Preparation, Characterization, and Properties of 1,1′-Azo-*o*-carbaboranes

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1-Amino-1,2-dicarbadodecaborane anions, *o*-$RCB_{10}H_{10}CNH_2^{2-}$ (R = H, Me, or Ph), are oxidized by K[MnO_4] in liquid NH_3 to give 1,1′-azo-*o*-carbaboranes, $RCB_{10}H_{10}CN{=}NCB_{10}H_{10}CR$ (3), whereas oxidation of $HCB_{10}H_{10}CCB_{10}H_{10}CNH_2^{4-}$ in the same solvent exclusively affords hydrazobis(*o*-carbaborane), $HCB_{10}H_{10}CCB_{10}H_{10}CNHNHCB_{10}H_{10}CCB_{10}H_{10}CH$. The reduction of (3) to the corresponding hydrazocarbaborane, $RCB_{10}H_{10}CNHNHCB_{10}H_{10}CR$ (2), has been successfully achieved. *closo-nido*-Azocarbaboranes, $RCB_{10}H_{10}CN{=}NCB_9H_{10}CR^-$ (4), and *nido-nido* ones, $RCB_9H_{10}CN{=}NCB_9H_{10}CR^{2-}$ (5), have also been prepared by the degradation of (3) with K[OH]. Their structure and properties are discussed on the basis of spectroscopic data.

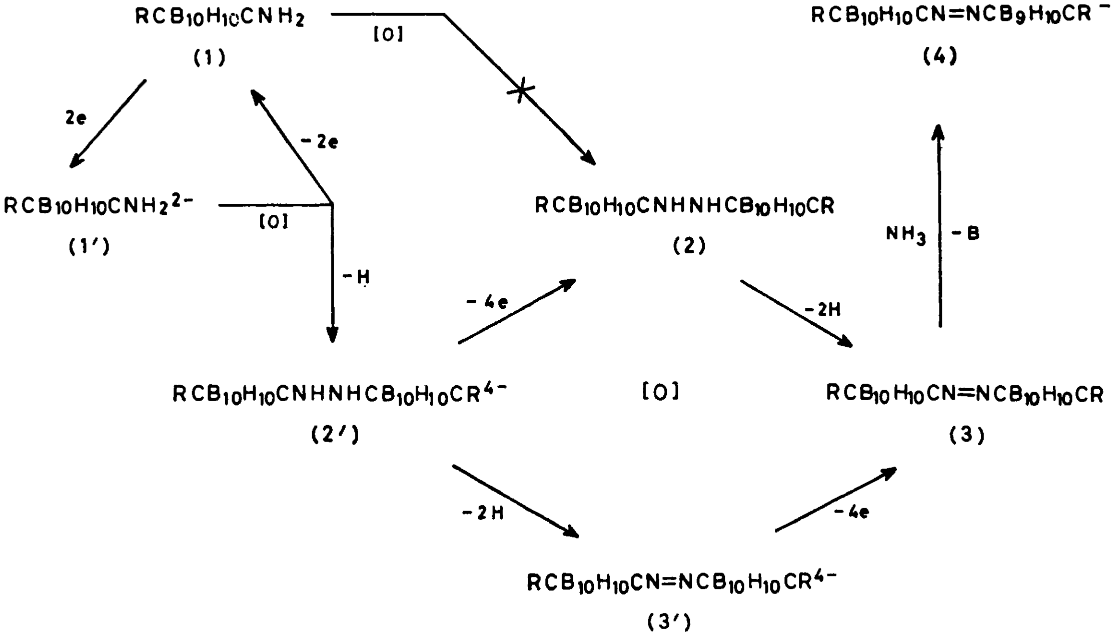
GENERAL azotization methods such as oxidation, diazonium coupling, and condensation of 1-amino-1,2-dicarbadodecaborane, *o*-$RCB_{10}H_{10}CNH_2$ (1), in order to obtain the corresponding *closo-closo*-1,1′-azo-*o*-carbaborane, $RCB_{10}H_{10}CN{=}NCB_{10}H_{10}CR$ (3), resulted in decomposition and/or recovery of (1). After many attempts we found a method to produce (3).[1] The object of this paper is to describe the relationship between the oxidation conditions and the yields of (3) as well as the characterization and properties of (3) and related compounds.

