Preparation and Properties of Alkyl- and Aryl-substituted *closo-closo*- and *closo-nido*-Hydrazocarbaboranes

By **Katsutoshi Aono** and **Tetsushi Totani**, Shionogi Research Laboratories, Shionogi and Co., Ltd., Fukushima-ku, Osaka, 553 Japan

closo-closo-1,1′-Azo-*o*-carbaboranes $RCB_{10}H_{10}CN{=}NCB_{10}H_{10}CR$ react with alkyl- and aryl-lithiums to afford the derivatives $RCB_{10}H_{10}CNHNR'CB_{10}H_{10}CR$ (R = H, Me, or Ph; R′ = alkyl or aryl group) (3) along with the hydrazocarbaboranes $RCB_{10}H_{10}CNHNHCB_{10}H_{10}CR$ (2). Further substitution of these compounds with alkyl halides resulted in the formation of the *NN*′-disubstituted compound $RCB_{10}H_{10}CNR''NR'CB_{10}H_{10}CR$ (4). The *closo-closo* compounds (2) and (4) can be converted into the corresponding *closo-nido* ones in the presence of piperidine base. By means of variable-temperature ^1H n.m.r. spectroscopy, the free-energy barriers to conformational interconversion have been estimated [15.5 kcal mol^{-1} for (3e; R = Me, R′ = Et), >22 kcal mol^{-1} for (4b; R = H, R′ = R″ = Et), and (4e; R = Me, R′ = R″ = Et)]. In addition, the existence of interconvertible diastereoisomers has been evidenced for $RCB_{10}H_{10}CNMeNMeCB_9H_{10}CR^-$ (6a; R = H) and (6b; R = Me) for which the free energies of activation are also estimated.

EXTENSIVE studies on *closo*-1,2-dicarbadodecaboranes (o-$C_2B_{10}H_{12}$) and their *nido* derivatives have been carried out and reviewed.[1] Regarding azo- and hydrazo-derivatives of *o*-carbaboranes, no description has been hitherto found. Since the preparation of azocarbaboranes was reported in a previous communication,[2] we now describe the preparation and properties of the title compounds.

RESULTS AND DISCUSSION

Preparation of closo-closo-*Hydrazocarbaboranes*.—Addition of alkyl- or aryl-lithium to azocarbaboranes (1) at room temperature afforded *N*-monosubstituted hydrazocarbaboranes (3), along with hydrazocarbaboranes (2), Scheme 1. In practice, compounds (3) were obtained in good yields (78—97%) while compounds (2) were obtained in less than 5% yield (Table 1). The similar

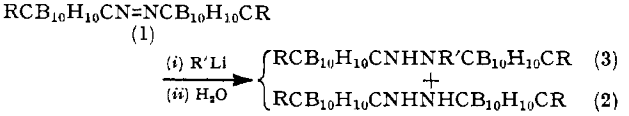
TABLE 1

Characterization data and yields for the *closo-closo*-hydrazocarbaboranes (3) and (4)

