

analogous complex cannot be isolated; this may be due to the tendency of monooxo-Tc(V) complexes to prefer (relative to the Re(V) analogues) five-coordinate geometry over six-coordinate geometry.^{17,22}

(3) The addition of further equivalents of hbtH leads rapidly to the formation of hbt, without any requirement for additional metal complex. The efficient conversion of large excesses of hbtH to hbt is accomplished by all the $[\text{MOX}_4]^-$, $[\text{MOX}(\text{S-phsal})]$, and $[\text{ReO}(\text{S-phsal})(\text{hbt})]$ complexes, and thus all of these species can be readily incorporated into the reaction cycle. Presumably, the hbt product is lost from $[\text{MO}(\text{S-phsal})(\text{hbt})]$ to generate a five-coordinate solvated species that can then accept another 1 mol of hbtH and continue the cycle.

When the metal(V)-promoted conversion of hbtH to hbt is conducted in methanol, the chemical fate of the released reducing power has not yet been determined. However, when this conversion is conducted in acetone, the formation of isopropyl alcohol can be detected within a few minutes after mixing the reagents. In this situation the small amount of metal(V) complex promotes hbtH reduction of acetone to yield isopropyl alcohol and hbt. Reduction of ketones is effected by the hydride ion but not by the hydrogen radical, and thus it appears as though the metal(V)-promoted conversion of hbtH to hbt proceeds by a 2-equiv mechanism rather than by a free-radical process. This is in contrast to the light-induced oxidation of hbtH, which proceeds with the formation of hydrogen radicals that are unable to reduce ketones.⁷

The studies reported herein are placed into a larger context by consideration of two literature reports on the reactivity of hbtH. First, hbtH reacts with high-valent metals such as Mo(V) and Mo(VI) without undergoing oxidation to hbt.⁶ This observation indicates that metal-promoted oxidation of hbtH is not a general reaction and strongly implies that there is some specific aspects of the $[\text{Tc}=\text{O}]^{3+}$ and $[\text{Re}=\text{O}]^{3+}$ cores which promotes conversion of hbtH to hbt. Second, hbtH has been used as an olefin reducing

agent,²⁶ but in this application the carbon-carbon double bond of α,β -unsaturated carbonyl compounds is reduced *without* concomitant reduction of the carbonyl group. This observation implies that in our studies it is not hbtH itself which reduces acetone but rather it is some activated metal center which effects the actual hydride transfer. In sum, it appears as though the five-coordinate, square-pyramidal, monooxo-Tc(V) and -Re(V) centers play an essential role in the conversion of hbtH to hbt, and it is reasonable to suppose that this conversion proceeds by a hydride transfer which involves the $\text{M}=\text{O}$ linkage. The details of this process, and the details of the subsequent reaction steps leading to carbonyl reduction, remain to be elucidated.

Acknowledgment. We are indebted to Prof. A. Barco, Prof. S. Benetti, and Dr. B. Wilcox for helpful discussions. We are grateful to Dr. S. Coppi for gas-chromatographic measurements and to M. Fratta for elemental analyses. Financial support was provided by the Italian Consiglio Nazionale delle Ricerche and Ministero della Pubblica Istruzione.

Registry No. hbtH, 7361-94-6; hbt, 3411-95-8; $\text{ReO}(\text{S-phsal})(\text{hbt})$, 116887-50-4; $\text{As}(\text{C}_6\text{H}_5)_4[\text{ReOCl}_4]$, 14853-14-6; $\text{As}(\text{C}_6\text{H}_5)_4[\text{ReOBr}_4]$, 14853-12-4; $\text{As}(\text{C}_6\text{H}_5)_4[{}^{99}\text{TcOCl}_3(\text{hbt})]$, 116887-52-6; $\text{As}(\text{C}_6\text{H}_5)_4[\text{ReOCl}_3(\text{hbt})]$, 116887-58-2; $\text{As}(\text{C}_6\text{H}_5)_4[{}^{99}\text{TcOBr}_3(\text{hbt})]$, 116887-54-8; $\text{As}(\text{C}_6\text{H}_5)_4[\text{ReOBr}_3(\text{hbt})]$, 116887-60-6; $\text{As}(\text{C}_6\text{H}_5)_4[{}^{99}\text{TcOBr}_4]$, 116887-56-0; $\text{As}(\text{C}_6\text{H}_5)_4[{}^{99}\text{TcOCl}_4]$, 97101-52-5; $\text{TcOCl}(\text{hbt})_2$, 113754-30-6; $\text{ReOCl}(\text{hbt})_2$, 116887-61-7; $\text{TcOBr}(\text{hbt})_2$, 116887-55-9; $\text{ReOBr}(\text{hbt})_2$, 116887-62-8; salicylaldehyde, 90-02-8; 2-aminothiophenol, 137-07-5.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom positional parameters, positional and thermal parameters, least-squares planes and deviations therefrom, and crystal data for the complex $\text{As}(\text{C}_6\text{H}_5)_4[\text{TcOCl}_3(\text{hbt})]$ and an ORTEP view of the cation $[\text{As}(\text{C}_6\text{H}_5)_4]^+$ (7 pages); a table of structure factor amplitudes (31 pages). Ordering information is given on any current masthead page.

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nido-Carborane Building-Block Reagents. 4.¹ Regiospecific Substitution at Boron in 2,3- $\text{R}_2\text{C}_2\text{B}_4\text{H}_6$ Cages. Evidence for Intramolecular C-H...H_{bridge} Interactions in 2,3- $\text{R}_2\text{C}_2\text{B}_4\text{H}_5$ -4-R' Derivatives

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Received August 3, 1988

Reactions of *nido*-2,3- $\text{R}_2\text{C}_2\text{B}_4\text{H}_5^-$ ions (R = ethyl, benzyl) with organic halides (R'X) generate B(4)-substituted derivatives together with the B(6)-substituted enantiomers. The formation of the $\text{R}_2\text{C}_2\text{B}_4\text{H}_5$ -4-R' products (R' = Me, Et, CH_2Ph , $(\text{CH}_2)_3\text{Ph}$, $\text{CH}_2\text{C}_6\text{H}_4\text{Me}$) is proposed to occur via $\text{R}_2\text{C}_2\text{B}_4\text{H}_5$ - $\mu(4,5)$ -R' bridged intermediates, which rapidly rearrange to the 4-substituted species. The reaction occurs cleanly, with $\leq 1\%$ contamination by other geometric isomers, and thus furnishes a useful regiospecific synthetic route to B-monosubstituted derivatives. In all cases examined, the products are air-stable liquids of low volatility that can be employed as building-block units in the synthesis of organometallic complexes and oligomers. Proton NMR spectra of several of the 2,3,4-trisubstituted products, supported by NOE experiments, indicate spin coupling between a C-CH₂ methylene proton and a B-H-B bridging hydrogen. The triethyl and tribenzyl derivatives were bridge-deprotonated by NaH, complexed to Fe^{2+} , and oxidatively fused to produce the hexasubstituted $\text{R}_6\text{C}_4\text{B}_8\text{H}_6$ carboranes, although the reaction was sluggish compared to those of the parent C,C'-disubstituted carboranes. The fused compounds are nonfluxional in solution, as determined from NMR spectra.