RESULTS AND DISCUSSION

TABLE 1

Oxidation conditions of $MeCB_{10}H_{10}CNH_2^{2-}$, (1b′)

Molar ratio K[MnO_4]/(1b′)	Temperature (θ_c/°C)	Liquid NH_3 (cm³)/(1b′) (g)	Yield (%)	Recovered (1b) (%)
4	−71	60	24.3	42.6
4	−58	80	43.9	42.1
4	−42	65	41.1	42.4
2	−71	55	10.7	56.9
2	−58	80	68.2	15.6
2	−58	40	71.3	11.3



SCHEME 1 Oxidation of $RCB_{10}H_{10}CNH_2^{2-}$ in liquid NH_3: [O] denotes K[MnO_4]; electrons from Na

Table 1 shows the relationship between the oxidation conditions of $MeCB_{10}H_{10}CNH_2{}^{2-}$ (1b′) and the yield of $MeCB_{10}H_{10}CN{=}NCB_{10}H_{10}CMe$ (3b). The optimum yield was obtained under the following conditions: molar ratio of K[MnO_4] : $MeCB_{10}H_{10}CNH_2{}^{2-}$, 2 : 1; oxidation temperature, −58 °C; and NH_3 as solvent which was removed at low temperature (−50 °C) after addition of dry toluene.† Accordingly, the use of more than four or less than two molar equivalents of K[MnO_4] to (1b′) leads to lower yields of (3b) even if the temperature is kept at *ca.* −58 °C. In each case in Table 1, (1b) was recovered as a result of reoxidation of the amino-carbaborane anion (1b′). It has been confirmed by detailed examination of the i.r. spectra of recovered

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† **CAUTION**. When the reaction mixture was concentrated to near dryness without addition of toluene or another inert solvent, detonation occurred.

(1b) that trace amounts of (2b) and the ionic species (4b) are present (Scheme 1). Unsubstituted azocarborane (3a) and the phenyl-substituted analogue (3c) were synthesized similarly in moderate yield [(3a) 58%, (3c) 73%]. However, the results for the two syntheses were not the same, despite the fact that essentially the same conditions were applied. In the synthesis of (3a), compound (2a) and considerable amounts of ionic product (4a) were isolated besides the expected products (3a) and (1a). With respect to (2a) (yield, 19%) formation, although only speculative, the potential-energy barrier for the pathway from (2a') to (3a) *via* (3a') would be relatively high compared to those of the corresponding oxidation pathway for methyl- and phenyl-substituted hydrazocarbaborane anion (2b') and (2c').[1] Contrary to the difficulty in converting (1) to (2) which involves the formation of an oxidative N–N bond, the dehydrogenation of (2) to generate (3) was readily performed even under ordinary conditions as follows; (2a—c) were converted quantitatively into (3a—c) with various oxidizing reagents in benzene or toluene at room temperature or under reflux. The degradation of (3a) with NH_3 as the solvent affords the *closo-nido*-azocarbaborane (4a), the i.r. and ^1H n.m.r. spectra of which convinced us that (4a) is the same compound as that derived in equation (1), described later.

TABLE 2

Characterization data and yields for the azo- and hydrazo-carbaboranes

	Compound	M.p. (θ_c/°C)	Analysis (%) *				Yield (%)
			C	H	B	N	
(3a)	$HCB_{10}H_{10}CN{=}NCB_{10}H_{10}CH$	270	16.15 (15.3)	7.20 (7.05)	68.75 (68.75)	8.85 (8.90)	58 (3a), 19 (2a), 9.5 (1a)
(3b)	$MeCB_{10}H_{10}CN{=}NCB_{10}H_{10}CMe$	225	21.2 (21.05)	7.80 (7.65)		8.25 (8.20)	79 (3b), <1 (2b), 8.0 (1b)
(3c)	$PhCB_{10}H_{10}CN{=}NCB_{10}H_{10}CPh$	243—244.5	41.25 (41.2)	6.60 (6.50)		5.95 (6.00)	73 (3c), 1.0 (2c), 15 (1c)
(2a)	$HCB_{10}H_{10}CNHNHCB_{10}H_{10}CH$	250	15.2 (15.2)	7.70 (7.65)	67.85 (68.35)	8.90 (8.85)	56
(2b)	$MeCB_{10}H_{10}CNHNHCB_{10}H_{10}CMe$	233—237	21.05 (20.9)	8.40 (8.20)		8.15 (8.15)	65
(2c)	$PhCB_{10}H_{10}CNHNHCB_{10}H_{10}CPh$	195—196	41.2 (41.0)	7.05 (6.90)		6.00 (6.00)	52
(2d)	$HCB_{10}H_{10}CCB_{10}H_{10}CNHNHCB_{10}H_{10}CCB_{10}H_{10}CH$	>300	16.2 (16.0)	7.30 (7.40)	71.4 (71.95)	4.60 (4.65)	58 (2d), 5 (1d)
(2e)	$[NMe_4][HCB_{10}H_{10}CCB_{10}H_{10}CNNHCB_{10}H_{10}CCB_{10}H_{10}CH]$	290 (decomp.)	21.4 (21.4)	8.30 (8.25)	62.55 (62.95)	6.00 (6.25)	
(2f)	$[NMe_4]_2[HCB_{10}H_{10}CCB_{10}H_{10}CNNCB_{10}H_{10}CCB_{10}H_{10}CH]$	225 (decomp.)	25.95 (25.75)	9.15 (8.90)	57.4 (57.9)	7.65 (7.50)	
(4a)	$[NMe_4][HCB_{10}H_{10}CN{=}NCB_9H_{10}CH]$	>300	25.70 (25.45)	9.25 (9.05)	53.85 (54.35)	11.25 (11.15)	80
(4b)	$[NMe_4][MeCB_{10}H_{10}CN{=}NCB_9H_{10}CMe]$	>300	29.70 (29.6)	9.65 (9.45)	50.0 (50.6)	10.4 (10.35)	88
(4c)	$[NMe_4][PhCB_{10}H_{10}CN{=}NCB_9H_{10}CPh]$	245—246	45.1 (45.3)	8.10 (8.00)	38.4 (38.75)	7.95 (7.95)	88
(5a)	$[NMe_4]_2[HCB_9H_{10}CN{=}NCB_9H_{10}CH]$	>300	32.25 (32.65)	10.8 (10.5)	43.8 (44.1)	12.75 (12.7)	72
(5b)	$[NMe_4]_2[MeCB_9H_{10}CN{=}NCB_9H_{10}CMe]$	>300	35.65 (35.85)	11.0 (10.75)	41.45 (41.45)	12.0 (11.95)	80
(5c)	$[NMe_4]_2[PhCB_9H_{10}CN{=}NCB_9H_{10}CPh]$	>300	47.95 (48.6)	9.15 (9.15)	31.85 (32.8)	9.25 (9.45)	25

