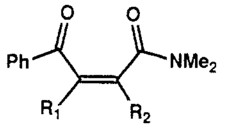
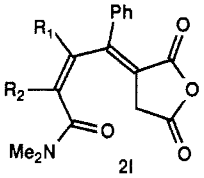
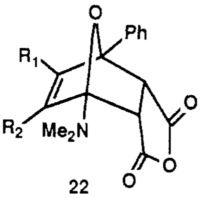
tion products **20** in high yield.[16c,17] The furans can be trapped from the reaction mixture using maleic anhydride, giving the adducts **21**.[17] The diels–Alder adducts **22** were not observed,[16a,b] but formation of **21** can be rationalized via one mode of rearrangement from **22**. The products from elimination of H_2O from **22** were also detected in two cases (**23a,b**).[16a,b]



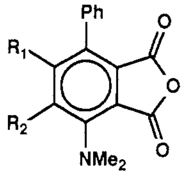
20



21



22



23

The general pathways available during reaction of (carbene)metal complexes with alkynes in the presence of CO are now clearer. While a simple series of steps can be written to rationalize formation of hydroquinones, pyrones, and furans, and factors which determine which product predominates in a given case are not evident.[18]

Registry No. **3**, 35797-88-7; **6a**, 104738-40-1; **6b**, 104738-41-2; **6c**, 104738-42-3; **6e**, 104738-43-4; **6f**, 104738-44-5; **6g**, 104738-45-6; **7a**, 104738-56-9; **8a**, 104738-57-0; **9**, 12245-44-2; **10**, 527-17-3; **11c**, 6237-59-8; **11d**, 104738-47-8; **11e**, 612-71-5; **12f**, 104738-48-9; **13d**, 104738-46-7; **13e**, 3140-01-0; **14e**, 104761-01-5; **20a**, 104738-55-8; **20b**, 104761-00-4; **21a**, 104738-49-0; **21e**, 104738-50-3; **21f**, 104738-51-4; **21g**, 104738-52-5; **23e**, 104738-53-6; **23g**, 104738-54-7; MeC≡CMe, 503-17-3; EtC≡CEt, 928-49-4; $EtO_2CC{\equiv}CCO_2Et$, 762-21-0; *t*-BuOC≡COBu-*t*, 66478-63-5; Ph≡CH, 536-74-3; *n*-PrC≡CH, 627-19-0; $MeC{\equiv}CCO_2Me$, 23326-27-4; maleic anhydride, 108-31-6.

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(16) (a) The parent 5-aminofuran appears to be unknown but has been implicated as a transient intermediate, disappearing by a Diels–Alder reaction and rearrangement of the adduct: Johnson, F.; Heeschen, J. P. *J. Org. Chem.* **1964**, *29*, 3252. (b) The 4-cyano-5-aminofuran derivatives have been isolated and converted to adducts related to 23 via a postulated Diels–Alder reaction: Gewald, K. *Chem. Ber*, **1966**, *99*, 1002. (c) oxidation products related to 20 from 2,3-diphenyl-5-(acylamino)furan have been reported: Ito, K.; yakushijin, K. *Heterocycles*, **1978**, 9.

(17) The oxidation products 20 and adducts 21 have been isolated and fully characterized.

(18) We wish to acknowledge financial support of this work by grants from the National Science Foundation and the National Institutes of Health.

New Synthetic Routes to the Small *closo*-Carboranes 2,3- and 2,4-$R_2C_2B_5H_5$

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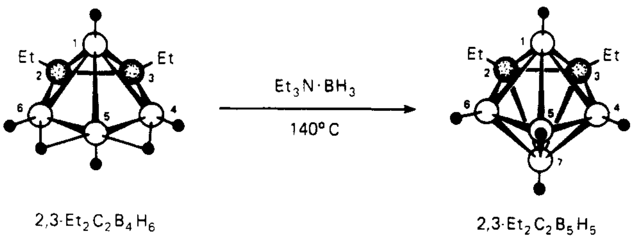
Summary: The reaction of *nido*-2,3-$Et_2C_2B_4H_6$ with triethylamine–borane at 140 °C has been found to result in the capping of the open face of the carborane, producing the *closo*-carborane 2,3-$Et_2C_2B_5H_5$ in good yields. Subsequent heating of 2,3-$Et_2C_2B_5H_5$ at ~320 °C results in the high yield isomerization of the carborane to *closo*-2,4-$Et_2C_2B_5H_5$.

