_3$). From a mixture of 9-Cl-1,7-$(Me_2S)_2B_{12}H_9$ (**10**) and 9,10-Cl_2-1,7-$(Me_2S)_2B_{12}H_8$ (**11**) the latter was isolated by column chromatography. There was no evidence for the formation of a CH_3SO_2-substituted boron product. This is in agreement with the results of Schaffer and Gabel, who found that *closo*-$[B_{12}H_{12}]^{2-}$ reacts with acyl chlorides in the presence of $AlCl_3$ yielding *B*-chlorinated derivatives rather than Friedel−Crafts acylation products.[13] The monochloride **10** was independently prepared from the reaction of **2** with *N*-chlorosuccinimide (1:1). In the ^{11}B NMR spectra of 9-X-1,7-$(Me_2S)_2B_{12}H_9$ (X = Cl, Br, I) the signal of the halogen-substituted boron atom appears further downfield as the substituent is changed from iodine to chlorine. The rest of the pattern essentially does not change. The same is true for the spectra of 9,10-X_2-1,7-$(Me_2S)_2B_{12}H_8$ (see the Supporting Information).

Reactions of 2 with Sulfenyl and Selenenyl Halides. Although $[(CH_3S)_3B_{12}H_9]^{2-}$ was obtained by Muetterties and co-workers from the reaction of $[B_{12}H_{12}]^{2-}$ with methyl disulfide under acidic conditions,[14] the yield was only 15%, and a mixture of isomers was most likely produced. To explore the possibility of the synthesis of polythiosubstituted compounds via reactions of **1**−**3** with sulfur electrophiles, commercially available (2,4-dinitrophenyl)sulfenyl chloride was used. It did not react with **2** in CH_2Cl_2 at room temperature. Addition of $AlCl_3$ resulted in substitution, but the reaction was not clean. Reflux of **2** with 2 equiv of the sulfenyl chloride in acetonitrile for 24 h resulted in formation

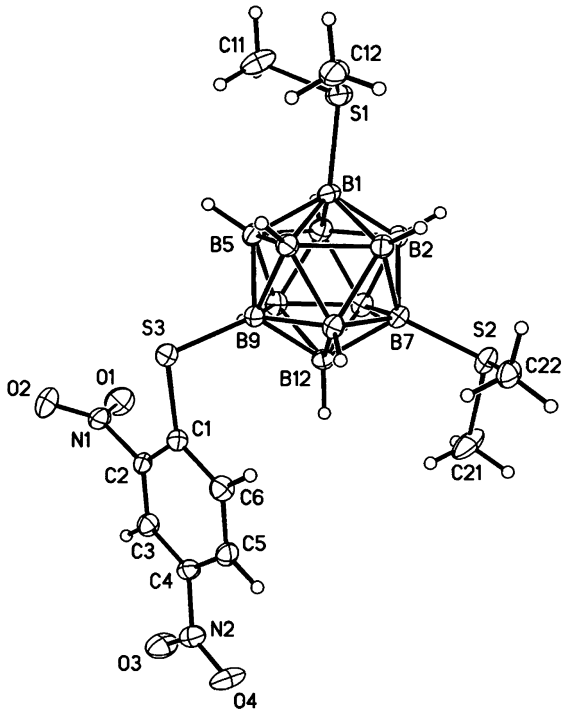


Figure 3. Molecular structure of 9-(2′,4′-$(NO_2)_2C_6H_3S$)-1,7-$(Me_2S)_2B_{12}H_9$ (**12**).

of 9-(2′,4′-$(NO_2)_2C_6H_3S$)-1,7-$(Me_2S)_2B_{12}H_9$ (**12**) as a main product (Scheme 2). This is in agreement with the combined directive effect of the two Me_2S groups previously established for halogenation. Prolonged reflux resulted in formation of disulfide (2,4-$(NO_2)_2C_6H_3S)_2$ as dark-brown crystals without any sign of 9,10-(2′,4′-$(NO_2)_2C_6H_3S)_2$-1,7-$(Me_2S)_2$-$B_{12}H_8$. The absence of the latter product is presumably due to insufficient electrophilicity of the sulfenyl chloride toward position 10, which is expected to possess only a very small negative charge in the trisubstituted boron cage. The molecular structure of **12** was determined by single-crystal X-ray diffraction analysis (Figure 3, Table 1).

Unlike 2,4-$(NO_2)_2C_6H_3SCl$, PhSeBr generated in situ from phenyl diselenide and bromine (1:1) in acetonitrile reacted with **2** upon reflux yielding mostly a diselenosubstituted product, 9,10-$(PhSe)_2$-1,7-$(Me_2S)_2B_{12}H_8$ (**13**) (Scheme 2). Presumably, this difference in behavior is due to the greater electrophilicity of the selenenyl bromide. A monoseleno derivative also formed as a minor product complicating the isolation of **13**. After two chromatographic procedures we were able to isolate **13** in 38% yield. The ^{11}B NMR spectrum of this compound is similar to that of **5**, but the signal of the selenium-substituted boron atoms is much sharper. A selenocyanate derivative $[(NCSe)B_{12}H_{11}]^{2-}$ was previously synthesized from $[B_{12}H_{12}]^{2-}$ using both chemical[15a] and electrochemical[15b] conditions.

Palladium-Catalyzed Boron−Carbon Cross-Coupling Reactions of Iodo Derivatives of 1,7- and 1,12-$(Me_2S)_2$-$B_{12}H_{10}$ with Grignard Reagents. A reaction of **7** and CH_3-

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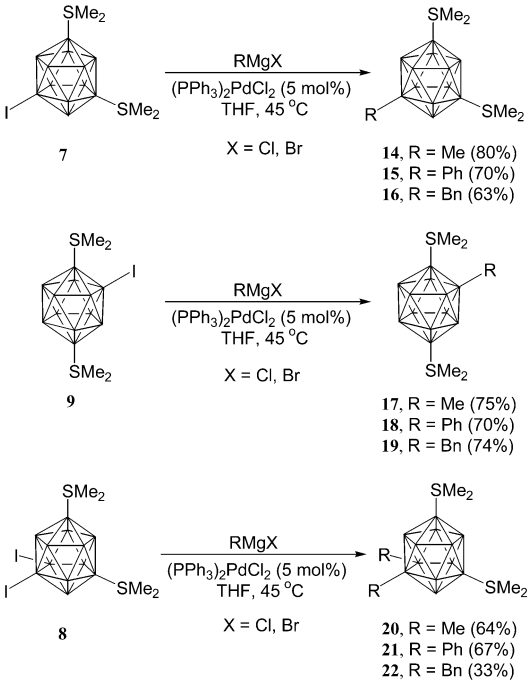
Scheme 3



