Organometallics **1990**, *9*, 1171-1176

methods; no absorption corrections were made. Details are given in Table VI. Programs used were the NRCVAX suite[32] and SHELX-76.[33] Scattering factors were taken from ref 34.

In $[CpMoCl(O)]_2(\mu\text{-}O)$ the H atoms were allowed to ride on the C atom to which they were attached (r(C-H) = 0.96 Å), and the isotropic thermal parameter of each hydrogen was varied independently. The positional parameters for $[CpMoCl(O)]_2(\mu\text{-}O)$ are given in Table VII and important distances and angles in Table V, and other relevant data have been deposited as supplementary material (see the paragraph at the end of the paper).

The disorder in $CpMoCl_2(O)$ is discussed above. In the final refinement the Mo, Cl, and O atoms were anisotropic. The C_5H_5 ring, which was disordered over two major sites, was refined as two independent rigid bodies, each of half-occupancy, with C-C distances of 1.42 Å and C-H distances of 0.96 Å. Each ring was assigned a single, isotropic, thermal parameter. The final difference Fourier synthesis had "ghost" peaks at approximately 0.85 Å from all atoms, these being due to the slippage discussed above. Positional parameters are listed in Table VIII, important distances and angles in Table I; other data have been deposited as supplementary material.

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Supplementary Material Available: Lists of hydrogen atom positions, U_{ij} values, bond distances and angles, distances to the least-squares planes, and anisotropic thermal parameters for $[CpMoCl(O)]_2(\mu\text{-}O)$ and $CpMoCl_2(O)$ (5 pages); lists of observed and calculated structure factors for $[CpMoCl(O)]_2(\mu\text{-}O)$ and $CpMoCl_2(O)$ (13 pages). Ordering information is given on any current masthead page.

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Organotransition-Metal Metallacarboranes. 15.[1] Regiospecific B-Alkylation of (arene)M($Et_2C_2B_3H_5$) (M = Fe, Ru) and (C_5Me_5)Co($Et_2C_2B_3H_5$) Sandwich Complexes

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The controlled introduction of hydrocarbon substituents onto specific boron locations in *nido*-metallcarborane complexes of the title classes has been achieved via bridge deprotonation followed by reaction with alkyl or arylalkyl halides. The monodeprotonated complex anions react with MeI, EtBr, *p*-$MeC_6H_4CH_2Br$, or *p*-$BrCH_2C_6H_4CH_2Br$ in THF to generate exclusively the B(5)-substituted derivative in each case. This pattern differs strikingly from the corresponding reactions of *nido*-$R_2C_2B_4H_5^-$ carborane anions, which had been shown in an earlier study to give the B(4)- (and equivalent B(6)-) alkylated products with 99% regiospecificity. In the present work, the *B*(*5*)-methyl complexes of Fe, Ru, and Co were each further alkylated via deprotonation/alkyl halide treatments, to give successively the *B*(*4,5*)-dimethyl and *B*(*4,5,6*)-trimethyl derivatives as desired. The alkylated products were isolated in generally high yields; for the three compound classes studied, the *B*-monomethyl complexes are extremely air-stable, but the sensitivity to air increases on further alkylation. Reactions of the $(C_6Me_6)Fe(Et_2C_2B_3H_3)^{2-}$ and $(C_5Me_5)Co(Et_2C_2B_3H_3)^{2-}$ dianions with alkyl iodides result in partial iodination at the B(4) position.

Introduction

In a series of papers we have described methods for the systematic preparation of C- and B-substituted derivatives[2,3] of *nido*-2,3-$C_2B_4H_8$, the conversion of these to arene-transition-metal-carborane double- and triple-decker sandwich complexes,[1,3,4] and the utilization of such complexes as building blocks in constructing stacked or linked-sandwich electron-delocalized systems.[1b,5] One of the long-range objectives of this work is the directed synthesis of electronically active polymers or solid-state networks that are stabilized by cyclic $R_2C_2B_3H_3^{4-}$ or pyramidal $R_2C_2B_4H_4^{2-}$ carborane units and can be tailored to exhibit specific desired properties.[2,3]

Prior to this work our synthetic strategies have centered on assembling sandwich or linked-sandwich systems from *nido*-carborane anions, metals, and arene (or cyclo-

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pentadienyl) ligands. Thus, in order to make multiunit double- and triple-decker systems, we employed polyarene ligands such as fulvalene ($(C_5H_4)_2$) or bis(tetramethylcyclopentadienyl)phenylene.[1b] An alternative approach would involve functionalizing parent metallacarborane clusters and then proceeding to link these by standard organomeallic reactions, but the required methods for attaching substituents to specific boron locations on *closo*-($R_2C_2B_4H_4$)M(ligand) or *nido*-($R_2C_2B_3H_5$)M(ligand) complexes have not been available. Until recently, the same was true of 2,3-$R_2C_2B_4H_6$ *nido*-carboranes; however, in a recent study[2c] we found that alkylation at the B(4) (or the equivalent B(6)) position in these molecules occurs with 99% regiospecificity upon attack of alkyl or arylalkyl halides on $R_2C_2B_4H_5^-$ monoanions. The B(4/6)-substituted carboranes can then readily be converted to metal sandwich complexes via routes described elsewhere.[1]

