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Pyrolysis Reactions of 1,5-$C_2B_3H_5$ and 1,6-$C_2B_4H_6$. Isolation of a New Four-Carbon Carborane, $C_4B_7H_{11}$, and the Boron–Carbon-Bonded Dimer and Trimers of 1,5-$C_2B_3H_5$. Improved Synthesis of the Mixed-Cage Carborane 2′:2-[1′,5′-$C_2B_3H_4$][1,6-$C_2B_4H_5$]

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The gas-phase pyrolysis reactions of 1,5-$C_2B_3H_5$ and 1,6-$C_2B_4H_6$ in a hot/cold reactor (400/0 °C) were studied. In agreement with previous reports, major products of the pyrolysis of 1,5-$C_2B_3H_5$ were found to be the boron–boron-linked dimer, 2:2′-[1,5-$C_2B_3H_4$]$_2$, and trimer, 2:2′,3′:2″-[1,5-$C_2B_3H_4$][1′,5′-$C_2B_3H_3$][1″,5″-$C_2B_3H_4$]. Also isolated from the reaction were a number of previously unknown compounds, including a boron–carbon-linked dimer, 1:2′-[1,5-$C_2B_3H_4$]$_2$, two boron–boron-, boron–carbon-linked trimers, 2:2′,1′:2″-[1,5-$C_2B_3H_4$][1′,5′-$C_2B_3H_3$][1″,5″-$C_2B_3H_4$] and 2:2′,3′:1″-[1,5-$C_2B_3H_4$][1′,5′-$C_2B_3H_3$][1″,5″-$C_2B_3H_4$], and a new tetracarbon nido carborane, $C_4B_7H_{11}$. The pyrolysis of 1,6-$C_2B_4H_6$ was found to give only polymerization; however, the copyolysis of 1,5-$C_2B_3H_5$ and 1,6-$C_2B_4H_6$ was found to produce the previously reported mixed-cage coupled carborane 2′:2-[1′,5′-$C_2B_3H_4$][1,6-$C_2B_4H_5$] in good yield.

Introduction

In recent years there has been great interest in our laboratory and others toward the synthesis of multicage boranes and carboranes. We have previously[2] reported that the mercury-sensitized photolysis of various small boranes and carboranes leads in certain cases to the formation of the corresponding coupled-cage products in good yields. These results sparked our interest in further investigations of the formation, chemistry,[2,3] and NMR[4] properties of linked-cage systems. Unfortunately, due to the apparent photochemical instability of 1,5-$C_2B_3H_5$ and 1,6-$C_2B_4H_6$, photochemical techniques could not be used to form linked-cage compounds based on these carboranes, although cophotolysis was found to yield the mixed-cage systems 2′:2-[1′,5′-$C_2B_3H_4$][1,6-$C_2B_4H_5$] and 1′:2-[1′,5′-$C_2B_3H_4$][1,6-$C_2B_4H_5$] in low yields.[2] Burg,[5] Onak,[6] and Fehlner[7] have previously demonstrated that the hot/cold thermolysis reactions of 1,5-$C_2B_3H_5$ yield boron–boron-linked multicage compounds, with the predominant product being the dimer, 2:2′-[1,5-$C_2B_3H_4$]$_2$, along with smaller amounts of the three-cage compound, 2:2′,3′:2″-[1,5-$C_2B_3H_4$][1′,5′-$C_2B_3H_3$][1″,5″-$C_2B_3H_4$]. These studies prompted our reinvestigation of the thermolysis reactions of 1,5-$C_2B_3H_5$ and 1,6-$C_2B_4H_6$ as a means of obtaining new linked-cage systems based on these carboranes. We have now been able to isolate and characterize a number of new compounds from these reactions including the boron–carbon-bonded dimer and trimers of 1,5-$C_2B_3H_5$ and a new four-carbon nido carborane, $C_4B_7H_{11}$. Full details of our studies are reported herein.

Table I. ^{11}B NMR (115.5 MHz) Data

compd^a	δ^b (J, Hz)	rel area	assignt
1:2′-[1,5-$C_2B_3H_4$]$_2$ (I)	8.7 (188)	2	B3′, B4′
	7.4 (s)^c	1	B2′
	5.6 (190)	3	B2, B3, B4
2:2′,1′:2″-[1,5-$C_2B_3H_4$]-[1′,5′-$C_2B_3H_3$][1″,5″-$C_2B_3H_4$] (II)	10.2 (s, br)^c	1	B2′
	9.0 (s, br)^{c,d}	1	B2
	8.6 (190)	2	B3″, B4″
	7.3 (s)	1	B2″
	4.2 (185)	2	B3′, B4′
	2.3 (185)	2	B3, B4
2:2′,3′:1″-[1,5-$C_2B_3H_4$]-[1′,5′-$C_2B_3H_3$][1″,5″-$C_2B_3H_4$] (III)	14.7 (vbr)^c	1	B2′
	9.1 (vbr)^{c,d}	1	B2
	7.5 (187)	1	B4′
	6.0 (s)^c	1	B3′
	5.4 (187)	3	B2″, B3″, B4″
	2.4 (187)	2	B3, B4
1,2,8,10-$C_4B_7H_{11}$ (IV)	−14.1 (150)	2	B7, B11
	−15.6 (190)	1	B9
	−16.6 (171)	2	B3, B6 or B4, B5
	−23.7 (172)	2	B4, B5 or B3, B6

^{a} All samples were run in pentane solvent with C_6D_6 lock. ^{b} All chemical shifts are relative to external $BF_3 \cdot O(C_2H_5)_2$; a negative sign indicates an upfield shift. ^{c} Abbreviations: s = singlet; br = broad; vbr = very broad. ^{d} Resonance is obscured and shift is estimated.

Experimental Section

Materials. The small closo carboranes, 1,5-$C_2B_3H_5$ and 1,6-$C_2B_4H_6$, were purchased from Chemical Systems Inc. and were purified by vacuum line fractionation until they were shown to contain no impurities by ^{11}B NMR. Gas–liquid chromatography (GLC) was conducted on a Varian Aerograph Model 920 gas chromatograph equipped with a 20 ft × 0.25 in. 6% tricresyl phosphate (TCP) on chromosorb P (60/80 mesh) column. The chromographic solvent was spectrophotometric grade pentane purchased from Aldrich Chemical Co., Inc., and was dried over P_2O_5.