	Compound	M.p. (θ_c/°C)	Analytical (%) *				Yield (%)
			C	H	N	Other	
(3a)	$HCB_{10}H_{10}CNHNMeCB_{10}H_{10}CH$	228—230	18.35 (18.15)	8.10 (7.95)	8.50 (8.50)		95 (3a), 1.0 (2a)
(3b)	$HCB_{10}H_{10}CNHNEtCB_{10}H_{10}CH$	175—176	20.8 (20.9)	8.10 (8.20)	8.15 (8.15)		74 (3b), 8.0 (2a)
(3c)	$HCB_{10}H_{10}CNHNPhCB_{10}H_{10}CH$	207—208	29.95 (30.6)	7.45 (7.20)	7.15 (7.15)		80 (3c), 5.0 (2a)
(3d)	$MeCB_{10}H_{10}CNHNMeCB_{10}H_{10}CMe$	194—195	23.6 (23.45)	8.70 (8.45)	7.80 (7.80)		77 (3d), 16 (2b)
(3e)	$MeCB_{10}H_{10}CNHNEtCB_{10}H_{10}CMe$	156—157	25.85 (25.8)	8.75 (8.65)	7.65 (7.50)		53 (3e), 39 (2b)
(3f)	$MeCB_{10}H_{10}CNHNBu^nCB_{10}H_{10}CMe$	162—163	29.9 (30.0)	9.10 (9.05)	6.70 (7.00)	53.7 (B) (54.0)	5.0 (3f), 87 (2b)
(3g)	$MeCB_{10}H_{10}CNHNPhCB_{10}H_{10}CMe$	187—189	34.1 (34.25)	7.90 (7.65)	6.55 (6.65)		95 (3g), 1.7 (2b)
(3h)	$MeCB_{10}H_{10}CNHN(C_6H_4Cl\text{-}p)CB_{10}H_{10}CMe$	182—183	31.8 (31.65)	6.60 (6.85)	5.95 (6.15)	7.55 (Cl) (7.80)	97 (3h), 0 (2b)
(3i)	$MeCB_{10}H_{10}CNHN(C_6H_4NMe_2\text{-}p)CB_{10}H_{10}CMe$	188—189	36.2 (36.25)	8.05 (8.05)	9.05 (9.05)		78 (3i), 0 (2b)
(3j)	$PhCB_{10}H_{10}CNHNMeCB_{10}H_{10}CPh$	160—162	42.4 (42.3)	7.25 (7.10)	5.75 (5.80)		75 (3j), 70 (2c)
(3k)	$PhCB_{10}H_{10}CNHNPhCB_{10}H_{10}CPh$	224—226	48.65 (48.5)	7.00 (6.65)	5.10 (5.15)		83 (3k), 5.0 (2c)
(4a)	$HCB_{10}H_{10}CNMeNMeCB_{10}H_{10}CH$	176—178	21.1 (20.9)	8.35 (8.20)	8.25 (8.15)	62.25 (B) (62.75)	52
(4b)	$HCB_{10}H_{10}CNEtNEtCB_{10}H_{10}CH$	112—113	25.5 (25.8)	8.65 (8.65)	7.55 (7.50)	57.5 (B) (58.0)	47
(4c)	$MeCB_{10}H_{10}CNMeNMeCB_{10}H_{10}CMe$	257	25.6 (25.8)	8.70 (8.65)	7.55 (7.50)	57.6 (B) (58.05)	95
(4d)	$MeCB_{10}H_{10}CNBu^nNMeCB_{10}H_{10}CMe$	188—189	31.8 (31.85)	9.40 (9.25)	6.70 (6.75)		50
(4e)	$MeCB_{10}H_{10}CNEtNEtCB_{10}H_{10}CMe$	184—185	30.0 (30.0)	9.05 (9.05)	6.95 (7.00)		72
(4f)	$MeCB_{10}H_{10}CN(SO_2Me)NMeCB_{10}H_{10}CMe$	175	22.0 (22.0)	7.55 (7.40)	6.5 (6.4)	7.50 (S) (7.35)	45
(4g)	$MeCB_{10}H_{10}CNMeNPhCB_{10}H_{10}CMe$	192—193	33.5 (33.95)	7.80 (7.90)	6.55 (6.55)		95
(4h)	$MeCB_{10}H_{10}CNMeN(C_6H_4Cl\text{-}p)CB_{10}H_{10}CMe$	180—181	33.5 (33.3)	7.10 (7.10)	6.10 (5.95)	7.70 (Cl) (7.55)	97

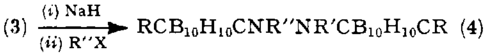
* Calculated values are given in parentheses.

reaction of azobenzene with phenyl-lithium indicated that the yield of *NNN'*-triphenylhydrazine was at most 20% and that the major product was hydrazobenzene.[3] The facile formation of (3) seems rather strange since the *o*-carbaboranyl group which possesses a nearly icosahedral structure is obviously very much bulkier than the phenyl group. It is understood, therefore, that the strong electron-withdrawing property of the *o*-carbaboranyl group decreases the electron density of the azo-nitrogen atoms of (1) and subsequently facilitates the nucleophilic attack of the R' anion. In the addition of alkyl-lithiums, the yield of (3) varied with the alkyl chain length. For example, the addition of methyl-, ethyl-, and n-butyl-lithium to (1b; R = Me) yielded 77% of (3d), 53% of (3e), and 5% of (3f) respectively (see Table 1). In addition, 1-methyl-*o*-carbaboranyl-lithium did not react with (1b). *N*-Metallation of (3) followed by treatment with alkyl halides resulted in *NN'*-disubstituted hydrazocarbaboranes (4), Scheme 2. In a similar alkylation, (2) can be converted into (3) which on further alkylation leads to (4). Tables 1 and 2 give the characterization data for (3) and (4).



$$\underset{(1)}{RCB_{10}H_{10}CN{=}NCB_{10}H_{10}CR} \xrightarrow[(ii)\ H_2O]{(i)\ R'Li} \left\{\begin{array}{ll} RCB_{10}H_{10}CNHNR'CB_{10}H_{10}CR & (3) \\ \quad + & \\ RCB_{10}H_{10}CNHNHCB_{10}H_{10}CR & (2) \end{array}\right.$$

SCHEME 1



$$(3) \xrightarrow[(ii)\ R''X]{(i)\ NaH} RCB_{10}H_{10}CNR''NR'CB_{10}H_{10}CR\ (4)$$

SCHEME 2

TABLE 2

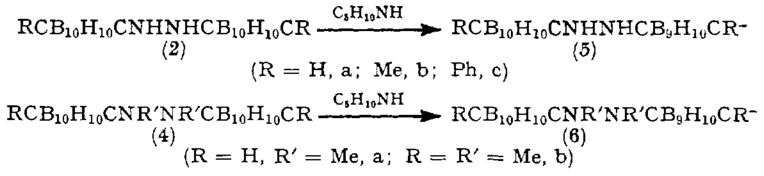
Hydrogen-1 n.m.r. data[a] for $RCB_{10}H_{10}CNHNR'CB_{10}H_{10}CR$ (3) and $RCB_{10}H_{10}CNR''NR'CB_{10}H_{10}CR$ (4)