* Calculated values are given in parentheses.

Characterization and Properties of the Products.—*closo-Azocarbaboranes*, $RCB_{10}H_{10}CN{=}NCB_{10}H_{10}CR$, (3). Analytical data were reported in part in a preliminary communication.[1] Only additional findings and supplementary data are therefore included in this paper. Compounds (3a—c) were readily reduced with $Li[AlH_4]$ to yield the hydrazo-*o*-carbaborane (2a—c). This reduction was accelerated by the addition of a catalytic amount of $TiCl_4$ [2] and consequently (1) was recovered. These oxidation–reduction processes can be written as in Scheme 2.

In the 1-aminobis(*o*-carbaborane) [3] system, oxidation proceeds to form the hydrazo-compound (2d) (Scheme 3).

$$\underset{(3a—c)}{RCB_{10}H_{10}CN{=}NCB_{10}H_{10}CR} \xrightleftharpoons[-2H]{+2H} RCB_{10}H_{10}CNHNHCB_{10}H_{10}CR \xrightleftharpoons[\substack{1.\ 2Na \\ 2.\ K[MnO_4]}\ \text{in liquid } NH_3]{+2H,\ Ti^{4+}} \underset{(1a—c)}{RCB_{10}H_{10}CNH_2}$$

SCHEME 2

Unexpectedly, further oxidation of the hydrazo-compound (2d) to the azo-compound did not occur, in contrast to the results of the oxidation for the 1-amino-*o*-carbaborane anion system. The compound (2d) is soluble in polar organic solvents such as alcohol, acetone, and ether and displays an orange-yellow colour, it is slightly soluble in benzene and dichloromethane without displaying any colour, and almost insoluble in water. The coloured solution shows acidity due to dissociation of the hydrazo-proton. In basic solution both hydrazo-protons are dissociated giving the orange colour (Scheme 4). The apparent pK_a values in alcoholic solution (75%) at 25 °C were determined by potentiometric titration ($pH = 2.40$ for 2×10^{-4} mol dm^{-3} 75% EtOH solution, $pK_1 = 2.24$, $pK_2 = 9.53$). Treatment of (2d) in neutral ($EtOH-H_2O$) and basic conditions ($EtOH-H_2O-Na[OH]$) in the presence of NMe_4^+ leads to the formation of NMe_4 salts of the monoanion (2e) and the dianion (2f) respectively (see Experimental section). Both salts regenerate (2d) when treated with hydrochloric acid. This strong acidity in comparison with that of (2a) ($pH = 9.30$ for 2×10^{-4} mol dm^{-3} 75% solution) might reflect the extreme electron-withdrawing character of the bis(carbaboranyl) group.

$$\underset{(1d)}{HCB_{10}H_{10}CCB_{10}H_{10}CNH_2} \xrightarrow[\text{liquid } NH_3]{4Na} HCB_{10}H_{10}CCB_{10}H_{10}CNH_2^{4-} \xrightarrow[\text{liquid } NH_3]{K[MnO_4]}$$

$$HCB_{10}H_{10}CCB_{10}H_{10}CNHNHCB_{10}H_{10}CCB_{10}H_{10}CH^{8-} \xrightarrow[\text{liquid } NH_3]{[O]} \underset{(2d)}{HCB_{10}H_{10}CCB_{10}H_{10}CNHNHCB_{10}H_{10}CCB_{10}H_{10}CH}$$