Physical Measurements. Boron-11 NMR spectra at 115.5 MHz and proton NMR spectra at 360 MHz were obtained on a Bruker WH-360 Fourier-transform spectrometer located in the Mid-Atlantic Regional NMR Facility at the University of Pennsylvania. Proton NMR spectra at 250 MHz and carbon-13 NMR spectra at 62.9 MHz were obtained on a Bruker WH-250 Fourier-transform spectrometer. Proton NMR spectra at 200 MHz were obtained on an IBM WH-200 Fourier-transform spectrometer. Proton NMR spectra at 100 MHz were recorded on a JEOL PS-100 Fourier-transform spectrometer; boron-11 spin decoupling was accomplished by using double-resonance techniques with a broad-band noise decoupler. Unit and high-resolution mass spectra were obtained on a Hitachi Perkin-Elmer RMH-2 mass spectrometer interfaced to a Kratos DS50-S data system. Infrared spectra were recorded on either a Perkin-Elmer 521 or 337 grating infrared spectrometer.

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Table II. ^{1}H NMR Data

compd^a	$\delta^{b,c}$ (J, Hz)	rel area	assignt
I^d	5.66 br	1	HC5
	5.40 t (2.0)^h	2	HC1′, HC5′
	4.49 q (188)	2	HB3′, HB4′
	4.48 q (188)	3	HB2, HB3, HB4
II^{e,g}	5.80 br	1	HC5′
	5.58 t (2.2)^h	2	HC1, HC5
	5.30 t (2.2)^h	2	HC1″, HC5″
III^{d,g}	5.72 t (1.9)^h	2	HC1, HC5
	5.68 br	1	HC5″
	5.54 d (2.0)	2	HC1′, HC5′
IV^f	2.50 q (186)	1	HB9
	2.45 q (146)	2	HB7, HB11
	2.33 q (168)	2	HB3, HB6 or HB4, HB5
	2.02 q (176)	2	HB4, HB5 or HB3, HB6
	1.19	4	HC1, HC2, HC8, HC10

^{a} All samples were run in pure C_6D_6 solvent. ^{b} All shifts downfield from $(CH_3)_4Si$. ^{c} Abbreviations: d = doublet; t = triplet; q = quartet; br = broad. ^{d} 250-MHz spectrum. ^{e} 200-MHz spectrum. ^{f} 360-MHz spectrum. ^{g} Samples too weak to accurately measure BH resonances. ^{h} J(CH–BH) measured from line-narrowed spectrum.

Table III. Infrared Spectra (cm^{-1})

compd	bands
I^a	2620 (vs), 1550 (vw), 1490 (m, sh), 1482 (m, sh), 1476 (m, sh), 1472 (m, sh), 1456 (s, sh), 1450 (s), 1409 (w, sh), 1245 (w), 1205 (w, sh), 1190 (w), 1105 (s), 1060 (m), 945 (w), 875 (w), 850 (w, sh), 805 (w)
II^{a,c}	2625 (m, sh), 2615 (s), 1480 (m, br), 1080 (m, vbr)
III^{a,c}	2602 (s), 1480 (m, br), 1460 (m, sh), 1453 (m), 1105 (s), 1069 (m, sh)
IV^b	2615 (vs), 2565 (s), 1745 (vw), 1078 (m), 1042 (w, br), 995 (m, sh), 990 (m), 968 (m)

^{a} Conditions: gas samples; 10 cm length 2 cm o.d. cells; NaCl windows. ^{b} Conditions: $CHCl_3$ solution vs. $CHCl_3$; NaCl windows. ^{c} Weak gas-phase spectra at low vapor pressure.

Table IV. ^{13}C NMR (62.9 MHz) Data

compd^a	δ^b (J, Hz)	rel area	assignt
IV	+29.5 d of q (J(^{13}C–H) = 161)^d (J(^{13}C–^{11}B) = 38)	2	C8, C10
	+28.6^c	1	C2
	−4.7 d (J(^{13}C–H) = 194)^d	1	C1

^{a} Sample run in C_6D_6 solvent. ^{b} Chemical shifts relative to $(CH_3)_4Si$; a negative sign indicates a upfield shift. Abbreviations: d = doublet; q = quartet. ^{c} Resonance obscured and shift estimated; appears as broad doublet, $J \approx$ 160–180 Hz. ^{d} Proton coupling was observed by running a gated decoupling sequence.

General Procedure. All reactions were run in a hot/cold reactor which consisted of an evacuated, cylindrical, quartz tube (27 cm × 16 mm inside diameter) equipped with a greaseless Teflon stopcock. During a reaction, the tube was maintained in a vertical position and its lower end (8 cm) was cooled with an ice bath, while the central portion was heated by a Variac-controlled tube furnace (6 cm wide). The furnace was warmed from 25 to 400 °C over the course of the initial hour, and that temperature was maintained for an additional 4 h. The reactor was then frozen at −196 °C, and the noncondensables (H_2) were measured with the aid of a Toepler pump. The volatile reaction materials were then fractionated on a vacuum line through traps maintained at −35, −95, and −196 °C and analyzed.

The known products, 2:2′-[1,5-$C_2B_3H_4$]$_2$, 2:2′,3′:2″-[1,5-$C_2B_3H_4$][1′,5′-$C_2B_3H_3$][1″,5″-$C_2B_3H_4$], and 2′:2-[1′,5′-$C_2B_3H_4$]-[1,6-$C_2B_4H_5$] were identified by comparison of their IR and ^{11}B and ^{1}H NMR spectral data with literature values.[2,5-7] Infrared, boron-11, carbon-13, and proton NMR data of the new compounds are presented in Tables I–IV.