Carbon-substituted $\text{RR}'\text{C}_2\text{B}_4\text{H}_6$ *nido*-carboranes are readily obtained via the base-promoted reaction of B_3H_9 and $\text{RC}\equiv\text{CR}'$ under mild conditions.² This method has provided a reliable, general synthetic route to a wide variety of alkyl-,²⁻⁴ arylalkyl-,²

aryl-,^{1b} and silylcarboranes⁵ as well as bis- and tris(carboranes)^{1b} having two or more *nido*- C_2B_4 cages linked by $-(\text{CH}_2)_n-$ chains;

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(2) See ref 1 and references therein.

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Table I. 115.8-MHz ^{11}B FT NMR Data

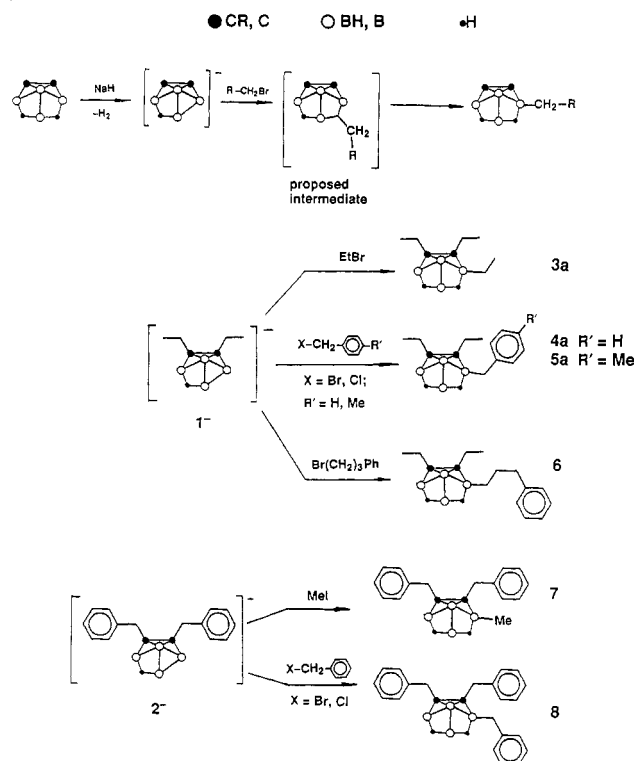
compd ^a	δ (J_{BH} , Hz) ^b	rel areas
2,3-Et ₂ C ₂ B ₄ H ₅ -4(6)-Et (3a)	7.40 ^c , -3.72 (148), -6.84 (146), -47.40 (171)	1:1:1:1
2,3-Et ₂ C ₂ B ₄ H ₅ -4(6)-CH ₂ Ph (4a)	5.77 ^c , -3.26 (142), -7.15 (162), -47.35 (174)	1:1:1:1
2,3-Et ₂ C ₂ B ₄ H ₅ -4(6)-CH ₂ -C ₆ H ₄ Me (5a)	6.23 ^c , -3.06 (157), -6.72 (147), -47.24 (177)	1:1:1:1
2,3-Et ₂ C ₂ B ₄ H ₅ -4(6)-(CH ₂) ₃ Ph (6)	6.21 ^c , -3.55 (152), -6.85 (134), -47.38 (175)	1:1:1:1
2,3-(PhCH ₂) ₂ C ₂ B ₄ H ₅ -4(6)-Me (7)	5.94 ^c , -3.34 (150), -5.44 (136), -47.06 (145)	1:1:1:1
2,3-(PhCH ₂) ₂ C ₂ B ₄ H ₅ -4(6)-CH ₂ Ph (8)	7.26 ^c , -2.73 (148), -5.29 (156), -46.45 (176)	1:1:1:1
H ₂ Fe[Et ₂ C ₂ B ₄ H ₅ -4(6)-Et] ₂ (11)	-0.27 (153), -1.12 ^d , -2.16 ^c , -19.58 (150)	1:1:1:1
Et ₆ C ₂ B ₈ H ₆ (13) ^e	7.48 ^c , -1.14 (112), -2.50 (133), -9.91 (138)	1:3:2:2
(PhCH ₂) ₆ C ₄ B ₈ H ₆ (14) ^f	6.94 ^c , 1.65 ^{d,g} , -0.57 ^d , -1.14 ^{d,g} , -3.25 ^d , -9.62 ^d , -10.44 ^{d,g}	~1:1:2:1:1:1:1

^a *n*-Hexane solutions. ^b Shifts relative to BF₃·OEt₂; positive values downfield. ^c Singlet (B-R). ^d *J* value not determinable. ^e Shifts given for the open-cage (A) form. Small peaks arising from the closed (B) form are also present in the spectrum (see text and Figure 4). ^f Mixture of positional isomers, all open-cage form (see text and Figure 5). ^g Shoulder.

indeed, in our experience almost all alkynes examined have been converted into their corresponding *nido*-carborane derivatives in this manner. In our laboratory, we have exploited this reaction in the designed synthesis of specific functionalized carboranes that can coordinate to transition metals via coordination at the C₂B₃ open face, at arenyl substituents attached to the cage, or both.² These complexes, in turn, can serve as building-block units for the construction of larger, multilevel electron-delocalized sandwich arrays (described elsewhere³) and may ultimately lead to polymers exhibiting low-dimensional electrical conductivity. Our progress in this area thus far has been described in the previous papers in this series¹ and in several earlier reports, and has recently been reviewed.^{3a}

As versatile as this chemistry has proved to be, it has nevertheless been limited to C-substituted derivatives and hence is dependent upon the availability of their R—C≡C—R' alkyne precursors. Clearly, from the standpoint of planned synthesis it is desirable to be able to use B-functionalized carboranes as well, since this not only expands the range of possibilities in preparing multidecker stacked systems but also allows investigation of the effects of B-substitution on such properties as metal-promoted fusion and base-induced "decapitation" (apex BH removal).^{3a} Few previous examples of B-organo-substituted derivatives of C₂B₄H₈ (or other small carboranes) have been reported, and certainly no general method for the controlled introduction of hydrocarbon substituents onto specific boron locations was available prior to this work. Onak et al.⁶ have prepared mixtures of *nido*-C₂B₄H₇-B-Me isomers from reactions of MeB₅H₈ and alkynes, while Hosmane and Grimes⁷ found that the bis(carborane) 5,5'-(Me₂C₂B₄H₅)₂, on air oxidation in benzene, affords Me₂C₂B₄H₅-4-Ph; also, C₂B₄H₇-4-CH₂SiMe₂Cl has been obtained⁸ by rearrangement of the 5-Me₂SiCl- derivative over AlCl₃. Wilczynski and Sneddon⁹ have prepared mixtures of B-alkenyl-R₂C₂B₄H₅ isomers via the Co-catalyzed addition of alkynes to the cage.

