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$(C_5Me_5)Co(Et_2C_2B_3H_4\text{–}R)$ Metallacarborane Sandwich Complexes as Versatile Synthons. Introduction of Electron-Withdrawing Substituents[1]

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As part of our development of small *nido*-metallacarborane complexes as organometallic building-blocks, the controlled syntheses of $(C_5Me_5)Co(Et_2C_2B_3H_4\text{–}R)$ and $(C_5Me_5)Co(Et_2C_2B_3H_3\text{–}R_2)$ derivatives in which R is an acyl, trifluoroacyl, ester, nitrile, nitro, chloro, bromo, or iodo group were investigated. The attack of electrophilic reagents (R^+) on the B–B edge of the $(C_5Me_5)Co(Et_2C_2B_3H_4)^-$ anion (1^-), which was demonstrated earlier (preceding article and earlier papers) to give regiospecific B(5)–R substitution, in the present work produced B(5)–R and/or B(4/6)–R derivatives. Efficient syntheses of the B(5)–chloro, –bromo, and –iodo derivatives were achieved via treatment of 1^- with $MeSO_2Cl$, $BrCH_2CN$ or $BrCH_2NO_2$, and CF_3I, respectively; further reaction of the monochloro compound gave the dichloro and trichloro species. In contrast to this B(5)-substitution pattern, reactions of 1^- with $C(O)CF_3Cl$ gave exclusively the B(4/6)–$C(O)CF_3$ derivative. Treatment of neutral 1 with *N*-halosuccinimides gave exclusively the monohalo [B(4/6)–X] derivatives (X = Cl, Br, I) in nearly quantitative yield; further halogenation of these species using the same reagents gave the B(4,6)–X_2 dihalo products quantitatively. The reaction of 1^- with acetyl chloride in THF at −78 °C did not form the expected B(5)–acetyl complex, giving instead the B(5)–(2-vinyl acetate) derivative **2** in good yield; the structure was proved via X-ray crystallography. Base-catalyzed cleavage of **2** readily afforded the B(5)–acetyl compound **3**. The formation of **2** does not involve the acetyl species **3** as an intermediate and is proposed to occur via formation of a B–C–B acetyl-bridged intermediate which undergoes O-acetylation and rearrangement to give **2**. The remarkable formation of **2** differs from the usual enol acetate formation in organic chemistry in that, in the present case, the only primary source of –(C=O)– is the acylating agent itself. New compounds were isolated in most cases as air-stable crystals and characterized via ^1H, ^{13}C, and ^{11}B NMR, IR, UV-visible, and mass spectra. Crystal data for **2**: space group $P2_1/n$; $Z = 4$; $a = 8.368$ (2), $b = 18.757$ (5), $c = 14.234$ (4) Å; $\beta = 97.25$ (2)°; $V = 2216$ (2) Å^3; $R = 0.037$ for 3856 reflections having $F_o^2 > 3.0\sigma(F_o^2)$.

Introduction

The synthetic utility of *nido*-$LM(R_2C_2B_3H_5)$ metallacarborane complexes (in which L is an aromatic hydrocarbon and M is Fe, Co, or Ru) is substantially enhanced by the addition of organic functional groups to the C_2B_3 ring.[1] Such derivatization is important in the development of this chemistry, for two reasons. As has been demonstrated in earlier work,[2-5] linking groups bound to the carborane ligand can be used to construct multicage metallacarborane oligomers and polymers; in principle, a wide variety of organic polymerization reactions could be employed once the necessary functional groups are introduced. Here we simply take advantage of the stability of the MC_2B_3 cage and its ability to survive a wide range of reaction conditions without degradation, not unlike the development of extraordinarily robust polymers from the icosahedral *m*-$C_2B_{10}H_{12}$ carborane.[6]

A different role for attached substituents arises when they influence the electronic properties of the C_2B_3 ring itself and thereby alter its chemistry, especially its ability to form sandwich complexes with metals. The importance of such effects became clear to us when we found, serendipitously, that attachment of electron-withdrawing groups such as acetyl and chloro to the middle boron [B(5)] promotes formation of tetradecker sandwiches via coordination of the C_2B_3 face to transition-metal ions.[7] This, in turn, creates the possibility of fine-tuning or tailoring the properties of $LM(R_2C_2B_3H_5)$ complexes via appropriate derivatization. Accordingly, the work described here was undertaken in order to develop efficient methods for introducing synthetically useful electron-withdrawing substituents.

An earlier report[8] from our laboratory described a straightforward method for regiospecific alkylation at B(5) (the middle boron) via reaction of a *nido*-$LM(R_2C_2B_3H_4)^-$ anion with alkyl halides, and the accompanying paper[1] extends this approach to the synthesis of a variety of B(5)–CH_2–R derivatives in which R is an active group. For the most part, these preparations proceeded similarly to those of the simple B(5)–alkyl compounds. However, in using this approach to introduce electron-withdrawing groups *directly* onto the carborane ring (without an intervening CH_2 unit), we found that the chemistry is more complex, in some cases leading to substitution at B(4/6), and in others taking entirely unexpected turns. These findings are described in the present report.

Results and Discussion

Synthesis of B(5)-Substituted Acetyl and Vinyl Ester Derivatives. In attempting to extend the B-alkylation[8] reaction of $(C_5Me_5)Co(Et_2C_2B_3H_5)$ (**1**, Scheme IA) to other types of organic groups, we initially chose the B(5)–acetyl species as a desirable target compound which

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[1] Organotransition-Metal Metallacarboranes. 24. Part 23: Piepgrass, K. W.; Grimes, R. N. Preceding paper in this issue.

[2] Recent reviews: (a) Grimes, R. N. *Chem. Rev.* **1992**, *92*, 251. (b) Grimes, R. N. Cyclocarborane-Stabilized Multidecker/Multicluster Sandwich Compounds and Linked Molecular Systems. In *Electron-Deficient Boron and Carbon Clusters*; Olah, G. A., Wade, K., Williams, R. E., Eds.; John Wiley and Sons: New York, 1991; Chapter 11, pp. 261-285.

[3] Attwood, M. D.; Davis, J. H., Jr.; Grimes, R. N. *Organometallics* **1990**, *9*, 1177.

[4] Davis, J. H., Jr.; Benvenuto, M. A.; Grimes, R. N. *Inorg. Chem.* **1991**, *30*, 1765.

[5] Benvenuto, M. A. Ph.D. Thesis, University of Virginia, 1991. Benvenuto, M. A.; Grimes, R. N. Submitted for publication.

[6] Peters, E. N. *Ind. Eng. Chem. Prod. Res. Dev.* **1984**, *23*, 28 and references therein.

[7] Piepgrass, K. W.; Davis, J. H., Jr.; Sabat, M.; Grimes, R. N. *J. Am. Chem. Soc.* **1991**, *113*, 681.

[8] Davis, J. H., Jr.; Attwood, M. D.; Grimes, R. N. *Organometallics* **1990**, *9*, 1171.

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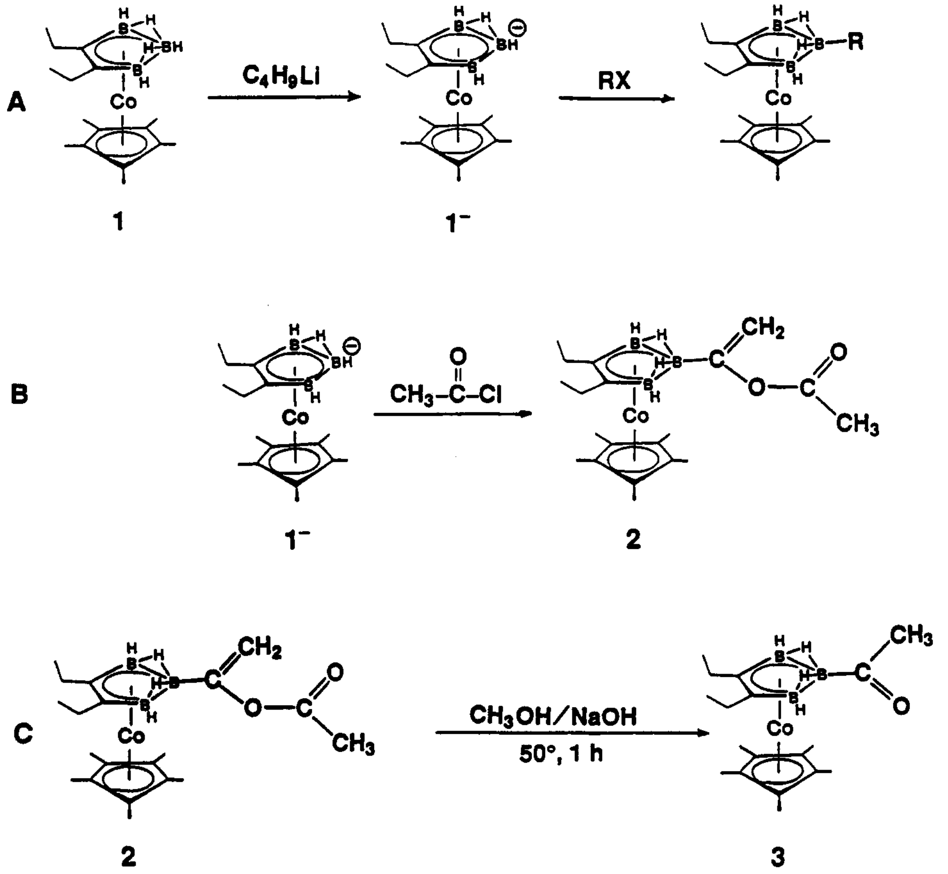
Scheme I



might serve as a useful precursor to metallacarborane-based oligomers and polymers via acyl polymerization reactions. To this end, the bridge-deprotonated anion 1^- was reacted with acetyl chloride in THF at −76 °C. Workup in air afforded in 55% yield (based on 1 consumed) a yellow air-stable solid 2 which clearly was *not* the intended B–acetyl complex 3, as shown by its ^{11}B, ^{1}H, and ^{13}C NMR and infrared spectra (Tables II–V).[9] A trace product isolated from this reaction was characterized as a THF-substituted derivative, (C_5Me_5)Co($Et_2C_2B_3H_3$-5-OC_4H_8) (4), an isomer of the previously reported B(4/6)-THF compound (27 in the preceding paper).

The multinuclear NMR and mass spectroscopic data at first suggested that 2 was an acetyl acetonate derivative, although the proton NMR spectrum was not entirely consistent with this assignment. However, a single-crystal X-ray diffraction study disclosed that 2 is in fact a B-(5)-vinyl ester complex (Scheme 1B), an unexpected result which is entirely in accord with the NMR data.[9]

The solid-state geometry of 2 is shown in Figure 1, and relevant data are listed in Tables VI–IX. All hydrogen atoms were located, and the structure exhibits no anomalous features. The MC_2B_3 cage parameters are closely similar to those in previously reported complexes of this class,[10] only one of which, [(C_5Me_5)Co($Me_2C_2B_3H_4$)-μ-HgCl],[10c] contains the Co(C_5Me_5) moiety. The C(2)–C(3) distance [1.412 (3) Å] is typical of *nido*-MC_2B_3 clusters, reflecting some multiple-bond character in the carborane C–C interaction. The vinyl ester group has an unusually short carboxyl [C(11)–O(2)] distance (1.187 (4) Å) and a relatively small C(9)–O(1)–C(11) angle [117.7 (2)°], consistent with an increase in s character in C(9) and O(1) which can be attributed to withdrawal of p electron density by the carborane ring ligand.