	R	R'	R''	
(2a)	H	H		4.92 (br,s) (2 H) N–H 3.82 (vbr,s) (2 H) C–H
(3a)	H	Me		4.20 (br,s) (1 H) N–N 3.97 (vbr,s) (2 H) C–H, C–H 2.87 (s) (3 H) N–Me
(3b)	H	Et		4.85 (br,s) (1 H) N–H 3.95 (vbr,s) (2 H) C–H, C–H 3.43 } (A_2X_3 pattern) (5 H) 1.12 } N–Et
(3c)	H	Ph		7.33 (m) (5 H) N–Ph 5.38 (br,s) (1 H) N–H 3.93 } (vbr,d) (2 H) C–H, 3.63 } C–H
(2b)	Me	H		4.93 (br,s) (2 H) N–H 2.08 (s) (6 H) C–Me
(3d)	Me	Me		4.33 (br,s) (1 H) N–H 3.07 (s) (3 H) N–Me 2.13 } (2 × s) (3 H, 3 H) C–Me, 2.10 } C–Me
(3e)	Me	Et		4.94 (br,s) (1 H) N–H 2.14 } (2 × s) (3 H, 3 H) 2.11 } C–Me, C–Me 3.65 } (ABX_3 pattern) (5 H) 1.24 } N–Et
(3f)	Me	Bu^n		4.93 (br,s) (1 H) N–H 3.05— 3.83[b] (2 H) $N–CH_2–$ 2.13 } (2 × s) (3 H, 3 H) 2.10 } C–Me, C–Me 0.67— 1.91[b] (7 H) $–CH_2CH_2CH_3$
(3g)	Me	Ph		7.33 (m) (5 H) N–Ph 5.63 (br,s) (1 H) N–H 2.39 } (2 × s) (3 H, 3 H) 2.03 } C–Me, C–Me
(3h)	Me	C_6H_4Cl-*p*		7.37 } (A_2B_2 pattern) (4 H) 7.17 } $N–C_6H_4Cl$-*p* 5.53 (br,s) (1 H) N–H 2.37 } (2 × s) (3 H, 3 H) 2.07 } C–Me, C–Me
(3i)	Me	$C_6H_4NMe_2$-*p*		7.03 } (A_2B_2 pattern) (4 H) 6.63 } $N–C_6H_4NMe_2$-*p* 5.50 (br,s) (1 H) N–H 3.00 (s) (6 H) NMe_2 2.37 } (2 × s) (3 H, 3 H) 2.03 } C–Me, C–Me
(2c)	Ph	H		7.44 (m) (10 H) C–Ph 4.37 (br,s) (2 H) N–H
(3j)	Ph	Me		7.50 (m) (10 H) C–Ph, C–Ph 4.08 (br,s) (1 H) N–H 2.70 (s) (3 H) N–Me
(3k)	Ph	Ph		7.33 (m) (15 H) C–Ph, C–Ph, N–Ph 5.12 (br,s) (1 H) N–H
(4a)	H	Me	Me	3.97 (vbr,s) (2 H) C–H, C–H 2.80 (s) (6 H) C–Me, C–Me
(4b)	H	Et	Et	3.95 (vbr,s) (2 H) C–H, C–H 3.30 } (ABX_3 pattern) (10 H) 1.33 } N–Et, N–Et
(4c)	Me	Me	Me	2.90 (s) (6 H) N–Me 2.08 (s) (6 H) C–Me
(4d)	Me	Me	Bu^n	2.98 (3 H) N–Me 2.93— 3.33[c] $N–CH_2–$ 2.12 } (2 × s) (3 H, 3 H) 2.08 } C–Me, C–Me 0.71— 1.63[b] (7 H) $–CH_2CH_2CH_3$
(4e)	Me	Et	Et	2.12 (s) (6 H) C–Me, C–Me 3.50 } (ABX_3 pattern) (10 H) 1.43 } N–Et, N–Et
(4f)	Me	Me	SO_2Me	3.43 (s) (3 H) SO_2Me 3.39 (s) (3 H) N–Me 2.23 } (2 × s) (3 H, 3 H) 2.17 } C–Me, C–Me
(4g)	Me	Ph	Me	7.45 (m) (5 H) N–Ph 3.37 (s) (3 H) N–Me 2.00 } (2 × s) (3 H, 3 H) 2.42 } C–Me, C–Me
(4h)	Me	C_6H_4Cl-*p*	Me	7.47 (m) (4 H) $N–C_6H_4Cl$-*p* 3.30 (s) (3 H) N–Me 2.37 } (2 × s) (3 H, 3 H) 2.02 } C–Me, C–Me

[a] δ(p.p.m.), from $SiMe_4$ in $CDCl_3$, relative area, and assignment. [b] Featureless signal. [c] Overlapped.