MgBr (4 equiv) in THF at 45 °C in the presence of 5 mol % of $(PPh_3)_2PdCl_2$ resulted in complete iodide substitution after 18 h (Scheme 3). It could be easily monitored by $^{11}B\{^1H\}$ NMR. As the B−I singlet of the starting material at −24.8 ppm is replaced by a new singlet at −4.5 ppm, the rest of the pattern essentially does not change. At the end no signals other than those of 9-CH_3-1,7-$(Me_2S)_2B_{12}H_9$ (**14**) can be seen in the spectrum of the reaction mixture. There are two signals in the ^1H NMR spectrum of **14**, one at 2.51 ppm due to Me_2S groups and another at 0.17 ppm (CD_2Cl_2) due to the methyl group on boron. Both location and broadness of the latter peak are in agreement with the data reported earlier by Hawthorne and co-workers[8] for the ^1H NMR for $[CH_3B_{12}H_{11}]^{2-}$. This conversion was achieved without use of CuI as a cocatalyst. The latter was reported to be essential for the reaction to succeed in the case of iodocarboranes.[4a,b] Similarly, CuI was used in the synthesis of [(naphthyl)-$(Bn_2NH)B_{12}H_{10}]^-$ from $[(Bn_2NH)B_{12}H_{10}I]^-$ and $[RB_{12}H_{11}]^{2-}$ (R = Me, Ph) from $[B_{12}H_{11}I]^{2-}$.[7,8] Interestingly, no reaction occurred when $(PPh_3)_2PdCl_2$ was replaced by $(dppf)PdCl_2$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene).

As judged by ^{11}B NMR, very little conversion occurred when **4** was treated with MeMgBr under similar conditions. This result is analogous to the carbon−carbon cross-coupling reactions where bromides are known to be less reactive than iodides due to a weaker tendency of a C−Br bond to undergo oxidative addition to Pd(0).

Using phenylmagnesium bromide instead of methylmagnesium bromide under the conditions described above, 9-Ph-1,7-$(Me_2S)_2B_{12}H_9$ (**15**) was prepared. The ^{11}B NMR spectrum of the reaction mixture, although not as clean as in the case of MeMgBr, was essentially that of the product and indicated complete conversion (no residual B−I signal). The signal of the phenyl substituted boron atom is shifted downfield from that of the methyl substituted boron by 1.2 ppm. A similar difference was observed between the chemical shifts of the *ipso*-boron atoms in $[CH_3B_{12}H_{11}]^{2-}$ and $[PhB_{12}H_{11}]^{2-}$.[8] Crystals of **15** suitable for X-ray study were obtained from the NMR sample in CD_3CN. The molecular structure is shown in Figure 4, and the relevant crystallographic data can be found in Table 2.

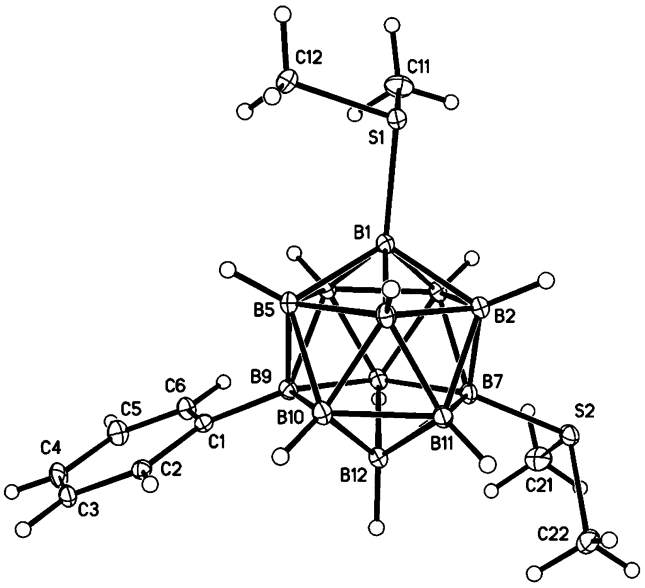


Figure 4. Molecular structure of 9-Ph-1,7-$(Me_2S)_2B_{12}H_9$ (**15**).

Similar to MeMgBr and PhMgBr, benzylmagnesium chloride yielded 9-Bn-1,7-$(Me_2S)_2B_{12}H_9$ (**16**) upon reaction with **7**. By ^{11}B NMR the benzyl-substituted derivative was found to be the main product of the reaction after 22 h of heating. In the ^1H NMR spectrum benzylic protons give rise to a broad singlet at 2.19 ppm, about 2 ppm downfield from the methyl signal in **14**. This broad signal becomes sharp upon broad-band boron decoupling. Although the benzylic carbon cannot be observed by routine $^{13}C\{^1H\}$ NMR, it can be detected indirectly in the $^1H-^{13}C$ HMQC spectrum at about 30 ppm in CD_2Cl_2 (see the Supporting Information). X-ray-quality crystals of this product were obtained by layering its solution in dichloromethane with hexane. The molecular structure is shown in Figure 5 (see Table 2 for crystallographic data). Attempts to use allylmagnesium bromide in a similar reaction produced no trace of the substitution product.