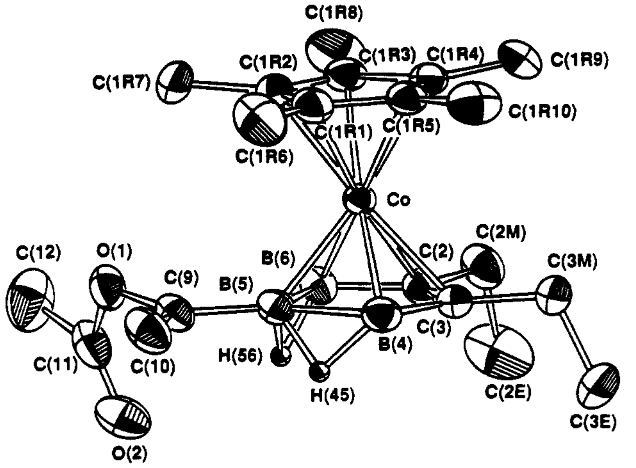


Figure 1. Molecular structure of 2 (terminal hydrogens omitted).

In a strange twist of the kind that sometimes occurs in research, our initial belief that 2 was an acetyl acetonate led us to attempt the formation of a Ni(acac)$_2$ complex via reaction of 2^- with nickel(II) bromide. Athough it was doomed to fail in its intended purpose, this was a truly fortuitous experiment[7] since it produced instead the quadruple-decker sandwich complex [(C_5Me_5)Co-($Et_2C_2B_3H_2$–C(O)Me)]$_2$Ni, representing a new class of metallacarborane species, and enabled us to develop a practical synthetic route to these previously inaccessible

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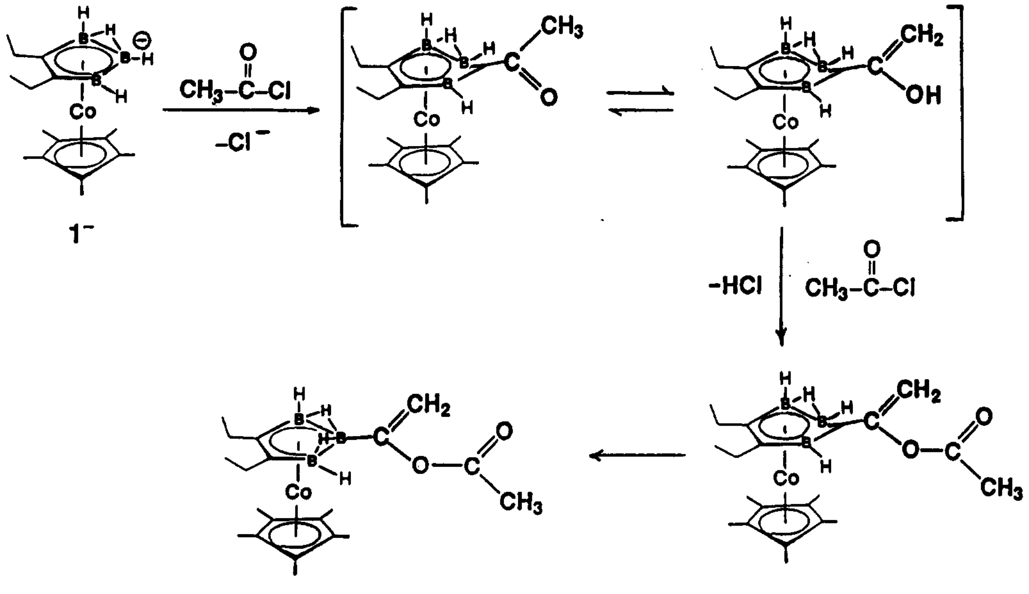
[9] A preliminary report of this work has appeared: Piepgrass, K. W.; Davis, J. H., Jr.; Sabat, M.; Grimes, R. N. *J. Am. Chem. Soc.* **1991**, *113*, 680.

[10] (a) Brennan, J. P.; Grimes, R. N.; Schaeffer, R.; Sneddon, L. G. *Inorg. Chem.* **1973**, *12*, 2276. (b) Pipal, J. R.; Maxwell, W. M.; Grimes, R. N. *Ibid.* **1978**, *17*, 1447. (c) Finster, D. C.; Grimes, R. N. *Ibid.* **1981**, *20*, 863. (d) Borodinsky, L.; Sinn, E.; Grimes, R. N. *Ibid.* **1982**, *21*, 1928.

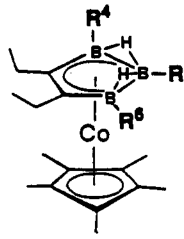
Scheme II



1^-

2

Table I. $(C_5Me_5)Co(Et_2C_2B_3H_2R^4R^5R^6)$ Major Products



compd	R^5	R^4, R^6	yield (%)[a]
2	$C(=CH_2)OC(O)Me$	H, H	25 (55)
3	C(O)Me	H, H	83[b]
5	H	$C(O)CF_3$, H	27 (46)
6	$C(O)CH_2C(O)OMe$	H, H	8 (18)
11	Cl	H, H	91 (92)
12	Cl	Cl, H	90[c]
13	Cl	Cl, Cl	21[d]
14	H	Cl, H	95[e]
15	H	Cl, Cl	99[e,f]
16	Me	Cl, H	81[g]
17	Me	Cl, Cl	56[h]
18	Br	H, H	56 (59),[i] 75[j]
20	H	Br, H	98[k]
21	H	Br, Br	99[k,l]
22	I	H, H	61 (64)
23	H	I, H	99[m]
24	H	I, I	99[m,n]
25	CN	H, H	11 (19)
26	H	CN, H	8 (13)

[a] Isolated yields, based on metallacarborane employed (yields based on 1 consumed are given in parentheses). [b] Prepared from 2. [c] Prepared from 11. [d] Prepared from 12. [e] From reaction with $(CH_2CO)_2NCl$. [f] Prepared from 14. [g] Prepared from $(C_5Me_5)Co(Et_2C_2B_3H_4$-5-Me). [h] Prepared from 16. [i] From reaction with $BrCH_2CN$. [j] From reaction with $BrCH_2NO_2$. [k] From reaction with $(CH_2CO)_2NBr$. [l] Prepared from 20. [m] From reaction with $(CH_2CO)_2NI$. [n] Prepared from 23.

compounds. A detailed account of this chemistry will be presented elswehere.[11]

Conversion of 2 to the desired acetyl derivative 3 was readily achieved by base-catalyzed cleavage, as shown in Scheme IC. The mechanism of formation of 2 from 1^- presents an intriguing problem. A priori, one might assume that the B(5)–acetyl species 3 is formed initially and subsequently reacts (in its enolate form) with acetyl chloride to generate 2; indeed, the formation of enol acetates via attack of acyl halides on enolate anions is well-known.[12] However, this route is effectively excluded in the present case, since we have established that 3 is not a precursor to 2. Treatment of 3 or its deprotonated anion 3^- with acetyl chloride generated no detectable 2, and there is no evidence that 3 is present in solution in the formation of 2 from 1^- and acetyl chloride. When this latter reaction was monitored (via TLC analysis) at room temperature as a function of time, 3 was not produced at detectable levels. A possible mechanism for the formation of 2, presented in Scheme II, involves initial reaction of an acetyl group at the nucleophilic B–B edge of 1^- to form the acetyl-bridged intermediate 2a. Formation of such bridged species has been proposed as a general pathway for the B(5)-alkylation of 1,[8] its iron–arene and ruthenium–arene analogues,[8] and the *nido*-$R_2C_2B_4H_6$ carboranes.[13] The formation of B–X–B bridged derivatives in which X is Si, Ge, Sn, or Pb has been demonstrated in reactions of group IV (14) alkyl halides with $B_5H_8^-$ and $R_2C_2B_4H_5^-$ anions.[14] In the B-alkylation of $C_2B_9H_{11}^{2-}$ via reactions with alkyl halides, μ-alkyl intermediates containing three-center, 2-electron B–C–B bonds have been isolated and characterized.[15]

In the postulated intermediate 2a, net transfer of electron density from the acetyl group to the carborane cage would polarize the carboxyl region, favoring the enolate form whose C–O^- unit would likely undergo O-acetylation followed by rearrangement (interchange of the organic moiety with H(5)) to generate 2 as shown. As is often the

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[11] Piepgrass, K. W.; Hölscher, M., Jr.; Sabat, M.; Grimes, R. N. Manuscript in preparation.

[12] The reaction of PhC(O)Cl with diethyl [lithio(trimethylsilyl)-methyl]phosphonate (Carey, F. A.; Court, A. S. *J. Org. Chem.* **1972**, *37*, 979) is an example of O-acylation in organosilicon chemistry; the preference for O- over C-acylation in this case was attributed to steric hindrance by the Me_3Si and $P(O)(OEt_2)$ substituents. In this reaction the acylation occurred at an oxygen present in the original substrate, in contrast to the formation of 2.

[13] Davis, J. H., Jr.; Grimes, R. N. *Inorg. Chem.* **1988**, *27*, 4213.

[14] (a) Gaines, D. F.; Iorns, T. V. *J. Am. Chem. Soc.* **1968**, *90*, 6617. (b) Thompson, M. L.; Grimes, R. N. *Inorg. Chem.* **1972**, *11*, 1925. (c) Tabereaux, A.; Grimes, R. N. *Inorg. Chem.* **1973**, *12*, 792.

[15] Knyazev, S. P.; Brattsev, V. A.; Stanko, V. I. *Zh. Obshch. Khim.* **1977**, *47*, 2627; *J. Gen. Chem. USSR (Engl. Transl.)* **1977**, *47*, 2398.