Scheme 3

$$\underset{(2d)}{HCB_{10}H_{10}CCB_{10}H_{10}CNHNHCB_{10}H_{10}CCB_{10}H_{10}CH} \rightleftharpoons$$

$$\underset{(2e)}{HCB_{10}H_{10}CCB_{10}H_{10}CNNHCB_{10}H_{10}CCB_{10}H_{10}CH^-} + H^+ \rightleftharpoons$$

$$\underset{(2f)}{HCB_{10}H_{10}CCB_{10}H_{10}CNNCB_{10}H_{10}CCB_{10}H_{10}CH^{2-}} + 2H^+$$

Scheme 4

closo-nido-*Azocarbaboranes,* $RCB_{10}H_{10}CN{=}NCB_9H_{10}CR^-$, (4), *and* nido-nido *dianions,* $RCB_9H_{10}CN{=}NCB_9H_{10}CR^{2-}$, (5). The selective degradation of *o*-carbaborane and its alkyl and aryl derivatives in basic media were studied in detail,[4] however, this type of reaction on a carbaborane cage that has other organic functional groups has not been well investigated. Applying the above procedure, *closo*-azocarbaborane, (3), was treated with K[OH] in ethanol. Degradation in ethanolic base proceeds smoothly at room temperature and hydrogen is evolved quantitatively according to equation (1). The i.r. and ^1H n.m.r. spectra of NMe_4 or Cs salts of the products are identical with those of (4) in Scheme 1.

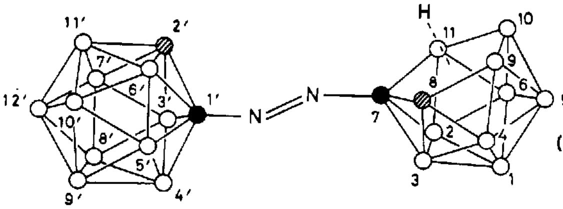
$$\underset{(3a-c)}{RCB_{10}H_{10}CN{=}NCB_{10}H_{10}CR} + R'O^- + 2R'OH \longrightarrow$$

$$\underset{(4a-c)}{RCB_{10}H_{10}CN{=}NCB_9H_{10}CR^-} + B(OR')_3 + H_2 \quad (1)$$

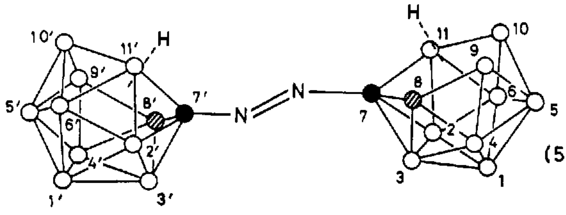
$$\underset{(4a-c)}{RCB_{10}H_{10}CN{=}NCB_9H_{10}CR^-} + R'O^- + 2R'OH \longrightarrow$$

$$\underset{(5a-c)}{RCB_9H_{10}CN{=}NCB_9H_{10}CR^{2-}} + B(OR')_3 + H_2 \quad (2)$$

The *closo-nido*-azocarbaboranes (4a—c) are subjected to further regiospecific degradation to afford *nido-nido*-azocarbaboranes (5a—c) as in equation (2). The proposed structures for compounds (4) and (5) are supported by the ^1H n.m.r., vibrational, and electronic spectra. The structure of (4a—c) indicates that the removal of boron atom 6 of the two chemically identical atoms 3 and 6 of (3a—c) has occurred as the result of the base degradation of the *closo*-azocarbaborane (3a—c). Two diastereoisomers for *nido-nido*-azocarbaboranes are possible, depending upon whether boron atom 3′ or 6′ of (4a—c) is removed by degradation. However, in the present investigation, no other isomer for (5a—c) has been detected by thin-layer chromatography or ^1H n.m.r. spectra. Hydrogen-1 n.m.r. spectra of (4a) exhibited *closo-* and *nido*-carbaborane C–H bonds at δ 4.63 and 2.75 respectively,[4] whereas a very broad singlet at δ 2.65 (2 H) for (5a) suggests that both carbaborane cages have been converted to the *nido* form. A similar relationship between the chemical shifts of both substituents bound to the *closo* and *nido* cages is still apparent in methyl- and phenyl-substituted derivatives as shown in Table 3.



(4a-c)



(5a-c)

● C
▨ CR (a, R = H; b, R = Me; c, R = Ph)
○ BH

The existence of an azo-group in *closo-nido* and *nido-nido* compounds is unequivocally established by their vibrational spectra. The i.r.- and Raman-active –N=N– stretching vibration for (4a) was observed at 1 509 and 1 512 cm^{-1} respectively. On the other hand, symmetrically substituted (5a) reveals only a Raman-active band at 1 515 cm^{-1}, as expected. The Raman frequencies for the –N=N– stretching mode in (4a) and (5a) shift to lower frequency relative to that in (3a). The Raman frequency due to N=N stretching of (3a) at 1 545 cm^{-1} is closer to that of azomethane (1 576 cm^{-1}) than that of azobenzene (1 442 cm^{-1} for the *trans* form of azobenzene). The Raman frequency of the azo-group for (3a—c) in the region 1 545—1 555 cm^{-1} implies that the conjugation of the azo-group with the carbaborane