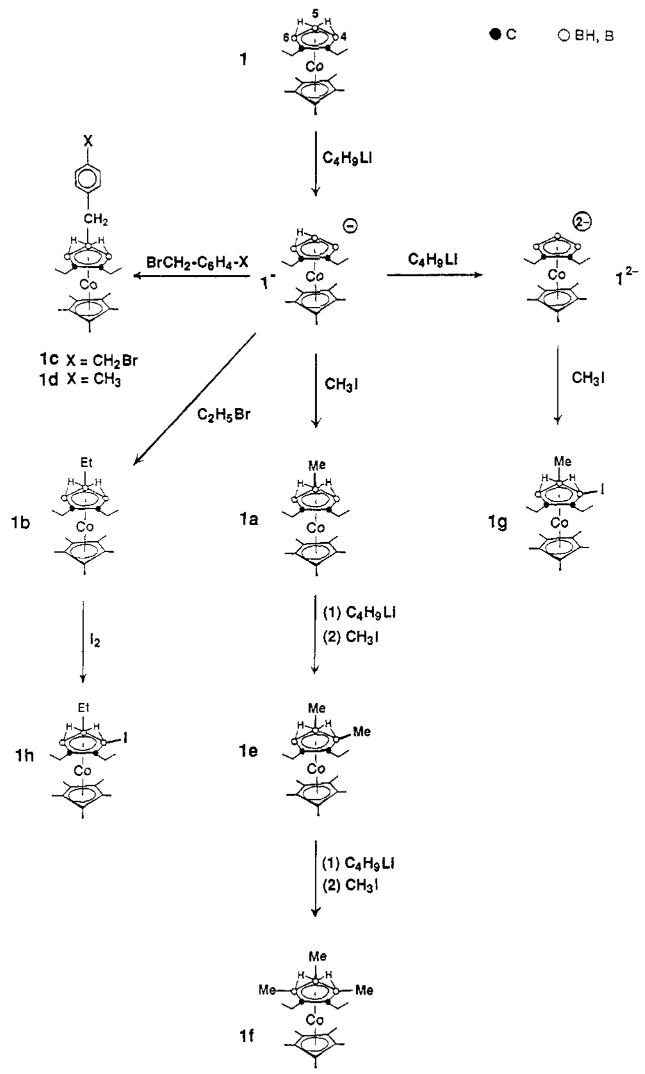
As we have sought to develop further the designed synthesis of multiunit linked sandwiches from monomers, the need for procedures to achieve controlled B-functionalization of carborane–metal complexes has become apparent. Here we report an effective means of accomplishing this, with an unexpected finding that greatly augments the synthetic utility of the method and, furthermore, provides a basis of comparison of the reactivities of the parent C_2B_4 *nido*-carboranes and their *nido*-MC_2B_3 analogues.

Results

An obvious strategy for alkylating *nido*-($R_2C_2B_3H_5$)M(ligand) complexes is to bridge-deprotonate them and treat the resulting anions with alkyl halides, in a sequence formally analogous to the alkylation of *nido*-$R_2C_2B_4H_6$ carboranes referred to above. Conceptually, this approach exploits the isostructural and isoelectronic relationship between these two classes (the $(C_5Me_5)Co$, (arene)Fe, and (arene)Ru ligand–metal units in the complexes are isolobal with the apex BH group of the carborane cage). In the present investigation, we examined the reactions of several varieties of *nido*-$(R_2C_2B_3H_4)M(\text{ligand})^-$ anionic complexes with organic halides and found that B-alkylation does, indeed, occur readily but with two remarkable and unexpected features. In all cases examined, the alkylation occurs solely at the central boron atom (B(5)), precisely opposite to the B(4/6)-substitution pattern exhibited by the $R_2C_2B_4H_5^-$ carboranes; moreover, in contrast to the latter species, which undergo only monosubstitution under these conditions, the metal complexes can be sequentially mono-, di-, and tri-B-alkylated with isolation of each species as a pure product.

Reactions of ($Et_2C_2B_3H_5$)Co(C_5Me_5) (1). Scheme I depicts the interaction of the monoanion 1^- and dianion 1^{2-} with several alkyl halides. Treatment of the monoanion in cold THF solution with 1 molar equiv of methyl iodide, ethyl bromide, α,α'-dibromoxylene, and α-bromoxylene gave respectively the B(5)-alkylated derivatives **1a–d**, in 60–98% isolated yield with no evidence of other isomers or polysubstituted products. These compounds, and all others reported herein, were isolated via column or high-performance liquid chromatography as yellow solids (cobalt and iron species) or nearly colorless oils or solids (ruthenium complexes) of moderate to high air stability, as discussed below. Characterization of the new derivatives is based on ^{11}B and ^1H NMR, infrared, and unit- and high-resolution mass spectroscopy (see Tables I–III and the Experimental Section). The attachment of organic substituents at specific boron locations was readily determined from the presence of singlet B-alkyl resonances in the proton-coupled ^{11}B NMR spectra. While the reaction mechanism was not examined directly, we postulate that the introduction of the organic group takes place initially at the unprotonated B–B edge, forming a B–C(R)–B-bridged intermediate that rearranges via exchange of the bridging alkyl with the terminal hydrogen on B(5) to generate the observed product. An analogous process has been proposed[2c] for the alkylation of *nido*-$R_2C_2B_4H_5^-$ ions, except that in that case the substituent terminates at the B(4) (B(6)) location; possible reasons for this difference will be examined later in the paper. In earlier work, this type of mechanism involving bridged intermediates was found or postulated to occur in reactions of group IV alkyl halides with the $B_5H_8^-$ ion[6] and in similar processes involving carboranes.[7]

Scheme I



The 5-methyl complex **1a** easily undergoes additional cycles of bridge deprotonation and methylation to give the *B(4,5)*-dimethyl and *B(4,5,6)*-trimethyl species **1e** and **1f** as shown. As was noted above, this finding represents a second major departure from the behavior of $R_2C_2B_4H_6$ carboranes (R = Et, CH_2Ph), whose anionic B(4/6)-monoalkyl derivatives are virtually inert to further reaction with alkyl halides.[2c]

As a further probe of the alkylation process, the parent monoanion 1^- was converted via deprotonation to the

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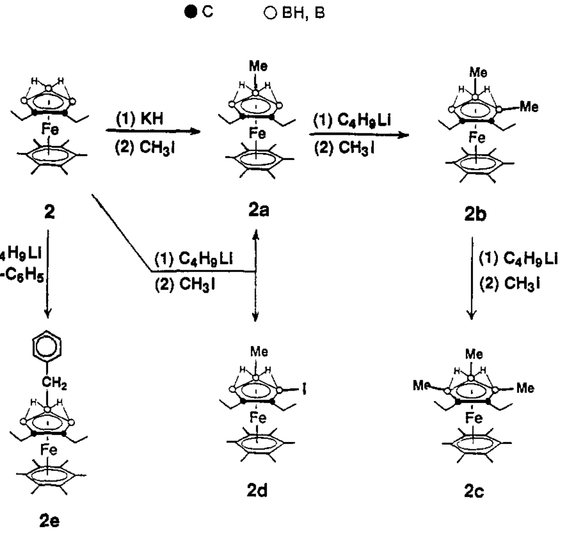
Table I. 115.8-MHz ^{11}B FT NMR Data