Table II. 115.8-MHz ^{11}B FT NMR Data for (C_5Me_5)Co(2,3-$Et_2C_2B_3H_2$-4-R^4-5-R^5-6-R^6) Complexes

compd	R^5	R^4, R^6	δ (J_{BH}, Hz)[a]	area ratio
1[b]	H	H, H	7.5 (146), 3.9 (134)[c]	1:2
2	C(=CH_2)OC(O)Me	H, H	11.7, −0.9 (125)	1:2
3	C(O)Me	H, H	7.8, 2.8 (116)	1:2
4	−OC_4H_8−	H[d]	11.6, 4.3 (<196)	1:2
5	H	C(O)CF_3, H	7.4 (153), 5.2 (156), −2.0	1:1:1
6	C(O)CH_2C(O)OMe	H, H	11.0, 1.3 (111)	1:2
8	H	CHOHCMe_3, H	5.9, 4.0, 1.4	1:1:1
9	$(CH_2)_4$OC(O)CMe_3	H, H	21.8, 0.8	1:2
10	$(CH_2)_4$OH	H, H	21.7, 0.0 (84)	1:2
11	Cl	H, H	20.6, −1.5 (137)	1:2
12	Cl	Cl, H	17.4, 8.7, −1.7 (138)	1:1:1
13	Cl	Cl, Cl	14.0, 8.6	1:2
14	H	Cl, H	14.5, 4.3 (108)	1:2
15	H	Cl, Cl	13.8, −0.3 (134)	2:1
16	Me	Cl, H	16.7, 9.7, −0.4 (124)	1:1:1
17	Me	Cl, Cl	12.7, 9.2	1:2
18	Br	H, H	12.9, 0.1 (145)	1:2
19	Br	Br, H	11.6, 5.6, −0.1 (126)	1:1:1
20	H	Br, H	9.5, 5.2 (150), 3.7 (140)	1:1:1
21	H	Br, Br	9.2, 2.1 (150)	2:1
22	I	H, H	2.5 (115), −2.6	2:1
23	H	I, H	7.9 (145), 5.0 (135), −0.93	1:1:1
24	H	I, I	6.4 (138), −2.1	1:2
25	CN	H, H	4.0 (134), 1.3	1:2
26	H	CN, H	7.0 (152), 4.8 (148), −5.3	1:2

[a] Shifts relative to $BF_3\cdot OEt_2$, positive values downfield; H—B coupling constant in hertz is given in parentheses, when resolved. Spectra were recorded in *n*-hexane solution except where otherwise indicated. [b] Davis, J. H., Jr.; Sinn, E.; Grimes, R. N. *J. Am. Chem. Soc.* 1989, *111*, 4776. [c] CH_2Cl_2 solution. [d] THF ring is proposed to bond to both B(5) and B(4,6).

Table III. 300-MHz ^1H FT NMR Data[a–c]

compd	δ
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 s, B—H—B)
2	5.16 (s, =CH_2), 5.03 (s, =CH_2), 2.15 (s, C(O)Me), 2.07 (m, CH_2), 1.85 (m, CH_2), 1.70 (s, C_5Me_5), 1.07 (t, CH_3), −4.9 (vbr, B—H—B)
3	2.18 (s, C(O)Me), 2.05 (m, CH_2), 1.88 (m, CH_2), 1.66 (s, C_5Me_5), 1.08 (t, CH_3), −5.2 (vbr, B—H—B)
4	3.94 (m, BCHO), 3.86 (m, OCH_2), 3.65 (dt, OCH_2), 2.13 (m, CH_2), 2.05 (m, CH_2), 1.89 (m, CH_2), 1.73 (s, C_5Me_5), 1.14 (t, CH_3), 1.10 (t, CH_3), −5.5 (vbr s, B—H—B), −6.0 (vbr s, B—H—B)
5	2.65 (m, CH_2), 2.07 (m, CH_2), 1.83 (m, CH_2), 1.70 (s, C_5Me_5), 1.09 (t, CH_3), 0.93 (t, CH_3), −5.38 (br s, B—H—B)
6	5.24 (s, $COCH_2CO$), 3.73 (s, OCH_3), 2.08 (m, CH_2), 1.90 (m, CH_2), 1.69 (s, C_5Me_5), 1.10 (t, CH_3), −5.1 (br s, B—H—B)
7	3.30 (br, BCH), 2.11 (m, CH_2), 1.87 (m, CH_2), 1.77 (s, C_5Me_5), 1.09 (t, CH_3), 0.90 (s, CMe_3), −5.36 (br s, B—H—B), −5.98 (br s, B—H—B)
8	4.04 (br t, BCH), 2.56 (m, CH_2), 2.11 (m, CH_2), 1.86 (m, CH_2), 1.71 (s, C_5Me_5), 1.10 (t, CMe_3), 0.84 (br t,[e] CH_3), −4.9 (vbr s, B—H—B), −5.5 (vbr s, B—H—B)
9	4.03 (t, OCH_2), 2.11 (m, CH_2), 1.85 (m, CH_2), 1.72 (s, C_5Me_5), 1.64 (m, CH_2), 1.37 (m, CH_2), 1.19 (s, CMe_3), 1.08 (t, CH_3), 0.84 (br t, BCH_2), −5.46 (br s, B—H—B)
10	3.63 (t, OCH_2), 2.11 (m, CH_2), 1.85 (m, CH_2), 1.72 (s, C_5Me_5), 1.61 (m, CH_2), 1.37 (m, CH_2), 1.08 (t, CH_3), 0.84 (br t, BCH_2), −5.45 (br s, B—H—B)
11	2.13 (m, CH_2), 1.87 (m, CH_2), 1.77 (s, C_5Me_5), 1.10 (t, CH_3), −3.98 (br s, B—H—B)
12	2.11 (m, CH_2), 1.84 (m, CH_2), 1.73 (s, C_5Me_5), 1.09 (t, CH_3), 1.07 (t, CH_3), −1.88 (br s, B—H—B), −3.77 (br s, B—H—B)
13	2.09 (m, CH_2), 1.70 (s, C_5Me_5), 1.09 (t, CH_3), −1.67 (br s, B—H—B)
14	2.14 (m, CH_2), 2.01 (m, CH_2), 1.85 (m, CH_2), 1.76 (s, C_5Me_5), 1.12 (t, CH_3), 1.05 (t, CH_3), −3.87 (br s, B—H—B), −5.77 (vbr s, B—H—B)
15	2.14 (m, CH_2), 1.95 (m, CH_2), 1.74 (s, C_5Me_5), 1.09 (t, CH_3), −3.66 (vbr s, B—H—B)
16	2.10 (m, CH_2), 1.84 (m, CH_2), 1.70 (s, C_5Me_5), 1.09 (t, CH_3), 1.04 (t, CH_3), −3.25 (br s, B—H—B), −5.11 (br s, B—H—B)
17	2.09 (m, CH_2), 1.67 (s, C_5Me_5), 1.07 (t, CH_3), −3.1 (vbr s, B—H—B)
18	2.14 (m, CH_2), 1.87 (m, CH_2), 1.77 (s, C_5Me_5), 1.09 (t, CH_3), −4.22 (br s, B—H—B)
19	2.13 (m, CH_2), 1.84 (m, CH_2), 1.72 (s, C_5Me_5), 1.10 (t, CH_3), 1.07 (t, CH_3), −2.25 (br s, B—H—B), −3.92 (br s, B—H—B)
20	2.18 (m, CH_2), 2.01 (m, CH_2), 1.90 (m, CH_2), 1.74 (s, C_5Me_5), 1.12 (t, CH_3), 1.05 (t, CH_3), −3.85 (vbr s, B—H—B), −5.63 (vbr s, B—H—B)
21	2.08 (m, CH_2), 1.78 (s, C_5Me_5), 1.11 (t, CH_3), −3.28 (vbr s, B—H—B)
22	2.16 (m, CH_2), 1.88 (m, CH_2), 1.71 (s, C_5Me_5), 1.09 (t, CH_3), −4.60 (br s, B—H—B)
23	2.15 (m, CH_2), 1.95 (m, CH_2), 1.77 (s, C_5Me_5), 1.14 (t, CH_3), 1.06 (t, CH_3), −3.89 (br s, B—H—B), −5.43 (br s, B—H—B)
24	2.08 (m, CH_2), 1.78 (s, C_5Me_5), 1.11 (t, CH_3), −3.28 (vbr s, B—H—B)
25	2.10 (m, CH_2), 1.90 (m, CH_2), 1.80 (s, C_5Me_5), 1.09 (t, CH_3), −5.6 (vbr s, B—H—B)
26	2.11 (m, CH_2), 1.86 (m, CH_2), 1.78 (s, C_5Me_5), 1.12 (t, CH_3), 1.09 (t, CH_3), −5.7 (vbr s, B—H—B)
27	2.09 (m, CH_2), 1.80 (m, CH_2), 1.68 (s, C_5Me_5), 1.2 (br m, CH_3), 1.07 (t, CH_3), −3.7 (vbr s, B—H—B), −5.37 (br s, B—H—B)

[a] Shifts relative to Me_4Si. Integrated peak areas in all cases are consistent with the assignments given. Legend: m = multiplet, s = singlet, d = doublet, t = triplet, q = quartet. [b] B—$H_{terminal}$ resonances are broad quartets and mostly obscured by other signals. [c] $CDCl_3$ solution. [d] Davis, J. H., Jr.; Sinn, E.; Grimes, R. N. *J. Am. Chem. Soc.* 1989, *111*, 4776. [e] Unresolved doublet of triplets.

case in reactions of 1^-, protonation to form neutral 1 is a competing process, in this case regenerating over 50% of the starting complex. The strong electron-withdrawing character of the 1^- cluster lends plausibility to this proposed mechanism and provides a rationale for its occurrence in this particular case, which is so far unique in boron cluster chemistry. (Electrophilic attack of acetyl chloride or benzoyl chloride on other carborane substrates having

Table IV. 75.5-MHz ^{13}C FT NMR Data[a,b]