TABLE 3

Physical data for the azocarbaborane derivatives

		ν(N=N')/cm^{-1}		
Compound	δ/p.p.m.	I.r.[a]	Raman[b]	$\lambda_{max.}$/nm[c]
(3a)	4.27 (C^2–H, $C^{2'}$–H), $CDCl_3$		1 545s	364 (32), 220 (12 500)[d]
(3b)	2.26 (C^2–Me, $C^{2'}$–Me), $CDCl_3$		1 550s	375 (22), 225 (9 800)[d]
(3c)	7.20 (C^2–Ph, $C^{2'}$–Ph), $CDCl_3$		1 555s	392 (58)[d]
(4a)	2.75 (C^8–H), CD_3CN 4.63 ($C^{2'}$–H)	1 509m	1 512vs	380 (5 200), 377 (4 700), 344 (5 000), 347 (5 400);[d] 230 (7 400, sh)[e]
(4b)	1.71 (C^8–Me), CD_3CN 2.14 ($C^{2'}$–Me)	1 494m	n.r.	390 (4 100, sh), 360 (5 400)[d]
(4c)	7.16 (C^8–Ph), CD_3CN 7.45 ($C^{2'}$–Ph)	1 500m	n.r.	400 (2 900), 360 (4 800)[d]
(5a)	2.65 (C^8–H, $C^{8'}$–H), CD_3CN		1 515vs	354 (2 200, sh), 309 (9 500)[e]
(5b)	1.62 (C^8–Me, $C^{8'}$–Me), CD_3CN		n.r.	376 (1 400, sh), 316 (15 000), 207 (28 000)[e]
(5c)	7.10 (C^8–Ph, $C^{8'}$–Ph), CD_3CN		n.r.	384 (1 000, sh), 313 (12 500), 210 (62 000, sh)[e]

[a] KBr discs. [b] Powdered solids; n.r. = not recorded. [c] Values of ϵ in dm^3 mol^{-1} cm^{-1} are given in parentheses. [d] In 1,2-dimethoxyethane. [e] In 95% EtOH.

cage is quite small. Moreover, the electronic spectra of (3a—c) exhibited an *R* band alone, due to the non-conjugated azo-group. These results are in accord with those for the benzocarbaborane molecule in which the degree of aromatic character in the benzenoid ring is slight.[5] Since the Raman-active –N=N– vibration in azobenzene is conjugated to the π electrons of the benzene ring, the Raman frequency values for (4a) and (5a), which fall approximately in the middle of those in azobenzene and azomethane, suggest a finite amount of conjugation between the *nido*-type cage and the azo-group. The electronic spectral results for the *nido* alkenyl-substituted carbaborane[6] and benzocarbaborane,[7] both of which have a conjugated π-electron system within the molecule, appear to be consistent with our data in a sense. An extraordinarily intense Raman line due to the –N=N– stretching vibration in the ionic species, (4a) and (5a), could be associated with a resonance of the Raman line with the excitation source as indicated in azobenzene derivatives.[8] The electronic spectrum of the monoanion (4a) in 95% EtOH exhibited absorption bands at $\lambda_{max.}$ 344 (ϵ, 5 000) and 377 nm (ϵ, 4 700 dm^3 mol^{-1} cm^{-1}). The dianion (5a), in the same solvent, displayed an absorption band at $\lambda_{max.}$ 309 nm (ϵ, 9 500) with a shoulder at 354 nm (ϵ, 2 200 dm^3 mol^{-1} cm^{-1}). Based on the electron-donating characteristics of the *nido*-carbaborane cage,[9] we tentatively assign these bands to charge transfer from the *nido* cage to the azo-group.

EXPERIMENTAL

All reactions were carried out under an atmosphere of nitrogen. Benzene and toluene were dried over molecular sieves prior to use. Other chemicals were reagent grade and used without further purification.

Infrared spectra were recorded on a Japan Spectroscopic Co. DS-402G spectrometer. Hydrogen-1 n.m.r. spectra (60 MHz) were obtained with a Varian T-60 spectrometer, mass spectra with a Hitachi RMU-6 spectrometer. Electronic spectra were recorded on a Hitachi 323 spectrophotometer. Raman spectra of powdered solids were measured at Osaka University on a JASCO R-1000 spectrometer using the 514.5 nm line of an argon-ion laser.