Preparation of closo-nido-*Hydrazocarbaboranes*.—Symmetric hydrazocarbaboranes (2)[2] and (4) can be degraded to yield the corresponding *closo-nido*-hydrazocarbaborane monoanions (5) and (6) respectively by treating them with piperidine base, Scheme 3.[4] Despite the high temperature (up to 80 °C) and prolonged reaction time (*ca.* 20 h), the *nido-nido* compound was not obtained. The hydrazo-group of the monoanions (5) is readily azotized in air. Table 3 lists the characterization data and yields for the *closo-nido*-hydrazocarbaboranes (5) and (6). Hydrogen-1 n.m.r. data of (5) and (6) are summarized in Table 4.

*Hydrogen-*1 *N.M.R. Spectra of* closo-closo-*Hydrazocarb-*



$$\underset{(2)}{RCB_{10}H_{10}CNHNHCB_{10}H_{10}CR} \xrightarrow{C_5H_{10}NH} \underset{(5)}{RCB_{10}H_{10}CNHNHCB_9H_{10}CR^-}$$

(R = H, a; Me, b; Ph, c)

$$\underset{(4)}{RCB_{10}H_{10}CNR'NR'CB_{10}H_{10}CR} \xrightarrow{C_5H_{10}NH} \underset{(6)}{RCB_{10}H_{10}CNR'NR'CB_9H_{10}CR^-}$$

(R = H, R′ = Me, a; R = R′ = Me, b)

SCHEME 3

TABLE 3

Characterization data and yields for the *closo-nido*-hydrazocarbaboranes (5) and (6)

	Compound	M.p. (θ_c/°C)	Analytical (%) * C	H	N	Other	Yield (%)
(5a)	$[C_5H_{10}NH_2][HCB_{10}H_{10}CNHNHCB_9H_{10}CH]$	212—213 (decomp.)	27.85 (27.6)	9.20 (9.20)	10.6 (10.6)		71
(5b)	$[C_5H_{10}NH_2][MeCB_{10}H_{10}CNHNHCB_9H_{10}CMe]$	199—201 (decomp.)	31.75 (31.45)	9.80 (9.60)	9.75 (10.0)		69
(5c)	$[C_5H_{10}NH_2][PhCB_{10}H_{10}CNHNHCB_9H_{10}CPh]$	205—207 (decomp.)	46.3 (46.35)	8.45 (8.15)	7.70 (7.70)		87
(6a)	$[NMe_4][HCB_{10}H_{10}CNMeNMeCB_9H_{10}CH]$	>300	29.25 (29.45)	10.20 (9.90)	10.55 (10.3)	50.0 (B) (50.35)	75
(6b)	$[NMe_4][MeCB_{10}H_{10}CNMeNMeCB_9H_{10}CMe]$	>300	33.0 (33.05)	10.15 (10.15)	9.75 (9.65)	46.3 (B) (47.1)	90

* Calculated values are given in parentheses.

TABLE 4

Hydrogen-1 n.m.r. data[a] for $RCB_{10}H_{10}CNHNHCB_9H_{10}CR^-$ (5) and $RCB_{10}H_{10}CNR'NR'CB_9H_{10}CR^-$ (6)

	R	R′	Solvent	
(5a)[b]	H		CD_3COCD_3	5.12 (br,s) (1 H) N–H (*closo*) 4.38 (br,s) (1 H) N–H (*nido*) 4.27 (vbr,s) (1 H) C–H (*closo*) 3.43 (s,) (12 H) NMe_4^+ ion 1.97 (vbr,s) (1 H) C–H (*nido*)
(5b)[b]	Me		$[^2H_5]$pyridine	6.87 (br,s) (1 H) N–H (*closo*) 5.57 (br,s) (1 H) N–H (*nido*) 3.30 (sh,s)[c] (12 H) NMe_4^+ ion 2.08 (s) (3 H) C–Me (*closo*) 2.02 (s) (3 H) C–Me (*nido*)
(5c)[d]	Ph		CD_3CN	7.37 (m)[d] (5 H) C–Ph (*closo*) 7.07[e] (5 H) C–Ph (*nido*) 4.57 (br,s) (1 H) N–H (*closo*) 3.73 (br,s) (1 H) N–H (*nido*) 3.11[e] (4 H) piperidinium ion 1.70[e] (6 H) piperidinium ion
(6a)[b]	H	Me	CD_3OD	4.38 (vbr,s) (1 H) C–H (*closo*) 2.76 (s) ($\sim\frac{3}{2}$ H), 2.70 (s) ($\sim\frac{3}{2}$ H) } N–Me (*closo*) 2.46 (s) ($\sim\frac{3}{2}$ H), 2.44 (s) ($\sim\frac{3}{2}$ H) } N–Me (*nido*) 2.07 (br,s) (1 H) C–H (*nido*)
(6b)[b]	Me	Me	CD_3OD	3.20 (s) (12 H) NMe_4^+ ion 2.90 (s) ($\sim\frac{9}{4}$ H), 2.82 (s) ($\sim\frac{3}{4}$ H) } N–Me (*closo*) 2.57 (s) ($\sim\frac{9}{4}$ H), 2.43 (s) ($\sim\frac{3}{4}$ H) } N–Me (*nido*) 2.33 (s) ($\sim\frac{3}{4}$ H), 2.05 (s) ($\sim\frac{9}{4}$ H) } C–Me (*closo*) 1.50 (s) ($\sim\frac{9}{4}$ H), 1.45 (s) ($\sim\frac{3}{4}$ H) } C–Me (*nido*)