Two different isomers of the small *closo*-carborane $C_2B_5H_7$ have previously been reported. The nonadjacent carbon compound 2,4-$C_2B_5H_7$ is formed by the thermolysis of *nido*-2,3-$C_2B_4H_8$[1] or in the complex pyrolytic reactions of pentaborane(9) with alkynes[2] and has been made on relatively large scales, although with poor selectivity. The 2,3-$R_2C_2B_5H_5$ isomer has previously been reported as a byproduct of the reaction of alkynes with B_8H_{12}[3] and has never been isolated in more than trace amounts. We report here the development of simple synthetic routes to both of these *closo*-$R_2C_2B_5H_5$ cage systems.

The synthesis of 2,3-$R_2C_2B_5H_5$ involves the reaction of the readily accessible[4] small carborane *nido*-2,3-$R_2C_2B_4H_6$ with triethylamine–borane at 140 °C. Thus, as is illustrated below, the reaction results in the capping of the open pentagonal face of the *nido*-carborane by a BH group derived from the amine–borane.



In a typical reaction, 0.547 g (4.16 mmol) of 2,3-$Et_2C_2B_4H_6$ and 3.4 g (29.7 mmol) of $Et_3N{\cdot}BH_3$ were reacted in vacuo at 140 °C for a total of 96 h with periodic (~every 8 h) removal of evolved hydrogen and triethylamine. The volatile components were then separated by vacuum line fractionation through a −0, −45, and −196 °C trap series. Stopping in the −45 °C trap was 0.346 g (2.45 mmol) of 2,3-$Et_2C_2B_5H_5$, corresponding to a 58.9% yield. The material was determined to be pure by ^{11}B and ^1H NMR[5] and by gas chromatographic analysis.[6]

Similar capping reactions of larger cage polyhedral boranes and carboranes have previously been reported by using either Lewis base–borane complexes or diborane(6) as reagents. For example, the reaction[7] of decaborane(14)

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(4) (a) Hosmane, N. S.; Grimes, R. N. *Inorg. Chem.* **1979**, *18*, 3294–3297. (b) Maynard, R. B.; Borodinsky, L.; Grimes, R. N. *Inorg. Synth.* **1983**, *22*, 211–214.

(5) ^{11}B NMR (64.2 MHz, ppm, C_6D_6): 7.03 (d, B4,6, J_{BH} = 170 Hz), 2.54 (d, B5, J_{BH} = 152 Hz), −14.21 (d, B1, 7, J_{BH} = 168 Hz). ^1H NMR (200 MHz, ^{11}B spin-decoupled, δ, C_6D_6): 4.52 (s, BH4,6 and BH5), 2.14 (q, CH_2), 0.95 (t, CH_3), 0.18 (s, BH1,7). Mass spectrum: cutoff at *m/e* 142.1610, calcd for $^{12}C_6{}^{11}B_5{}^1H_{15}$ 142.1639.

(6) 6% Tricresyl phosphate on Chromosorb P, 60/80 mesh, 100 °C: 2,3-$Et_2C_2B_5H_5$, Rv = 2.4; 2,4-$Et_2C_2B_5H_5$, *R*v = 0.7; 2,3-$Et_2C_2B_4H_6$, Rv = 1.0.

(7) Miller, H. C.; Muetterties, E. L. *Inorg. Synth.* **1967**, *10*, 88–91.

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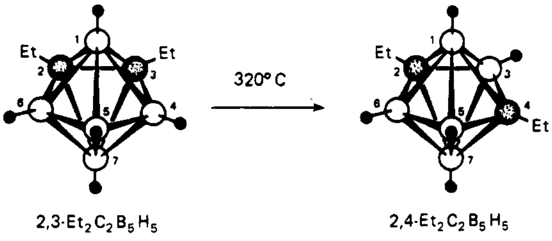
with Et_3NBH_3 yields $(Et_3NH^+)_2B_{12}H_{12}^{2-}$ and the reaction[8] of *arachno*-1,3-$C_2B_7H_{13}$ with B_2H_6 gives *closo*-1,6-$C_2B_8H_{10}$. Onak[9] has previously examined the reaction of *nido*-2,3-$C_2B_4H_8$ with diborane(6) at 220 °C but found that, due to the rapid decomposition of diborane(6) at these temperatures, no *closo*-carboranes are produced. Indeed, our studies have indicated that a minimum temperature of 140 °C is necessary to activate the 2,3-$Et_2C_2B_4H_6$ for reaction and that only Lewis base–borane complexes, such as triethylamine–borane, which are stable to decomposition at these temperatures are suitable BH-capping reagents. In the present case it was also found that the *closo*-2,3-$Et_2C_2B_5H_5$ product undergoes slow attack by triethylamine at 140 °C; therefore, it is necessary to periodically remove the triethylamine which is evolved during the reaction in order to achieve good yields. We have also employed other borane complexes containing less nucleophilic bases, such as $C_6H_5N(Et)_2{\cdot}BH_3$ and $(n\text{-}Bu)_3P{\cdot}BH_3$, and have obtained similar yields without removal of the base during the reaction; however, longer reaction times and higher temperatures were required.