For our purposes, we required a way of achieving B-organo substitution in reasonable yield at a specific boron location, thereby avoiding the problem of isomer separation. Icosahedral-fragment *nido*-C₂B₉H₁₁²⁻ anions and their derivatives are known to undergo electrophilic B-alkylation by treatment with alkyl halides,¹⁰ al-

Scheme I**Table II.** 300-MHz ^1H FT NMR Data

compd	$\delta^{a,b}$	rel areas
3a	2.45 m (CH ₂), 2.37 m (CH ₂), 2.34 m (CH ₂), 1.19 t (CH ₃), -1.5 q (BH), -2.15 (BHB)	2:2:2:3:3:2:2
4a	7.20 m (C ₆ H ₅), 2.64 m (4-CH ₂), 2.45 m (2-CH ₂), 2.44 m (3-CH ₂), 2.31 m (3-CH ₂), 1.21 m (3-CH ₃), 1.06 m (2-CH ₃), -0.79 q (BH), -1.68 s (BHB), -2.13 s (BHB)	5:2:2:1:1:3:3:3:1:1
6	7.22 m (C ₆ H ₅), 2.68 m (CH ₂), 2.44 m (CH ₂), 2.34 m (CH ₂), 2.22 m (CH ₂), 1.79 m (CH ₂), 1.20 t (CH ₃), 1.07 t (CH ₃)	5:2:2:2:2:3:3:3:3
7	7.21 m (C ₆ H ₅), 3.75 m (CH ₂), 0.58 m (CH ₃)	10:4:3
8	7.13 m (C ₆ H ₅), 3.89 m (2-CH ₂), 3.72 m (3-CH ₂), 2.63 m (4-CH ₂), -0.6 q (BH), -1.35 s (BH), -2.05 s (BH)	15:2:2:2:2:1:1
11^c	2.64 m (C-CH ₂), 2.43 m (C-CH ₂ , B-CH ₂), 2.21 m (C-CH ₂), 2.02 m (C-CH ₂ , B-CH ₂), 2.02 m (C-CH ₂ , B-CH ₂), 1.14 m (C-CH ₃), 1.04 m (B-CH ₃), 0.67 m (C-CH ₃), -10.45 d (Fe-H)	1:1:1:1:4:3:3:2:2

^a CDCl₃ solution. ^b Shifts relative to (CH₃)₄Si. Key: m = multiplet, s = singlet, d = doublet, t = triplet, q = quartet. ^c Mixture of two isomers.

though the position of substitution varies and rearrangement to new isomers at room temperature is observed in some cases.^{10c} Despite the possibility of such complications in our system, we have explored the application of this type of reaction to *nido*-

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Table III. Infrared Absorptions (cm⁻¹; NaCl Plates)^a

compd	absorptions
3a	3214 m, br, 3000 sh, 2968 s, 2927 s, 2910 sh, 2902 sh, 2877 sh, 2836 sh, 2598 s, 2385 s, 2352 sh, 2287 w, 1950 m, 1918 m, 1458 s, 1392 s, 1335 s
4a	3082 w, 3025 m, 3000 sh, 2977 vs, 2935 s, 2877 s, 2590 vs, 1491 sh, 1450 vs, 1433 sh, 704 vs
6	3027 m, 2959 vs, 2931 vs, 2676 sh, 2656 sh, 2593 vs, 1496 s, 1453 vs, 935 w, 744 s, 697 vs
7	3243 w, br, 3099 w, 3066 m, 3025 s, 2976 sh, 2960 sh, 2918 vs, 2844 vs, 2606 vs, 2352 w, 2344 w, 1942 w, 1598 m, 1499 vs, 1450 vs, 728 vs, 698 vs
8	3065 sh, 3063 m, 3027 s, 2951 sh, 2925 m, 2923 sh, 2600 vs, 1601 m, 1495 vs, 1476 w, 1474 sh, 1453 vs, 1075 w, 1069 w, 1030 w, 960 w, 746 s, 725 sh, 697 vs

^aKey: vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, br = broad.

RR'C₂B₄H₅⁻ anions and find that it is indeed a viable synthetic route to the desired B-monosubstituted species. The present paper describes this work as well as some chemistry of the B-organo-substituted carborane products.

Results and Discussion

Reactions of Alkyl and Arylalkyl Halides with nido-R₂C₂B₄H₅⁻ Anions (R = Et, CH₂Ph). The C,C'-diethyl- and C,C'-dibenzylcarborane anions 1⁻ and 2⁻ (readily generated via bridge deprotonation¹¹ of the neutral species in glyme or THF) reacted easily with a variety of primary halides to generate the B(4)-substituted products 3a-8, together with their B(6) enantiomers (Scheme I). These compounds were isolated as colorless to pale yellow air-stable liquids and characterized from their ¹¹B and ¹H FT NMR, infrared, electronic, and unit- and high-resolution mass spectra (Tables I-III and Experimental Section). In several reactions the B(4/6) isomer was the only detectable product; in all other cases, very small amounts (≤1%) of the 5-substituted isomers (3b-5b) were found. No evidence of substitution at B(1) was observed under any conditions. Thus, the reaction is clean and highly regioselective, generating essentially a single geometric isomer.

The reaction mechanism probably entails the initial formation of a carbon-bridged intermediate (R₂C₂B₄H₅-μ(4,5)-R') which rapidly undergoes exchange of the bridging methylene carbon with the terminal H(4) atom (Scheme I). This is analogous to the observed^{10d} pathway of alkylation of C₂B₉H₁₁²⁻ and is also reminiscent of the sequence noted some time ago in the reactions of group IV halides with the C₂B₄H₇⁻ anion, in which the μ-MR₃-C₂B₄H₇ isomers (M = Si, Ge, Sn, Pb; R = H, Me) were isolated and characterized.¹² Similarly, μ-ClCH₂SiMe₂-C₂B₄H₇ undergoes quantitative rearrangement to the B(4)-substituted derivative.⁸ In the present case, however, the proposed R₂C₂B₄H₅-μ-R' intermediates isomerized too rapidly to permit their isolation or detection.

These findings raised the possibility of extending this reaction scheme through additional deprotonation/alkylation cycles to form di- and tri-B-substituted derivatives. We found that Et₂C₂B₄H₅-4-R derivatives (R = Et, CH₂Ph) are easily bridge-deprotonated by NaH in THF to give the Et₂C₂B₄H₄-4-R⁻ anions; however, treatment of the latter species with ethyl bromide or benzyl halides gave no evidence of the desired products (see concluding section). The only experiment in which higher B-substituted derivatives were observed involved a sample of the 2,3-diethyl-4-benzylcarborane (4a), which was allowed to stand for days in contact with benzyl chloride in air, after which Et₂C₂B₄H₄(CH₂Ph)₂ (9) and Et₂C₂B₄H₃(CH₂Ph)₃ (10) were identified from mass spectra. Since these species are not produced

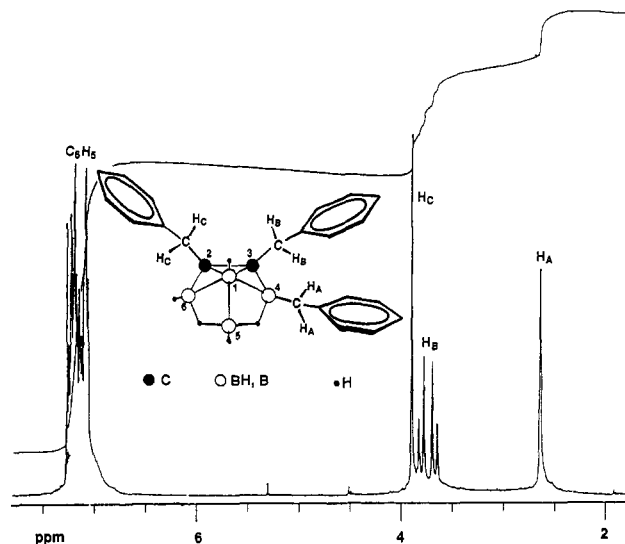


Figure 1. CH₂-C₆H₅ region of the 300-MHz proton FT NMR spectrum of 2,3,4-(PhCH₂)₃C₂B₄H₅ (8) in CDCl₃.