compd	δ
2	169.8 (C=O), 160 (br, C_2B_3), 111.8 (t, =CH_2), 92.6 (C_5), 23.0 (t, CH_2), 21.6 (q, $COCH_3$), 17.6 (q, CH_3), 9.8 (q, C_5Me_5)
3	113 (br, C_2B_3), 93.1 (C_5), 37.2 (q, $COCH_3$), 23.0 (t, CH_2), 17.5 (q, CH_3), 9.9 (q, C_5Me_5)
4	113 (br, C_2B_3), 106 (br, C_2B_3), 92.5 (C_5), 74 (br, BCH), 68.6 (t, OCH_2), 32.2 (t, CH_2), 27.9 (t, CH_2), 22.8 (t, *Et* CH_2), 21.8 (t, *Et* CH_2), 18.8 (q, CH_3), 16.8 (q, CH_3), 10.4 (q, C_5Me_5)
5	117 (br, C_2B_3), 112 (br, C_2B_3), 94.0 (C_5), 22.8 (t, CH_2), 19.7 (t, CH_2), 17.6 (q, CH_3), 17.2 (q, CH_3), 9.9 (q, C_5Me_5)
6	185 (br, C=O), 172.6 (CO_2), 113 (br, C_2B_3), 96.7 (C_5), 51.1 (OCH_3), 23.0 (CH_2), 17.5 (CH_3), 9.8 (C_5Me_5)
7	110 (br, C_2B_3), 92.8 (C_5), 35.5 (CMe_3), 27.0 (Me_3), 22.9 (CH_2), 17.6 (CH_3), 10.0 (C_5Me_5)
9	179 (br, C=O), 111 (br, C_2B_3), 92.4 (C_5), 64.8 (OCH_2), 39.2 (CMe_2), 31.4 (CH_2), 29.0 (CH_2), 27.7 (Me_3), 22.9 (*Et* CH_2), 17.9 (*Et* CH_3), 14.7 (br, BCH_2), 10.0 (C_5Me_5)
10	111 (br, C_2B_3), 92.4 (C_5), 63.4 (OCH_2), 35.6 (CH_2), 28.8 (CH_2), 22.9 (*Et* CH_2), 17.9 (*Et* CH_3), 10.0 (C_5Me_5)
11	111 (br, C_2B_3), 93.6 (C_5), 22.7 (CH_2), 17.7 (CH_2), 9.6 (C_5Me_5)
12	109 (br, C_2B_3), 105 (br, C_2B_3), 94.3 (C_5), 23.1 (t, CH_2), 20.0 (t, CH_2), 17.9 (q, CH_3), 15.7 (q, CH_3), 9.0 (q, C_5Me_5)
13	103 (br, C_2B_3), 95.1 (C_5), 20.2 (CH_2), 15.9 (CH_3), 8.4 (C_5Me_5)
14	110 (br, C_2B_3), 104 (br, C_2B_3), 92.9 (C_5), 22.7 (CH_2), 19.3 (CH_2), 17.2 (CH_3), 15.1 (CH_3), 9.2 (C_5Me_5)
15	104 (br, C_2B_3), 93.7 (C_5), 19.6 (CH_2), 15.3 (CH_3), 8.5 (C_5Me_5)
16	110 (br, C_2B_3), 104 (br, C_2B_3), 93.2 (C_5), 23.3 (CH_2), 20.1 (CH_2), 18.2 (CH_3), 15.9 (CH_3), 9.3 (C_5Me_5), −4 (br, BCH_3)
17	105 (br, C_2B_3), 94.0 (C_5), 20.2 (CH_2), 16.0 (CH_3), 8.6 (C_5Me_5), −6 (br, BCH_3)
18	111 (br, C_2B_3), 93.7 (C_5), 22.6 (CH_2), 17.7 (CH_3), 9.8 (C_5Me_5)
19	111 (br, C_2B_3), 105 (br, C_2B_3), 94.5 (C_5), 23.0 (CH_2), 20.8 (CH_2), 18.0 (CH_3), 15.7 (CH_3), 9.1 (C_5Me_5)
20	110 (br, C_2B_3), 105 (br, C_2B_3), 93.6 (C_5), 23.0 (CH_2), 20.6 (CH_2), 18.0 (CH_3), 15.7 (CH_3), 9.9 (C_5Me_5)
21	105 (br, C_2B_3), 93.0 (C_5), 20.1 (CH_2), 15.2 (CH_3), 9.1 (C_5Me_5)
22	112 (br, C_2B_3), 93.6 (C_5), 22.4 (CH_2), 17.8 (CH_3), 10.0 (C_5Me_5)
23	110 (br, C_2B_3), 106 (br, C_2B_3), 93.7 (C_5), 23.2 (CH_2), 22.3 (CH_2), 18.1 (CH_3), 16.9 (CH_3), 10.0 (C_5Me_5)
24	105 (br, C_2B_3), 94.0 (C_5), 20.5 (CH_2), 15.3 (CH_3), 8.7 (C_5Me_5)
25	127 (br, BCN), 113 (br, C_2B_3), 93.8 (C_5), 22.6 (CH_2), 17.5 (CH_2), 9.8 (C_5Me_5)
26	128 (br, BCN), 112 (br, C_2B_3), 93.8 (C_5), 22.6 (CH_2), 21.6 (CH_2), 17.6 (CH_3), 17.1 (CH_3), 9.8 (C_5Me_5)

[a] $CDCl_3$ solution. [b] Shifts relative to Me_4Si; all spectra broad-band-decoupled except where couplings are indicated.

a C_2B_3 open face, e.g. $C_2B_9H_{12}^-$ anions,[16] generates the expected B–acyl derivatives with no evidence of a vinyl ester analogous to 3. Similarly, treatment of C-lithiated 1,2- or 1,7-$C_2B_{10}H_{12}$ clusters with acetyl chloride affords C–acetyl carboranes[17]). Moreover, reactions of 1^- with acyl halides other than acetyl chloride gave no species analogous to 2 (vide infra).

From the standpoint of organic chemistry, the formation of 2 from 1^- is remarkable in that the acylating agent is itself the only source of –C=O– in this system, in contrast to the usual case wherein acylation occurs on an existing carboxyl-containing substrate.[12]

Reactions with Other Acyl Halides. The treatment of 1^- with trifluoroacetyl chloride gave, on workup in air, the B(4)–trifluoroacetyl derivative 5 (obtained as a racemic mixture with the equivalent B(6)–C(O)CF_3 compound). This structure is clearly evident from the 1:1:1 ^{11}B NMR pattern, and indicates that powerful electron-withdrawing groups such as trifluoroacetyl may end up on B(4/6) rather than B(5) as is the case with alkyl or organomethyl substituents.[1,8] A rationale for this observation is that the introduction of strong electron attractors perturbs the normal electron distribution in the C_2B_3 ring, inducing higher negative charge on B(4/6) relative to B(5). The latter situation is found in unsubstituted *nido*-$R_2C_2B_4H_6$ carboranes, whose deprotonated anions alkylate preferentially at B(4/6)[13]—an observation that is consistent with MNDO calculations[18] on parent 2,3-$C_2B_4H_8$ which place the higher negative charge on B(4) and B(6).

In the present work the trifluoracetyl reaction was the only case in which the addition of a functional group to *unsubstituted* 1^- occurred in significant yield at B(4/6). As will be seen, B(4/6)-substituted trace products (e.g., 8) were found, and cyano addition produced both B-substituted isomers, but only C(O)CF_3 provided a clear-cut example of selective B(4/6) substitution on the 1^- anion. This appears to correlate with the extremely high electrophilicity of the latter group.

Treatment of 1^- with methylmalonyl chloride gave the B(5)–C(O)CH_2C(O)OMe derivative (6) in moderately low yield, but a reaction with trimethylacetyl chloride over an extended period at room temperature afforded only a very small amount of the B(5)–trimethylacetyl product 7, which was characterized by ^1H NMR and mass spectroscopy. When this reaction was conducted over a much shorter time, a different set of products was isolated, consisting of the B(4/6)–CHOHCMe_3 (8) and B(5)–$(CH_2)_4$OC(O)-CMe_3 (9) derivatives, both isolated in low yield, and the B(5)–$(CH_2)_4$OH species (10) which was the main product. The last two compounds are assumed to have formed via addition of THF to the metallacarborane substrate, followed by opening of the OC_4H_8 ring to give 10 and subsequent acetylation to form 9. In both reactions, large amounts of neutral 1 were recovered.

Synthesis of Chloro, Bromo, and Iodo Derivatives. In the course of this investigation a variety of reagents and conditions were employed in attempts to prepare B-halogenated derivatives of 1. Here we report only the synthetically most important findings.

Chlorination of 1^- was effected via treatment with methanesulfonyl chloride, which produced the B(5)–Cl species 11 almost quantitatively, accompanied by a trace of the B(4/6,5)–dichloro compound 12; in contrast to many other reactions of 1^- in THF, reprotonation of the anion to form 1 was almost nil. Stepwise treatment of 11 with additional equivalents of methanesulfonyl chloride gave 12 and the B(4,5,6)-trichloro derivative 13 in high and moderate yield, respectively. In these reactions and in the corresponding B(5)-bromination and -iodination, described below, the presumed mechanism is analogous to that of the alkyl additions,[8] i.e., electrophilic attack at the B–B edge of 1^- with the halogen ultimately binding to B(5), the most negative boron position.

An alternative, and synthetically complementary, approach to halogenation employing *N*-halosuccinimides generated exclusively B(4/6)–halo derivatives via an assumed free radical mechanism, in which substitution occurs at the relatively electropositive B(4) and B(6) positions adjacent to carbon. Treatment of neutral 1 with *N*-

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[16] Brattsev, V. A.; Knyazev, S. P.; Stanko, V. I. *Zh. Obshch. Khim.* **1976**, *46*, 1419.

[17] Zakharkin, L. I.; L'vov, A. I. *Zh. Obshch. Khim.* **1967**, *37*, 1217.

[18] Dewar, M. J. S.; McKee, M. L. *Inorg. Chem.* **1980**, *19*, 2662.