[a] δ/p.p.m., relative area, assignment. [b] Tetramethylammonium salt. [c] Sharp singlet. [d] Piperidinium salt. [e] Featureless signal.

aboranes.—The *o*-carbaboranyl group interacts with the *C*-substituents, mainly through an inductive mechanism.[5] A similar interaction of the amino-nitrogen atom with the *o*-carbaboranyl group was suggested by the ^{13}C n.m.r. study of the *C*-amino-*o*-carbaborane.[6] Some properties of the *C*-amino-group in *C*-amino-*o*-carbaboranes revealed a similarity to those of aliphatic amines.[7] These may assume a bipyramidal geometry for the *closo-closo*-hydrazocarbaboranes. The idealized *staggered* conformations and their mirror images are shown in Figure 1 as Ia—If. Each conformation is drawn by arbitrarily adopting *ca.* 60° dihedral angles.

The ^1H n.m.r. spectra of the *closo-closo*-hydrazocarbaboranes at room temperature did not show any sign of the existence of diastereomeric isomers. Compound (4c) in CD_2Cl_2 solution was cooled to −90 °C, but the n.m.r. spectrum remained essentially unchanged. A significant broadening of the *N*-methyl signal observed at −90 °C might be due to a slowing down of the $N-CH_3$ bond rotation[8] and partial collapsing of the B–H signals is due to the quadrupole induced $^1H-^{10}B,^{11}B$ spin decoupling.[9] The n.m.r. results do not always prove the existence of only one stable conformer because a rapid exchange among *gauche* lone-pair conformers Ia $\rightleftharpoons$ Ib $\rightleftharpoons$ Ic $\rightleftharpoons$ Id, even if they exist, may take place through the non-eclipsing inversion processes whose known barriers for alkylated hydrazines are relatively low ($\Delta G^\ddagger$ = 6.8—8.2 kcal mol^{-1} *).[10]

A molecular model for (4c) assumed to have normal bond angles and bond lengths similar to those of hydrazine itself suggests unlike conformations of Ib, Ic, Id, and If in which a severe non-bonded interaction between *gauche* *o*-carbaboranyl groups having a nearly icosahedral structure would exist. In most of the acyclic alkyl hydrazines, electronic repulsion of the lone pairs excludes

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* Throughout this paper: 1 cal = 4.184 J.

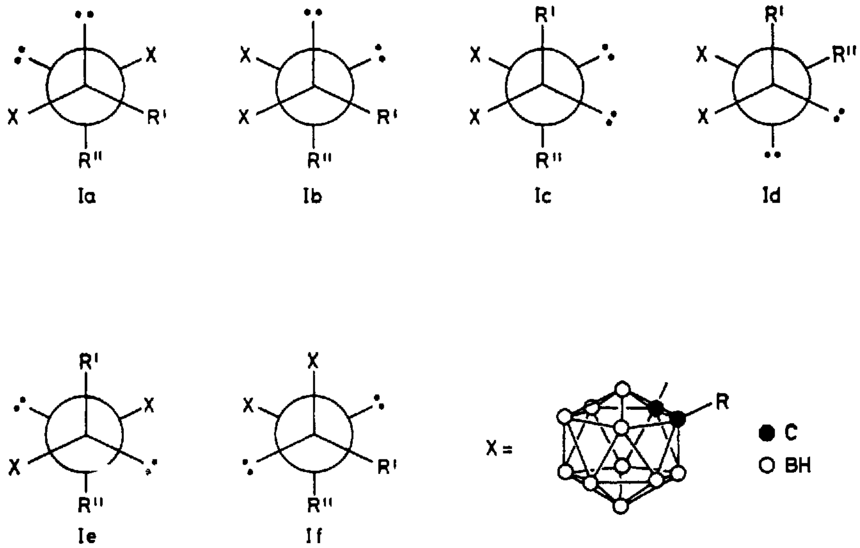

FIGURE 1 Possible staggered conformations for *closo*-*closo*-hydrazocarbaboranes. Each mirror image is abbreviated