It was of interest to explore cross-coupling reactions of **9** possessing a Me_2S substituent on the boron vertex next to the iodine-substituted boron atom. It seems that the dimethyl sulfide group does not interfere as the yields of **17**−**19** synthesized from **9** were comparable to those of **14**−**16** prepared from **7** (Scheme 3). The ^1H NMR spectrum of **19** reveals two different Me_2S signals, one of them being shifted upfield substantially compared to the Me_2S signal in the parent compound **3** (about 0.2 ppm). Since only the upfield signal correlated with that of the aromatic protons 2 and 6 in the NOESY experiment (see the Supporting Information), we assigned it to the Me_2S group on B(1). Crystals of **19** were grown by slow evaporation of dichloromethane from

Table 2. Crystallographic Data for 9-Ph-1,7-$(Me_2S)_2B_{12}H_9$ (**15**), 9-Bn-1,7-$(Me_2S)_2B_{12}H_9$ (**16**), and 2-Bn-1,12-$(Me_2S)_2B_{12}H_9$ (**19**)

	15	**16**	**19**
chem formula	$C_{10}H_{26}B_{12}S_2$	$C_{11}H_{28}B_{12}S_2$	$C_{11}H_{28}B_{12}S_2$
fw	340.15	354.17	354.17
space group	Pbca	$P2_1/c$	$P\bar{1}$
a, Å	13.3469(10)	13.1588(10)	7.9365(10)
b, Å	11.8991(10)	9.4695(10)	10.3822(10)
c, Å	23.7024(10)	16.8791(10)	12.5820(10)
α, deg			95.078(10)
β, deg		98.039(10)	98.175(10)
γ, deg			101.251(10)
V, Å^3	3764.3(5)	2082.6(3)	999.24(18)
Z	8	4	2
ρ(calcd), g cm^{-3}	1.200	1.130	1.177
cryst size, mm	0.38 × 0.38 × 0.19	0.35 × 0.35 × 0.12	0.46 × 0.31 × 0.31
temp, °C	−123	−73	−123
radiatn (*λ*, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
μ, mm^{-1}	0.271	0.247	0.258
R_1[a] [$I > 2\sigma(I)$]	0.0362	0.0349	0.0303
wR_2[b] (all data)	0.0939	0.0998	0.0823

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

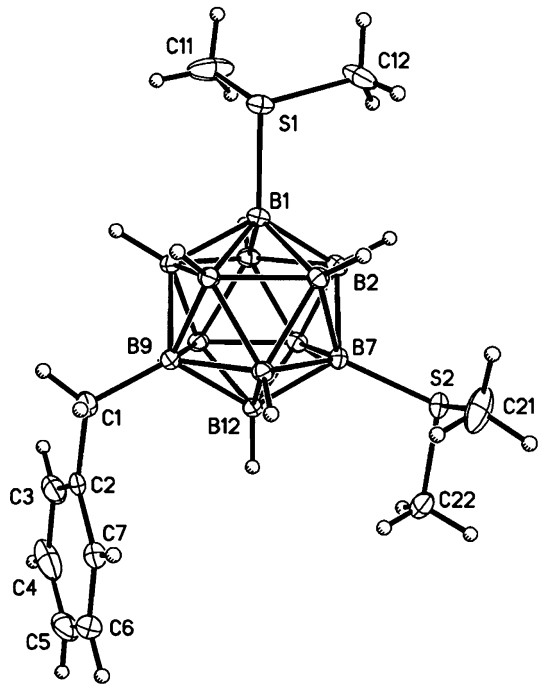


Figure 5. Molecular structure of 9-Bn-1,7-$(Me_2S)_2B_{12}H_9$ (**16**).

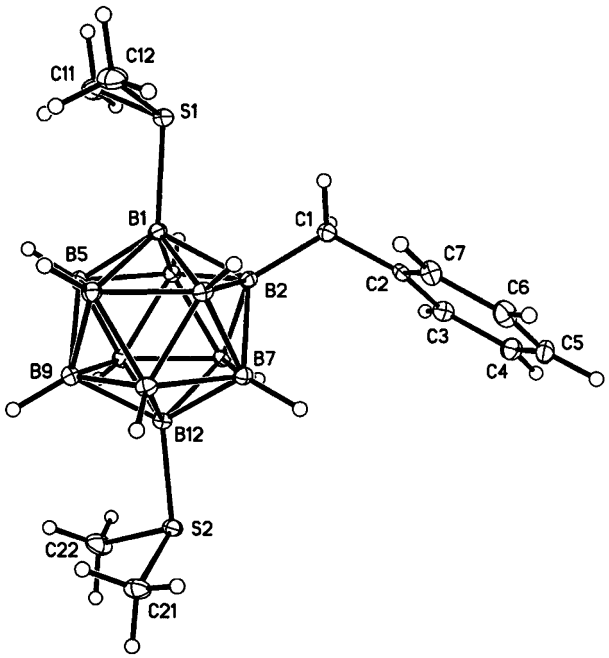


Figure 6. Molecular structure of 2-Bn-1,12-$(Me_2S)_2B_{12}H_9$ (**19**).

the NMR sample. Its molecular structure is shown in Figure 6, and the relevant crystallographic data can be found in Table 2.

Similarly, when reacted with MeMgBr, diiodide **8** produced 9,10-Me_2-1,7-$(Me_2S)_2B_{12}H_8$ (**20**). The methyl carbon atoms cannot be observed by routine $^{13}C\{^1H\}$ NMR but can be detected indirectly in the $^1H-^{13}C$ HMQC spectrum at about 3 ppm in CD_3CN (see the Supporting Information). Reaction of **8** with excess PhMgBr under similar conditions produced the expected 9,10-Ph_2-1,7-$(Me_2S)_2B_{12}H_8$ (**21**) in 67% yield after chromatography. The ^{11}B NMR spectrum of this compound has only four signals instead of the expected five due to the accidental overlap of the signal of intensity 4 and one of the signals of intensity 2. Interestingly, a similar reaction with excess benzylmagnesium chloride resulted in a mixture of three boron products. The major product identified as 9,10-Bn_2-1,7-$(Me_2S)_2B_{12}H_8$ (**22**) was isolated in a significantly lower yield compared to those of **20** and **21**. As expected, **22** displayed five signals in its ^{11}B NMR spectrum. The first minor product, which is separable from **22**, possesses eight signals in its ^{11}B NMR spectrum. Three of them are singlets including the highest upfield signal indicating the presence of iodine in the molecule (see the Supporting Information); therefore, it is most likely to be 9-Bn-10-I-1,7-$(Me_2S)_2B_{12}H_8$. The second minor product, which could not be separated from **22**, displayed two singlets in the downfield region of the ^{11}B NMR spectrum (see the Supporting Information). The intramolecular activation of a C−H bond of the benzyl substituent in a *σ*-(10-dodecaboranyl)palladium iodide complex resulting from 9-Bn-10-I-1,7-$(Me_2S)_2B_{12}H_8$ could be responsible for its formation.[16]

(16) Intramolecular C−H activation leading to *ortho*-palladation via Pd(IV) intermediates has been reported in the literature. For example, see: Alsters, P. L.; Engel, P. F.; Hogerheide, M. P.; Copijn, M.; Spek, A. L.; van Koten, G. *Organometallics* **1993**, *12*, 1831−1844.