Pyrolysis of 1,5-$C_2B_3H_5$. When a 1.7-mmol (103.8-mg) sample of 1,5-$C_2B_3H_5$ (initial pressure 0.75 atm) was pyrolyzed, extensive polymerization was noted on the walls of the reactor in the form of an opaque tan solid. The area directly exposed to the hot zone showed extensive decomposition in the form of a clear amber film. Upon completion of the reaction, a liquid was seen to have formed at the bottom of the tube and 0.72 mmol H_2 evolved. Fractionation of the products yielded 7.6 mg stopping at −35 °C, 23.0 mg stopping at −95 °C, and 9.9 mg stopping at −196 °C. The material at −196 °C consisted of 1,5-$C_2B_3H_5$ and a trace (3%) of 1,6-$C_2B_4H_6$ as seen in the ^{11}B NMR spectrum. The liquid stopping at −95 °C was separated by GLC on the TCP column at 50 °C to give three compounds: the unknown C–B-bonded isomer 1:2′-[1,5-$C_2B_3H_4$]$_2$ (I) (R_v = 2.5 (relative to R_v = 1.0 for 1,6-$C_2B_4H_6$), 16%, liquid, calculated mass for $^{12}C_4{}^{11}B_6{}^1H_8$ 122.1185, found 122.1190), the B–B-bonded isomer 2:2′-[1,5-$C_2B_3H_4$]$_2$,[5-7] (R_v = 3.0, 83%), and the compound 2′:2-[1′,5′-$C_2B_3H_4$][1,6-$C_2B_4H_5$][2] (R_v = 7.0, trace, 1.5%).[8] The yields of I and 2:2′-[1,5-$C_2B_3H_4$]$_2$ based on consumed 1,5-$C_2B_3H_5$ were 4% and 21%, respectively. The material stopping at −35 °C was separated by GLC on a 85 °C TCP column to give four compounds: three trimer isomers, 2:2′,1′:2″-[1,5-$C_2B_3H_4$][1′,5′-$C_2B_3H_3$][1″,5″-$C_2B_3H_4$] (II) (R_v = 0.7, 5%, liquid, calculated mass for $^{12}C_6{}^{11}B_9{}^1H_{11}$ 182.1699, found 182.1713), 2:2′,2′:1″-[1,5-$C_2B_3H_4$][1′,5′-$C_2B_3H_3$][1″,5″-$C_2B_3H_4$] (III) (R_v = 0.85, 5%, liquid, calculated mass for $^{12}C_6{}^{11}B_9{}^1H_{11}$ 182.1699, found 182.1704), and 2:2′,3′:2″-[1,5-$C_2B_3H_4$][1′,5′-$C_2B_3H_3$][1″,5″-$C_2B_3H_4$][5,7] (R_v = 1.00, 24%, solid), and the new four-carbon carborane $C_4B_7H_{11}$ (IV) (R_v = 2.5, 64%, mp 204–205 °C in a sealed capillary (uncorrected), calculated mass for $^{12}C_4{}^{11}B_7{}^1H_{11}$ 136.1512, found 136.1510). The yields, based on total consumed 1,5-$C_2B_3H_5$, were as follows: II, 0.4%; III, 0.4%; 2:2′,3′:2″-[1,5-$C_2B_3H_4$][1′,5′-$C_2B_3H_3$][1″,5″-$C_2B_3H_4$], 2%; IV, 5%. Sixty percent of the starting material was lost to polymerization.

An equimolar mixture of 1,5-$C_2B_3H_5$ and B_2H_6 (0.5 mmol each) was also reacted as above. Analysis by GLC of the products showed that significant amounts of $B_{10}H_{14}$ had formed; however, the relative abundances of the other products were essentially unchanged. Similarly, neither gas-phase reactions (400/0 °C) nor solution (diethyl ether) reactions of diborane with 2:2′-[1,5-$C_2B_3H_4$]$_2$ were found to yield $C_4B_7H_{11}$.

Pyrolysis of 1,6-$C_2B_4H_6$. The pyrolysis of 0.84 mmol of 1,6-$C_2B_4H_6$ resulted in the formation of a white, polymeric material on the walls of the reactor; however, decomposition was not as extensive as in the 1,5-$C_2B_3H_5$ pyrolysis. The reaction yielded 0.06 mmol of H_2 and only a trace amount of liquid stopping at −95 °C. This material gave a very weak signal in the ^{11}B NMR spectrum and could not be identified. Stopping at −196 °C was 0.65 mmol of unreacted 1,6-$C_2B_4H_6$.

Copyrolysis of 1,5-$C_2B_3H_5$ and 1,6-$C_2B_4H_6$. The reaction of an equimolar mixture of 1,5-$C_2B_3H_5$ and 1,6-$C_2B_4H_6$ (1.0 mmol each) evolved 0.4 mmol of H_2 and resulted in a polymeric buildup on the walls of the reactor. Vacuum-line fractionation of the products yielded 1.0 mg stopping at −35 °C, 28.2 mg stopping at −95 °C, and 0.9 mmol of unreacted substrates stopping at −196 °C. This last fraction was found to consist of 0.2 mmol of 1,5-$C_2B_3H_5$ and 0.7 mmol of 1,6-$C_2B_4H_6$ by ^{11}B NMR analysis. The material stopping at −95 °C was separated by GLC as described above to yield 1:2′-[1,5-$C_2B_3H_4$]$_2$ (I), 3%, 2:2′-[1,5-$C_2B_3H_4$]$_2$, 32%, and 2′:2-[1′,5′-$C_2B_3H_4$][1,6-$C_2B_4H_5$], 65%. The yield of the last coupled species based on consumed 1,6-$C_2B_4H_6$ is 47% (17.5% based on consumed 1,5-$C_2B_3H_5$). Chromatography of the trace (1.0 mg) material stopping at −35 °C showed that the majority of the sample consisted of the same ratio of low volatile products as in the 1,5-$C_2B_3H_5$ experiment except there were additional peaks at R_v = 1.2, 0.3%, R_v = 1.3, 4.6%, and R_v = 1.5, 14% (relative to R_v = 1.0 for 2:2′,3′:2″-[1,5-$C_2B_3H_4$][1′,5′-$C_2B_3H_3$][1″,5″-$C_2B_3H_4$]). The compound at R_v = 1.5 contained the following resonances in the ^{11}B NMR spectrum (ppm, J in Hz): 8.8 (s), 1.96 (J = 185), −11.7 (J = 170), and −16.1 (J = 190) in the ratio of 2:3:1:2.

Thermolysis of $C_4B_7H_{11}$ (IV). Thermolysis reactions of IV were conducted in sealed Pyrex tubes, and the product material was analyzed by ^{11}B NMR. There was no evidence of reaction when a sample of IV was heated at 240 °C for 16 h; however, heating at 330 °C for 20 h resulted in significant decomposition as evidenced by the formation of noncondensables and insoluble solids. The volatile products of the

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[8] Small quantities of 2:2′-[1,5-$C_2B_3H_5$]$_2$ can be purified from 1:2′-[1,5-$C_2B_3H_5$]$_2$, without chromatography, by vacuum-line fractionation into a −78 °C trap.

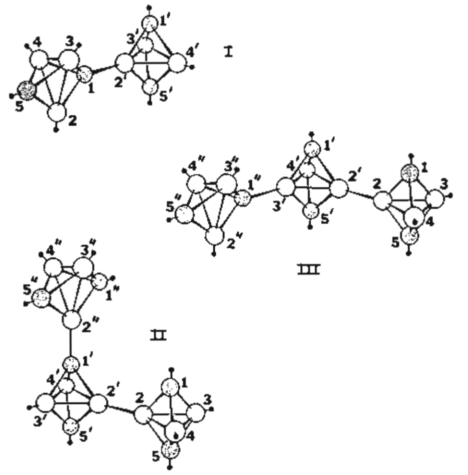


Figure 1. Proposed structures of 1:2′-[1,5-$C_2B_3H_4$]$_2$ (I), 2:2′,1′:2″-[1,5-$C_2B_3H_4$][1′,5′-$C_2B_3H_3$][1″,5″-$C_2B_3H_4$] (II), and 2:2′,3′:1″-[1,5-$C_2B_3H_4$][1′,5′-$C_2B_3H_3$][1″,5″-$C_2B_3H_4$] (III).

latter reaction were fractionated, and the material stopping in a −45 °C trap was seen by ^{11}B NMR to consist primarily of starting material with additional small resonances at −13.0 (d), −14.0 (d), −22.9 (d), and −45.5 ppm (d). Pyrolysis of IV at 450 °C for 2 h resulted in extensive decomposition with the appearance of the same impurity resonances in the ^{11}B NMR.