Preparation of Azocarbaboranes, $HCB_{10}H_{10}CN{=}NCB_{10}H_{10}CH$, (3a).—*General procedure for oxidation of* 1-*amino*-o-*carbaboranes* via *their dianion intermediates*. Anhydrous NH_3 (*ca.* 25 cm^3) was condensed at –65 °C into a 200-cm^3 four-necked flask equipped with a mechanical stirrer, thermometer, dropping funnel, and nitrogen inlet. Under a blanket of nitrogen, with stirring, 1-amino-*o*-carbaborane $HCB_{10}H_{10}CNH_2$[10] (530 mg, 3.32 mmol) was added and allowed to dissolve, followed by the slow addition of Na metal (155 mg, 6.73 mg atoms) in small pieces. The solution turned blue when the final piece of the Na had been added. With vigorous stirring, finely ground K[MnO$_4$] (1.10 g, 6.96 mmol) was added to the solution in small portions over 5 min at –60 to –55 °C. A stream of nitrogen was passed rapidly over the mixture below –50 °C until the volume was reduced to *ca.* 10 cm^3 (it should not be reduced to dryness), toluene (35 cm^3) was added from a dropping funnel, and the remaining NH_3 was removed under reduced pressure below –50 °C. The mixture turned green and was allowed to warm to room temperature. It was then filtered in air and washed several times with small portions of toluene.* The combined filtrate and washings were evaporated using a rotary evaporator to leave a yellowish solid crude product (400 mg). The product was washed with portions of acetonitrile (3 × 1 cm^3) on a sintered-glass filter and the residual white solid was recrystallized from dichloromethane–hexane to afford colourless crystals of $HCB_{10}H_{10}CN{=}NCB_{10}H_{10}CH$, 307 mg (58%).

Isolation of the by-products. The combined acetonitrile solutions used to wash the azocarbaborane were concentrated to near dryness. The yellow residue was dissolved in the minimum amount of dichloromethane and treated on a silica gel column. Elution with dichloromethane gave a colourless liquid, and subsequent elution with acetone gave a yellow liquid. From the colourless liquid, the hydrazocarbaborane $HCB_{10}H_{10}CNHNHCB_{10}H_{10}CH$ (8 mg, 1.5%), characterized by comparison of its i.r. spectrum with that of (2a) prepared below, and the starting aminocarbaborane (1a) (50 mg, 9.5%) were sepa-

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* **CAUTION**. After filtration, the solid residue on the filter must be immediately decomposed with water, because, when left in the atmosphere, it often burns.

rated by fractional recrystallization from hexane. Removal of the solvent from the yellow eluted product left a yellow solid which could be dissolved in water. Addition of aqueous $[NMe_4]Cl$ to the aqueous solution precipitated a yellow solid, which was filtered off and recrystallized from dichloromethane–hexane to give pale yellow needles (24 mg), m.p. >300 °C. The i.r. spectrum of a Nujol mull of this unknown ionic compound contained absorptions at 3 040w, 2 510vs, 1 500w, 1 490(sh), 1 480s, 1 410w, 1 230w, 1 130w, 1 073w, 1 010m, 942m, 730m, and 718m cm^{-1}. The ^1H n.m.r. spectrum of a CD_3CN solution of this compound contained two broad CH resonances at 2.75 and 4.63 p.p.m. and a NMe_4^+ resonance at 3.08 p.p.m. with relative intensity 1 : 1 : 12. From these data and elemental analysis, the structure of this ion was believed to be a *nido-closo*-azocarbaborane monoanion, as determined by comparison of the data with those of $HCB_{10}H_{10}CN{=}NCB_9H_{10}CH^-$ (4a) prepared by base degradation of (3a).

Preparation of Hydrazocarbaboranes. Reduction of Azocarbaboranes (3a—c) *with* $Li[AlH_4]$.—$HCB_{10}H_{10}CNHNHCB_{10}H_{10}CH$, (2a). To a solution of (3a) (157 mg, 0.5 mmol) in diethyl ether (15 cm^3), was added, with stirring, a solution of $Li[AlH_4]$ (95 mg, 2.5 mmol) in diethyl ether (10 cm^3) dropwise over a period of 10 min at room temperature and stirring continued for 30 min. The mixture assumed a light green colour. To the resulting mixture, cooled on an ice-bath, was added saturated aqueous $[NH_4]Cl$ (2 cm^3) with vigorous stirring. The ether layer was separated, washed with water, and dried over anhydrous $Na_2[SO_4]$. After removal of the solvent under reduced pressure, the residue was chromatographed on silica gel using dichloromethane–hexane (1 : 1) as the eluant and recrystallized from dichloromethane–hexane to afford colourless crystals of (2a) (88 mg, 56%). Mass spectrum cut-off at $m/e = 320$, corresponding to the $^{12}C_4{}^1H_{24}{}^{11}B_{20}{}^{14}N_2^+$ ion; i.r. (Nujol mull): 3 300m (NH stretch), 3 050w (CH stretch), 2 560s (BH stretch), 1 240w, 1 125w, 1 070m, 1 010m, 940w, 910w, 855w, 720 cm^{-1}.