The palladium-catalyzed substitution of iodine by an alkyl or aryl group in iodocarboranes and boranes is likely to take place via a mechanism[8] similar to the one generally accepted for the palladium-catalyzed carbon−carbon cross-coupling reactions. However, no boron cage intermediates have been isolated as yet.[17] The ^{11}B NMR spectrum of a solution containing equimolar amounts of **7** and $Pd(PPh_3)_4$ in THF did not change after stirring for 1 day at room temperature. The spectrum of the same solution taken 3 months later revealed a new singlet at −2 ppm, which grew at the expense of the B−I signal of the starting borane, along with other new signals. Heating resulted in further increase in intensity of the former signal at the expense of the latter. The signal at −2 ppm might be due to the formation of the (σ-dodecaboranyl)palladium iodide complex, although its isolation was not attempted. The ^{31}P NMR spectrum of the solution after heating showed two major signals at 24.2 and 24.0 ppm, which fall within the expected range for the above intermediate (for comparison, the chemical shift of $(PPh_3)_2$-Pd(Ph)(I) is 22.3 ppm[18]).

Experimental Section

General Data. Chromatography was performed on Selecto silica gel (230−400 mesh). Fractions obtained after chromatography were analyzed by TLC using the palladium dichloride stain. ^{1}H NMR spectra were obtained on Bruker DRX-500, DPX-400, and AC-300 spectrometers at 500.1, 400.1, and 300.1 MHz, respectively, and referenced to TMS using residual proton signals of deuterated solvents. ^{13}C NMR spectra were obtained on Bruker DRX-500, DPX-400, AC-300, and DPX-250 spectrometers operating at 125.8, 100.6, 75.5, and 62.9 MHz, respectively, and referenced to TMS using deuterated solvent signals. ^{11}B spectra were obtained on the Bruker DRX-500 spectrometer at 160.5 MHz and referenced externally to $BF_3{\cdot}OEt_2$ in C_6D_6 ($\delta = 0.00$ ppm). Coupling constants are reported in hertz. The mass spectra were recorded on Micromass QTOF Electrospray (ESI) and VG-70 (EI) mass spectrometers.

X-ray Structure Determinations. Single-crystal X-ray diffraction data were collected on a Nonius Kappa CCD diffractometer for compounds **7**, **12**, **15**, **16**, and **19.** An Enraf-Nonius CAD4 diffractometer was employed for compound **5**. Both instruments employ graphite-monochromated Mo Kα radiation. For data collected on the CCD system, a single crystal was mounted on the tip of a glass fiber coated with Fomblin oil (a pentafluoro polyether). Unit cell parameters were obtained by indexing the peaks in the first 10 frames and refined by employing the whole data set. All frames were integrated and corrected for Lorentz and polarization effects using the Denzo-SMN package (Nonius BV, 1999).[19] Absorption correction was applied using the SORTAV program.[20] Structures were solved by direct methods and refined using SHELXTL97 (difference electron density calculation, full-matrix least-squares refinements) structure solution package.[21] Data merging was performed using the data preparation program supplied by SHELXTL97. All non-hydrogen atoms were located and refined anisotropically. All hydrogens on boron atoms are located and refined isotropically. Hydrogen atoms on carbons are calculated assuming standard C−H geometries. For data collected on the CAD4 diffractometer, unit cell parameters were obtained by a least-squares refinement of the angular settings from 25 reflections, well distributed in reciprocal space and lying in the 2θ range of 24−30°. Diffraction data were corrected for Lorentz and polarization effects and empirical absorption (empirically from ψ scan data). There are no unusual structural features or distances and angles in these molecular structures that require discussion.

9-Br-1,7-$(Me_2S)_2B_{12}H_9$ (4). A 50 mL round-bottomed flask equipped with a magnetic stirbar was charged with 0.2807 g of **2** (1.063 mmol) and 15 mL of dichloromethane. To the resulting solution, 5.6 mL of 0.192 M solution of Br_2 in CH_2Cl_2 (1.075 mmol) was added within 15 min. After the addition the volatile materials were removed under reduced pressure leaving behind a yellowish solid. Upon recrystallization from 1-propanol, 0.3126 g (86%) of the product was obtained as white needlelike crystals. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 2.541 and 2.536 (2 s, S(CH_3)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz): δ 26.2. ^{11}B NMR (CD_3CN, 160.5 MHz): δ −8.7 (s, B(9)), −10.2 (s, B(1,7)), −12.6 (d, B(10)), −13.9 (d, B(5,12) or B(4,8)), −14.3 (d, B(4,8) or B(5,12)), −15.9 (d, J_{BH} = 144, B(6,11)), −17.2 (d, B(3)), −20.0 (d, J_{BH} = 145, B(2)). MS (EI): calcd for $C_4H_{21}{}^{10}B_2{}^{11}B_{10}S_2{}^{79}Br$, m/z = 342.1458; obsd, m/z = 342.1452 (M^+).

9,10-Br_2-1,7-$(Me_2S)_2B_{12}H_8$ (5).[22] A 50 mL round-bottomed flask equipped with a magnetic stirbar was charged with 0.1316 g of 9-Br-1,7-$(Me_2S)_2B_{12}H_9$ (0.384 mmol) and 15 mL of dichloromethane. To the resulting solution 1.0 mL of a 0.396 M solution of Br_2 in CH_2Cl_2 (0.396 mmol) was added. After the solution was stirred overnight, the volatile materials were removed under reduced pressure. The crude product was recrystallized from 1-propanol twice to yield 0.0804 g of the title compound as a white solid (50%). ^{1}H{^{11}B} NMR (CD_3CN, 500 MHz): δ 2.52 (s, 12H, S(CH_3)$_2$), 2.02 (br s, 2H, H(5,12)), 1.90 (br s, 4H, H(4,6,8,11), 1.66 (br s, 2H, H(2,3)). ^{13}C{^{1}H} NMR (CD_3CN, 125.8 MHz): δ 26.0. ^{11}B NMR (CD_3CN, 160.5 MHz): δ −8.6 (s, B(9,10)), −9.9 (s, B(1,7)), −11.0 (d, J_{BH} = 144, B(5,12)), −14.7 (d, J_{BH} = 144, B(4,6,8,11)), −19.9 (d, J_{BH} = 142, B(2,3)). MS (EI): calcd for $C_4H_{20}{}^{10}B_2{}^{11}B_{10}S_2{}^{79}Br^{81}Br$, m/z = 422.0543; obsd, m/z = 422.0534 (M^+).