compd[a,b]	δ (J_{BH}, Hz)	rel areas
$(Et_2C_2B_3H_5)Co(C_5Me_5)$ (**1**)[c]	7.47 (146), 3.94 (134)[d]	1:2
$(Et_2C_2B_3H_4$-5-Me$)Co(C_5Me_5)$ (**1a**)	19.38,[e] −0.95 (117)	1:2
$(Et_2C_2B_3H_4$-5-Et$)Co(C_5Me_5)$ (**1b**)	23.02,[e] −0.57	1:2
$(Et_2C_2B_3H_4$-5-$CH_2C_6H_4CH_2Br)Co$-(C_5Me_5) (**1c**)	21.61,[e] −0.81[f]	1:2
$(Et_2C_2B_3H_4$-5-$CH_2C_6H_4Me)Co$-(C_5Me_5) (**1d**)	23.45,[e] 0.52 (113)	1:2
$(Et_2C_2B_3H_3$-4(6),5-$Me_2)Co(C_5Me_5)$ (**1e**)	16.13,[e] 7.59,[e] 0.22 (121)	1:1:1
$(Et_2C_2B_3H_2$-4,5,6-$Me_3)Co(C_5Me_5)$ (**1f**)	12.11,[e] 7.66[e]	1:2
$(Et_2C_2B_3H_3$-4(6)-I-5-Me$)Co(C_5Me_5)$ (**1g**)	19.56,[e] −0.77 (110), −5.60[e]	1:1:1
$(Et_2C_2B_3H_3$-4(6)-I-5-Et$)Co(C_5Me_5)$ (**1h**)	23.06,[e] −1.02 (104), −6.23[e]	1:1:1
$(Et_2C_2B_3H_5)Fe(C_6Me_6)$ (**2**)[g]	5.19 (141), 1.62 (137)	1:2
$(Et_2C_2B_3H_4$-5-Me$)Fe(C_6Me_6)$ (**2a**)	16.51,[e] −3.16 (116)	1:2
$(Et_2C_2B_3H_3$-4(6),5-$Me_2)Fe(C_6Me_6)$ (**2b**)	13.09,[e] 3.96,[e] −3.15 (116)	1:1:1
$(Et_2C_2B_3H_2$-4,5,6-$Me_3)Fe(C_6Me_6)$ (**2c**)	9.07,[e] 3.67[e]	1:2
$(Et_2C_2B_3H_4$-4(6)-I-5-Me$)Fe(C_6Me_6)$ (**2d**)	16.44,[e] −3.39 (121), −6.50 (35)[h]	1:1:1
$(Et_2C_2B_3H_4$-5-$CH_2Ph)Fe(C_6Me_6)$ (**2e**)	19.67,[e] −3.16 (118)	1:2
$(Et_2C_2B_3H_5)Ru(MeC_6H_4CHMe_2)$ (**3**)[c]	0.48 (138), −3.08 (138)	1:2
$(Et_2C_2B_3H_4$-5-Me$)Ru$-$(MeC_6H_4CHMe_2)$ (**3a**)	14.40,[e] −3.97 (117)	1:2
$(Et_2C_2B_3H_3$-4,5-$Me_2)Ru$-$(MeC_6H_4CHMe_2)$ (**3b**)	12.20,[e] 5.03,[e] −4.61 (117)	1:1:1
$(Et_2C_2B_3H_2$-4,5,6-$Me_3)Ru$-$(MeC_6H_4CHMe_2)$ (**3c**)	10.39,[e] 4.35[e]	1:2

[a] Shifts relative to $BF_3\cdot OEt_2$, positive values downfield. [b] *n*-hexane solution. [c] Reference 1a. [d] CH_2Cl_2 solution. [e] Singlet. [f] Coupling not resolved. [g] Reference 9. [h] Assigned to H_{bridge}–$H_{terminal}$ coupling.

Scheme II



dianion 1^{2-}, which in turn was treated with 2 equiv of methyl iodide in the expectation of producing a *B,B'*-dimethyl derivative. However, the only isolated product was the 4(6)-iodo-5-methyl species **1g** (Scheme I), indicating that the dominant reaction of the anion following introduction of the methyl unit on B(5) is addition of iodine (or iodide). This latter property was further explored by reacting **1b** with elemental iodine, which produced the 4(6)-iodo-5-ethyl complex **1h**.