Reduction of Azocarbaborane (3b) *to Aminocarbaborane* (1b) *with* $Li[AlH_4]$ *catalyzed by* $TiCl_4$.—To a solution of (3b) (100 mg, 0.29 mmol) in diethyl ether (10 cm^3) was added, with stirring, a solution of $Li[AlH_4]$ (1.5 mmol) in diethyl ether (6 cm^3) and a few drops of $TiCl_4$. The mixture was stirred at room temperature for 2 h, and was cooled on an ice-bath; saturated aqueous $[NH_4]Cl$ was added to the cooled mixture. The ether layer was separated, washed with water, and dried over $Na_2[SO_4]$. After removal of the solvent, the residue was recrystallized from hexane to afford colourless crystals whose i.r. spectrum was identical with that of an authentic sample of 1-amino-2-methyl-*o*-carbaborane, (1b). The yield was 45 mg or 45%.

Oxidation of Hydrazocarbaboranes to Azocarbaboranes.—The hydrazocarbaboranes (2a—c) were readily oxidized to the corresponding azocarbaboranes with various oxidizing reagents such as $K[MnO_4]$, MnO_2, and nickel peroxide. Examples of the reactions are as follows. (*a*) A mixture of (2a), excess of $K[MnO_4]$, and benzene was stirred for 30 min at room temperature; (3a) was obtained in nearly quantitative yield (98%). (*b*) A mixture of (2b), excess of MnO_2, and toluene was refluxed for 12 h; (3b) was obtained in 92% yield. (*c*) A mixture of (2c), excess of nickel peroxide, and benzene as the solvent was refluxed for 4 h; (3c) was obtained in 95% yield.

Preparation of closo-nido *Monoanions of Azocarbaborane Derivatives*.—A typical preparation is given here.

$HCB_{10}H_{10}CN{=}NCB_9H_{10}CH^-$, (4a). To a solution of $K[OH]$ (250 mg, 4.46 mmol) in absolute ethanol (150 cm^3), was added fine crystalline (3a) (940 mg, 2.99 mmol) at 20 °C. The mixture was vigorously stirred at 20 °C for 45 min, giving a yellow solution and 72 cm^3 (3.0 mmol) of hydrogen. The solution was neutralized with dilute hydrochloric acid and the solvent was rotary evaporated to dryness. The residue was extracted three times with portions (30 cm^3) of hot dichloromethane. The combined extracts were concentrated and recrystallized from dichloromethane–hexane to afford pale yellow crystals of the potassium salt of the monoanion (4a) (957 mg, 93%). The caesium salt was precipitated by addition of 20% aqueous CsCl (1 cm^3) to a solution of the potassium salt (200 mg) in cold water (5 cm^3). Recrystallization of the precipitate from dichloromethane–hexane afforded pale yellow crystals of $Cs[HCB_{10}H_{10}CN{=}NCB_9H_{10}CH]$ (196 mg, 72%), m.p. >300 °C (Found: C, 11.25; H, 5.15; B, 46.4; N, 6.45. $C_4H_{22}B_{19}CsN_2$ requires C, 11.0; H, 5.10; B, 47.05; N, 6.40%). The tetramethylammonium salt was precipitated by adding 10% aqueous $[NMe_4]Cl$ (2 cm^3) to an aqueous solution of the potassium salt (200 mg). The precipitate was recrystallized from dichloromethane–hexane to afford pale yellow crystals of $[NMe_4][HCB_{10}H_{10}CN{=}NCB_9H_{10}CH]$ (189 mg, 80%).

Preparation of nido-nido *Dianions of Azocarbaborane Derivatives*.—A typical preparation is given here.

$HCB_9H_{10}CN{=}NCB_9H_{10}CH^{2-}$, (5a). A mixture of the potassium salt of (4a) (274 mg, 0.80 mmol), $K[OH]$ (90 mg, 1.6 mmol), and absolute ethanol (20 cm^3) was stirred at 50—55 °C for 8 h, and cooled. After removal of the solvent under reduced pressure, the residue was dissolved in water (10 cm^3) and the mixture filtered. The caesium salt was precipitated by addition of 20% aqueous CsCl (1 cm^3) to one-half its volume of the filtrate. The precipitate was collected and recrystallized from acetonitrile–dichloromethane to afford pale yellow crystals of $Cs_2[HCB_9H_{10}CN{=}NCB_9H_{10}CH]$, 152 mg (68%). The tetramethylammonium salt was precipitated by adding 10% aqueous $[NMe_4]Cl$ (2 cm^3) to the remainder of the filtrate. The precipitate was recrystallized from acetonitrile–dichloromethane to afford pale yellow crystals of $[NMe_4]_2[HCB_9H_{10}CN{=}NCB_9H_{10}CH]$, 125 mg (71%).