2-Br-1,12-$(Me_2S)_2B_{12}H_9$ (6).[23] A 50 mL round-bottomed flask equipped with a magnetic stirbar was charged with 0.3286 g of **3** (1.244 mmol) and 0.280 g of Br_2−dimethyl sulfide complex (1.261 mmol). Dichloromethane (25 mL) was added, and the solution was stirred overnight. A second portion of Br_2SMe_2 was added to the solution (0.200 g, 0.901 mmol), and stirring was continued for an additional 1 day followed by addition of a third portion of Br_2-SMe_2 (0.080 g, 0.360 mmol). After an additional 2 days of stirring, the ^{11}B NMR spectrum indicated that the reaction was complete.

(17) Recently Grushin et al.[18] attempted to observe intermediates of boron−carbon cross-coupling reactions of 9-iodo-*meta*-carborane. No substantial change in the ^{31}P spectrum of the toluene-d_8 solution containing 9-iodo-*meta*-carborane and $(PPh_3)_4Pd$ (ratio 10:1) was detected even after 3 h of heating at 70 °C. Unfortunately, this was not complemented by observation of ^{11}B NMR of the same solution. It was concluded that the equilibrium constant for the oxidative addition of the carboranyl boron−iodine bond to a zerovalent palladium is very unfavorable.

(18) Marshall, W. J.; Young, R. J.; Jr., Grushin, V. V. *Organometallics* **2001**, *20*, 523−533.

(19) Otwinowsky, Z.; Minor, W. In *Methods in Enzymology, Vol. 276: Macromolecular Crystallography*; Carter, C. W., Jr., Sweet, R. M., Eds.; Academic Press: New York, 1997; Part A, pp 307−326.

(20) (a) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, *33*-38. (b) Blessing, R. H. *J. Appl. Crystallogr.* **1997**, *30*, 421−426.

(21) *SHELXTL*, version 5.10; Bruker Analytical X-ray Systems: Madison, WI, 1997.

(22) Although the procedure below uses **4** as a starting material, **5** can be prepared directly from **2** using 2 equiv of bromine.

(23) Bromine-dimethyl sulfide complex is used in this procedure solely due to the convenience of handling a solid reagent. For its preparation see Olah, G. A.; Vankar, Y. D.; Arvanaghi, M.; Prakash, G. K. S. *Synthesis* **1979**, 701−721. Bromine can be used instead as described above for the synthesis of **4**.

The resulting solution was washed with aqueous $Na_2S_2O_3$ and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the crude product was recrystallized from 1-propanol yielding 0.2958 g of **6** as white crystals (69%). ^{1}H NMR (CD_3CN, 500 MHz): δ 2.58 and 2.49 (2 s, S(CH_3)$_2$). ^{13}C{^{1}H} NMR (CD_3CN, 62.9 MHz): δ 26.0, 25.4. ^{11}B NMR (CD_3CN, 160.5 MHz): δ −8.6 (s, 2B), −10.9 (s, 1B), −14.5 (d, 4B), −16.6 (d, 2B), −17.3 (d, 2B), −19.0 (d, 1B). MS (EI): calcd for $C_4H_{21}{}^{10}B_2{}^{11}B_{10}S_2{}^{79}Br$, m/z = 342.1458; obsd, m/z = 342.1459 (M^+).

General Procedure for Synthesis of Iodo-Substituted Boranes. A 250 mL three-necked round-bottomed three-neck flask equipped with a condenser, magnetic stirbar, and a rubber septum was charged with $(Me_2S)_2B_{12}H_{10}$ (4.2−4.6 mmol) and 80−100 mL of acetonitrile. Under nitrogen a calculated volume of 0.77 M solution of iodine monochloride in dichloromethane required for either mono- or diiodination was added by syringe. The resulting solution was refluxed for 2−2.5 h (sand bath) in the case of monoiodination and overnight (10−11 h) in the case of diiodination. The volatile materials were removed under reduced pressure followed by dissolution of a residue in CH_2Cl_2. The resulting solution was washed with aqueous $Na_2S_2O_3$ and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the crude product was recrystallized form EtOH (95%) (**7**, **9**) or acetone−EtOH (95%) (**8**).

9-I-1,7-$(Me_2S)_2B_{12}H_9$ (7). From the reaction of **2** (1.1705 g, 4.432 mmol) with 4.44 mmol of ICl, 1.5730 g of **7** was isolated as white crystals (91%). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 2.55 and 2.54 (2s, S(CH_3)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100.6 MHz): δ 26.2. ^{11}B NMR (CD_2Cl_2, 160.5 MHz): δ −9.4 (s, B(1,7)), −12.3 (d, 1B), −13.7 (d, 2B), −14.2 (d, 2B), −15.6 (d, 2B, J_{BH} = 147), −16.9 (d, 1B), −18.6 (d, 1B, J_{BH} = 141), −24.8 (s, B(9)). MS (ESI): calcd for $C_4H_{21}{}^{11}B_{12}S_2INa$, m/z = 415.1145; obsd, m/z = 415.1144 [(M + Na)$^+$].

9,10-I_2-1,7-$(Me_2S)_2B_{12}H_8$ (8). From the reaction of **2** (1.1117 g, 4.210 mmol) with 8.47 mmol of ICl, 1.6169 g of the title compound was isolated as white crystals (75%). ^{1}H{^{11}B} NMR (CD_3CN, 500 MHz): δ 2.53 (s, 12H, S(CH_3)$_2$), 2.19 (br s, 2H, H(5,12)), 2.08 (br s, 4H, H(4,6,8,11), 1.99 (br s, 2H, H(2,3)). ^{13}C-{^{1}H} NMR (CD_3CN, 125.8 MHz): δ 26.0. ^{11}B NMR (CD_3CN, 160.5 MHz): δ −8.1 (s, B(1,7)), −11.4 (d, B(5,12)), −13.3 (d, B(4,6,8,11)), −17.2 (d, B(2,3)), −22.3 (s, B(9,10)). MS (ESI): calcd for $C_4H_{20}{}^{10}B_2{}^{11}B_{10}S_2I_2Na$, m/z = 539.0187; obsd, m/z = 539.0179 [(M + Na)$^+$].