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

compd	δ^{a-c}
1[d]	2.09 m (CH_2), 1.89 m (CH_2), 1.76 s (C_5Me_5), 1.10 m (CH_3), −5.54 br (B–H–B)
1a	2.13 m (CH_2), 1.85 m (CH_2), 1.73 s (C_5Me_5), 1.08 m (CH_3), 0.34 br s (B–CH_3), −5.4 br s (B–H–B)
1b	2.27 br m (B–CH_2), 2.11 m (CH_2), 1.89 m (CH_2), 1.72 s (C_5Me_5), 1.09 m (CH_3), 0.97 m (CH_3), −5.5 br s (B–H–B)
1c	7.22 d (C_6H_4), 7.08 d (C_6H_4), 5.15 br s (BH), 4.48 s (CH_2), 2.60 br s (B–CH_2), 2.30 m (CH_2), 1.91 m (CH_2), 1.78 s (C_5Me_5), 1.18 m (CH_3), −5.4 br s
1d	7.00 s (C_6H_4), 2.15 s (CH_3), 2.13 br s (CH_2), 2.09 m (CH_2), 1.85 m (CH_2), 1.77 s (C_5Me_5), 1.02 m (CH_3), −5.7 br s (B–H–B)
1e	2.10 m (CH_2), 1.87 m (CH_2), 1.68 s (C_5Me_5), 1.08 m (CH_3), 1.02 m (CH_3), 0.36 br s (B–CH_3), 0.27 br s (CH_3), −4.7 br s (B–H–B), −5.5 br s (B–H–B)
1f	2.07 m (CH_2), 1.89 m (CH_2), 1.62 s (C_5Me_5), 1.01 m (CH_3), 0.38 br s (CH_3), 0.19 br s (CH_3) −4.80 br (B–H–B)
1g	2.13 m (CH_2), 1.90 m (CH_2), 1.68 s (C_5Me_5), 1.08 m (CH_3), 0.35 br s (B–CH_3), −3.5 br d (B–H–B, −4.8 br s (B–H–B)
1h	2.20 m (CH_2), 2.14 m (B–CH_2), 1.90 m (CH_2), 1.67 s (C_5Me_5), 1.12 m (CH_3), 1.07 m (CH_3), 1.00 m (CH_3), −3.5 br d (B–H–B), −5.3 br s (B–H–B)
2	2.14 s (C_6Me_6), 1.89 m (CH_2), 1.77 m (CH_2), 1.04 t (CH_3), −6.80 br s (B–H–B)
2a	2.13 s (C_6Me_6), 1.93 m (CH_2), 1.72 m (CH_2), 1.03 t (CH_3), 0.19 s (B–CH_3), −5.99 br s (B–H–B)
2b	2.08 s (C_6Me_6), 1.93 m (CH_2), 1.79 m (CH_2), 1.03 t (CH_3), 0.94 t (CH_3), 0.31 s (B–CH_3), 0.10 s (B–CH_3), −5.49 br s (B–H–B), −6.03 br s (B–H–B)
2c	2.04 s (C_6Me_6), 1.84 m (CH_2), 0.96 t (CH_3), 0.34 s (B–CH_3), 0.02 s (B–CH_3), −5.60 br s (B–H–B)
2d	2.11 s (C_6Me_6), 1.97 m (CH_2), 1.79 m (CH_2), 1.02 m[e] (CH_3), 0.20 s (B–CH_3), −4.05 br s (B–H–B), −5.63 br s (B–H–B)
2e	7.19 m (C_6H_4), 7.04 m (C_6H_4), 2.26 s (C_6Me_6), 2.20 s (C_6Me_6), 2.14 s (B–CH_2), 1.90 m (CH_2), 1.76 m (CH_2), 0.99 t (CH_3), −6.04 br s (B–H–B)
3[d]	5.41 d (C_6H_4), 5.33 d (C_6H_4), 2.58 m ($CHMe_2$), 2.10 m (CH_2), 2.09 s ($CH_3C_6H_4$), 1.94 m (CH_2), 1.21 d ($CHMe_2$), 1.09 m (CH_3CH_2), −5.54 s (B–H–B)
3a	5.15 s[f] (C_6H_4), 2.63 m ($CHMe_2$), 2.18 s ($CH_3C_6H_4$), 2.09 m (CH_2), 1.91 m (CH_2), 1.26 d ($CHMe_2$), 1.08 t (CH_3), 0.32 s (B–CH_3), −4.72 s (B–H–B)
3b	5.17 d (C_6H_4), 5.07 q (C_6H_4), 4.98 d (C_6H_4), 2.62 m ($CHMe_2$), 2.11 s ($CH_3C_6H_4$), 1.98 m (CH_2), 126 d ($CHMe_2$), 1.23 d ($CHMe_2$), 1.07 m (CH_3), 0.37 s (B–CH_3), 0.32 s (B–CH_3), −4.01 s (B–H–B), −4.70 s (B–H–B)
3c	5.03 d (C_6H_4), 4.97 d (C_6H_4), 2.53 m ($CHMe_2$), 2.05 s ($CH_3C_6H_4$), 1.98 m (CH_2), 1.17 d ($CHMe_2$), 1.03 t (CH_3), 0.35 s (B–CH_3), 0.28 s (B–CH_3), −4.00 s (B–H–B)

[a] $CDCl_3$ solution. [b] Shifts relative to $(CH_3)_4Si$. Integrated peak areas in all cases are consistent with the assignments given. Legend: m = multiplet, s = singlet, d = doublet, t = triplet, q = quartet, br = broad. [c] B–$H_{terminal}$ resonances are broad quartets and are mostly obscured by other signals. [d] Reference 1a. [e] Overlapping triplets arising from nonequivalent *C*-ethyl groups. [f] Coincidental superposition of nonequivalent phenyl proton resonances.

Reactions of $(Et_2C_2B_3H_5)Fe(C_6Me_6)$ (2). In order to elaborate further the alkyl-substitution chemistry of *nido*-MC_2B_3 species, the behavior of complex **2**, an isoelectronic analogue of the cobalt species **1**, was examined. Deprotonation of the neutral complex in cold THF to form the monoanion, followed by addition of 1 equiv of methyl iodide, gave the 5-methyl product **2a** nearly quantitatively, with no other products detected (Scheme II). The deprotonation step must be conducted carefully to ensure that no dianion is formed. Preferably, KH or NaH should be employed since only monodeprotonation occurs with

Table III. Infrared Absorptions (cm^{-1}, Neat Films on KBr Plates)[a]