In the present study it was also found that thermolysis of 2,3-$Et_2C_2B_5H_5$ (0.114 g, 0.81 mmol) in a sealed glass tube in vacuo for 47.5 h at ~320 °C gave the nonadjacent carbon isomer 2,4-$Et_2C_2B_5H_5$ (0.093 g, 0.66 mmol) in high yield[10] (81%). Such thermally induced cage rearrangements, leading to separation of cage carbon atoms, are well-known[11] for adjacent carbon carboranes, and this isomerization reaction thus provides a convenient, selective synthetic route to the 2,4-isomer.



2,3-$Et_2C_2B_5H_5$ 2,4-$Et_2C_2B_5H_5$

The *closo*-$C_2B_5H_7$ cage system is the most stable small carborane and has, in fact, been used[12] as the backbone structure of a number of high-temperature polymers. The development, reported here, of new rational synthetic routes to both the 2,3- and 2,4-isomers promises to result in renewed interest in the chemistry and properties of these carboranes.

Acknowledgment. We thank the Army Research Office and the National Science Foundation for the support of this work.

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[10] The isomeric purity of the product was again confirmed by spectroscopic and gas chromatographic analysis.[6] ^{11}B NMR (64.2 MHz, ppm, C_6D_6): 8.25 (d, B3, J_{BH} = 166 Hz), 5.77 (d, B5,6, J_{BH} = 169 Hz), −17.71 (d, B1,7, J_{BH} = 177 Hz); ^1H NMR (200 MHz, ^{11}B spin-decoupled, δ, C_6D_6): 4.60 (s, BH3), 4.26 (s, BH5,6), 2.26 (q, CH_2), 0.93 (t, CH_3), 0.54 (s, BH1,7).

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Effects of Temperature and Supporting Electrolyte on the Electrochemical Oxidation of (Benzene)tricarbonylchromium and Other π-Hydrocarbon Complexes

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Summary: The electrochemical oxidation of $(C_6H_6)Cr(CO)_3$ and other π-hydrocarbon complexes can be made chemically reversible in dichloromethane by using low temperatures or by using tetrabutylammonium hexafluorophosphate as the supporting electrolyte.

The electrochemical oxidation of $(C_6H_6)Cr(CO)_3$ (1) has been the subject of numerous studies.[1–7] Normally the one-electron oxidation of 1 at room temperature is followed by rapid decomposition leading to Cr(II) or Cr(III) and free benzene. The stability of $(arene)Cr(CO)_3^+$ radical cations can be enhanced by alkylation or metalation of the arene ring[6–11] or by using pure trifluoroacetic acid (TFAA) as the solvent.[4] The success of TFAA in this regard is no doubt due to its low intrinsic nucleophilicity as well as its ability to lower the reactivity of the supporting electrolyte anion via hydrogen bonding.[4,12–14] Nevertheless, the serious corrosive and toxic properties of TFAA render it inconvenient as a routine solvent for electrochemical studies. We have previously shown[15–17] that cyclic voltammetry at temperatures down to −95 °C in the relatively nonpolar and nonnucleophilic solvent dichloromethane is a convenient procedure for studying reactive metalloporphyrin complexes. Herein we demonstrate that low-temperature cyclic voltammetry (LTCV) in dichloromethane is a useful way to study organometallics such as 1 that display chemically irreversible redox processes at room temperature. Also reported is the surprising observation that the radical cations produced from the room-temperature oxidation of 1 and other π-hydrocarbon complexes are much more persistent when the supporting electrolyte is changed

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