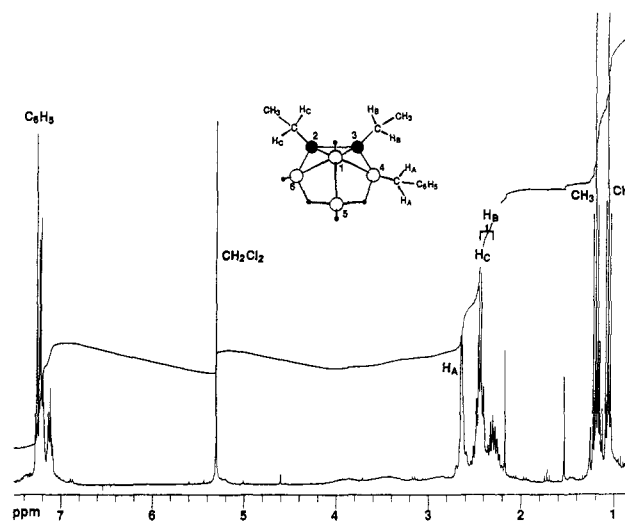


Figure 2. CH₂-C₆H₅/CH₂-CH₃ region of the 300-MHz proton FT NMR spectrum of 2,3-Et-4-(PhCH₂)-C₂B₄H₅ (4a) in CDCl₃.

in the solution reactions of 4a, it is likely that their formation in this case occurred via a free-radical process, which did not appear synthetically useful for our purposes and was not pursued.

NMR Studies. The primary structural features of the B-substituted derivatives are readily apparent from their NMR spectra, which are typical of nido-dicarbaboranes (e.g., the apical-boron ¹¹B NMR signals near δ -50 ppm), although the solution ¹H NMR spectra of several of these compounds exhibit unusual features that are suggestive of possible intramolecular H...H interactions. The 2,3,4-trisubstituted derivatives 3a-8 are asymmetric, and consequently the three organic substituents are inequivalent (even when they are identical, as in 3a and 8); hence, the CH₂ protons give rise to six resonances in each compound (Figures 1 and 2). Assignment of these peaks is straightforward, since CH₂-R protons generate multiplets (e.g., quartets or pairs of quartets) when R is methyl but simpler patterns when R is phenyl; also, CH₂ units attached to boron are identified by relatively broad lines and shifts near δ 2.6.¹³ While one cannot

- (13) For example, in the C,C'-diethyl-B-benzyl derivative 4a, the singlet arising from the B-CH₂-Ph methylene protons appears at δ 2.64 and is clearly distinguishable from the C-CH₂-Me multiplets, which are observed between δ 2.3 and δ 2.5. Similarly, in the tribenzyl species 8, one finds the C-benzyl CH₂ resonances at δ 3.7-3.9, corresponding to that of the C,C'-dibenzyl derivative,¹⁴ which is a pair of doublets centered at δ 3.91 (this value supersedes that reported in ref 14, which is incorrect); the singlet peak observed at δ 2.63 in 8 then is unambiguously assigned to the B-CH₂-Ph methylene protons.

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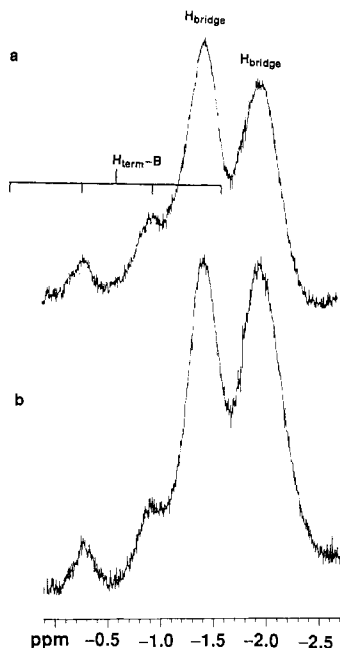


Figure 3. H_{bridge} region of the ^1H NMR spectra of **8**: (a) normal spectrum; (b) spectrum during selective irradiation of the C(3)- CH_2 low-field resonance.

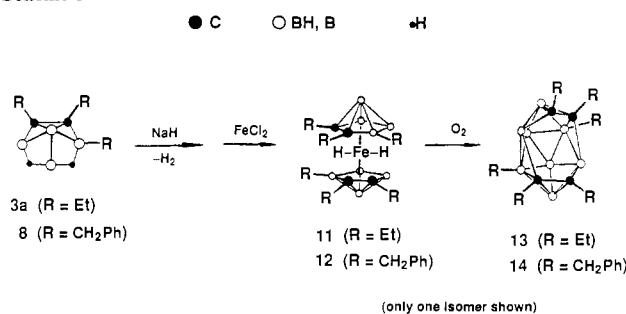
unambiguously distinguish the C(2)- CH_2 and C(3)- CH_2 resonances from each other, it is reasonable to assume that the latter signal will appear at higher field owing to shielding arising from the substituent on neighboring B(4); the assignments in Table II are based on this presumption, although we do not exclude the alternative possibility.

In examining the proton spectra we suspected that one or both B-H-B protons might be involved in spin-spin coupling with alkyl hydrogens on the substituents, and accordingly NOE experiments were conducted. The presence of a C(3)- CH_2 - H_{bridge} NOE interaction has been demonstrated in two ways. In the normal proton spectrum of **8** (Figure 3a), the two B-H-B resonances (superimposed on a B- H_{terminal} quartet) are of unequal integrated areas, but when the proton resonance of the C(3)-methylene protons is irradiated, there is a marked increase in intensity of one of the B-H-B signals (Figure 3b); further, when the B-H-B resonance is irradiated, the C(3)-methylene quartet is measurably sharpened and strengthened. No effects on any other resonances are observed on irradiation, establishing that there is a specific through-space interaction between a C(3)- CH_2 proton and one (presumably the nearest) of the two bridging hydrogen atoms on the open face.

This type of conformation is also seen in the 2,3-diethyl-4-benzyl derivative **4a**, whose proton NMR spectrum appears in Figure 2. Here the spectrum is more complex owing to splitting by the methyl hydrogens; thus, one sees quartets for the methylene protons on C(2)- CH_2 -Me (H_C) and a single resonance for those on B(4)- CH_2 -Ph (H_A). Each of the (H_B) protons generates a doublet of quartets as expected, although the downfield quartet is partially obscured by the C(2)-methylene resonance. Again, NOE experiments provide evidence of interaction between one of these methylene hydrogens and one of the B-H-B bridges: irradiation of the high-field C(3)- CH_2 quartet produces an increase in intensity of one B-H-B resonance, while irradiation of the latter peak has a similar effect on the C(3)-methylene signal.

It is remarkable that this kind of intramolecular proton-proton interaction occurs even in the case of a substituent as small as ethyl, and we were led to search for similar effects in the other 2,3- $\text{R}_2\text{C}_2\text{B}_4\text{H}_5$ -4- CH_2 - R' species prepared in this study. However, the C,C'-dibenzyl-B-methyl derivative **7** did not exhibit NOE evidence of methylene-bridge hydrogen interaction as was observed in the other compounds. This finding may in some way be a

Scheme II



consequence of the small steric bulk of the B-methyl group, although we are not prepared to speculate further on this point. In the remaining compounds, except for **1**, observation of such effects was precluded by extensive overlap of resonances in the region of interest.