Results

Under the reaction conditions employed, the pyrolysis of 1,5-$C_2B_3H_5$ was found to give extensive polymerization and at least seven different compounds in isolable quantities. The volatile products were initially separated into two fractions by vacuum-line fractionation. The material passing a −35 °C trap and stopping in a −95 °C trap was separated by GLC to give a trace amount of the mixed-cage compound 2′:2-[1′,5′-$C_2B_3H_4$][1,6-$C_2B_4H_5$][2] and two of the three possible isomers of the dimer, [$C_2B_3H_4$]$_2$. The known boron–boron-bonded isomer 2:2′-[1,5-$C_2B_3H_4$]$_2$[5-7] was formed in 21% yield, while the new boron–carbon-linked species, 1:2′-[1,5-$C_2B_3H_4$]$_2$, was formed in 4% yield.

The compound 1:2′-[1,5-$C_2B_3H_4$]$_2$ (I) is isolated from the chromatograph as a clear, volatile liquid that is moderately air sensitive. The proposed structure (Figure 1) is supported by the NMR data given in Tables I and II. Thus, the ^{11}B NMR spectrum indicates three types of boron environments in the relative ratio 2:1:3 the sharp singlet of intensity 1 being assigned to the boron atom B2′ bonded to the C1 carbon atom through an exopolyhedral σ bond. The ^{11}B-decoupled proton NMR spectrum shows two types of B–H units in the ratio of 2:3 and two C–H resonances in a relative ratio 1:2, which is consistent with a boron–carbon cage linkage. Line narrowing of the proton spectrum reveals a triplet structure for the hydrogens bound to the carbons C1′ and C5′ which is due to long-range coupling to the two boron-bonded (B4′ and B5′) hydrogens. The resonance assigned to the C5-bound hydrogen is broadened; however, the quartet structure expected from coupling with the B2-, B3-, and B4-bound hydrogens was not observed.

The reaction products that stopped in a −35 °C trap were also separated by GLC to give the known boron–boron-, boron-boron-linked trimer 2:2′,3′:2″-[1,5-$C_2B_3H_4$][1′,5′-$C_2B_3H_3$][1″,5″-$C_2B_3H_4$] in 2% yield, smaller quantities of the two possible trimers containing one boron–boron bond and one boron–carbon bond, 2:2′,1′:2″-[1,5-$C_2B_3H_4$][1′,5′-$C_2B_3H_3$]-[1″,5″-$C_2B_3H_4$] (II) and 2:2′,3′:1″-[1,5-$C_2B_3H_4$][1′,5′-$C_2B_3H_3$][1″,5″-$C_2B_3H_4$] (III), and the condensed cage compound $C_4B_7H_{11}$ (IV) in 5% yield.

The structures proposed for compounds II and III (Figure 1) are again assigned based on the spectroscopic data given in the tables. For compound II, the ^{11}B NMR spectrum shown in Figure 2 is seen to contain three doublets of equal intensity assigned to the three sets of chemically different B–H pairs in the molecule. The sharp singlet of intensity 1 is assigned to the boron atom B2″ bonded to the carbon atom of the center cage. The two broad peaks at low field are then assigned to resonances from the B2 and B2′ borons which are involved in the exopolyhedral boron–boron linkage. The proton NMR indicates three types of CH groups in the ratio 1:2:2. The intensity 2 resonances each show a triplet structure upon line narrowing indicating coupling with two BH protons and are therefore assigned to the HC1, HC5 and HC1″, HC5″ hydrogens of the end cages. The intensity 1 resonance is then assigned to the HC5′ group of the central cage.

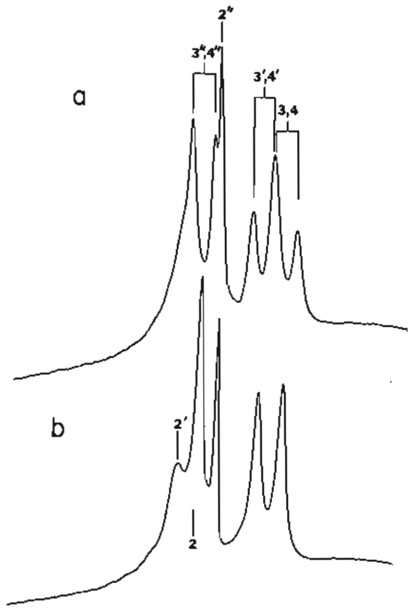


Figure 2. ^{11}B NMR spectra (115.5 MHz) of 2:2′,1′:2″-[1,5-$C_2B_3H_4$][1′,5′-$C_2B_3H_3$][1″,5″-$C_2B_3H_4$] (II): (a) proton-spin coupled; (b) proton-spin decoupled. Proposed assignments are made by comparison with the known shifts of other 1,5-$C_2B_3H_5$ dimers and trimers.

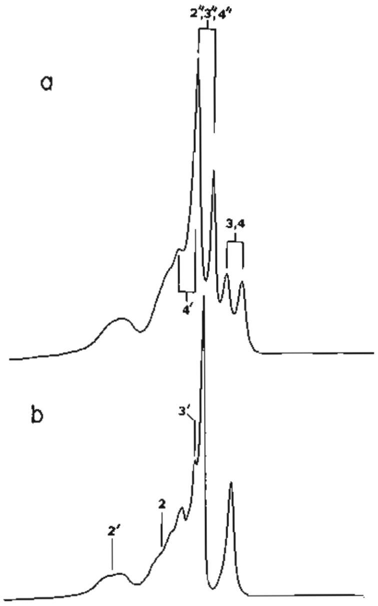
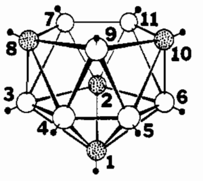


Figure 3. ^{11}B NMR spectra (115.5 MHz) of 2:2′,3′:1″-[1,5-$C_2B_3H_4$][1′,5′-$C_2B_3H_3$][1″,5″-$C_2B_3H_4$] (III): (a) proton-spin coupled; (b) proton-spin decoupled. The proposed assignments are in agreement with the chemical shifts of the known 1,5-$C_2B_3H_5$ dimers and trimers.