2-I-1,12-$(Me_2S)_2B_{12}H_9$ (9). From the reaction of **3** (1.2209 g, 4.623 mmol) with 4.62 mmol of ICl, 1.6300 g of **9** was isolated as a white powder (90%). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 2.61 (s, 6H, B(1)S(CH_3)$_2$), 2.52 (s, 6H, B(12)S(CH_3)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125.8 MHz): δ 26.1, 25.7. ^{11}B NMR (CD_2Cl_2, 160.5 MHz): δ −7.8 and − 8.1 (2s, B(1) and B(12)), −13.5 (d, B(3,6)), −13.8 (d, B(7,11)), −16.0 (d, B(4,5) and B(8,10)), −16.9 (d, B(9)), −25.8 (s, B(2)). MS (ESI): calcd for $C_4H_{21}{}^{10}B_2{}^{11}B_{10}S_2INa$, m/z = 413.1221; obsd, m/z = 413.1232 [(M + Na)$^+$].

9-Cl-1,7-$(Me_2S)_2B_{12}H_9$ (10). A 25 mL round-bottomed flask equipped with a magnetic stirbar was charged with 0.2640 g of **2** (1.000 mmol), 0.1337 g of *N*-chlorosuccinimide (1.001 mmol) and 10 mL of acetonotrile. The resulting solution was refluxed for 1 h followed by solvent removal in vacuo. The residue was partitioned between dichloromethane (10 mL) and water (10 mL). The organic phase was washed twice with water and dried with $MgSO_4$. After solvent removal the crude product was obtained as a white powder (0.2778 g, 93% yield) and purified by column chromatography. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 2.54 and 2.53 (2s, S(CH_3)$_2$). ^{13}C-{^{1}H} NMR (CD_2Cl_2, 125.8 MHz): δ 25.9. ^{11}B NMR (CH_2Cl_2, 160.5 MHz): δ −2.4 (s, B(9)), −10.7 (s, B(1,7)), −13.5 (d, B(10)), −14.9 (d, B(5,12)), −15.4 (d, B(4,8)), −17.2 (d, B(6,11)), −18.6 (d, B(3)), −21.9 (d, J_{BH} = 139, B(2)). MS (ESI): calcd for $C_4H_{21}{}^{10}B_2{}^{11}B_{10}S_2{}^{35}ClNa$, m/z = 321.1860; obsd, m/z = 321.1871 [(M + Na)$^+$].

9,10-Cl_2-1,7-$(Me_2S)_2B_{12}H_8$ (11). A 50 mL round-bottomed flask equipped with a magnetic stirbar was charged with 0.1104 g of **2** (0.418 mmol). Dichloromethane (10 mL), mesyl chloride (0.070 mL, 0.90 mol), and aluminum trichloride (0.2086 g, 1.560 mmol) were added under nitrogen, and the mixture was stirred overnight. The resulting solution was washed with aqueous 1 M HCl and water. After drying over $MgSO_4$, the solvent was removed under reduced pressure. The crude product, containing both mono- and dichlorosubstituted derivatives, was chromatographed on silica gel using CH_2Cl_2 as an eluent. The title compound (lower spot on TLC) was isolated as a white crystalline material, but the yield was not determined. ^{1}H{^{11}B} NMR (CD_3CN, 500 MHz): δ 2.51 (s, 12H, S(CH_3)$_2$), 1.89 (br s, 2H, H(5,12)), 1.78 (br s, 4H, H(4,6,8,11), 1.45 (br s, 2H, H(2,3)). ^{13}C{^{1}H} NMR (CD_3CN, 125.8 MHz): δ 26.0. ^{11}B NMR (CD_3CN, 160.5 MHz): δ −2.5 (s, B(9,10)), −11.2 (s, B(1,7)), −13.5 (d, J_{BH} = 141, B(5,12)), −15.5 (d, J_{BH} = 142, B(4,6,8,11)), −21.5 (d, J_{BH} = 141, B(2,3)). MS (EI): calcd for $C_4H_{20}{}^{10}B_2{}^{11}B_{10}S_2{}^{35}Cl_2$, m/z = 332.1575; obsd, m/z = 332.1583 (M^+).

9-(2′,4′-$(NO_2)_2C_6H_3S$)-1,7-$(Me_2S)_2B_{12}H_9$ (12). A solution of **2** (1.0169 g, 3.851 mmol) and (2,4-dinitrophenyl)sulfenyl (1.8833 g, 7.706 mmol) in 100 mL of acetonitrile was placed in a 250 mL three-necked round-bottomed flask equipped with a condenser and stirbar and refluxed for 24 h under nitrogen. The resulting solution was filtered, and the volatile materials were removed under reduced pressure. Dichloromethane (200 mL) was added to the residue, and the mixture was stirred overnight. After filtration the solvent was removed under reduced pressure, and the crude product was chromatographed on silica gel using CH_2Cl_2 as an eluent. The product was further purified by recrystallization from ethanol (95%) yielding three crops of orange crystals having the identical NMR spectra. Those were combined to give 1.1857 g of **12** (67%). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 8.54 (d, 1H, $^4J_{HH}$ = 2.5, H_3), 8.43 (d, 1H, $^3J_{HH}$ = 8.9, H_6), 8.14 (d, 1H, $^3J_{HH}$ = 8.9; $^4J_{HH}$ = 2.5, H_5), 2.55 (s, 6H, S(CH_3)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125.8 MHz): δ 149.8, 147.8, 144.0, 135.0, 125.1, 120.1, 26.2. ^{11}B NMR (CD_2Cl_2, 160.5 MHz): δ −6.5 (s, B(9)), −9.6 (s, B(1,7)), −13.7 (d, 1B), −14.4 (d, 2B), −15.1 (d, 2B), −15.8 (d, 2B), −17.2 (d, 1B), −18.0 (d, 1B). MS (ESI): calcd for $C_{10}H_{24}O_4N_2{}^{11}B_{12}S_3Na$, m/z = 487.1913; obsd, m/z = 487.1909 [(M + Na)$^+$].