Preparation of $HCB_{10}H_{10}CCB_{10}H_{10}CNHNHCB_{10}H_{10}CCB_{10}H_{10}CH$, (2d). *Oxidation of* $HCB_{10}H_{10}CCB_{10}H_{10}CNH_2$ (1d) via *its Tetra-anionic Intermediate*.—The starting material (1d) (m.p. 240 °C, sublimes) was readily prepared from bis(*o*-carbaborane)[11] by a known *C*-amination method.[10] To a solution of (1d) (1.2 g, 4.0 mmol) in liquid NH_3 (*ca.* 30 cm^3) was slowly added, with stirring at −65 °C, Na metal (370 mg, 16 mg atoms) in small pieces. After a few minutes finely ground $K[MnO_4]$ (2.7 g, 17 mmol) was added in small portions over 5 min at −60 to −55 °C with vigorous stirring. Ammonia was removed by the same process as described for (3a) and the mixture was allowed to stand to warm to room temperature. The mixture was filtered to separate the dark green solid from the toluene solution. The solid was washed with three portions (40 cm^3) of acetone. The combined acetone solutions were rotary evaporated to give a dark red oily residue. This was dissolved in dichloromethane (25 cm^3), filtered from a small amount of black solid, and treated with 3 mol dm^{-3} hydrochloric acid (10 cm^3). A white solid was separated from the colourless liquid. This was filtered off, washed with water and dichloromethane, and recrystallized from methanol–benzene. White crystals of (2d) resulted (0.7 g, 58%). Infrared (Nujol mull): 3 365m (NH stretch), 2 585vs (BH stretch), 1 270m, 1 152w, 1 120w, 1 073m, 1 056m, 1 037m, 1 019m, 1 010w, 925w, 905w, 780w, 735m, and 719 cm^{-1}. $\lambda_{max.}$ (in methanol): 281 (3 510) and 398 nm (18 100 dm^3 mol^{-1} cm^{-1}); in C_6H_6, no maximum was observed above 250 nm. From the toluene solution separated above, 5% of the starting material, (1d), was recovered.

Isolation of $HCB_{10}H_{10}CCB_{10}H_{10}CNNHCB_{10}H_{10}CCB_{10}H_{10}$-$CH^-$ (2e) *and* $HCB_{10}H_{10}CCB_{10}H_{10}CNNCB_{10}H_{10}CCB_{10}H_{10}$-$CH^{2-}$ (2f).—Compound (2d) and excess of $[NMe_4]Cl$ were dissolved in 80% ethanol. Evaporation of ethanol precipitated an orange-red NMe_4 salt of (2e). Infrared (Nujol mull): 3 310w (NH stretch) 3 062w (CH stretch), 2 558vs (BH stretch), 1 510m, 1 485s, 1 417w, 1 347m, 1 240w, 1 155w, 1 123w, 1 073m, 1 053m, 1 030m, 1 015m, 1 005m, 948m, 926w, 908w, 855w, 732m, and 724 cm^{-1}. $\lambda_{max.}$ (in MeOH): 398 (17 600) and 281 nm (4 000 dm^3 mol^{-1} cm^{-1}). Similar treatment under basic conditions, precipitated the dark red $[NMe_4]_2$ salt of (2f). Infrared (Nujol mull): 3 040w (CH stretch), 2 600(sh) and 2 556vs (BH stretch), 1 495s, 1 485vs, 1 417w, 1 287w, 1 245w, 1 165w, 1 137w, 1 073m, 1 060m, 1 030m, 1 007w, 945m, 905w, 855w, 765m, 729m, and 720m cm^{-1}. $\lambda_{max.}$ (in MeOH): 398 (19 000) and 280 nm (4 500 dm^3 mol^{-1} cm^{-1}).

[0/1588 *Received*, *17th October*, 1980]

REFERENCES

[1] T. Totani, K. Aono, H. Nakai, and M. Shiro, *J. Chem. Soc., Chem. Commun.*, 1979, 1051.

[2] G. A. Olah, *J. Am. Chem. Soc.*, 1959, **81**, 3165.

[3] K. Aono and T. Totani, unpublished work.

[4] M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe, and P. A. Wegner, *J. Am. Chem. Soc.*, 1968, **90**, 862; M. F. Hawthorne, D. A. Owen, and J. W. Wiggins, *Inorg. Chem.*, 1971, **10**, 1304.

[5] D. S. Matteson and N. K. Hota, *J. Am. Chem. Soc.*, 1971, **93**, 2893.

[6] D. A. T. Young, T. E. Paxson, and M. F. Hawthorne, *Inorg. Chem.*, 1971, **4**, 786.

[7] D. S. Matteson and R. E. Grunzinger, jun., *Inorg. Chem.*, 1974, **13**, 671.

[8] K. Kumar and P. R. Carey, *Can. J. Chem.*, 1977, **55**, 1444.

[9] R. G. Alder and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1970, **92**, 6174.

[10] L. A. Polyakova, K. A. Bilevich, V. I. Bregadze, and O. Yu. Okhlobystin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1972, **8**, 1895.

[11] J. A. Dupont and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1964, **86**, 1643.