significant populations of *trans* lone-pair conformations.[10] Since, in the present compound, any special electronic or electrostatic interactions to stabilize *trans* lone-pair conformations are improbable, the conformation Ie, although sterically favourable, is not preferred. Thus the remaining *gauche* lone-pair conformation, Ia, may be expected to be the most stable one.* The ^1H n.m.r. spectrum of the ethyl group of the *N*-ethyl derivatives $MeCB_{10}H_{10}CNHNEtCB_{10}H_{10}CMe$ (3e), $HCB_{10}H_{10}CNEtNEtCB_{10}H_{10}CH$ (4b), and $MeCB_{10}H_{10}CNEtNEtCB_{10}H_{10}CMe$ (4e) exhibited an ABX_3 pattern at room temperture. On raising the temperature, the ABX_3 pattern of the compound (3e) changed to an A_2X_3 pattern below 70 °C but those of (4b) and (4e) remained essentially unchanged until 160 °C (upper temperature limit in $C_2D_2Cl_4$ solution). At room temperature, with irradiation at the frequency of the X_3 part triplet, the complicated AB part changed to a simple AB type quartet. On increasing the temperature, with the irradiation kept constant, the AB quartet of (3e) coalesced to a singlet (Figure 2) as expected.

The ^1H n.m.r. behaviour described above suggests that these compounds have substantial energy barriers to interconversion between mirror-image conformations of an enantiomeric mixture. Since, like (4c), these *N*-ethyl derivatives are probably predominant in the bipyramidal *gauche* lone-pair conformation Ia (Figure 1) and its mirror image in the ground state, the interconversion between the enantiomers may proceed by either two eclipsing inversions or the combination of a low-energy rotation and a non-eclipsing inversion.[10] Such an interconversion exchanges the magnetic environments of the prochiral methylene protons of the ethyl group. It seems unlikely that the non-equivalence of the methylene protons is caused merely by hindered rotation of the N-CH_2 bond, because if the molecular rigidity is lost by the rapid interconversion process described above, the N-CH_2 bond may also be rotated rapidly accompanied by relaxing of steric hindrance during the process. The estimated free-energy barriers ($\Delta G^\ddagger$) are 15.5 kcal mol^{-1} for (3e) and >22 kcal mol^{-1} for (4b) and (4e) (Table 5), which are considerably higher than the barriers (*ca.* 11 kcal mol^{-1}) for bipyramidal alkylated hydrazines.[11]

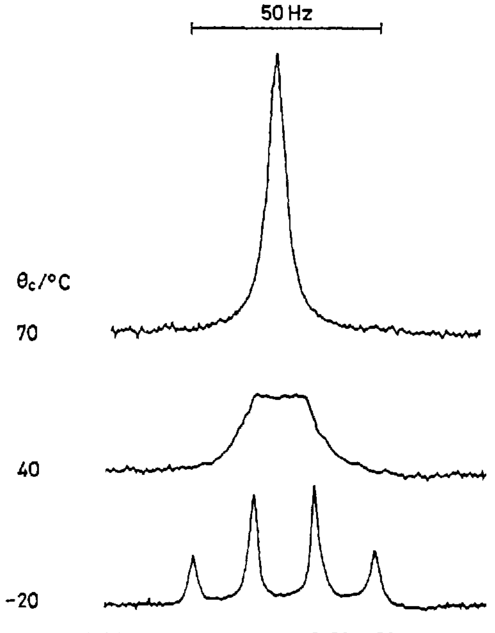

FIGURE 2 Variable-temperature 100 MHz ^1H n.m.r. spectra of the methylene protons of the *N*-ethyl group of (3e) with irradiation at the frequency of the methyl resonance

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* An *X*-ray diffraction study of $MeCB_{10}H_{10}CNMeNMeCB_{10}H_{10}CMe$ (4c) indicates that the nitrogen atoms assume a bipyramidal geometry, the lone pairs occupy nearly perpendicular positions, and the two *o*-carbaboranyl groups occupy *trans* positions, corresponding to Ia in Figure 1 where R = R′ = R″ = Me (M. Shiro, personal communication).

TABLE 5

Hydrogen-1 n.m.r. parameters and free-energy barriers to the conformational interconversion in *closo-closo*-[(3e), (4b), and (4e)] and *closo-nido*-hydrazocarbaboranes [(6a) and (6b)]

Compound	Solvent	$\|\Delta\nu_{AB}\|$/Hz	J_{AB}/Hz ($\pm$0.2)	T_c/K ($\pm$2)	$\Delta G^\ddagger$ at T_c/ kcal mol^{-1}
(3e)	$CDCl_3$	28.2 [a]	16.0	313 [b]	15.5 $\pm$ 0.5 [c]
(4b)	$C_2D_2Cl_4$	23.4 [a]	14.5	>433	>22 [d]
(4e)	$C_2D_2Cl_4$	22.4 [a]	15.0	>433	>22 [d]
			Ratio of isomers		
(6a) [e]	[$^2H_5$]pyridine	2.0 [f]	1 : 1	358	20.0 $\pm$ 0.2 [d]
(6b) [e]	[$^2H_5$]pyridine	17.7 [g]	1 : 3	360	19.5 $\pm$ 0.2 [d]
					18.7 $\pm$ 0.2 [d]