9,10-$(PhSe)_2$-1,7-$(Me_2S)_2B_{12}H_8$ (13). A 50 mL three-necked round-bottomed three-neck flask equipped with a condenser, magnetic stirbar, and a rubber septum was charged with 0.3880 g of 98% phenyl diselenide (1.218 mmol) and 15 mL of acetonitrile. Under nitrogen 8.0 mL of 0.149 M solution of bromine in acetonitrile was added by syringe, and the resulting mixture was stirred in the dark for 1 h. After the addition of 0.3217 g of **2** (1.218 mmol) the solution was refluxed for 21 h. The volatile materials were removed under reduced pressure followed by the addition of dichloromethane to the residue. The resulting solution was fitered, washed with aqueous NaCl, and dried over $MgSO_4$. After removal of the solvent, an oily residue left which crystallized upon trituration with ethanol (95%). The crude product was chromatographed twice on silica gel using dichloromethane as an eluent yielding 0.2566 g of the product as a yellowish powder (38%). ^{1}H NMR (CD_3CN, 500 MHz): δ 7.63−7.61 (m, 4H, $Ph_{2,6}$), 7.17−7.13 (m, 6H, $Ph_{3,4,5}$), 2.45 (s, 12H, S(CH_3)$_2$). ^{13}C{^{1}H} NMR (CD_3CN, 125.8 MHz): δ 136.5, 133.4, 129.0, 126.6, 25.9. ^{11}B NMR (CD_3CN, 160.5 MHz):

δ −7.0 (s, B(9,10)), −9.0 (s, B(1,7)), −12.7 (d, B(5,12)), −14.2 (d, J_{BH} = 143, B(4,6,8,11)), −17.8 (d, J_{BH} = 139, B(2,3)). MS (ESI): calcd for $C_{16}H_{30}{}^{10}B_2{}^{11}B_{10}S_2{}^{78}Se^{80}SeNa$, *m*/*z* = 597.1216; obsd, *m*/*z* = 597.1232 [(M + Na)$^+$].

General Procedure for Synthesis of *B*-Monoalkyl and *B*-Monoaryl Derivatives of 2 and 3. In a typical experiment a 50 mL three-necked round-bottomed flask equipped with a condenser and magnetic stirbar was charged with 0.5 mmol of iodide **7** or **9** and 4−5 mol % of $(PPh_3)_2PdCl_2$. Dry THF was condensed (15−20 mL), and the resulting solution was placed in ice−water bath. After 30 min of stirring, a Grignard reagent (2 mmol, solution in ether) was added by a syringe, and the ice−water bath was replaced by an oil bath at 40−45 °C. Heating was continued for 1−2 days depending on the completeness of reaction, which was checked by ^{11}B NMR. Methanol was added to destroy an excess Grignard reagent followed by filtration and solvent removal in vacuo. The residue was partitioned between dichloromethane−aqueous HCl (1 M), and the organic phase was washed with distilled water, dried over $MgSO_4$, and filtered. After solvent removal under reduced pressure, the crude product was purified by chromatography.

9-Me-1,7-$(Me_2S)_2B_{12}H_9$ (14). Yield: 80%. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 2.51 (s, 12H, S(CH_3)$_2$), 0.17 (br s, 3H, BCH_3). ^{11}B NMR (CD_2Cl_2, 160.5 MHz): δ −4.8 (s, B(9)), −10.0 (s, B(1,7)), −12.7 (d, B(10)), −14.0 (d, B(5,12) or B(4,8)), −14.7 (d, B(4,8) or B(5,12)), −16.4 (d, B(6,11)), −17.7 (d, B(3)), −21.1 (d, J_{BH} = 138, B(2)). MS (ESI): calcd for $C_5H_{24}{}^{10}B_2{}^{11}B_{10}S_2Na$, *m*/*z* = 301.2411; obsd, *m*/*z* = 301.2417 [(M + Na)$^+$].

9-Ph-1,7-$(Me_2S)_2B_{12}H_9$ (15). Yield: 70%. ^{1}H NMR (CD_3CN, 500 MHz): δ 7.47 (d, 2H, $^3J_{HH}$ = 7.1, H_2, H_6), 7.09 (dd, 2H, H_3, H_5), 7.05 (tt, 1H, H_4), 2.52 (s, 12H, S(CH_3)$_2$). ^{13}C{^{1}H} NMR (CD_3CN, 125.8 MHz): δ 134.2, 127.6, 126.1, 26.1. ^{11}B NMR (CD_3CN, 160.5 MHz): δ −3.3 (s, B(9)), −8.7 (s, B(1,7)), −12.6 (d, B(10)), −13.7 (d, 2B), −14.3 (d, 2B), −15.3 (d, 2B), −16.6 (d, B(3)), −18.5 (d, J_{BH} = 138, B(2)).

9-Bn-1,7-$(Me_2S)_2B_{12}H_9$ (16). Yield: 63%. ^{1}H NMR (CD_2Cl_2, 500 MHz): 7.13 (m, 2H, Ph), 7.06 (m, 2H, Ph), 6.96 (dd, 1H, Ph), 2.47 (s, 12H, S(CH_3)$_2$), 2.19 (br s, 2H, BCH_2). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125.8 MHz): δ 148.7, 129.2, 127.7, 123.3, 26.2. ^{11}B NMR (CD_2Cl_2, 160.5 MHz): δ −3.3 (s, B(9)), −10.0 (s, B(1,7)), −13.3 (d, B(10)), −14.4 (d, 2B), −15.2 (d, 2B), −16.4 (d, 2B), −17.8 (d, B(3)), −20.4 (d, J_{BH} = 137, B(2)). MS (ESI): calcd for $C_{11}H_{28}{}^{11}B_{12}S_2Na$, *m*/*z* = 379.2647; obsd, *m*/*z* = 379.2654 [(M + Na)$^+$].