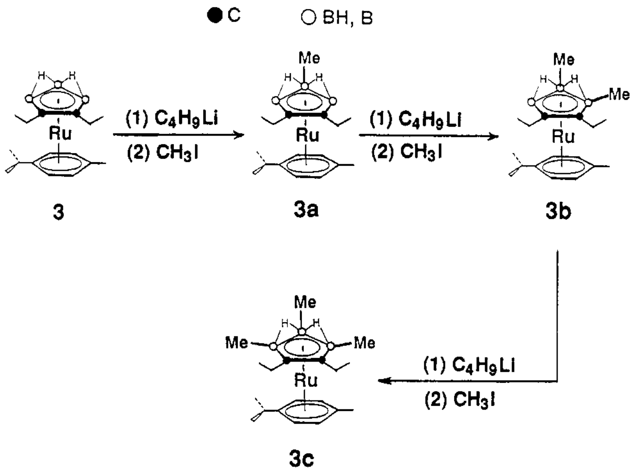
compd	abs
1a	2985 s, 2964 m, 2960 m, 2925 s, 2913 s, 2867 s, 2834 vs, 2503 s, 2484 m, 2362 s, 2339 s, 2337 s, 1482 s, 1466 s, 1450 s, 1384 m, 1376 s, 1303 s, 1076 s, 1030 s, 895 s, 889 s, 769 s, 740 s
1b	2960 vs, 2958 vs, 2941 vs, 2924 vs, 2868 vs, 2857 vs, 2855 vs, 2495 vs, 2491 vs, 2361 vs, 2337 vs, 1734 vs, 1700 vs, 1685 vs, 1653 vs, 1457 vs
1c	3054 s, 2986 s, 2963 s, 2927 s, 2869 vs, 2856 vs, 2361 vs, 2339 vs, 2337 vs, 1457 s, 1438 s, 1422 s, 1420 s, 1265 w, 896 s, 738 vw, 706 w, 668 s
1d	2999 vs, 2993 vs, 2961 vs, 2924 vs, 2882 vs, 2867 vs, 2495 vs, 2491 vs, 2364 vs, 2361 vs, 1734 vs, 1718 vs, 1700 vs, 1696 vs, 1685 vs, 1653 vs, 1559 vs, 1539 vs, 1521 vs, 1512 vs, 1507 vs, 1473 vs, 1465 vs, 1457 vs, 1448 vs, 1437 vs, 1419 vs, 1375 vs
1e	2957 s, 2927 s, 2910 s, 2906 s, 2864 s, 2478 s, 1468 vs, 1454 vs, 1449 vs, 1383 s, 1377 s, 1301 s, 1074 vs, 1029 vs, 887 vs
1f	2963 m, 2957 w, 2925 m, 2903 m, 2864 m, 1576 m, 1560 m, 1465 m, 1457 m, 1447 m, 1376 m, 1304 m, 1075 m, 1047 m, 1028 m, 901 m
1g	2964 s, 2943 s, 2940 s, 2926 s, 2912 s, 2867 s, 2494 s, 2361 s, 2339 s, 2337 s, 1653 s, 1457 s, 1419 s, 1383 s, 1377 s
1h	2960 s, 2927 vs, 2866 vs, 2503 vs, 2362 s, 2339 vs, 2337 vs, 1457 s, 1377 s
2a	3016 m, 2959 s, 2923 vs, 2856 s, 2489 s, 2011 w, br, 1931 w, 1519 w, 1453 m, 1446 s, 1435 sh, 1381 m, 1101 w, 1069 m, 1000 m, 953 w, 893 s, 772 m, 614 w, 552 w
2b	3016 m, 2957 s, 2923 vs, 2853 s, 2460 m, 1912 w, br, 1619 w, 1614 w, 1463 m, 1446 m, 1381 m, 1299 m, 1199 w, 1105k w, 1068 m, 1014 m, 941 w, 888 m, 849 w, 758 w, 555 w
2c	3014 w, 2957 s, 2923 vs, 2923 vs, 2853 s, 1878 w, br, 1742 m, 1574 m, 1454 m, 1445 m, u381 m, 1300 m, 1109 w, 1070 m, 1054 m, 1030 m, 901 w, 891 w, 880 w, 722 w
2d	3016 w, 2957 s, 2923 vs, 2852 s, 2487 s, 2010 w, br, 1448 m, 1430 m, 1387 s, 1382 s, 1305 m, 1185 vw, 1103 vw, 1068 m, 1025 w, 1015 w, 889 w, 798 w, 773 w, 731 m, 668 m
2e	3021 m, 2956 s, 2923 vs, 2854 s, 2480 s, 1916 w, br, 1599 w, 1489 m, 1463 s, 1452 s, 1367 m, 1214 m, 1066 w, 1012 w, 892 m, 776 m, 757 m, 700s
3a	3054 w, 2960 vs, 2927 s, 2867 s, 2489 s, 1935 w, br, 1585 w, br, 1531 m, 1463 s, 1452 m, 1446 s, 1380 m, 1364 sh, 1305 m, 1277 w, 1070 w, 1053 m, 1034 m, 1005 w, 898 s, 843 m, 802 m, 777 m
3b	3054 w, 2960 vs, 2927 s, 2867 s, 2491 s, 1927 w, br, 1633 w, br, 1554 m, 1537 m, 1477 s, 1467 m, 1460 s, 1380 m, 1305 s, 1189 w, 1083 w, 1070 w, 1053 m, 1032 m, 1018 w, 889 s, 825 sh, 841 m, 802 w, 760 w
3c	3044 w, 2961 vs, 2926 s, 2889 s, 2867 s, 2827 m, 1962 vw, 1882 w, 1842 w, 1554 m, 1650 w, 1574 s, 1535 w, 1459 m, 1446 s, 1381 m, 1361 w, 1331 w, 1300 s, 1220 w, 1112 m, 1087 w, 1070 m, 1050 m, 1036 m, 895 s, 875 m, 839 m, 823 w, 786 m

[a] Legend: vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, br = broad.

these reagents. When *tert*-butyllithium is used, even a small excess produces some dideprotonation; addition of methyl iodide then produces the 4-iodo-5-methyl derivative (**2d**), with a consequently lower yield of the desired species **2a** (the iodination is analogous to the reaction of the cobalt complex dianion 1^{2-} with methyl iodide, described above). This problem can be avoided by precise delivery of 1 molar equiv of the LiC_4H_9 reagent, which affords essentially only the monoanion, whose alkylation proceeds in 87% isolated yield with no iodinated side product. As will be shown, the use of *tert*-butyllithium proved advantageous in subsequent alkylation steps.

Treatment of the monomethyl complex **2a** with KH and subsequent reaction with methyl iodide afforded the 4,5-dimethyl product **2b**, but the deprotonation step was relatively sluggish in comparison to that with the parent complex 2, and some unreacted **2a** was recovered. Clearly, the presence of the 5-methyl group significantly reduces the acidity of the B–H–B protons, possibly reflecting an increase in electron density in the bridging region that lowers the polarity of the $B-H_{bridge}$ bonds.[8] (Kinetic factors arising from the heterogeneous nature of the NaH or KH reactions and the presumably slower diffusion of the alkylated vs the parent complex may also be involved.) As expected, when *tert*-butyllithium was employed in place of KH, the deprotonation proceeded more readily and the alkylation to form **2b** was effected in 91% isolated yield (Scheme II). Similar behavior was noted in the deprotonation of **2b** via *tert*-butyllithium and the alkylation of the anion to generate the *B(4,5,6)*-trimethyl derivative **2c**.

Scheme III



The corresponding reaction of the monoanion 2^- with α-bromotoluene proceeded as anticipated, giving the 5-substituted product **2e** with 100% regiospecificity. The analogous *p*-(α-bromotolyl) complex can be similarly prepared from α,α'-dibromoxylene and reacted with a second metallacarborane anion to give a phenylene-linked dimetallic system, as described in the accompanying paper.[9]

Reactions of $(Et_2C_2B_3H_5)Ru(MeC_6H_4CHMe_2)$ (3). The scope of the preceding chemistry was extended to the (cymene)ruthenium carborane complex **3** (cymene = *p*-isopropyltoluene), which like **1** and **2** has been utilized as a building-block unit in the synthesis of triple-decker and linked sandwiches.[1] By the same procedure as was employed for the iron complexes above, successive deprotonations via *tert*-butyllithium and additions of methyl iodide gave the 5-methyl, 4,5-dimethyl, and 4,5,6-trimethyl derivatives **3a–c**, respectively, in 84–92% isolated yield (Scheme III). As in the previous cases, each reaction generated a single pure isomer with no evidence of side products. In contrast to the cobalt and iron complexes, which were isolated as bright yellow solids, **3a** and **3b** are very light brown oils while **3c** is a slightly brown solid.