In *nido*-2,3- $\text{R}_3\text{C}_2\text{B}_4\text{H}_5$ derivatives having one or more substituents attached to basal borons, one might anticipate chemical consequences, especially in the bridge deprotonation/metal complexation/ligand fusion sequence, which is characteristic of *nido*- C_2B_4 carboranes.^{3a} Since this process obviously involves the C_2B_3 face, increased basal substitution is expected to significantly slow the reaction (via steric hindrance) in comparison to those of the corresponding 2,3-disubstituted derivatives. Recent work in our laboratory^{1a,1b,11} has shown that, even in the disubstituted species, the presence of a sufficiently bulky group (e.g., indenylmethyl, fluorenylmethyl, or phenyl) on one or both cage carbon atoms severely hinders such reactions and, if two such groups are present, can even block metal complexation and fusion altogether. Consequently, it was of interest to explore the corresponding chemistry of the trisubstituted derivatives generated in this study.

Metal-Promoted Fusion of Trisubstituted *nido*- $\text{R}_2\text{C}_2\text{B}_4\text{H}_5$ -4- R'^- Anions. The oxidative fusion of *nido*- C_2B_4 ligands via complexation with Fe^{2+} or other metal ions to give C_4B_6 cages has been extensively investigated,^{2,3a,15-17} but only with C-substituted substrates. Inasmuch as the fusion is believed to proceed via interligand B-B linkage, the presence of organic groups on basal boron(s) of the *nido*- C_2B_4 ligands might be expected to interfere with the fusion process. In order to examine this question, the 2,3,4-triethyl and 2,3,4-tribenzyl derivatives (**3a** and **8**) were deprotonated by NaH in THF and treated with FeCl_2 to form red complexes (Scheme II). By analogy to the iron complexes previously obtained from *nido*- $\text{R}_2\text{C}_2\text{B}_4\text{H}_5^-$ ligands, these species were assumed to be $\text{H}_2\text{Fe}(\text{R}_2\text{C}_2\text{B}_4\text{H}_3\text{-4-R})_2$ (**11**, R = Et; **12**, R = CH_2Ph). This was confirmed via isolation of the bis(triethylcarborane)iron complex **11** and its characterization from NMR and mass spectra, which exhibit the features typical of this class of complex (including a high-field Fe-H proton NMR signal). As shown in Scheme II, both iron complexes did undergo fusion on exposure to oxygen, and the hexasubstituted $\text{R}_6\text{C}_4\text{B}_6\text{H}_6$ products (**13**, R = Et; **14**, R = CH_2Ph) were isolated in good yield as air-stable white solids.

These observations are qualitatively comparable to the complexation/fusion behavior of *nido*- $\text{R}_2\text{C}_2\text{B}_4\text{H}_5^-$ ions having no B substituent,¹⁵⁻¹⁷ but the reactions of **3a** and **8** are sluggish in comparison to those of their non-B-substituted counterparts. For example, although the formation of the bis(diethylcarborane)iron complex $\text{H}_2\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)_2$ from $\text{Et}_2\text{C}_2\text{B}_4\text{H}_5^-$ and FeCl_2 in THF occurs within minutes at -30°C ,¹⁸ the corresponding reaction of the 2,3,4-triethylcarborane anion to form **11** is slow even at 0°C and requires warming to room temperature for completion. The fusions of these iron complexes contrast even more dramatically: while the bis(diethylcarborane) complex forms $\text{Et}_4\text{C}_4\text{B}_6\text{H}_6$ in

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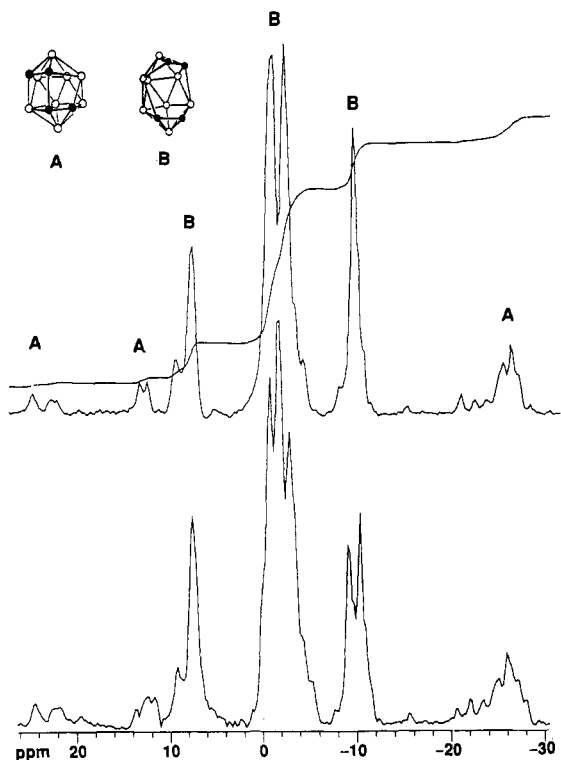


Figure 4. 115.8-MHz ^{11}B FT NMR spectra of $\text{Et}_4\text{C}_4\text{B}_8\text{H}_8$ (**13**) in *n*-hexane: top, proton decoupled; bottom, undecoupled.

minutes on exposure¹⁸ to O_2 , the bis(triethylcarborane) species **11** displays no color change in 1 h and requires overnight treatment with O_2 augmented by FeCl_3 to achieve fusion in good yield. Similar effects were noted in the 2,3,4-tribenzylcarborane system **8** and its iron complex **12**, in comparison to the 2,3-dibenzylcarborane and its corresponding iron complex: the metal-complexation and fusion reactions of the latter species¹⁶ are much more facile than those of the tribenzyl compounds.

Solution Properties of the Hexasubstituted Fusion Products. Previous studies¹⁹ have shown that tetra-C-substituted $\text{R}_4\text{C}_4\text{B}_8\text{H}_8$ carboranes exhibit interesting fluxional behavior involving equilibria between open-cage and quasi-closed-cage forms, except when R is bulky (e.g., benzyl), in which case only the open form is seen.^{1,2} Therefore, it is worthwhile to compare the ^{11}B NMR spectra of the hexasubstituted derivatives **13** and **14** (Figures 4 and 5) with those of their tetrasubstituted counterparts $\text{Et}_4\text{C}_4\text{B}_8\text{H}_8$ ¹⁹ and $(\text{PhCH}_2)_4\text{C}_4\text{B}_8\text{H}_8$.¹⁶ The spectra of **13** and **14** are more complex, which undoubtedly reflects the presence of geometric isomers arising from the chirality of the 2,3- $\text{R}_2\text{C}_2\text{B}_4\text{H}_3$ -4- R'_2 ligands; as discussed elsewhere,^{16,17} fusion of such ligands can occur in at least two ways to give distinguishable stereoisomers that differ in the relative positions of the substituents. In both **13** and **14**, the isomer mixtures were not resolvable via chromatography.

The spectrum of **13** (Figure 4), like that of the corresponding tetraethyl compound, contains resonances attributable to both closed (A) and open (B) forms. However, in contrast to that of the tetraethyl species,¹⁹ the spectrum of **13** does not change with time, so that the ratio of open to closed cage isomers is fixed. Despite the complexity of the spectrum, it is apparent that the open/closed ratio in **13** is slightly larger than that in $\text{Et}_4\text{C}_4\text{B}_8\text{H}_8$, indicating that the *B*-ethyl groups in **13** influence the dynamics of cage rearrangement via intramolecular steric interaction, which favors the open form.