Table V. Infrared Absorptions (cm^{-1}, Neat Films on KBr Plates)^{a,b}

compd	absorptions
2	2960 (vs), 2927 (s), 2910 (sh), 2867 (s), 2514 (s), 1869 (m br), 1750 (vs),^{c} 1448 (m), 1379 (vs), 1368 (vs), 1363 (sh), 1237 (vs),^{c} 1201 (vs),^{c} 1026 (s), 895 (s, vinyl), 873 (s), 773 (s)
3	2961 (vs), 2928 (s), 2912 (sh), 2866 (s), 2520 (s), 1886 (br m), 1851 (br m), 1654 (vs), 1610 (m), 1454 (s), 1446 (s), 1428 (m), 1383 (s), 1340 (m), 1199 (s), 1029 (s), 944 (m), 846 (m), 773 (s)
4	3295 (m), 2960 (vs), 2924 (vs), 2869 (s), 2522 (s), 1856 (m), 1518 (w), 1478 (m), 1468 (m), 1461 (m), 1450 (s), 1380 (s), 1376 (s), 1042 (vs), 1029 (s), 922 (m), 774 (w), 740 (w)
5	2965 (s), 2928 (s), 2871 (m), 2554 (m), 2518 (m), 1868 (m), 1673 (s), 1481 (m), 1469 (m), 1453 (m), 1384 (m), 1282 (m), 1189 (vs), 1131 (vs), 1083 (s), 1030 (m), 899 (m), 704 (s), 636 (w)
7	3611 (w), 2959 (s), 2922 (vs), 2919 (vs), 2864 (m), 2849 (s), 2499 (m), 1477 (m), 1466 (m), 1463 (m), 1453 (m), 1389 (w), 1377 (m), 1362 (m), 1213 (w), 1165 (w), 1027 (w), 996 (w), 982 (w), 912 (w), 867 (w)
8	3251 (br w), 3167 (br w), 2961 (vs), 2927 (vs), 2868 (s), 2538 (s), 2509 (s), 1866 (m), 1729 (m), 1637 (m), 1632 (s), 1621 (m), 1614 (m), 1474 (s), 1470 (s), 1461 (m), 1453 (m), 1388 (w), 1381 (m), 1360 (m), 1157 (w), 1030 (w), 905 (w), 833 (w)
9	2960 (vs), 2927 (vs), 2868 (s), 2491 (s), 1918 (w), 1869 (w), 1729 (vs), 1506 (m), 1480 (s), 1464 (m), 1457 (s), 1452 (m), 1376 (s), 1366 (m), 1284 (s), 1155 (vs), 1052 (w), 1029 (m), 895 (m), 775 (m)
10	3297 (br m), 2960 (vs), 2926 (vs), 2867 (s), 2491 (s), 1932 (w), 1713 (w), 1504 (w), 1480 (m), 1466 (m), 1450 (m), 1430 (w), 1376 (m), 1072 (w), 1059 (w), 1027 (m), 1001 (w), 950 (w), 894 (w), 776 (w)
11	2965 (vs), 2929 (vs), 2868 (s), 2526 (vs), 2332 (s), 1888 (w), 1469 (s), 1451 (s), 1377 (vs)
13	2873 (vs), 2935 (s), 2872 (m), 1469 (m), 1456 (s), 1448 (s), 1437 (m), 1405 (m), 1377 (vs), 1364 (s), 1333 (m), 1105 (m), 1012 (vs), 913 (s), 810 (s), 777 (s), 712 (m), 667 (m), 584 (m), 490 (m)
14	2962 (vs), 2927 (s), 2868 (m), 2544 (m), 2507 (m), 2361 (m), 2338 (w), 1384 (m), 1365 (m)
15	2970 (vs), 2930 (m), 2857 (w), 2554 (m), 1480 (m), 1451 (s), 1379 (m), 1110 (m), 1080 (m), 1061 (m), 1011 (m), 950 (m)
16	2959 (vs), 2927 (vs), 2909 (vs), 2866 (s), 2488 (s), 1916 (br w), 1523 (w), 1467 (s), 1449 (s), 1379 (s), 1305 (m), 1161 (w), 1085 (m), 1031 (m), 888 (m), 813 (m), 775 (m)
17	2961 (vs), 2923 (vs), 2868 (sh), 2852 (s), 1466 (s), 1456 (s), 1429 (m), 1380 (m), 1362 (m), 1307 (m), 1096 (w), 1028 (m), 1015 (m), 950 (w), 803 (m), 762 (m)
18	2928 (s), 2919 (s), 2911 (s), 2525 (s), 2508 (s), 1869 (m), 1559 (m), 1472 (s), 1465 (m), 1456 (s), 1448 (s), 1375 (vs), 1050 (w), 1027 (s), 965 (m), 821 (m), 802 (vs), 767 (vs)
19	2965 (vs), 2928 (vs), 2868 (s), 2855 (s), 2529 (s), 1874 (w), 1536 (w), 1479 (m), 1466 (m), 1458 (m), 1450 (s), 1430 (s), 1378 (vs), 1184 (w), 1052 (w), 1030 (w), 980 (w), 971 (m), 924 (w), 855 (m), 816 (m), 804 (w), 755 (m), 664 (w)
20	2965 (vs), 2927 (s), 2869 (m), 2545 (m), 2497 (m), 2342 (w), 1490 (s), 1450 (s), 1381 (s), 1361 (s)
21	2961 (vs), 2925 (vs), 2868 (s), 2514 (m), 1844 (w), 1450 (m), 1429 (m), 1382 (s), 1376 (s), 1041 (m), 801 (m), 790 (m)
22	3260 (s), 3233 (s), 2961 (vs), 2945 (m), 2925 (s), 2910 (s), 1558 (m), 1465 (vs), 1381 (s), 1025 (s), 951 (s), 800 (m), 782 (vs), 762 (vs), 742 (m), 602 (m)
23	2960 (s), 2927 (vs), 2867 (s), 2546 (m), 2493 (m), 1450 (s), 1431 (m), 1370 (s), 1355 (s)
24	2959 (s), 2923 (s), 2851 (s), 2561 (m), 1456 (m), 1425 (m), 1420 (m), 1363 (m), 925 (m)
25	2964 (vs), 2928 (s), 2910 (s), 2866 (s), 2545 (s), 2521 (vs), 1814 (m), 1566 (m), 1472 (vs), 1465 (s), 1456 (s), 1378 (vs), 1074 (w), 1027 (s), 949 (m), 872 (m), 774 (m), 734 (w)
26	2962 (vs), 2925 (vs), 2855 (s), 2549 (m), 2513 (m), 1635 (m), 1437 (s), 1378 (m), 1028 (w), 919 (w)

[a] Microcrystalline films obtained by evaporation of solutions. [b] Legend: vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, br = broad. [c] Characteristic of acetate.

Table VI. Experimental X-ray Diffraction Parameters and Crystal Data for (C_5Me_5)Co(2,3-$Et_2C_2B_3H_4$-5-C(=CH_2)OC(O)Me) (2)

space group	$P2_1/n$
a, Å	8.368 (2)
b, Å	18.757 (5)
c, Å	14.234 (4)
β, deg	97.25 (2)
V, Å^3	2216
Z	4
μ, cm^{-1} (Mo Kα)	7.8
transm factors	0.88–1.22
λ, Å	0.7107
D(calcd), g cm^{-3}	1.19
cryst size, mm	0.38 × 0.32 × 0.27
2θ range, deg	2–55
no. of reflns measd	5113
no. of reflns obsd ($I > 3.00\sigma(I)$)	3856
R	0.037
R_w	0.053
largest peak in final diff map, e/Å^3	0.33

chlorosuccinimide in THF gave the B(4/6)–Cl derivative **14** in 95% isolated yield; subsequent reaction of **14** with the same reagent afforded the B(4,6)-dichloro species **15**, again in 95% yield. No evidence of B(5)-substitution was seen in either procedure.

Alkylhalo-B,B′-disubstituted and B,B′,B″-trisubstituted complexes of **1** were prepared from the B-methyl derivative[8] (C_5Me_5)Co($Et_2C_2B_3H_4$-5-Me) via bridge-deprotonation to form the anion **1$^-$** followed by treatment with methanesulfonyl chloride to give the 5-methyl-4/6-chloro species **16**. Repetition of this sequence with the latter compound gave the 5-methyl-4,6-dichloro derivative **17**.

Electrophilic bromination of **1$^-$** was most efficiently accomplished with bromoacetonitrile and bromonitromethane, which produced the B(5)–Br complex **18** in 56 and 75% isolated yields, respectively. The former reaction also gave a trace of the B(4/6,5)–dibromo species **19**, as well as a 19% yield of the B(5)–CH_2CN derivative (see preceding paper[1]). The treatment of neutral **1** with *N*-bromosuccinimide, as expected, gave the B(4/6)–Br derivative **20**, and further bromination of the latter species gave the B(4,6)–Br_2 complex **21**, both reactions proceeding essentially quantitatively.

The analogous iodo derivatives were synthesized similarly. The B(5)–iodo complex **22** was prepared in good yield by reaction of **1$^-$** with iodotrifluoromethane, while the reaction of **1** with *N*-iodosuccinimide generated the B(4/6)–iodo product **23**; iodination of **23** with the same reagent gave the B(4,6)–diiodo species **24**. Again, both procedures gave quantitative yields.

Synthesis of Cyano and Nitro Derivatives. The reaction of **1$^-$** with *p*-toluenesulfonyl cyanide afforded, on workup, both the B(5)–CN and B(4/6)–CN complexes (**25** and **26**, respectively) in a total yield of about 20% with considerable recovery of neutral **1**. The preparation of a nitro-substituted derivative was less successful, a treatment of **1$^-$** with $NO_2^+BF_4^-$ affording the B(4/6)–NO_2 species **27** in very low yield, identified by proton NMR and mass spectra.

Attempted Syntheses of Fluoro, Vinyl, Benzoyl, and Malonyl Derivatives. Reactions of **1$^-$** with excess

Table VII. Positional and Thermal Parameters for 2

Positional Parameters

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Co	0.34956 (3)	0.15858 (1)	0.82704 (2)	H(2EC)	0.3833	0.1397	0.4964
O(1)	0.5019 (2)	0.3590 (1)	0.8307 (1)	H(3MA)	0.1250	0.0276	0.6917
O(2)	0.4667 (3)	0.3889 (1)	0.6774 (1)	H(3MB)	0.0107	0.0621	0.7569
C(2)	0.3331 (3)	0.1387 (1)	0.6834 (1)	H(3EA)	−0.1170	0.0359	0.6026
C(2M)	0.4033 (4)	0.0781 (1)	0.6314 (2)	H(3EB)	−0.1020	0.1170	0.6226
C(2E)	0.3811 (6)	0.0926 (2)	0.5260 (2)	H(3EC)	0.0052	0.0806	0.5574
C(3M)	0.0683 (3)	0.0719 (1)	0.6998 (2)	H(4)	0.0341	0.2121	0.8079
C(3)	0.1784 (3)	0.1367 (1)	0.7130 (2)	H(6)	0.5619	0.2163	0.7069
C(3E)	−0.0547 (5)	0.0788 (2)	0.6135 (3)	H(6RA)	0.1936	0.2115	1.0141
C(9)	0.3396 (3)	0.3337 (1)	0.8261 (2)	H(6RB)	0.3219	0.2151	1.0960
C(10)	0.2395 (4)	0.3718 (1)	0.8700 (2)	H(6RC)	0.3578	0.2610	1.0229
C(1R1)	0.3592 (4)	0.1664 (1)	0.9717 (2)	H(7RA)	0.7190	0.2130	1.0222
C(11)	0.5525 (4)	0.3816 (1)	0.7498 (2)	H(7RB)	0.6761	0.2469	0.9176
C(12)	0.7313 (4)	0.3943 (2)	0.7648 (3)	H(7RC)	0.5830	0.2782	0.9763
C(1R2)	0.5157 (3)	0.1725 (1)	0.9448 (2)	H(8RA)	0.7548	0.0537	0.8950
C(1R3)	0.5496 (3)	0.1089 (1)	0.8973 (2)	H(8RB)	0.7710	0.1371	0.8533
C(1R4)	0.4133 (2)	0.0630 (1)	0.8953 (2)	H(8RC)	0.6701	0.0523	0.7916
C(1R5)	0.2963 (3)	0.0992 (1)	0.9421 (1)	H(9RA)	0.4433	−0.0428	0.9004
C(1R6)	0.2783 (5)	0.2202 (2)	1.0296 (2)	H(9RB)	0.4561	−0.0152	0.7907
C(1R7)	0.6347 (4)	0.2317 (2)	0.9714 (3)	H(9RC)	0.2997	−0.0264	0.8538
C(1R8)	0.7051 (3)	0.0909 (2)	0.8586 (3)	H(10RA)	0.1431	0.0517	1.0187
C(1R9)	0.4027 (3)	−0.0115 (1)	0.8577 (2)	H(10A)	0.2656	0.4174	0.8965
C(1R10)	0.1378 (3)	0.0685 (2)	0.9609 (2)	H(10B)	0.1213	0.3496	0.8719
B(4)	0.1340 (3)	0.2011 (1)	0.7702 (2)	H(10RB)	0.0949	0.0273	0.9132
B(5)	0.3068 (3)	0.2594 (1)	0.7759 (2)	H(10RC)	0.0559	0.0985	0.9403
B(6)	0.4327 (3)	0.2051 (1)	0.7127 (2)	H(12A)	0.7685	0.3996	0.7126
H(2MA)	0.3622	0.0306	0.6455	H(12B)	0.7516	0.4352	0.8128
H(2MB)	0.5159	0.0728	0.6627	H(12C)	0.7943	0.3615	0.8166
H(2EA)	0.4903	0.1046	0.5486	H(45)	0.1658	0.2616	0.7310
H(2EB)	0.4256	0.0604	0.4866	H(56)	0.3511	0.2642	0.6921