Discussion

The nearly identical deprotonation/alkylation chemistry of the $(Et_2C_2B_3H_5)M$(ligand) complexes examined in this study, involving three different metal–ligand combinations, suggests that these properties are quite general for this class of complex. This has obvious advantages in directed synthesis, since it allows the efficient preparation of in-

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(8) Brice, V. T.; Shore, S. G. *Inorg. Chem.* **1973**, *12*, 309.

(9) Attwood, M. D.; Davis, J. H., Jr.; Grimes, R. N. *Organometallics*, following paper in this issue.

dividual pure isomers having substituents at specific, predictable boron locations. Moreover, from a practical synthetic viewpoint, it is fortuitous that the substitution patterns uncovered in this work dovetail nicely with the previously studied alkylation of R$_2$C$_2$B$_4$H$_6$ carboranes.[2c] Thus, the B(4/6)-monosubstituted derivatives obtained in the latter case can be metal-complexed to give the corresponding (R$_2$C$_2$B$_4$H$_3$-4(6)-R′)M(ligand) species, which on decapitation (apex BH removal) yield the analogous (R$_2$C$_2$B$_3$H$_4$-4(6)-R′)M(ligand) products. Alternatively, as shown in the present work, one can start with an unsubstituted (R$_2$C$_2$B$_3$H$_5$)M(ligand) complex and obtain the 5-, 4,5-, or 4,5,6-substituted materials as desired, with essentially total regiospecificity.

The striking difference in behavior of the R$_2$C$_2$B$_4$H$_5^-$ anions and their (R$_2$C$_2$B$_3$H$_4$)M(ligand)$^-$ analogues toward alkyl halides is intriguing. Undoubtedly, both types of species initially form an alkyl-bridge intermediate via introduction of the hydrocarbon group into the nucleophilic B–B edge of the cage,[2c,6,7] with subsequent rearrangement in which the alkyl bridging unit and a terminal hydrogen on B(4) or B(5) exchange places. Why does the rearrangement proceed differently in the two cases? In the absence of obvious steric influences, the explanation must center on charge distribution within the respective cage frameworks. This implies that borons 4 and 6 are more negative in the parent carborane, while B(5) has the higher negative charge in the MC$_2$B$_3$ complexes. This idea is consistent with published MNDO calculations[10] on 2,3-C$_2$B$_4$H$_8$, which indicate that B(4) and B(6) are indeed more negative than B(5). We know of no corresponding study on (R$_2$C$_2$B$_3$H$_5$)M(arene) complexes, but it is interesting to note that, in the formally analogous (C$_2$B$_3$H$_7$)Fe(CO)$_3$ molecule, the middle boron (B(5)) is calculated to have the higher negative charge.[11]

A remarkable trend was noted in the relative air stability of the complexes in this work. The parent compounds **1**–**3** survive exposure as solids to moist air over periods of 1–2 weeks, thereafter showing signs of slow degradation; in solution the process is somewhat faster. In contrast, the B(5)-monoalkyl derivatives appear to be completely air-stable as solids or THF solutions, exhibiting no reaction even on prolonged standing in air. However, the introduction of second and third B-alkyl groups *lowers* the stability: the 4,5-dialkyl species are comparable in stability to the parent compounds, while the 4,5,6-trialkyl complexes are even more reactive, degrading somewhat upon exposure to air for 2 or 3 days. While these observations are qualitative, they are consistent for the three classes involving different transition metals and, hence, are surely significant. This pattern can reasonably be explained in terms of a conventional metal–C$_2$B$_3$ ring bonding model. The addition of electron-releasing alkyl groups to the carborane ring can be expected to facilitate "forward" bonding from the ligand to the metal but would also tend to reduce the π-acidity of the ring and hence inhibit the metal-to-ring back-bonding interaction (at the same time, the metal oxidation state is lowered, making the metal more susceptible to oxidation). In the B-monoalkyl species, the first effect evidently predominates and there is a net strengthening of the metal–ligand binding, but on further alkylation the second effect overrides and the complex is less strongly bound. The implication of this finding for the utilization of these complexes in designed synthesis is clear: optimal stability is achieved in the B-monoalkyl complexes.

The clean, facile nature of these alkyl halide interactions with *nido*-metallacarborane complexes suggested to us that similar reactions of selected organic dihalides could provide an efficient and controllable method for linking individual metal sandwich units. This has proved to be the case, and an exploration of this approach is presented in the following article.[9]

Experimental Section

Except where otherwise indicated, materials, instrumentation, and general procedures were identical with those described in earlier publications in this series.[1] Infrared spectra were recorded on a Mattson Cygnus FTIR spectrometer. The unit-resolution mass spectra of all new compounds contain strong parent envelopes that closely match the patterns calculated from elemental composition; in addition, high-resolution mass measurements are reported below for all products. Complexes **1**–**3** were prepared as reported elsewhere.[1a,b,12]

Synthesis of (Et$_2$C$_2$B$_3$H$_4$-5-Me)Co(C$_5$Me$_5$) (1a). Complex **1**[1a] (0.25 g, 0.80 mmol) was placed in a 100-mL round-bottom flask attached to a vacuum line and fitted with a septum cap, 25 mL of dry tetrahydrofuran (THF) was added, and the solution was placed in a dry ice/2-propanol bath. To the cooled, yellow solution was added, via syringe, 0.47 mL of a 1.7 M solution of *tert*-butyllithium in hexane (0.80 mmol). The solution was warmed to room temperature, during which time a color change from yellow to deep red-orange was noted. After the mixture was stirred at room temperature for 10 min, 0.80 mmol of MeI was added via syringe; within seconds, the solution faded to yellow, reminiscent of the color of the original (neutral) complex **1**. After it was stirred for a further 10 min, the solution was opened to the air and the solvent removed by rotary evaporation. The yellow residue was taken up in hexane and column chromatographed on silica gel in hexane, producing a single yellow band, which was collected and the solvent slowly evaporated in air to give lemon yellow air-stable crystals of **1a** (0.188 g, 0.57 mmol, 72% yield). Exact mass: calcd for ^{59}Co^{12}C$_{17}$^{11}B$_3$^{1}H$_{32}^+$, 328.2115; found, 328.2115.