In the case of **14**, the spectrum (Figure 5) indicates that *only* the open form is present, as is observed also for $(\text{PhCH}_2)_4\text{C}_4\text{B}_8\text{H}_8$.¹⁶ Again, the spectrum does not change with time, so that **14**, like its tetrabenzyl analogue, is nonfluxional and is locked into an

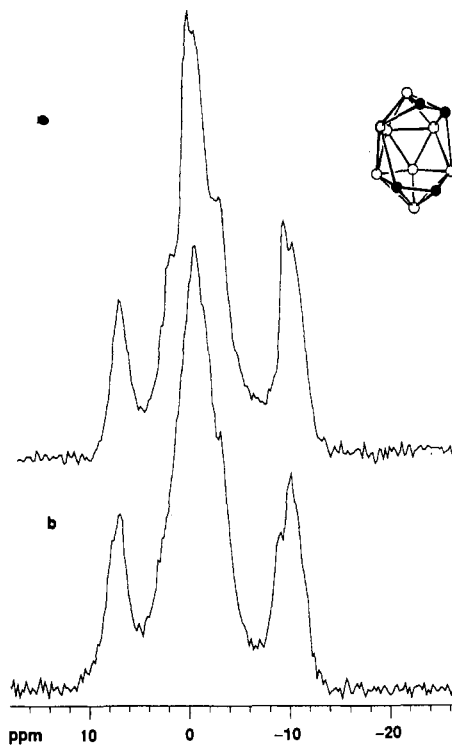


Figure 5. 115.8-MHz ^{11}B FT NMR spectra of $(\text{PhCH}_2)_6\text{C}_4\text{B}_8\text{H}_6$ (**14**) in *n*-hexane: (a) proton decoupled; (b) undecoupled.

open-cage configuration. These findings are readily accounted for by the large steric bulk of the benzyl units, which causes the closed-cage (A) geometry to be unfavorable.

General Observations

This work provides a controlled regiospecific route to B(4/6)-organosubstituted derivatives of *nido*- $\text{R}_2\text{C}_2\text{B}_4\text{H}_6$, thereby extending the versatility of carboranes of this class as building-block units in synthesis.³ For example, while the *C,C'*-dibenzyl derivative $(\text{PhCH}_2)_2\text{C}_2\text{B}_4\text{H}_6$ is trifunctional (in that the C_2B_3 open face and the phenyl rings present three sites for metal complexation), the tribenzylcarborane **8** is tetrafunctional and thereby opens up new modes of possible linkage via transition-metal centers. Consequently, the accessibility of B-functionalized *nido*-carboranes should facilitate the task of designing materials (e.g., electron-delocalized metallocarborane polymers) having desired properties associated with particular structural features.³

The fact that only mono-B-substitution is observed under the conditions employed is significant; even when alkylation of the *dianions* of **1** and **2** is attempted, only monosubstituted products are isolated. This is understandable when it is recognized that the *nido*-carborane anions in general can function both as a nucleophile—accepting electropositive groups at the B–B edge—and as a base, abstracting a proton from substrate proton donors. In the boron-unsubstituted species (e.g., **1**[−] and **2**[−]), the former property is usually dominant, leading to reasonable yields of the B-monofunctional products in most cases. In the B(4)-substituted anions, the lone bridging hydrogen probably adopts the B(5)–B(6) location, since one expects the B(4)–B(5) edge, adjacent to the substituent, to provide a more stable site for a localized negative charge. In that event, attack of an incoming group is electronically favored at B(4)–B(5) but is hindered by the substituent on B(4); hence, the base-character of the carborane anion predominates and the result is regeneration of the neutral carborane (as observed) rather than introduction of a second organic group.

It is important to recognize that the substitution at B(4,6) is truly regiospecific, since the statistical expectation for attack at B(4,6) vs B(5), if no selective driving force were operative, would be a 2:1 mixture of these isomers. Assuming that a B–C–B bridged intermediate is formed initially as suggested above, the rearrangement to the B(4,6)- rather than the B(5)-substituted derivative is probably dictated by higher negative charge on B(4,6).

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This hypothesis is supported by MNDO calculations²⁰ on $C_2B_4H_8$, although earlier PRDDO calculations had indicated that B(5) is slightly more negative.²¹ While B(1) is the most negative site in the molecule,^{20,21} there is no evidence of substitution at that location, as expected from the proposed mechanism; direct migration from a bridging to an apical location would be highly unlikely.

The presence of an ethyl or benzyl substituent on B(4) does not prevent either the formation of a bis(carboranyl)iron complex or fusion of the latter to generate a tetracarbon carborane product, but it does detectably slow both processes, particularly in the case of the benzyl derivative. With respect to the fusion of the triethyl- and tribenzylcarborane ligands in the $H_2Fe(R_2C_2B_4H_5-R)_2$ complexes, it is not surprising that the process is sluggish in comparison to the C,C'-disubstituted species, since interligand repulsion must be significantly increased when organic groups are attached to basal boron atoms. In light of these findings, the fusion properties of tri- and tetra-B-substituted *nido*- C_2B_4 complexes are clearly of interest and will be examined as these compounds become available.

Experimental Section

Except where otherwise indicated, materials, instrumentation, and general procedures were identical with those described in earlier publications in this series.¹ The carboranes $Et_2C_2B_4H_6$ (**1**) and $(PhCH_2)_2C_2B_4H_6$ (**2**) were prepared as reported elsewhere.^{14,22}

Synthesis of 2,3-Et₂C₂B₄H₅-4-Et (3a). An 0.84-g (6.4-mmol) sample of **1** was distilled in vacuo into a monoglyme suspension of 0.30 g (6.4 mmol) of NaH, and the mixture was allowed to react at room temperature until H₂ evolution had ceased. Ethyl bromide (5.0 g, 46 mmol) was added to the solution at 0 °C, and the mixture was warmed to room temperature and stirred overnight. The contents were opened to the air and filtered through 2 cm of silica, and the solvent was removed by rotary evaporation. The yellow liquid residue was transferred to a vacuum line and distilled for 4 h at room temperature through traps at 0 and -80 °C. The material in the -80 °C trap was identified as unreacted **1** (0.365 g). The 0 °C trap contained 0.22 g (1.3 mmol, 39% yield based on **1** consumed) of **3a** as a clear colorless liquid that exhibits no change in air over several hours. Exact mass: calcd for $^{12}C_8^{11}B_4^1H_{20}^+$, 160.1937; found, 160.1939.

The ¹¹B NMR spectrum of **3a** contains very small peaks (≤1% of total peak area) at δ 12 (singlet, B-Et) and -7 (shoulder, B-H), which were assigned to the $Et_2C_2B_4H_5$ -5-Et isomer (**3b**). The apex BH signal for **3b** is not observed and is presumably under the corresponding **3a** peak.