Thermal Parameters

atom	*U*11	*U*22	*U*33	*U*12	*U*13	*U*23
Co	0.0329 (1)	0.0346 (1)	0.0347 (1)	−0.0007 (1)	0.0039 (1)	0.0042 (1)
O(1)	0.079 (1)	0.049 (1)	0.053 (1)	−0.0192 (8)	0.0133 (8)	0.0001 (7)
O(2)	0.102 (2)	0.078 (1)	0.068 (1)	0.008 (1)	0.024 (1)	0.028 (1)
C(2)	0.055 (1)	0.042 (1)	0.038 (1)	0.001 (1)	0.0088 (9)	0.0012 (8)
C(2M)	0.090 (2)	0.047 (1)	0.057 (1)	0.007 (1)	0.019 (1)	−0.004 (1)
C(2E)	0.208 (4)	0.098 (3)	0.059 (2)	0.054 (3)	0.049 (2)	−0.008 (2)
C(3M)	0.059 (1)	0.053 (1)	0.061 (1)	−0.015 (1)	−0.009 (1)	0.005 (1)
C(3)	0.047 (1)	0.042 (1)	0.041 (1)	−0.0023 (9)	−0.0027 (9)	0.0050 (9)
C(3E)	0.108 (2)	0.095 (2)	0.094 (2)	−0.043 (2)	−0.046 (2)	0.016 (2)
C(9)	0.066 (1)	0.038 (1)	0.043 (1)	0.002 (1)	0.013 (1)	0.005 (1)
C(10)	0.102 (2)	0.046 (1)	0.065 (2)	0.015 (1)	0.025 (1)	−0.002 (1)
C(1R1)	0.081 (2)	0.049 (1)	0.037 (1)	0.001 (1)	0.004 (1)	0.005 (1)
C(11)	0.086 (2)	0.044 (1)	0.065 (2)	−0.011 (1)	0.024 (1)	0.001 (1)
C(12)	0.096 (2)	0.114 (3)	0.089 (2)	−0.046 (2)	0.030 (2)	−0.007 (2)
C(1R2)	0.067 (2)	0.055 (1)	0.050 (1)	−0.019 (1)	−0.016 (1)	0.015 (1)
C(1R3)	0.036 (1)	0.061 (1)	0.063 (1)	−0.002 (1)	−0.005 (1)	0.020 (1)
C(1R4)	0.040 (1)	0.044 (1)	0.046 (1)	0.0009 (9)	−0.0016 (8)	0.010 (1)
C(1R5)	0.048 (1)	0.052 (1)	0.040 (1)	−0.003 (1)	0.0059 (9)	0.013 (1)
C(1R6)	0.164 (4)	0.071 (2)	0.050 (1)	0.006 (2)	0.031 (2)	−0.008 (1)
C(1R7)	0.120 (3)	0.078 (2)	0.087 (2)	−0.052 (2)	−0.049 (2)	0.023 (2)
C(1R8)	0.035 (1)	0.103 (2)	0.142 (3)	0.013 (1)	0.012 (2)	0.040 (2)
C(1R9)	0.075 (2)	0.041 (1)	0.071 (2)	0.009 (1)	0.003 (1)	0.011 (1)
C(1R10)	0.055 (1)	0.097 (2)	0.070 (2)	−0.007 (1)	0.020 (1)	0.032 (2)
B(4)	0.039 (1)	0.048 (1)	0.051 (1)	0.004 (1)	0.003 (1)	0.007 (1)
B(5)	0.047 (1)	0.041 (1)	0.041 (1)	0.002 (1)	0.010 (1)	0.004 (1)
B(6)	0.050 (1)	0.043 (1)	0.042 (1)	−0.001 (1)	0.014 (1)	0.001 (1)

methanesulfonyl fluoride or with 1 equiv of benzoyl chloride or malonyl chloride gave no isolable products; in each case neutral 1 was recovered in ca. 50% yield. Treatment of the metallacarborane anion with vinyl bromide gave only a trace of a product which was tentatively identified from its proton NMR and mass spectra as a B—CH=CH_2 derivative (28), with substantial recovery of 1.

Summary

As was noted in the Introduction, this work was designed with two purposes in mind: to explore the chemical reactivity of 1^- toward electrophilic reagents and, at a practical level, to develop efficient routes to derivatives containing electron-withdrawing groups for use in the synthesis of multidecker complexes. In general, the pattern observed in reactions with organomethyl halides,[1,8] in which monosubstitution takes place selectively at B(5), was repeated here; a notable exception was trifluoroacetyl addition, which occurred only at B(4/6). As discussed above, these findings can be at least qualitatively explained on the basis of charge distribution in the C_2B_3 carborane ring and the relative electrophilicity of the attacking reagents. The contrasting reactions of *N*-halosuccinimides with neutral 1, which are assumed to proceed via a free radical mechanism, afford exclusively B(4/6)-halogenated

Table VIII. Bond Distances (Å) in 2

Co–C(2)	2.066 (2)	C(3M)–C(3E)	1.505 (4)
Co–C(3)	2.066 (2)	C(3)–B(4)	1.529 (4)
Co–C(1R1)	2.056 (2)	C(9)–C(10)	1.318 (4)
Co–C(1R2)	2.055 (2)	C(9)–B(5)	1.573 (3)
Co–C(1R3)	2.061 (2)	C(1R1)–C(1R2)	1.415 (4)
Co–C(1R4)	2.076 (2)	C(1R1)–C(1R5)	1.410 (3)
Co–C(1R5)	2.074 (2)	C(1R1)–C(1R6)	1.515 (4)
Co–B(4)	2.043 (2)	C(11)–C(12)	1.504 (4)
Co–B(5)	2.042 (3)	C(1R2)–C(1R3)	1.417 (4)
Co–B(6)	2.044 (2)	C(1R2)–C(1R7)	1.507 (4)
O(1)–C(9)	1.432 (3)	C(1R3)–C(1R4)	1.426 (3)
O(1)–C(11)	1.345 (3)	C(1R3)–C(1R8)	1.514 (4)
O(2)–C(11)	1.187 (4)	C(1R4)–C(1R5)	1.424 (3)
C(2)–C(2M)	1.516 (3)	C(1R4)–C(1R9)	1.495 (3)
C(2)–C(3)	1.412 (3)	C(1R5)–C(1R10)	1.502 (3)
C(2)–B(6)	1.527 (3)	B(4)–B(5)	1.807 (4)
C(2M)–C(2E)	1.513 (4)	B(5)–B(6)	1.787 (4)
C(3M)–C(3)	1.522 (3)	B(4)–H(4)	1.07
		B(4)–H(45)	1.31
		B(5)–H(45)	1.27
		B(5)–H(56)	1.30
		B(6)–H(6)	1.12
		B(6)–H(56)	1.32

Table IX. Selected Bond Angles (deg) in 2

C(2M)–C(2)–C(3)	123.5 (2)	C(1R2)–C(1R1)–C(1R5)	108.3 (2)
C(2M)–C(2)–B(6)	121.0 (2)	C(1R2)–C(1R1)–C(1R6)	125.8 (3)
C(3)–C(2)–B(6)	115.4 (2)	C(1R5)–C(1R1)–C(1R6)	125.7 (3)
C(2)–C(3)–C(3M)	123.3 (2)	C(1R1)–C(1R2)–C(1R3)	108.0 (2)
C(2)–C(3)–B(4)	115.6 (2)	C(1R1)–C(1R2)–C(1R7)	126.6 (3)
C(3M)–C(3)–B(4)	120.8 (2)	C(1R3)–C(1R2)–C(1R7)	125.0 (3)
C(2)–C(2M)–C(2E)	110.0 (2)	C(1R2)–C(1R3)–C(1R4)	108.1 (2)
C(3)–C(3M)–C(3E)	111.9 (2)	C(1R2)–C(1R3)–C(1R8)	126.5 (3)
C(3)–B(4)–B(5)	104.8 (2)	C(1R4)–C(1R3)–C(1R8)	125.4 (3)
B(4)–B(5)–B(6)	98.7 (2)	C(1R3)–C(1R4)–C(1R5)	107.3 (2)
C(9)–B(5)–B(4)	130.5 (2)	C(1R3)–C(1R4)–C(1R9)	125.6 (2)
C(9)–B(5)–B(6)	130.7 (2)	C(1R5)–C(1R4)–C(1R9)	126.9 (2)
C(2)–B(6)–B(5)	105.5 (2)	C(1R1)–C(1R5)–C(1R4)	108.3 (2)
O(1)–C(9)–C(10)	117.0 (2)	C(1R1)–C(1R5)–C(1R10)	126.5 (2)
O(1)–C(9)–B(5)	115.1 (2)	C(1R4)–C(1R5)–C(1R10)	125.1 (2)
C(10)–C(9)–B(5)	127.7 (2)	B(4)–H(45)–B(5)	89.1
C(9)–O(1)–C(11)	117.7 (2)	B(5)–H(56)–B(6)	86.4
O(1)–C(11)–O(2)	124.0 (3)		
O(1)–C(11)–C(12)	110.1 (3)		
O(2)–C(11)–C(12)	125.9 (3)		

products. In combination, these approaches allow considerable synthetic versatility, as they can be employed sequentially to generate mixed-halogen and di- and trisubstituted derivatives if desired.

In some cases, notably the syntheses of the vinyl and nitro derivatives, the preparative routes chosen gave unsatisfactory results. Fortunately, for synthetic purposes, however, the most highly sought products—the mono- and dihalo and acetyl species—were obtained in good to excellent yields. These compounds are amenable to transition-metal complexation leading to formation of multidecker sandwich complexes.[7,11] As a general observation, the extensive derivatization described in this and the accompanying paper, together with prior work, demonstrates clearly the stability of transition-metal metallacarboranes such as 1 under a wide variety of experimental conditions and underline their value as synthetic building block reagents.

Experimental Section

Except where otherwise indicated, materials, instrumentation, analyses, and general procedures were as described in earlier publications in this series.[1] All new products gave unit-resolution mass spectra in good agreement with calculated patterns based on natural isotope distributions, supported by high-resolution mass measurements or elemental analyses. Visible–UV spectra were recorded in CH_2Cl_2 solution.

Reaction of 1^- with Acetyl Chloride. A 0.52-g (1.7-mmol) sample of 1 was deprotonated by treatment with *n*-butyllithium under vacuum in THF at −76 °C as described elsewhere.[1] To this solution was added, via syringe, 2.1 mmol of acetyl chloride at −76 °C, and the resulting dark orange-brown solution was stirred for 3 days at room temperature, after which the greenish yellow solution was opened to air, the solvent was removed by evaporation, the dark brown solid residue was taken up in CH_2Cl_2, and the resulting solution was filtered through 2 cm of silica. The filtrate was evaporated, and the dark brown residue was chromatographed on a silica column in 1:1 hexane/CH_2Cl_2, giving two yellow bands of which the first was 1 (0.290 g, 54%). The second band was yellow-brown $(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_4\text{-}5\text{-}C({=}CH_2)\text{-}OC(O)Me)$ (2) (0.160 g, 0.400 mmol, 24%). Further elution with the same solvent afforded a yellow band which was collected as a few milligrams of yellow oil and characterized as $(C_5Me_5)Co\text{-}(2,3\text{-}Et_2C_2B_3H_4\text{-}5\text{-}OC_4H_8)$ (4). Exact mass for 2: calcd for $^{59}Co^{16}O_2{}^{12}C_{20}{}^{11}B_3{}^1H_{34}{}^+$, 398.2170; found, 398.2156. Visible–UV absorptions (nm; percent absorbance given in parentheses): 370 (12%), 298 (95%), 244 (81%). Anal. Calcd for $CoOC_{20}B_3H_{37}$ (4): C, 62.41; H, 9.69. Found: C, 62.34; H, 9.63. Visible–UV absorptions: 286 (81%), 234 (32%).