2-Me-1,12-$(Me_2S)_2B_{12}H_9$ (17). Yield: 75%. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 2.50 (s, 6H, S(CH_3)$_2$), 2.49 (s, 6H, S(CH_3)$_2$), 0.20 (br s, 3H, BCH_3). ^{13}C{^{1}H} NMR (CD_3CN, 125.8 MHz): δ 26.1, 25.7. ^{11}B NMR (CD_2Cl_2, 160.5 MHz): δ −6.6 (s, B(2)), −7.8 (s, B(1), B(12)), −14.2 (d, *J* = 136, B(3,6), B(7,11)), −16.7 (d, *J* = 132, B(4,5), B(8,10)), −19.5 (d, *J* = 138, B(9)). MS (ESI): calcd for $C_5H_{24}{}^{10}B_2{}^{11}B_{10}S_2Na$, *m*/*z* = 301.2411; obsd, *m*/*z* = 301.2433 [(M + Na)$^+$].

2-Ph-1,12-$(Me_2S)_2B_{12}H_9$ (18). Yield: 70%. ^{1}H NMR (CD_3CN, 500 MHz): δ 7.52 (br d, 2H, $^3J_{HH}$ = 6.5, H_2, H_6), 7.18−7.12 (m, 3H, H_3, H_5, H_4), 2.48 (s, 6H, S(CH_3)$_2$), 2.28 (s, 6H, S(CH_3)$_2$). ^{13}C{^{1}H} NMR (CD_3CN, 125.8 MHz): δ 134.7, 128.1, 126.9, 26.0, 25.3. ^{11}B NMR (CD_3CN, 160.5 MHz): δ −4.7 (s, B(2)), −6.6 (s, B(1,12)), −13.5 (d, 2B), −14.6 (d, 2B), −15.3 (d, 2B), −16.1 (d, 2B), −16.8 (d, B(9)). MS (ESI): calcd for $C_{10}H_{26}{}^{10}B_2{}^{11}B_{10}S_2Na$, *m*/*z* = 363.2571; obsd, *m*/*z* = 363.2578 [(M + Na)$^+$].

2-Bn-1,12-$(Me_2S)_2B_{12}H_9$ (19). Yield: 74%. ^{1}H NMR (CD_2Cl_2, 500 MHz): 7.17−7.10 (m, 4H, Ph), 7.02−6.99 (m, 1H, Ph), 2.46 (s, 6H, B(12)S(CH_3)$_2$), 2.33 (s, 6H, B(1)S(CH_3)$_2$), 2.27 (br s, 2H, BCH_2). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125.8 MHz): δ 147.4, 129.5, 128.0, 124.0, 26.1, 26.0. ^{11}B NMR (CD_2Cl_2, 160.5 MHz): δ −5.2 (s, B(2)), −7.9 (s, B(1), B(12)), −14.7 (d, J_{BH} = 141, B(3,6), B(7,11)), −16.7 (d, J_{BH} = 139, B(4,5), B(8,10)), −19.0 (d, J_{BH} = 137, B(9)). MS (ESI): calcd for $C_{11}H_{28}{}^{10}B_2{}^{11}B_{10}S_2Na$, *m*/*z* = 377.2728; obsd, *m*/*z* = 377.2706 [(M + Na)$^+$].

Preparation of *B*-Dialkyl and *B*-Diaryl Derivatives of 2. The procedure was analogous to that for the preparation of the monoalkyl and monoaryl derivatives except diiodide **8** was used as a starting material.

9,10-Me_2-1,7-$(Me_2S)_2B_{12}H_8$ (20). Yield: 64%. ^{1}H NMR (CD_3CN, 500 MHz): δ 2.46 (s, 12H, S(CH_3)$_2$), 0.08 (s, 6H, BCH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125.8 MHz): δ 26.1. ^{11}B NMR (CD_3CN, 160.5 MHz): δ − 4.4 (s, B(9,10)), −9.9 (s, B(1,7)), −12.2 (d, J_{BH} = 134, B(5,12)), −14.3 (d, *J* = 135, B(4,6,8,11)), −20.2 (d, J_{BH} = 137, B(2,3)). MS (ESI): calcd for $C_6H_{26}{}^{10}B_2{}^{11}B_{10}S_2Na$, *m*/*z* = 315.2568; obsd, *m*/*z* = 315.2580 [(M + Na)$^+$].

9,10-Ph_2-1,7-$(Me_2S)_2B_{12}H_8$ (21). Yield: 67%. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.39−7.37 (m, 4H, Ph), 7.03−6.99 (m, 6H, Ph), 2.56 (s, 12H, S(CH_3)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125.8 MHz): δ 134.2, 126.9, 125.6, 26.2. ^{11}B NMR (CH_2Cl_2, 160.5 MHz): δ −3.5 (s, B(9,10)), −10.4 (s, B(1,7)), −14.8 (d, J_{BH} = 135, B(5,12), B(4,6,8,11)), −18.9 (d, J_{BH} = 142, B(2,3)). MS (ESI): calcd for $C_{16}H_{30}{}^{10}B_2{}^{11}B_{10}S_2Na$, *m*/*z* = 439.2887; obsd, *m*/*z* = 439.2899 [(M + Na)$^+$].

9,10-Bn_2-1,7-$(Me_2S)_2B_{12}H_8$ (22). Yield: 33%. ^{1}H NMR (CD_2Cl_2, 500 MHz): 7.16−7.11 (m, 8H, Ph), 6.99−6.96 (m, 2H, Ph), 2.40 (s, 12H, S(CH_3)$_2$), 2.26 (br s, 4H, BCH_2). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125.8 MHz): δ 148.7, 129.5, 127.7, 123.3, 26.1. ^{11}B NMR (CD_2Cl_2, 160.5 MHz): δ −3.5 (s, B(9,10)), −10.8 (s, B(1,7)), −13.7 (d, J_{BH} = 135, B(5,12)), −15.8 (d, *J* = 136, B(4,6,8,11)), −20.6 (d, J_{BH} = 135, B(2,3)). MS (ESI): calcd for $C_{18}H_{34}{}^{10}B_2{}^{11}B_{10}S_2Na$, *m*/*z* = 467.3202; obsd, *m*/*z* = 467.3196 [(M + Na)$^+$].

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Supporting Information Available: Six crystallographic files in CIF format, ^{11}B−^{11}B{^{1}H} COSY spectra of **8** and **9**, ^{11}B{^{1}H} NMR spectra of **4**, **5**, **7**, **8**, **10**, **11**, and both minor products from the reaction of **8** with excess BnMgCl, ^{1}H−^{13}C HMQC spectra of **16** and **20**, and the NOESY spectrum of **19**. This material is available free of charge via the Internet at http://pubs.acs.org.

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