In agreement with the proposed structure for compound III given in Figure 1, the ^{11}B NMR spectrum (Figure 3) shows



IV

Figure 4. Proposed structure of $C_4B_7H_{11}$ (IV).

three sets of doublets in the ratio 1:3:2. The resonance attributed to the boron atom (B3′) involved in the boron–carbon linkage appears as a sharp singlet in the proton-decoupled spectrum, although it is obscured in the coupled spectrum. The two resonances assigned to the boron atoms involved in the boron–boron single bond, B2 and B2′, are extensively broadened which would be expected because of $^{11}B-^{11}B$ coupling between these two atoms. We have previously observed similar coupling interactions between chemically inequivalent boron atoms involved in boron–boron cage linkages in related cage systems[2,4] such as the mixed carborane 2′:2-[1′,5′-$C_2B_3H_4$]-[1,6-$C_2B_4H_5$] discussed below. The proton NMR spectrum of III shows as expected three CH resonances in the ratio of 1:2:2 which appear as multiplets characteristic of their coupling to the boron-attached protons. Thus, the resonances of intensity 2 appear as a doublet and a triplet, supporting their assignment to the HC1′, HC5′ and HC1, HC5 groups, while the resonance of intensity 1, which is unusually broad, is assigned to the HC5″ proton.

Compound IV, which was the major component of the material stopping in the −35 °C trap, was obtained as an air-stable solid that forms triangular crystals upon sublimation and, in spite of its relatively high melting point (204.5 °C), can be easily transferred in vacuo.

The NMR data for IV showed no evidence for an exopolyhedral linkage of any type but instead supports the formulation of IV as a single-cage, 11-vertex carborane containing 4 carbon atoms and 7 boron atoms. Skeletal electron-counting theory[9] predicts an open-cage structure consisting of a monocapped pentagonal antiprism for an 11-vertex, 26-electron system ($2n + 4$) such as IV. All known examples of isoelectronic cage systems including, for example, $SeSB_9H_9$,[10] $B_8C_2H_{10}S$,[11] $C_2B_9H_{13}$ (2 isomers),[12] and (η-C_5H_5)Co-$(CH_3)_4C_4B_6H_6$ (2 isomers)[13] have been either confirmed or proposed to adopt this structure. A number of different arrangements of the cage boron and carbon atoms are possible within this cage geometry; however, the spectroscopic data are consisent with the 1,2,8,10-$C_4B_7H_{11}$ structure shown in Figure 4.

The ^{11}B NMR spectrum of IV (Figure 5) shows four doublet resonances of intensities 2:1:2:2, indicating the seven boron atoms are each coupled to a terminal hydrogen. It is significant that the coupling constant of the downfield doublet is appreciably smaller (146 Hz) than the other resonances (176–186 Hz) and that the infrared spectrum of IV exhibits two B–H stretching frequencies, 2615 and 2585 cm^{-1}, since Todd has observed similar effects in other 11-vertex nido heteroboranes such as $B_9H_9Se_2$.[14] Twelve different geometric isomers are possible for $C_4B_7H_{11}$ with this cage structure given the multiplicities observed in the ^{11}B NMR. However, it has been previously noted that a boron atom lying between two heteroatoms on the face of such a system appears unusually sharp, probably due to reduced $^{11}B-^{11}B$ spin coupling.[10] Therefore, the sharp doublet of intensity 1 in the spectrum of IV may be assigned to the boron atom, B9, situated between two carbon atoms, C8 and C10, on the open face and the sharp doublet of intensity 2 may be assigned to the remaining two borons, B7 and B11, on the face. The fact that there are three pairs of equivalent boron nuclei then requires that the remaining two carbon atoms, C1 and C2, lie on the plane bisecting the two carbon atoms on the face. Todd has also noted that 11-membered heteroboranes, not involving a metal atom, exhibit a high-field doublet above −34 ppm that can be attributed to the "apical" boron atom located at the bottom of the cage.[15] This resonance is absent in the ^{11}B NMR spectrum of $C_4B_7H_{11}$, the resonance at highest field occurring at −23.7 ppm, strongly suggesting a carbon atom at this "apical" position.

The normal and line-narrowed proton decoupled spectra of IV are shown in Figure 5b,c. The two upfield resonances, which are assigned to the B3,6 and B4,5 borons, appear as broadened multiplets (21 Hz coupling) in the line-narrowed spectrum. The origin of the unique line shape at elevated temperatures (see Figure 5) is still under investigation; however, the multiplet structure (7-Hz coupling) appears to be

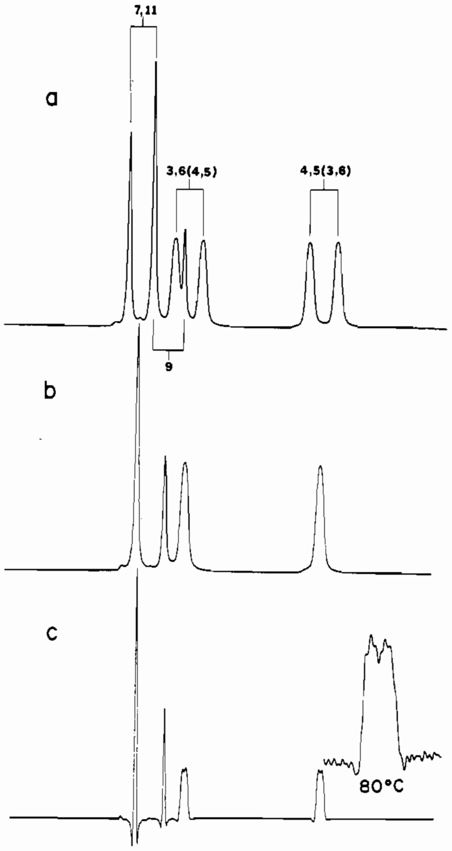


Figure 5. ^{11}B NMR spectra (115.5 MHz) and proposed assignments of 1,2,8,10-$C_4B_7H_{11}$ (IV): (a) proton-spin coupled; (b) proton-spin decoupled; (c) proton-spin decoupled with line narrowing at 25 °C. The expansion exhibits the structure of the upfield resonance at elevated temperature.

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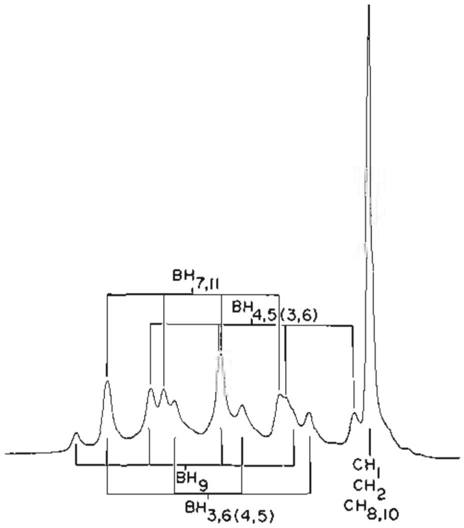

Figure 6. ^{1}H NMR spectrum (360 MHz) and proposed assignments of 1,2,8,10-$C_4B_7H_{11}$ (IV).