Synthesis of 1b–f. The remaining monoanion alkylations utilized the procedure employed for preparing **1a**. In each case, the appropriate neutral complex was first monodeprotonated with an equimolar quantity of 1.7 M *tert*-butyllithium in hexanes, after which the alkyl bromide was added (via tip-tube or syringe) and workup was conducted as described above. Details of the individual syntheses follow.

(Et$_2$C$_2$B$_3$H$_4$-5-Et)Co)(C$_5$Me$_5$) (1b). Complex **1a** (0.258 g, 0.82 mmol) and excess ethyl bromide gave 0.244 g (0.71 mmol, 87%) of **1b** as air-stable orange crystals. Exact mass: calcd for ^{59}Co^{12}C$_{18}$^{11}B$_3$^{1}H$_{34}^+$, 342.2272; found, 342.2277.

(Et$_2$C$_2$B$_3$H$_4$-5-CH$_2$C$_6$H$_4$CH$_2$Br)Co(C$_5$Me$_5$) (1c). Complex **1a** (0.237 g, 0.75 mmol) and 0.199 g (0.75 mmol) of α,α'-dibromo-*p*-xylene gave 0.220 g (0.44 mmol, 60%) of brown solid **1c**. Exact mass: calcd for ^{59}Co^{12}C$_{24}$^{11}B$_3$^{81}Br^{1}H$_{37}^+$, 198.1669; found, 498.1687.

(Et$_2$C$_2$B$_3$H$_4$-5-CH$_2$C$_6$H$_4$Me)Co(C$_5$Me$_5$) (1d). Compound **1a** (0.268 g, 0.85 mmol) and 0.079 g (0.85 mmol) of α-bromo-*p*-xylene gave 0.310 g (0.74 mmol, 87%) of bright yellow crystalline **1d**. Exact mass: calcd for ^{59}Co^{12}C$_{24}$^{11}B$_3$^{1}H$_{38}^+$, 418.2585; found, 418.2583.

(Et$_2$C$_2$B$_3$H$_3$-4(6),5-Me$_2$)Co(C$_5$Me$_5$) (1e). Complex **1a** (0.124 g, 0.38 mmol) and 0.38 mmol of MeI gave 0.128 g (0.37 mmol, 98%) of **1e** as yellow air-stable crystals. Exact mass: calcd for ^{59}Co^{12}C$_{18}$^{11}B$_3$^{1}H$_{34}^+$, 342.2272; found, 342.2274.

(Et$_2$C$_2$B$_3$H$_2$-4,5,6-Me$_3$)Co(C$_5$Me$_5$) (1f). Compound **1e** (0.240 g, 0.70 mmol) and 0.70 mmol of MeI gave 0.236 g (0.66 mmol, 95%) of **1f** as dark yellow, slightly air-sensitive crystals. Exact mass: calcd for ^{59}Co^{12}C$_{19}$^{11}B$_3$^{1}H$_{36}^+$, 356.2428; found, 356.2430.

Synthesis of (Et$_2$C$_2$B$_3$H$_3$-4(6)-I-5-Me)Co(C$_5$Me$_5$) (1g). A 0.102-g (0.30-mmol) quantity of **1a** was dideprotonated in THF solution via addition of 0.36 mL (0.60 mmol) of 1.7 M *tert*-butyllithium in hexane, after which a large excess (0.5 mL) of methyl iodide was added. The solution immediately changed from deep red to brown. Evaporation of the solvent, extraction of the residue

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in hexane, and filtration through silica gave a yellow solution, which on evaporation afforded 93 mg (0.20 mmol, 67%) of **1g** as waxy orange crystals. Exact mass: calcd for $^{59}\mathrm{Co}^{12}\mathrm{C}_{17}{}^{11}\mathrm{B}_3{}^{127}\mathrm{I}^1\mathrm{H}_{31}{}^+$, 454.1082; found, 454.1078.

Synthesis of ($\mathbf{Et_2C_2B_3H_3}$-4(6)-I-5-Et)Co($\mathbf{C_5Me_5}$) (1h). Compound **1b** (0.250 g, 0.73 mmol) was dissolved in THF in air, and to the stirred yellow solution was added, dropwise, 0.18 g (0.73 mmol) of I_2 in THF and a catalytic amount (5 mg) of $\mathrm{RuCl_3{\cdot}}x\mathrm{H_2O}$. The dark brown solution was stirred at room temperature for 1 h, after which the solvent was removed by evaporation. Chromatography of the residue on silica in dichloromethane gave dark orange, air-stable crystals of **1h** (0.330 g, 0.71 mmol, 97%). Exact mass: calcd for $^{59}\mathrm{Co}^{12}\mathrm{C}_{18}{}^{11}\mathrm{B}_3{}^{127}\mathrm{I}^1\mathrm{H}_{33}{}^+$, 468.1238; found, 468.1238.

Synthesis of ($\mathbf{Et_2C_2B_3H_4}$-5-Me)Fe($\mathbf{C_6Me_6}$) (2a). (a) Deprotonation of 2 with Use of KH. In an apparatus similar to that shown in Figure 3a of ref 1a, 0.152 g (0.450 mmol) of **2**[12] was placed in a side arm attached to the upper flask (A), which contained an excess of KH in THF, flask A was frozen in liquid nitrogen, and the apparatus was evacuated on a vacuum line. The KH suspension was warmed to room temperature, the complex **2** was added via rotation of the side arm, and the mixture was stirred 1 h at room temperature, during which time the solution color changes from yellow to orange. The solution was filtered in vacuo through a medium frit into the lower flask, which was cooled in liquid nitrogen. The flask was placed in a −78 °C bath, and an excess of MeI (0.90 mmol) was added through the rubber septum, which produced an initial color change from orange to red-orange. When the solution was warmed to room temperature with stirring, the color reverted to yellow. The flask was opened to the air, the contents were rotary-evaporated to dryness and extracted with hexane, and the extract was filtered through silica and again evaporated to dryness. Final purification on a silica preparative TLC plate gave 0.150 g (0.426 mmol, 95%) of lemon yellow **2a**. Exact mass: calcd for $^{56}\mathrm{Fe}^{12}\mathrm{C}_{19}{}^{11}\mathrm{B}_3{}^1\mathrm{H}_{35}{}^+$, 352.2367; found, 352.2374.