Conversion of 2 to $(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_4\text{-}5\text{-}C(O)Me)$ (3). A 0.275-g (0.574-mmol) sample of 2 was dissolved in 50 mL of methanol, 42 mg of NaOH was added, and the solution was heated at 50 °C for 1 h, which produced a color change to pale green. Following addition of excess NH_4Cl the solution was evaporated, the residue was taken up in CH_2Cl_2, the solution was filtered, and the filtrate was evaporated. The residue was chromatographed on a silica column in 50:50 hexane/CH_2Cl_2, producing several light yellow bands which were 2 and minor cleavage products, and a major band which was dark yellow 3, obtained on evaporation of the solution as a crystalline solid (0.204 g, 0.476 mmol, 83%). Exact mass: calcd for $^{59}Co^{16}O^{12}C_{18}{}^{11}B_3{}^1H_{32}{}^+$, 356.2064; found, 356.2057. Visible–UV absorptions: 334 (14%), 288 (95%), 236 (49%).

Synthesis of $(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_4\text{-}4/6\text{-}C(O)CF_3)$ (5). Compound 1 (0.301 g, 0.96 mmol) was placed in a two-neck round-bottom flask fitted with a septum. The flask was evacuated on a vacuum line, 50 mL of dry THF was added by distillation, and the reactor was cooled to −78 °C, at which point 0.56 mL of *tert*-butyllithium (1.7 M in hexane, 0.96 mmol) was added via syringe. The solution slowly turned orange as it was warmed to room temperature and stirred for 30 min. The flask was again cooled to −78 °C and 1.04 mmol of trifluoroacetyl chloride was condensed into the mixture, causing an immediate color change to red. After stirring at −78 °C for 10 min, the cold bath was removed and stirring was continued for 1.5 h, during which the solution turned brown and then green. The mixture was opened to the air, solvent was removed by rotary evaporation, the residue was taken up in hexane, and the solution was filtered through 2 cm of silica. The column was then washed with dichloromethane. The hexane wash was taken to dryness and column-chromatographed on silica in hexane, affording one yellow band which was recovered 1 (0.125 g, 42%). The CH_2Cl_2 wash was taken to dryness and chromatographed on a silica column using 2:1 hexane/CH_2Cl_2, giving one major orange band which was collected as yellow-orange crystalline 5 (0.108 g, 0.26 mmol, 27%). Anal. Calcd for $CoF_3OC_{18}B_3H_{29}$: C, 52.76; H, 7.13; F, 13.91. Found: C, 54.27; H, 7.55; F, 13.13. Visible–UV absorptions: 400 (11%), 348 (24%), 290 (92%), 262 (79%), 240 (51%).

Synthesis of $(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_4\text{-}5\text{-}C(O)CH_2C(O)\text{-}OMe)$ (6). According to the above procedure, 0.34 mL (3.17 mmol) of methylmalonyl chloride was added to 1^- in THF at −78 °C. The solution turned red and became darker as it was stirred for 30 min. The flask was placed in a salt–ice water bath, causing a rapid color change to brown, and was stirred for 2 h. The bath was removed and the solution stirred overnight, during which it became olive green. Workup as above gave 1 (0.287 g, 54%) in the hexane wash, and the CH_2Cl_2 solution with thin-layer-chromatographed to give 6 (0.055 g, 0.14 mmol, 8%). Anal. Calcd for $CoO_3C_{20}B_3H_{34}$: C, 58.04; H, 8.28. Found: C, 58.16; H, 8.45.

Reactions of 1^- with Trimethylacetyl Chloride. (a) $Me_3CC(O)Cl$ (0.16 mL, 1.30 mmol) was added to 0.257 g (0.82 mmol) of 1^- in THF at −78 °C, and the solution was raised to 0 °C over a 4-h period. After overnight stirring at room temperature, the brown solution was worked up as above and the residue of the CH_2Cl_2 wash was chromatographed on a TLC plate in 1:1 hexane/CH_2Cl_2, affording a yellow band which was further purified by TLC in hexane to give 5 mg (1%) of $(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_4\text{-}5\text{-}CHOHCMe_3)$ (7), identified from its proton NMR and mass spectra. Visible–UV absorptions for 7: 334 (16%), 290 (95%), 286 (94%), 240 (50%).

(b) $Me_3CC(O)Cl$ (0.24 mL, 1.95 mmol) was added to 0.317 g (1.00 mmol) of 1^- in THF at −78 °C. After 15 min the −78 °C bath was removed and the solution was stirred for 4 h at room temperature, at which point it was olive green. The solvent was removed, the residue was washed with hexane followed by CH_2Cl_2, and the silica was stripped with MeOH. The hexane wash contained 1 (60 mg, 19%). The CH_2Cl_2 wash was chromatographed on a TLC plate in 1:1 hexane/CH_2Cl_2, giving 6 mg (2%) of $(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_4\text{-}4/6\text{-}CHOHCMe_3)$ (8) and 10 mg (2%) of $(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_4\text{-}5\text{-}(CH_2)_4OC(O)CMe_3)$ (9). The methanol wash was column-chromatographed in CH_2Cl_2 to give one band, consisting of 60 mg (16%) of $(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_4\text{-}5\text{-}(CH_2)_4OH)$ (10). Anal. Calcd for $CoOC_{21}B_3H_{40}$ (8): C, 63.07; H, 10.08. Found: C, 66.19; H, 10.64. Visible–UV absorptions for 8: 340 (14%), 288 (88%), 248 (57%), 238 (55%). Visible–UV absorptions for 9: 332 (17%), 288 (93%), 240 (52%). Anal. Calcd for $CoOC_{20}B_3H_{38}$ (10): C, 62.25; H, 9.93. Found: C, 63.08; H, 10.22. Visible–UV absorptions for 10: 332 (15%), 288 (91%), 238 (57%).

Synthesis of $(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_4\text{-}5\text{-}Cl)$ (11). Methanesulfonyl chloride (0.5 mL, 6.46 mmol) was added to 1^- (1.058 g, 3.37 mmol) at 0 °C, producing an immediate color change to brown. The bath was removed and the solution stirred for 2 h, during which it turned yellow-green. The solution was stirred an additional 2 h and rotary-evaporated, and the residue was washed with CH_2Cl_2 and column-chromatographed in hexane. Three bands were obtained, consisting of 1 (16 mg, 1.5%), 11 (1.067 g, 3.06 mmol, 91%), and a trace of the dichloro derivative 12. Anal. Calcd for $CoClC_{16}B_3H_{29}$: C, 55.19; H, 8.39. Found: C, 56.19; H, 8.51. Visible–UV absorptions: 380 (26%), 308 (95%), 254 (83%).

Synthesis of $(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_3\text{-}4/6,5\text{-}Cl_2)$ (12). Methanesulfonyl chloride (0.10 mL, 1.29 mmol) was added to 11^- (0.417 g, 1.14 mmol) at −78 °C, producing an immediate color change to red. The bath was removed and the solution stirred for 30 min, which produced a pale green color. The solution was stirred an additional 3.5 h and rotary-evaporated, and the residue was washed with CH_2Cl_2 and column-chromatographed in hexane. A large yellow band was obtained, the first part of which (9 mg) was a mixture of 11 and 12 and the remainder of 12 (0.394 g, 1.03 mmol, 90%). Anal. Calcd for $CoCl_2C_{16}B_3H_{28}$: C, 50.22; H, 7.38. Found: C, 51.27; H, 7.48.

Synthesis of $(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_2\text{-}4,5,6\text{-}Cl_3)$ (13). Methanesulfonyl chloride (0.08 mL, 1.04 mmol) was added to 12^- (0.421 g, 1.10 mmol) at −78 °C, producing an immediate color change to red. The bath was removed and the solution stirred for 2 h, during which it turned green. The solution was stirred for 3 days (producing a lighter green color) and rotary-evaporated, and the residue was washed with CH_2Cl_2 and column-chromatographed in hexane. The first band was 12 (60 mg, 14%), and the second was 13 (0.094 g, 0.23 mmol, 21%). Compound 13 decomposes slowly on silica. Anal. Calcd for $CoCl_3C_{16}B_3H_{27}$: C, 46.07; H, 6.52. Found: C, 47.14; H, 6.72. Visible–UV absorptions: 292 (85%), 248 (31%), 236 (35%).

Synthesis of $(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_4\text{-}4/6\text{-}Cl)$ (14) and $(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_3\text{-}4,6\text{-}Cl_2)$ (15). A 100-mg (0.318-mmol) sample of 1 was dissolved in 50 mL of THF, 42 mg (0.318 mmol) of *N*-chlorosuccinimide was added, and the solution was stirred in vacuo and monitored periodically by ^{11}B NMR spectroscopy. There was no immediate color change, but the initially yellow solution slowly turned green and the change was complete after 4 h. Removal of solvent via rotary evaporation, followed by solution of the residue in hexane and elution on a silica column, afforded 106 mg (0.31 mmol, 95%) of orange, crystalline, air-stable 14.

A 100-mg sample of 14 was dissolved in THF, 1.5 equiv of *N*-chlorosuccinimide was added with no immediate color change, and the solution was stirred with periodic monitoring by ^{11}B NMR spectroscopy. Over a 4-h period the solution turned aqua blue. The reaction reached completion in 4 h, after which the solvent was removed, the residue was extracted in hexane, and the solution was filtered through 3 cm of silica gel. Evaporation of the solvent gave 109 mg (0.29 mmol, 99%) of pure orange crystalline 15.

In an alternative procedure, 15 was also prepared directly from 1 via reaction of a 100-mg sample with 2.5 equiv of *N*-chlorosuccinimide, with workup as above to give an essentially quantitative yield of crystalline product. Anal. Calcd for $CoClC_{16}B_3H_{29}$ (14): C, 55.19; H, 8.39. Found: C, 55.44; H, 8.31.

Synthesis of $(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_3\text{-}4/6\text{-}Cl\text{-}5\text{-}Me)$ (16). Methanesulfonyl chloride (0.10 mL, 1.29 mmol) was added to 0.185 g (0.56 mmol) of $(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_3\text{-}5\text{-}Me)^-$ (see ref 8) at −78 °C, producing an immediate color change to red. The solution was stirred at 0 °C for 1 h and then at room temperature for 1 h, after which it was taken to dryness and the residue washed through silica with CH_2Cl_2 and column-chromatographed in hexane. The first band obtained was cobaltacarborane starting material (20 mg, 11%) and the second was 16 (0.164 g, 0.45 mmol, 81%). Anal. Calcd for $CoClC_{17}B_3H_{31}$: C, 56.37; H, 8.63. Found: C, 56.91; H, 8.81. Visible–UV absorptions: 332 (18%), 290 (92%), 242 (62%).