Synthesis of 2,3-Et₂C₂B₄H₅-4-CH₂Ph (4a). To a solution of 0.78 g (5.9 mmol) of **1** in THF at -78 °C was added, via a syringe through a septum, 2.5 mL of a 2.5 M solution of *n*-butyllithium in hexane. The solution was warmed to room temperature and stirred for 30 min, after which it was cooled to -78 °C and benzyl chloride (0.64 mL, 5.6 mmol) was added via syringe. The solution was warmed to room temperature, stirred overnight, and opened to the air, and the solvent was removed by rotary evaporation. The residue was extracted with 50 mL of 1:1 (v/v) *n*-hexane/ether, the resultant mixture was filtered through 1 cm of silica, and the solvent was removed. The liquid residue was transferred via pipet to a vessel that was attached to a vacuum line, and the liquid was heated in vacuo at 70 °C while the distillate was collected in 0 and -78 °C traps. The -78 °C material was unreacted **1** (0.320 g, 2.4 mmol), while the trap at 0 °C contained 0.120 g (0.54 mmol, 15% based on carborane consumed) of **4a**, obtained as a colorless liquid that is unchanged in air over a period of days. Exact mass: calcd for $^{12}C_{13}^{11}B_4^1H_{22}^+$, 222.2094; found, 222.2096.

As in the case of **3a** above, the ¹¹B NMR spectrum of **4a** contained small peaks at δ 11 (singlet, B-benzyl) and -5.8 (doublet, B-H) which indicated the presence of ≤1% 2,3-Et₂C₂B₄H₅-5-CH₂Ph (**4b**). Again, the apex BH peak of **4b** is not visible and is assumed to be superimposed on that of **4a**.

Visible-UV absorptions (nm) of **4a** in CH₂Cl₂: 232 (84%), 265 (4%), 270 (2%).

Synthesis of 2,3-Et₂C₂B₄H₅-4-CH₂C₆H₄Me (5a). A procedure identical with that employed in the synthesis of **4a** was conducted with xylyl chloride in place of benzyl chloride. From 1.24 g (9.4 mmol) of **1**, following deprotonation with excess NaH in THF and reaction with 0.69

g (9.4 mmol) of xylyl bromide, was obtained 0.67 g (2.8 mmol, 30% yield) of **5a** after purification via chromatography on silica.

Synthesis of 2,3-Et₂C₂B₄H₅-4-(CH₂)₃Ph (6). A solution of 0.77 g (5.9 mmol) of **1** in THF was deprotonated with NaH (0.28 g, 5.9 mmol). The solution was filtered, 1.0 g of 1-bromo-3-phenylpropane (corresponding to a 10% molar deficiency, ensuring complete consumption of the reagent) was added, the mixture was stirred at room temperature overnight and opened to the air, and solvent was removed by rotary evaporation. The residue was extracted with 50 mL of 1:1 dichloromethane/ether, the resulted mixture was filtered through 1 cm of silica, and the solvent was again removed by evaporation. The yellow liquid residue was placed on a vacuum line and distilled for 2 h at 100 °C and 5×10^{-5} Torr in a short-path arrangement through traps at 0 and -78 °C. After it was cooled to room temperature, the residue in the distillation bulb was characterized as pure **6**, yield 0.410 g (1.60 mmol, 66% based on **1** consumed). The condensates at 0 and -78 °C were respectively unreacted 1-bromo-3-phenylpropane and unreacted **1** (0.44 g). Compound **6** is a viscous, nonvolatile, pale yellow air-stable liquid. Exact mass: calcd for $^{12}C_{15}^{11}B_4^1H_{26}^+$, 250.2407; found, 250.2412. Visible-UV absorptions (nm): 232 (95%), 264 (15%), 270 (14%), 282 (5%), 304 (2%).

Synthesis of 2,3-(PhCH₂)₂C₂B₄H₅-4-Me (7). The dibenzylcarborane **2** (1.08 g, 4.2 mmol) was deprotonated with NaH (0.20 g, 4.2 mmol) in THF, and to the resulting solution of Na⁺(PhCH₂)₂C₂B₄H₅⁻ was added 0.34 mL (4.2 mmol) of methyl iodide via syringe at room temperature. After stirring overnight, the solution was opened to the air and the THF stripped off via rotary evaporation. The bright yellow liquid residue was extracted with 200 mL of 1:1 *n*-hexane/ether, the resultant mixture was filtered through 2 cm of silica, and the solvent was removed in vacuo. At this point a mass spectrum of the residue showed the presence of **7** as the main component together with **2** and a monoiodo derivative of **2**. Preparative thick-layer chromatography on silica in *n*-hexane gave three bands having *R_f* values of 0.05, 0.30 (**7**), and 0.35 (unreacted **2**; 0.38 g, 1.5 mmol). The isolated **7** (0.40 g, 1.40 mmol, 52% based on carborane consumed) was isomerically pure but revealed traces of **2** on mass spectral analysis. Compound **7** is a pale yellow, air-stable liquid.

Synthesis of 2,3-(PhCH₂)₂C₂B₄H₅-4-CH₂Ph (8). A 1.27-g (5.0-mmol) sample of **2** was deprotonated with 0.24 g (5.0 mmol) of NaH in THF at room temperature, and to the solution was added 0.85 g (5.0 mmol) of benzyl bromide. The mixture was refluxed at 60 °C for 1.5 h in THF, cooled to room temperature, and opened to the air, and solvent was stripped off by evaporation. The residue was extracted with 200 mL of diethyl ether, the resultant mixture was filtered through 1 cm of silica, and the ether was removed by evaporation to give a yellow liquid residue (0.8 g), which was chromatographed on preparative silica plates in *n*-hexane. Two bands were obtained, one of which (*R_f* 0.35) was **2** (0.264 g, 1.0 mmol) and the other of which (*R_f* 0.13) was **8** (0.160 g, 0.46 mmol, 12% based on **2** consumed), obtained as an air-stable colorless liquid. Exact mass: calcd for $^{12}C_{23}^{11}B_4^1H_{26}^+$, 346.2407; found, 346.2417. Visible-UV absorptions (nm): 232 (95%), 266 (16%), 272 (12%).

Observation of B,B'-Dibenzyl- and B,B',B''-Tribenzyl-C,C'-diethylcarboranes. A solution of the *B*-monobenzyl derivative **4a** (0.69 g) in 1.7 mL of benzyl chloride was allowed to stand in an open flask exposed to air and light for 2 weeks, during which the colorless solution turned yellow and solid material precipitated. The solution was filtered and the benzyl chloride removed in vacuo to give a yellow sludge, which was taken up in 50 mL of diethyl ether; the resultant mixture was filtered through silica to give a bright yellow solution. The solvent was removed by rotary evaporation to give a yellow oil, which was chromatographed on 0.25-mm silica plates in 10% ethanol/hexane. Three bands were eluted, of which the major one was **4a** (0.67 g). The minor bands (*R_f* 0.42 and 0.45) were identified from their mass spectra (parent envelopes closely matching the calculated intensities) as $Et_2C_2B_4H_4(CH_2Ph)_2$ (**9**) and $Et_2C_2B_4H_3(CH_2Ph)_3$ (**10**), respectively. The quantities of these materials collected were insufficient for further characterization.