(b) Deprotonation of 2 with Use of *tert*-Butyllithium. A solution of 0.108 g (0.320 mmol) of **2** in ca. 20 mL of dry THF was placed in a 50-mL round-bottom flask, which was frozen in liquid nitrogen, evacuated, and placed in a −78 °C bath, and 0.320 mmol of *tert*-butyllithium in hexane was added via injection through a septum as in the case of **1a**. Excess MeI (0.5 mL) was added, and the solution was worked up as above to give 98 mg (0.278 mmol, 87%) of **2a**. When the quantity of *tert*-butyllithium was less carefully controlled, so that a small excess was present (causing formation of some $\mathbf{2}^{2-}$ dianion, vide infra), the yield of **2a** was only 34%, accompanied by ($\mathrm{Et_2C_2B_3H_3}$-4(6)-I-5-Me)Fe($\mathrm{C_6Me_6}$) (**2d**) in 9% yield. Exact mass of **2d**: calcd for $^{56}\mathrm{Fe}^{12}\mathrm{C}_{19}{}^{11}\mathrm{B}_3{}^{127}\mathrm{I}^1\mathrm{H}_{34}{}^+$, 478.1334; found, 478.1339.

Synthesis of ($\mathbf{Et_2C_2B_3H_3}$-4(6),5-$\mathbf{Me_2}$)Fe($\mathbf{C_6Me_6}$) (2b). (a) Deprotonation of 2a with Use of KH. The apparatus and procedure employed for the KH deprotonation of **2**, described above, were used to prepare the $\mathbf{2a}^-$ monoanion from 0.151 g (0.429 mmol) of **2a** and excess KH in THF. Reaction with an excess of MeI and workup as above gave 0.103 g (0.281 mmol, 77% based on **2a** consumed) of yellow crystalline **2b**, accompanied by 23 mg of unreacted 2. Exact mass of **2b**: calcd for $^{56}\mathrm{Fe}^{12}\mathrm{C}_{20}{}^{11}\mathrm{B}_3{}^1\mathrm{H}_{37}{}^+$, 366.2524; found, 366.2526.

(b) Deprotonation of 2a with Use of *tert*-Butyllithium. By the procedure of method b above, 0.098 g (0.278 mmol) of **2a** was treated with an exactly equimolar amount of *tert*-butyllithium, and excess MeI was added, producing similar color changes. Workup as before gave 0.093 g (0.254 mmol, 91%) of **2b**.

Synthesis of ($\mathbf{Et_2C_2B_3H_2}$-4,5,6-$\mathbf{Me_3}$)Fe($\mathbf{C_6Me_6}$) (2c). Deprotonation of 0.093 g (0.254 mmol) of **2b** in THF was conducted with an equimolar quantity of *tert*-butyllithium via procedure b above; the deprotonated species was treated with an excess of MeI and the product worked up as before to give 0.079 g (0.208 mmol, 82%) of yellow **2c**. Exact mass: calcd for $^{56}\mathrm{Fe}^{12}\mathrm{C}_{21}{}^{11}\mathrm{B}_3{}^1\mathrm{H}_{39}{}^+$, 380.2680; found, 380.2688.

Synthesis of ($\mathbf{Et_2C_2B_3H_4}$-5-$\mathbf{CH_2Ph}$)Fe($\mathbf{C_6Me_6}$) (2e). The above procedure b was employed with 0.142 g (0.42 mmol) of **2** and an equimolar amount of *tert*-butyllithium to generate the 2^- ion, which was reacted with an excess of α-bromotoluene (0.1 mL) to give 78 mg (0.18 mmol, 43%) of bright yellow solid **2e**. Exact mass: calcd for $^{56}\mathrm{Fe}^{12}\mathrm{C}_{25}{}^{11}\mathrm{B}_3{}^1\mathrm{H}_{39}{}^+$, 428.2680; found, 428.2684.

Synthesis of 3a–c. The procedure employed in the deprotonation of 2 with *tert*-butyllithium and subsequent alkylations and product isolations, described above, was applied to the ruthenium complex 3. In each case, deprotonation resulted in a slight darkening of the initially golden brown solution, which on addition of an excess of methyl iodide reverted to the original color. Workup was conducted as for the iron complexes, with final purification on a silica column in hexane. Details of the individual syntheses follow.

($\mathbf{Et_2C_2B_3H_4}$-5-Me)Ru($\mathbf{MeC_6H_4CHMe_2}$) (3a). Complex **3**[1a] (0.310 g, 0.873 mmol) gave 0.282 g (0.764 mmol, 88%) of **3a** as a viscous light brown oil. Exact mass: calcd for $^{102}\mathrm{Ru}^{12}\mathrm{C}_{17}{}^{11}\mathrm{B}_3{}^1\mathrm{H}_{31}{}^+$, 370.1742; found, 370.1727.

($\mathbf{Et_2C_2B_3H_3}$-4,5-$\mathbf{Me_2}$)Ru($\mathbf{MeC_6H_4CHMe_2}$) (3b). Complex **3a** (0.217 g, 0.588 mmol) gave 0.206 g (0.538 mmol, 92%) of **3b** as a very viscous light brown oil. Exact mass: calcd for $^{102}\mathrm{Ru}^{12}\mathrm{C}_{18}{}^{11}\mathrm{B}_3{}^1\mathrm{H}_{33}{}^+$, 384.1899; found, 384.1862.

($\mathbf{Et_2C_2B_3H_2}$-4,5,6-$\mathbf{Me_3}$)Ru($\mathbf{MeC_6H_4CHMe_2}$) (3c). Complex **3b** (0.193 g, 0.504 mmol) gave 0.168 g (0.423 mmol, 84%) of **3c** as a very light brown solid. Exact mass: calcd for $^{102}\mathrm{Ru}^{12}\mathrm{C}_{19}{}^{11}\mathrm{B}_3{}^1\mathrm{H}_{35}{}^+$, 398.2055; found, 398.2027.

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