Synthesis of $(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_2\text{-}4,6\text{-}Cl_2\text{-}5\text{-}Me)$ (17). Methanesulfonyl chloride (0.07 mL, 0.90 mmol) was added to 16^- (0.242 g, 0.66 mmol) at −78 °C, producing an immediate color change to red. The solution was stirred at room temperature for 4 days, during which it turned black. The solution was taken to dryness and the residue washed through silica with CH_2Cl_2 and column-chromatographed in 1:1 hexane/CH_2Cl_2 to give 17 (0.148 g, 0.37 mmol, 56%). Anal. Calcd for $CoCl_2C_{17}B_3H_{30}$: C, 51.47; H, 7.62. Found: C, 52.05; H, 7.82. Visible–UV absorptions: 338 (17%), 288 (88%), 250 (45%), 238 (42%).

Synthesis of $(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_4\text{-}5\text{-}Br)$ (18). Bromoacetonitrile (0.40 mL, 5.74 mmol) was added to 1^- (0.336 g, 1.07 mmol) at 0 °C, causing an immediate color change to dark brown. The mixture was stirred at room temperature for 4 h with no appreciable change in color. The solvent was removed, the residue washed with CH_2Cl_2, and the solution was column-chromatographed starting with hexane. The first band was 1 (16 mg, 5%), followed by 18 (0.234 g, 0.60 mmol, 56%) and $(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_3\text{-}4/6,5\text{-}Br_2)$ (19, 5 mg, 1%). The same procedure using bromonitromethane in place of bromoacetonitrile gave 18 in 75% yield. Anal. Calcd for $BrCoC_{16}B_3H_{29}$ (18): C, 48.94; H, 7.44. Found: C, 49.14; H, 7.45. Visible–UV absorptions: 288 (86%), 248 (33%), 236 (42%). Anal. Calcd for $Br_2CoC_{16}B_3H_{28}$ (19): C, 40.75; H, 5.98. Found: C, 42.96; H, 6.23. Visible–UV absorptions: 366 (6%), 332 (14%), 292 (90%), 240 (54%).

Synthesis of $(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_4\text{-}4/6\text{-}Br)$ (20) and $(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_3\text{-}4,6\text{-}Br_2)$ (21). The procedures described above for the synthesis of 14 and 15 were followed using *N*-bromosuccinimide. Reaction of 100 mg (0.318 mmol) of 1 with 57 mg (0.32 mmol) of the brominating agent produced an immediate color change from yellow to brownish-yellow and was complete in <5 min, affording on workup 122 mg (0.31 mmol, 98%) of orange crystalline 20. Bromination of this species with 1.5 equiv of *N*–bromosuccinimide resulted in a color change from orange to dark orange-brown. The reaction reached completion in <5 min and gave 119 mg (0.34 mmol, 99%) of orange crystalline 21. The latter compound was also obtained quantitatively on treatment of 1 with 2.5 equiv of the same reagent. Anal. Calcd for $CoBrC_{16}B_3H_{29}$ (20): C, 48.94; H, 7.44. Found: C, 49.11; H, 7.56. Anal. Calcd for $CoBr_2C_{16}B_3H_{28}$ (21): C, 40.75; H, 5.98. Found: C, 40.85; H, 6.18.

Synthesis of $(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_4\text{-}5\text{-}I)$ (22). Iodotrifluoromethane (2.93 mmol) was condensed into a solution of 1^- (0.99 mmol) at −78 °C, producing an immediate blood red color. The solution was stirred at −78 °C for 10 min and then at room temperature for 1.5 h, during which the solution turned dark orange. Following removal of solvent, the residue was washed with hexane and column-chromatographed in pentane, producing two bands of which the first was 1 (16 mg, 5%) and the second was 22 (0.264 g, 0.60 mmol, 61%). Anal. Calcd for $ICoC_{16}B_3H_{29}$: C, 43.71; H, 6.65. Found: C, 43.86; H, 6.66. Visible–UV absorptions: 328 (13%), 290 (88%), 244 (41%), 236 (45%).

Synthesis of $(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_4\text{-}4/6\text{-}I)$ (23) and $(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_3\text{-}4,6\text{-}I_2)$ (24). The procedures described above for the synthesis of 14 and 15 were followed using *N*-iodosuccinimide. Reaction of 100 mg (0.318 mmol) of 1 with 72 mg (0.32 mmol) of the iodinating agent produced an immediate color change from yellow to brownish–orange and was complete in <5 min, affording on workup 140 mg (0.31 mmol, 99%) of orange crystalline **23**. Iodination of this species with 1.5 equiv of *N*-bromosuccinimide, which produced an immediate color change from orange to dark orange-brown, gave 127 mg (0.34 mmol, 99%) of orange crystalline **24**. The latter compound was also obtained quantitatively on treatment of **1** with 2.5 equiv of *N*-iodosuccinimide. Anal. Calcd for $CoIC_{16}B_3H_{29}$ (**23**): C, 43.71; H, 6.65. Found: C, 44.17; H, 6.61.

Synthesis of $(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_4\text{-}5\text{-}CN)$ (25) and $(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_4\text{-}4/6\text{-}CN)$ (26). *p*-Toluenesulfonyl cyanide (0.627 g, 3.46 mmol) was added via a tip-tube to a solution of 1^- (0.290 g, 0.92 mmol) at −78 °C, producing a brownish-yellow solution. The bath was removed and the solution stirred for 30 min, after which the solvent was removed and the residue was washed with CH_2Cl_2 and then column-chromatographed starting with hexane, which produced **1** (0.124 g, 43% recovery). The solvent was changed to 1:1 hexane/CH_2Cl_2, affording one band which was collected and placed on a TLC plate in the same solvent. Two bands were obtained, the first of which was **25** (35 mg, 0.10 mmol, 11%) and the second was **26** (23 mg, 0.07 mmol, 8%). Anal. Calcd for $CoNC_{17}B_3H_{29}$ (**25**): N, 4.13; C, 60.27; H, 8.63. Found: N, 4.09; C, 60.53; H, 8.62. Visible–UV absorptions: 288 (87%), 244 (27%), 234 (32%). Anal. Calcd for $CoNC_{17}B_3H_{29}$ (**26**): N, 4.13; C, 60.27; H, 8.63. Found: N, 3.92; C, 60.50; H, 8.60. Visible–UV absorptions: 286 (95%), 248 (50%), 234 (43%).

Synthesis of $(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_4\text{-}4/6\text{-}NO_2)$ (27). Nitronium tetrafluoroborate (4.5 mL of 0.5 M solution in sulfolane, 2.25 mmol) was added to 1^- (0.301 g, 0.96 mmol) at −78 °C. The solution immediately turned brown. After stirring at −78 °C for 30 min and at room temperature for 30 min, the solvent was removed and the residue washed with hexane followed by CH_2Cl_2. The hexane wash was column-chromatographed in hexane, affording only **1** (0.048 g, 16% recovery). The CH_2Cl_2 wash was chromatographed on a silica column in 1:1 hexane/CH_2Cl_2, giving a band of **1** followed by a small band of **27** (5 mg, 0.01 mmol, 1.5%), identified by ^1H NMR and mass spectroscopy.

Reaction of 1^- with Vinyl Bromide. Vinyl bromide (1.03 mmol) was reacted with 1^- (0.303 g, 0.96 mmol) under the conditions of the preceding synthesis, affording on workup only **1** (55% recovery) and a trace of an air-sensitive compound whose ^1H NMR and mass spectra were consistent with the formulation as a vinyl derivative, $(C_5Me_5)Co(2,3\text{-}Et_2C_2B_3H_4CH{=}CH_2)$ (**28**).

Other Attempted Reactions of 1^-. Treatment of 1^- with excess methanesulfonyl fluoride gave only **1** (46% recovery). Reaction with excess *p*-toluenesulfonyl isocyanate resulted in the loss of all starting material and gave no characterizable product. Reactions of 1^- with 1 equiv of benzoyl chloride or malonyl chloride gave only **1** in ca. 50% recovery.

X-ray Structure Determination on 2. Relevant crystal data and experimental parameters are listed in Table VI. Intensities were collected on a Nicolet P3m diffractometer (Mo Kα, λ = 0.7107 Å). The unit cell was determined using the setting angles of 20 high-angle reflections. The intensities of three standard reflections were monitored showing no significant decay. Empirical absorption corrections were made using the program DIFABS[19] with transmission factors in the range 0.88–1.22. All calculations were performed on a VAXstation 3520 computer using the TEXSAN 5.0 crystallographic software package.[20] The structure was solved by heavy-atom techniques (Patterson and Fourier maps). Full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms yielded the final *R* of 0.037. All hydrogen atoms were located from the difference Fourier maps and included as fixed contributions to the structure factors. Only those reflections for which $I > 3.0\sigma(I)$ were used in the final refinement of the structural parameters.

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Tungsten–Oxo Complexes with Amido Ligands: A Simple Example of the Stereochemical and Dynamic Consequences of Competing π-Donor Effects

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Complexes of tungsten(VI) of the type $WO(CH_2Bu^t)_2(NR_2)Cl$ **1** and $WO(CH_2Bu^t)_3(NR_2)$ **2** (**1a**, **2a**, R = Et; **1b**, **2b**, R = Me; **2c**, R = pyrrolidinate) have been synthesized and characterized. The proton NMR spectra of these compounds indicated that the stereochemistry was different from that of the chloride analogues. Further, the variable-temperature NMR data showed these complexes to be stereochemically nonrigid where exchange of the NR_2 group or equilibration of the neopentyl groups occurred. The structure of $WO(CH_2Bu^t)_3(NEt_2)$ (**2a**) was established by X-ray diffraction and is in agreement with the NMR observations; the amido ligand adopts a position cis to the oxo, with the NR_2 group parallel to the W═O vector. This ligand arrangement results from the competing π-donor demands of the amido and oxo ligands. $C_{19}H_{43}NOW$ crystallizes in the monoclinic space group $P2_1/c$ (No. 14), $a = 9.632$ (2) Å, $b = 12.961$ (3) Å, $c = 18.192$ (4) Å, $\beta = 104.62$ (2)°, $V = 2197.6$ Å^3, $Z = 4$, ρ(calcd) = 1.467 g cm^{-3}, $R_F = 0.0276$, $R_{wF} = 0.0514$.

Introduction

For several years we have been interested in high-oxidation-state organometallic chemistry, particularly that of W(VI) and Mo(VI). The role played by strong π-donor ligands (e.g., oxo, imido) or moderate π-donors (e.g., alkoxo) was critical in the stabilizing and the fine tuning of the reactivity of such metal centers in catalysis. The amido anion NR_2^- has been used extensively as a ligand in early transition metal chemistry[1-3] and is generally considered

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