[a] Refers to methylene protons of *N*-ethyl group at 100 MHz ($\pm$0.5 Hz). [b] The coalescence temperature (T_c) was determined from the decoupled spectra. [c] Calculated at the coalescence temperature T_c using appropriate expressions for the exchange rate at the coalescence temperature, $k_c = \pi(\Delta\nu_{AB}^2 + 6J_{AB}^2)^{\frac{1}{2}}/\sqrt{2}$. [d] Calculated at the coalescence temperature T_c based upon the rate at which the computed line shape shows coalescence. [e] Potassium salt. [f] Refers to *N*-methyl signals (b in Figure 3) at 60 MHz. The value given was extrapolated from low-temperature measurements ($\pm$0.3 Hz). [g] Refers to *C*-methyl signals (c in Figure 4) at 60 MHz. The value given was extrapolated from low-temperature measurements ($\pm$0.5 Hz).

Exceptionally, the ethyl group resonance of $HCB_{10}H_{10}CNHNEtCB_{10}H_{10}CH$ (3b) appeared as an A_2X_3 pattern at room temperature (Table 2), and down to −90 °C. At low temperatures a significant broadening of the A_2 part was observed but it was accompanied by a similar broadening of the X_3 part, therefore it could be regarded as some other process. Considering the free-energy barrier of *ca.* 15.5 kcal mol^{-1} for (3e), a lower barrier to the corresponding interconversion process in (3b) would be unlikely, since the methyl group in (3e) can be oriented to a site of minimum steric interaction by $CH_3CB_{10}H_{10}C$–N bond rotation and so a large difference in terms of steric effects between the $CH_3CB_{10}H_{10}C$ and $HCB_{10}H_{10}C$ moieties is improbable. Therefore, the observed A_2X_3 pattern for (3b), especially at low temperature, may be attributable to an accidental very small chemical-shift difference between the methylene protons.

*Hydrogen-*1 *N.M.R. Spectra of* closo-nido-*Hydrazocarbaboranes*.—The ^1H n.m.r. data of the *closo-nido* derivatives at room temperature are summarized in Table 4. Interestingly, the spectrum of $HCB_{10}H_{10}CNMeNMeCB_9H_{10}CH^-$ (6a) exhibited two couples of nearly equal-intensity signals due to the methyl groups at different magnetic environments. The very broad signals of C–H protons had apparently one maximum. Variable-temperature n.m.r. spectra in [$^2H_5$]pyridine solution indicated that each doublet coalesced to a singlet at higher temperatures (Figure 3).

Spectral patterns of $MeCB_{10}H_{10}CNMeNMeCB_9H_{10}CMe^-$ (6b) resemble those of (6a); the spectrum at room temperature in CD_3OD solution consisting of four methyl signals possessing the same integrated intensity at δ 2.90, 2.57, 2.05, and 1.50 p.p.m., besides the rather weak satellite lines having the same intensity as one another (Table 4). Variable-temperature n.m.r. spectra in [$^2H_5$]pyridine solution indicated coalescence of each pair at higher temperatures (Figure 4). No splitting at room temperature, and unusual slight broadening at higher

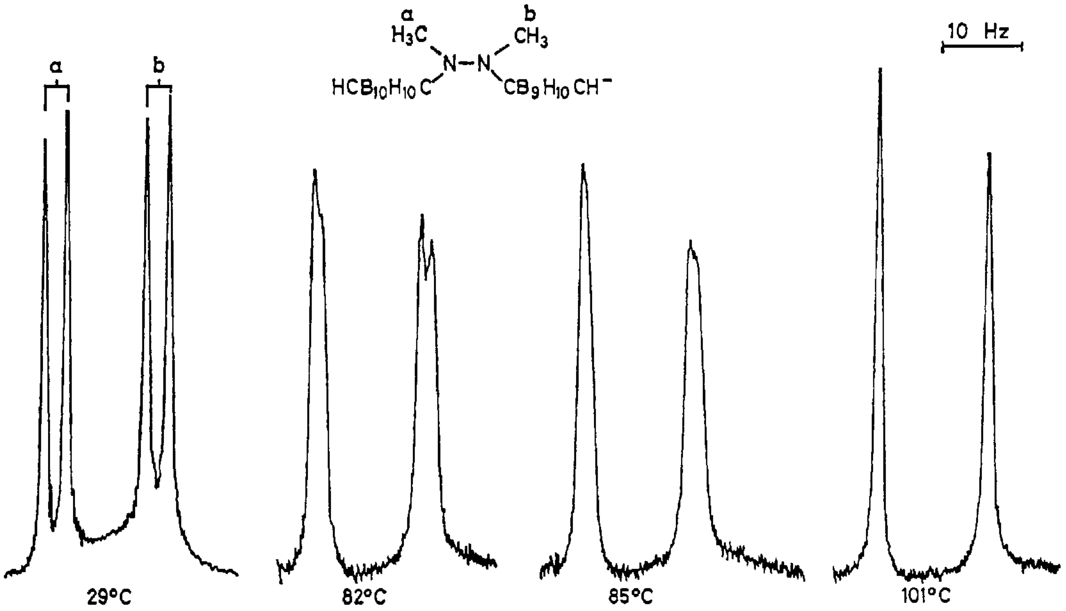

FIGURE 3 Variable-temperature 60 MHz ^1H n.m.r. spectra of the methyl groups of (6a) in [$^2H_5$]pyridine solution. A broad CH(*nido*) signal overlaps with the methyl signal