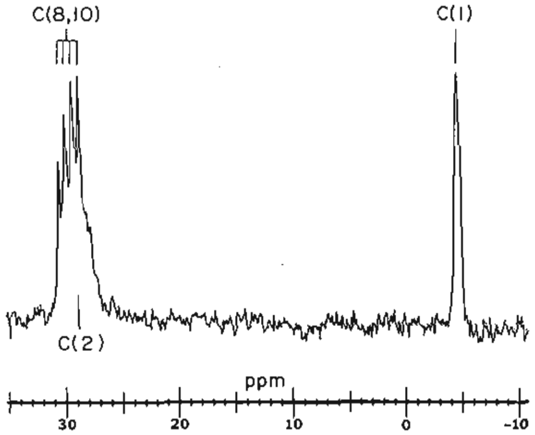

Figure 7. Proton-spin-decoupled 62.9-MHz ^{13}C NMR spectrum and proposed assignments of 1,2,8,10-$C_4B_7H_{11}$ (IV).

associated with coupling interactions between B4, B5 and B3, B6 only, since the B9 and B7, B11 resonances are too sharp to be extensively coupled to either B4, B5 or B3, B6.

The 360-MHz proton NMR spectrum of IV in Figure 6 shows, as expected, four overlapping B–H quartets in the ratio 1:2:2:2. The assignments given in the figure are consistent with the relative chemical shifts and coupling constants observed in the ^{11}B NMR spectrum. Surprisingly, only a single peak, which must arise from the overlap of three separate resonances, HC1, HC2, and HC8, HC10, is observed for the four CH protons. The presence of three different types of carbon atoms in the compound is confirmed, however, in the proton-decoupled ^{13}C NMR spectrum, shown in Figure 7, which indicates three resonances in the ratio of 2:1:1. The appearance of an upfield resonance in the spectrum is consistent with the assignment of a carbon atom to the apical 1-position in the structure. The line width of this resonance is relatively sharp, indicating little coupling to the cage borons. The coupled spectrum shows, of course, a doublet (J = 194 Hz) due to ^{13}C–H coupling. The overlapping downfield resonances integrate to a relative area 3 and are assigned to the C8, C10 and C2 carbons. Both resonances show ~160-Hz coupling for $J(^{13}C{-}^{1}H)$ in the coupled spectrum. Significantly, the C8, C10 resonance appears as a quartet in the proton-decoupled spectrum (Figure 7) due to ^{13}C–^{11}B coupling. Similar ^{13}C–^{11}B couplings have previously been observed by ^{13}C NMR for 2,3-$C_2B_4H_8$[16a] (J = 50 Hz) and by ^{11}B NMR in a ^{13}C-enriched sample of 1,5-$C_2B_3H_5$ (J = 18 Hz).[16b] The observed coupling constant, J = 38 Hz, in IV is also consistent with other reported ^{13}C–^{11}B couplings.[17] Strong interactions between cage atoms on the open face of an 11-vertex nido cage system are not unprecedented; for example, ^{11}B–^{31}P coupling (J = 52 Hz) has been observed between adjacent boron and phosphorus atoms located on the open face of the isoelectronic cluster 7,9-$B_9H_{10}CHPCH_3$.[18] The apparent lack of coupling of C8, C10 to boron atoms (B3, B4 or B5, B6) in the lower belt is unusual but is consistent with the reduced coupling observed between the boron atoms in the two rings. It is surprising that the C8, C10 signal appears as only a quartet, indicating that each carbon atom must be strongly coupled to only one boron atom, since each carbon occupies a site between two boron atoms on the face; however, a similar selective coupling was also observed in 7,9-$B_9H_{10}CHPCH_3$. For IV either C8–B9 and C10–B9 or C8–B7 and C10–B11 interactions are possible but due to the low natural abundance of ^{13}C it is not possible to observe the nature of the coupling by ^{11}B NMR.

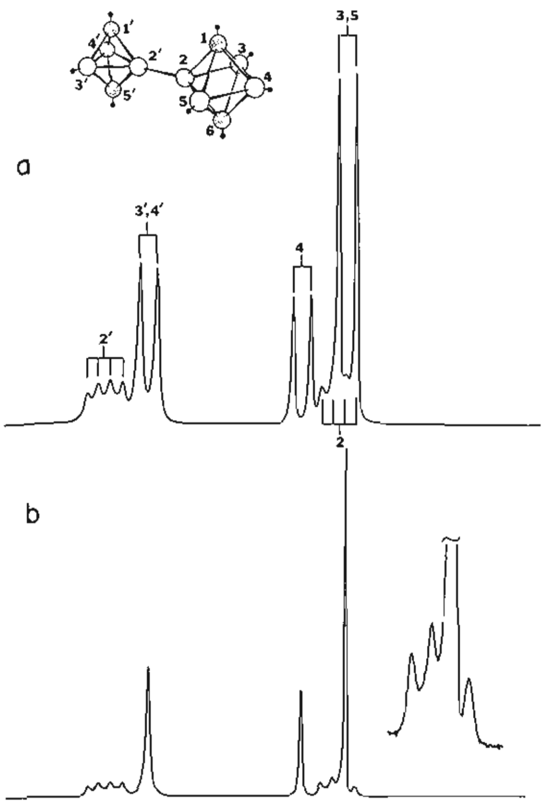

Figure 8. (a) ^{11}B NMR spectrum (115.5 MHz) and structure of 2':2-[1',5'-$C_2B_3H_4$][1,6-$C_2B_4H_5$]. (b) Proton-spin-decoupled spectrum of the same compound with a small degree of computer line narrowing to enhance the upfield B2 resonance (enlarged).

In contrast to the results obtained for 1,5-$C_2B_3H_5$, the pyrolysis of 1,6-$C_2B_4H_6$ under similar reaction conditions resulted in only decomposition with the evolution of hydrogen and no discrete products could be isolated.

The copyrolysis of 1,5-$C_2B_3H_5$ and 1,6-$C_2B_4H_6$ was also investigated and found to yield as the major product the mixed-cage carborane 2':2-[1',5'-$C_2B_3H_4$][1,6-$C_2B_4H_5$]. This

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compound has previously been obtained in low yields from the cophotolysis of 1,5-$C_2B_3H_5$ and 1,6-$C_2B_4H_6$;[2] however, the copyrolysis reaction gives the compound in reasonable yields (47% based on consumed 1,6-$C_2B_4H_6$) and is therefore a significant synthetic improvement.