Synthesis of H₂Fe(Et₂C₂B₄H₅-4-Et)₂ (11). A THF solution of the carborane monoanion **3a**⁻ prepared from 0.365 g (2.3 mmol) of **3a** and an equimolar amount of NaH was filtered in vacuo onto solid FeCl₂ (0.30 g, 2.5 mmol) that was maintained at liquid-nitrogen temperature. The mixture was warmed to -18 °C (benzyl alcohol slush) and stirred for 1 h, and the temperature was slowly raised to 0 °C, at which point the colorless solution acquired a red-orange color. After being stirred for 1 h, the solution was warmed to room temperature and stirred for 15 min as the color changed to deep red-brown. The THF was removed by evaporation in vacuo, the mixture was placed in a drybox and extracted with *n*-hexane, and the resultant solution was chromatographed on a silica column in hexane. One major, deep red band was collected and the solvent removed on a Schlenk line. The red oil residue was placed in a sublimator on the vacuum line and the product sublimed on a -78 °C cold finger by heating at 70 °C for 1.5 h at 5×10^{-5} Torr. The sublimate was dissolved in *n*-hexane in the drybox and the solvent again

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removed on a Schlenk line to give a red-black oil (0.218 g, 0.58 mmol, 51.3% based on carborane reagent employed).

Synthesis of $\text{Et}_4\text{C}_4\text{B}_8\text{H}_6\text{Et}_2$ (13**).** The iron complex **11** prepared in the preceding synthesis was opened to the air, 5 mL of dry THF was added, the solution was pipetted into an open flask, and 0.1 g of FeCl_3 was added. Dioxygen was bubbled into the solution, producing no detectable color change after 1 h. The O_2 treatment was continued for 12 h, which gave a brown suspension, from which solvent was removed by evaporation to give a brown sludge, which was extracted with *n*-hexane. The resultant solution was placed on a 5-cm silica column and eluted with 200 mL of 50:50 *n*-hexane/dichloromethane. The colorless eluent was rotary-evaporated to give 0.411 g of a viscous, colorless liquid. Thin-layer chromatography on silica in *n*-hexane gave one band, R_f 0.68, which was extracted with dichloromethane and rotary-evaporated to give 0.125 g (0.40 mmol, 68% yield) of **13**. Exact mass: calcd for $^{12}\text{C}_{16}^{11}\text{B}_8^{1}\text{H}_{36}^+$, 316.3562; found, 316.3579. Visible-UV absorptions (nm): 234 (68%), 258 (76%), 296 (88%).

Synthesis of $(\text{PhCH}_2)_4\text{C}_4\text{B}_8\text{H}_6(\text{CH}_2\text{Ph})_2$ (14**).** Following the procedure employed in the preceding two syntheses, 0.119 g (0.34 mmol) of the tribenzylcarborane **8** was deprotonated with 0.38 mmol of NaH in THF, and 0.34 mmol of FeCl_2 was added. The red iron complex **12** was not isolated in this case, but its solution was warmed to room temperature

and stirred overnight. Workup identical with that used for **13** above gave a colorless liquid, which was thin-layer chromatographed on silica to give four bands. Band 1 (R_f 0.03) was **14**, 0.070 g (62% yield). Bands 2 and 3 (R_f 0.11 and 0.19) were unidentified non-boron-containing materials, and band 4 (R_f 0.32) was the starting carborane **8**. Crystals of **14** were grown in 4:1 *n*-hexane/dichloromethane solution. Visible-UV absorptions (nm): 254 (60%), 284 (58%), 300 (59%).

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Registry No. **1**, 80583-48-8; **2**, 105472-14-8; **3a**, 116910-63-5; **4a**, 116910-64-6; **5a**, 116910-65-7; **6**, 116910-66-8; **7**, 116910-67-9; **8**, 116910-68-0; **9**, 116910-69-1; **10**, 116910-70-4; **11**, 116926-52-4; **12**, 116926-53-5; **13**, 116910-71-5; **14**, 116910-72-6; $\text{Na}^+(\text{PhCH}_2)_2\text{C}_2\text{B}_4\text{H}_5^-$, 116926-51-3; FeCl_2 , 7758-94-3; benzyl chloride, 100-44-7; xylol chloride, 104-82-5; xylol bromide, 104-81-4; 1-bromo-3-phenylpropane, 637-59-2; methyl iodide, 74-88-4; benzyl bromide, 100-39-0; ethyl bromide, 74-96-4.

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New Multidentate Ligands. 29. Stabilities of Metal Complexes of the Binucleating Macrocyclic Ligand BISBAMP and Dioxygen Affinity of Its Dinuclear Cobalt(II) Complex

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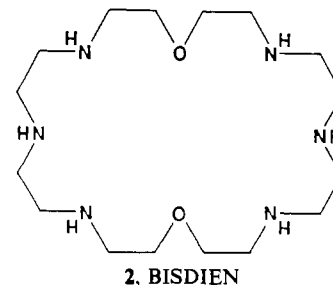
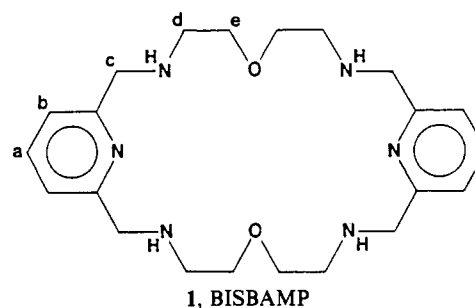
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The macrocyclic ligand 3,9,17,23,29,30-hexaaza-6,20-dioxatricyclo[23.3.1.1^{11,15}]triaconta-1(28),11,13,15(30),25,26-hexaene, BISBAMP, has been prepared and isolated as the hexahydrochloride. The protonation constants of BISBAMP are determined from potentiometric measurements at 25.0 °C and $\mu = 0.100$ M (KNO_3). The stability constants of the mononuclear and binuclear Co(II), Ni(II), Cu(II), and Zn(II) complexes are reported. The formation of monoprotonated binuclear BISBAMP complexes with the metal ions is observed, as well as several protonated and hydroxo species. The dinuclear complexes show a strong tendency toward hydroxide ion bridging between the metal ions. The stability of the Co(II) dioxygen complex has been determined, and the potentiometric data reveal that dioxygen complex formation occurs in basic solution and that the (μ -hydroxo)(μ -peroxo)dinuclear cobalt(III) complex forms several hydroxo species.

Introduction

Metal complexes of binucleating macrocyclic ligands may serve as models for certain metalloproteins that require the presence of two metal centers. Thus, it has been proposed that type III copper proteins contain two Cu(II) ions with a hydroxo bridge.¹ In oxyhemocyanin two Cu(II) ions are doubly bridged by a peroxo and an oxygen-donor ligand.² In bovine superoxide dismutase an imidazolate ion acts as a bridge between Cu(II) and Zn(II).³ In order to mimic the structure of these proteins, a large number of synthetic ligands have been prepared. For ligands with an appropriate disposition of donor atoms, it has been possible to show the presence of hydroxo,⁴ imidazolato,⁵ azido,^{6,7} and thiocyanato⁷⁻⁹ bridges between metal ions. Although these results show an increasing understanding of the synthetic and structural aspects of the problem, there are still few reports dealing with solution studies in which the interaction between the macrocycle and the metal ions is analyzed over a wide range of conditions¹⁰⁻¹⁴ in order to determine the complex species formed and the corresponding equilibrium constants for their formation.

In this paper, the synthesis of the macrocyclic compound 3,9,17,23,29,30-hexaaza-6,20-dioxatricyclo[23.3.1.1^{11,15}]triaconta-1(28),11,13,15(30),25,26-hexaene, BISBAMP (**1**), is reported. It has been isolated as the hexahydrochloride with the purity required for potentiometric equilibrium determinations. This



compound is structurally related to BISDIEN (**2**, 1,4,7,13,16,19-hexaaza-10,22-dioxacyclotetracosane),^{11,15} BIS-

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