We had previously noted[2] that no readily identifiable singlets, which could be assigned to the B2 and B2' boron atoms, were apparent in the ^{11}B NMR spectrum of 2':2-[1',5'-$C_2B_3H_4$][1,6-$C_2B_4H_5$] at 32.1 MHz, and we had proposed that these two resonances were extensively broadened because of ^{11}B–^{11}B coupling between B2 and B2'. As can be seen in Figure 8, the ^{11}B NMR spectra at 115.5 MHz confirms this interpretation. The resonance assigned to the B2' boron clearly shows the quartet structure in both the coupled (a) and proton-spin-decoupled (b) spectra that would be expected to arise from direct coupling with the B2 boron. The B2 resonance is partially obscured in the coupled spectrum (a) but again clearly shows a quartet structure in the proton-spin-decoupled spectrum (b). Similar boron–boron interactions have now been reported for several coupled cage compounds such as 1:2'-[B_5H_8]$_2$,[4a] 1:5'-[2,4-$C_2B_5H_6$]$_2$,[4a] and 1:2'-[$B_{10}H_{13}$]$_2$,[19] in which the cages are linked by chemically inequivalent boron atoms. The coupling constant (J = 126 Hz) observed for 2':2-[1',5'-$C_2B_3H_4$][1,6-$C_2B_4H_5$] is one of the largest that has been reported and is consistent with the expected high s-orbital character of an exopolyhedral bond between these small carboranes. Further studies[4b] are now in progress concerning boron–boron couplings in these and related systems.

Also isolated in the copyrolysis reaction were small amounts of the dimers and trimers of 1,5-$C_2B_3H_5$ and of the four-carbon carborane $C_4B_7H_{11}$, in essentially the same relative ratio as observed for the 1,5-$C_2B_3H_5$ pyrolysis. Trace amounts of an additional compound were isolated in insufficient amounts for complete characterization; however, the boron-11 NMR spectrum (see Experimental Section) is consistent with a formulation of the compound as the mixed-cage trimer 2:2',3':2''-[1,5-$C_2B_3H_4$][1',5'-$C_2B_3H_3$][1'',6''-$C_2B_4H_5$].

Discussion

Burg[5] first studied the thermolysis reactions of 1,5-$C_2B_3H_5$ and reported that, when the vapor of the carborane was heated at 350 °C in a reactor containing an internal cold finger, the boron–boron-coupled carborane 2:2'-[1,5-$C_2B_3H_4$]$_2$, was obtained in 18% yield along with trace amounts of a possible three-cage compound. Later, Onak[6] also isolated 2:2'-[1,5-$C_2B_3H_4$]$_2$ along with its boron-substituted methyl derivatives from the thermal reaction of trimethylboron with 1,5-$C_2B_3H_5$. Fehlner[7] then investigated the thermolysis of 1,5-$C_2B_3H_5$, again using a hot/cold reactor containing an internal cold finger, and succeeded in producing both 2:2'-[1,5-$C_2B_3H_4$]$_2$ and a trimer that was characterized as the boron-linked compound 2:2',3':1''-[1,5-$C_2B_3H_4$][1',5'-$C_2B_3H_3$][1'',5''-$C_2B_3H_4$].

In the present study we have investigated the thermolysis reactions of both 1,5-$C_2B_3H_5$ and 1,6-$C_2B_4H_6$ again using hot/cold techniques but employing a reactor and conditions that allowed more extensive secondary reactions, thus increasing the probability of forming larger cage systems. In agreement with the earlier studies cited above, the major product of the reaction of 1,5-$C_2B_3H_5$ was found to be the boron–boron-coupled dimer 2:2'-[1,5-$C_2B_3H_4$]$_2$. However, we were also able to isolate a second dimer in lower yield, which was identified as the boron–carbon-linked compound 1:2'-[1,5-$C_2B_3H_4$]$_2$. Likewise, in addition to the previously known boron–boron-linked trimer we were able to isolate two new trimers, 2:2',1':2''-[1,5-$C_2B_3H_4$][1'5,'-$C_2B_3H_3$][1'',5''-$C_2B_3H_4$] (II) and 2:2',3':1''-[1,5-$C_2B_3H_4$][1',5'-$C_2B_3H_3$][1'',5''-$C_2B_3H_4$] (III), each having one boron–boron and one boron–carbon linkage. In both the known boron-bonded trimer and compound III (Figure 1) the three cages are linked through a 120° angle, whereas in compound II this angle is 90°. Thus, compound III and the boron-bonded trimer can be viewed as linkage isomers, while compound II is a geometric isomer of both of them.

No evidence was found for the formation of a carbon–carbon-linked dimer or trimers. This fact along with the low yields obtained for the boron–carbon-linked isomers indicates a reduced reactivity at the carbon site and is consistent with the relative bond strengths of C–H vs. B–H bonds.[20]

Surprisingly, one of the major products of the thermolysis of 1,5-$C_2B_3H_5$ was found not to be a linked cage compound but rather a fused-cage carborane, $C_4B_7H_{11}$. This is the newest member of a growing family of four-carbon carboranes that already includes $C_4B_2H_6$,[21,22] $R_4C_4B_2R'_2$,[22,23] $R_4C_4B_4H_4$,[24] $R_4C_4B_4R'_4$,[25] $R_4C_4B_8H_8$,[26] and $R_4C_4B_7H_9$[27] (R, R' = H or alkyl) and is the first such large cage compound[28] to be characterized that does not have alkyl substituents at the carbon cage atoms.

A number of isomers based on a capped-pentagonal-antiprism structure would be possible for IV, but as discussed above, the spectroscopic data are consistent with the 1,2,8,10-$C_4B_7H_{11}$ structure shown in Figure 4. It should be noted, however, that other structures such as a 1,7,9,11-$C_4B_7H_{11}$ cage, although considered less likely, cannot be rigorously excluded. Final confirmation of the structure of IV will therefore require a crystallographic investigation.

The relatively severe reaction conditions and our failure to observe isomerization reactions before decomposition at elevated temperatures suggest that IV is the thermodynamically favored isomer. Additional support for the 1,2,8,10-$C_4B_7H_{11}$ structure comes from the fact that this structure maximizes the carbon–carbon separation in the cage, which is a well-documented[29] trend in carborane cage rearrangements. This structure is also the only possible structure in which each carbon atom is adjacent to four boron atoms, maximizing the boron–carbon interactions in the cage. One other unique aspect of this structure is that strong bonding interactions can be enhanced in the C2, B3, B4, B5, B6, and B7, C8, B9, C10, B11 rings, which is in agreement with both the strong intraring couplings observed in the ^{13}C NMR spectrum between C8, C10 and B7, B11 (or B9) and in the ^{11}B NMR spectrum between B3, B6 and B4, B5 and with the apparent lack of any such inter-ring couplings.

The mechanism of formation of IV from 1,5-$C_2B_3H_5$ is probably unrelated to the process leading to the coupled cage compounds, since the formation of cage linkages requires B–H bond scission with the evolution of hydrogen, whereas the formation of a fused cage does not. This cage fusion reaction may, in fact, be related to the 1,5-$C_2B_3H_5$ polymerization reaction, since Burg[5] has noted that polymerization occurs without the formation of hydrogen. Furthermore, theoretical studies[30] have indicated that 1,5-$C_2B_3H_5$ is a unique carborane

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that can be formulated as a bicyclic compound with little boron–boron bonding. Such a system contains strained four-membered C–B–C–B rings which should be susceptible to ring-opening reactions generating open polyhedral faces suitable for cage fusions. Indeed, the proposed 1,2,8,10-$C_4B_7H_{11}$ structure can be envisioned as containing two such open-cage $C_2B_3H_5$ fragments: 1,8,3,4,7-$C_2B_3H_5$ and 2,10,5,6,11-$C_2B_3H_5$ cages. The thermally induced process leading to the formation of IV thus may be formally related to the metal-promoted cage fusions of nido carboranes which have been used to generate the other large-cage four-carbon carborane systems.[26]

The formation of $C_4B_7H_{11}$ from 1,5-$C_2B_3H_5$ is also quite unusual since the molecule contains one more B–H unit than two $C_2B_3H_5$ groups. Two reasonable possibilities for a reaction sequence were suggested. First, diborane, produced by decomposition of 1,5-$C_2B_3H_5$, could be involved in the reaction to produce IV. Supporting this possibility was the report[31] that mass spectroscopic evidence for a compound of the same formula had been obtained as a product of the pyrolysis of 2,4-$C_2B_4H_8$ and diborane. Second, since 1,5-$C_2B_3H_5$ is known[5] to thermally convert to 1,6-$C_2B_4H_6$ and both 1,6-$C_2B_4H_6$ and 2:2′-[1,5-$C_2B_3H_4$][1,6-$C_2B_4H_5$] were observed as minor products of the reaction, 1,6-$C_2B_4H_6$ could combine with 1,5-$C_2B_3H_5$ to produce IV. It was found, however, that neither additional diborane nor 1,6-$C_2B_4H_6$ affected the yield of IV formed in the 1,5-$C_2B_3H_5$ pyrolysis reaction. Thus, the mechanism of formation of this unusual species is unknown and is the subject of continuing investigation in this laboratory.

The pyrolysis reactions of 1,6-$C_2B_4H_6$ were found to yield only polymerization, but when equimolar quantities of 1,5-$C_2B_3H_5$ and 1,6-$C_2B_4H_6$ were pyrolyzed, the mixed-cage carborane 2′:2-[1′,5′-$C_2B_3H_4$][1,6-$C_2B_4H_5$] was formed in good yield based on consumed 1,6-$C_2B_4H_6$, suggesting that reactive fragments derived from 1,5-$C_2B_3H_5$ are the key species in the reaction. This reaction method is a significant improvement over the previous photochemical procedure,[2] and we would expect that the reaction yields could be further improved by employing more efficient quenching of the product.

Further investigations are now in progress concerning the synthesis and properties of the compounds reported herein and related linked- and fused-cage polyhedral boranes. The results of these studies will be reported in future publications.

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Registry No. I, 85709-78-0; II, 85709-79-1; III, 85701-87-7; IV, 85701-88-8; 1,5-$C_2B_3H_5$, 20693-66-7; 1,6-$C_2B_4H_6$, 20693-67-8; B_2H_6, 19287-45-7.

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Preparation and Coordination Geometry of Quadridentate Ethylenediaminetetraacetate Complexes of Ruthenium(II) and -(III)

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Complexes of $Ru^{II}(H_2edta)L$ (L = bis(pyridine), bis(4-methylpyridine), 1,10-phenanthroline, 2,2′-bipyridine, 1,2-bis(diphenylphosphino)ethane, and dimethylglyoximate) and $Ru^{III}(H_2edta)L$ (L = $(SCN)_2$, acetylacetonate, dimethylglyoximate, and diethyldithiocarbamate) were prepared by substitution reactions on $Ru^{II}(Hedta)H_2O^-$ and $Ru^{III}(Hedta)H_2O$, respectively. Substitution of the ligands L on $Ru(H_2edta)(py)_2$ and $Ru(H_2edta)(C_6H_5CN)_2$ with a variety of other entering ligands was investigated. The carboxylic acid functions in the free glycinate arms in $[Ru^{II}(Hedta)CO]K{\cdot}2H_2O$ and $Ru(H_2edta)(py)_2$ were shown to react with diazomethane and *p*-toluidine. The complexes were characterized by analytical and spectroscopic procedures, including ^{13}C NMR, and were shown to accommodate L in the equatorial positions, giving rise to molecules possessing a C_2 axis. The complexes prepared in this work, together with complexes with π-acceptor ligands reported in an earlier study, were investigated by cyclic voltammetry. Resistance to oxidation was found to depend on the ligand L and followed the sequence NO, CO > RCN > bipyridine, phenanthroline > pyridine > N_2(terminal) > SCN^- > N_2(bridging) > acetylacetonate > dimethylglyoximate. The effect of the ligand L on the stability of the oxidation state of the complex is discussed.

Introduction

In an earlier study[1] we reported the preparation of complexes of the type $Ru(H_nedta)L_n$ (L = N_2, CO, NO (n = 1) and L = RCN (n = 2)) by substitution of the ligand on $Ru^{II}(Hedta)H_2O^-$ in dilute acid solution and in the presence of H_2/Pt. Matsubara and Creutz[2] investigated the kinetics of substitution on $Ru^{III}(edta)H_2O^-$ and on $Ru^{II}(edta)H_2O^{2-}$ and found rate constants higher than those of corresponding ruthenium complexes with oxygen and nitrogen donors, especially in the case of ruthenium(III) in which substitution was faster by as much as 10 orders of magnitude. Thus, the ready preparation of the complexes can be explained as proceeding by substitution on ruthenium(II) or on ruthenium(III) followed by rapid electron transfer.

In this paper we report the preparation and properties of complexes of ruthenium(II) and ruthenium(III) containing quadridentate edta, in which the remaining two positions are occupied by a variety of ligands, mainly bidentate, ranging in their coordinating ability from strong π-acceptors to σ- and π-donors.

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