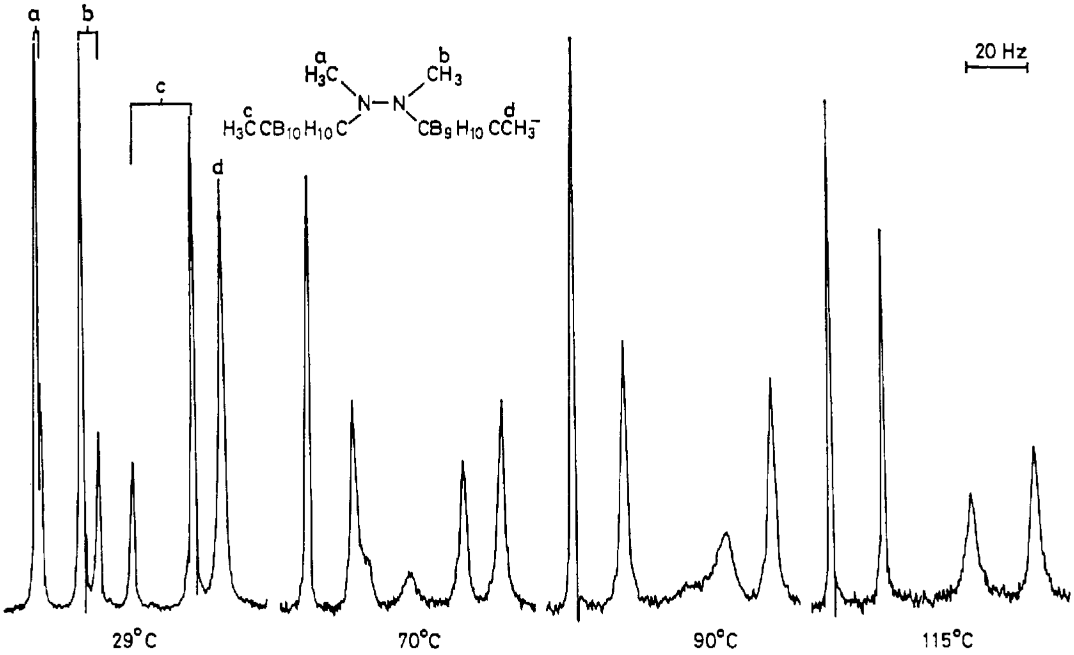

FIGURE 4 Variable-temperature 60 MHz ^1H n.m.r. spectra of the methyl groups of (6b) in $[^2H_5]$pyridine solution

temperatures, of the C–Me (*nido*) resonance were observed in $[^2H_5]$pyridine solution. The free-energy barriers to these exchange processes were calculated from a comparison of the observed and calculated spectral line shapes [(6a): 20.0 kcal mol^{-1}, (6b): 19.5 kcal mol^{-1} (for the process major isomer to minor isomer), 18.7 kcal mol^{-1} (for the reverse process)] (Table 5).

The above temperature-dependent n.m.r. behaviour may be associated with the existence of two interconvertible diastereoisomers which result from chirality around the nitrogen atoms and chirality of the *nido* ion. In the degradation of the *o*-carbaboranyl group (X) with piperidine, two enantiomeric *nido* ions (Y and Y′) must be formed by removal of the boron-3 atom and the boron-6 atom respectively (Figure 5). Accordingly, when the XNR′NR′ moiety of the *closo-nido*-hydrazocarbaboranes exists in a pair of enantiomeric conformations, in combination with enantiomeric *nido* ions, there exist four stereoisomers (IIA, IIA′, IIB, and IIB′) in which two diastereoisomeric pairs of enantiomers exist, see Figure 5. When a rate of interconversion between enantiomeric XNR′NR′ moieties, *i.e.* IIA $\rightleftharpoons$ IIB (and its mirror image set IIA′ $\rightleftharpoons$ IIB′), is slow on the n.m.r. time scale, two kinds of signals corresponding to each diastereoisomer IIA (IIA′) and IIB (IIB′) must be observable, as in the case for (6a) and (6b). Because of uncertainty over the proposed bipyramidal *gauche* lone-pair conformation (Figure 5), although it is the preferred one as regards steric interaction between the two bulky groups (X and Y or Y′) as well as the electronic repulsions between the lone pairs, it is difficult to assign the n.m.r. signals to each diastereoisomer at present. It should be noted that when the XNR′NR′ moiety exists in more than two diastereoisomeric and chiral conformations which are separated by a substantial energy barrier, in combination with a chiral *nido* ion, more than four diastereoisomers would exist. This being so, many

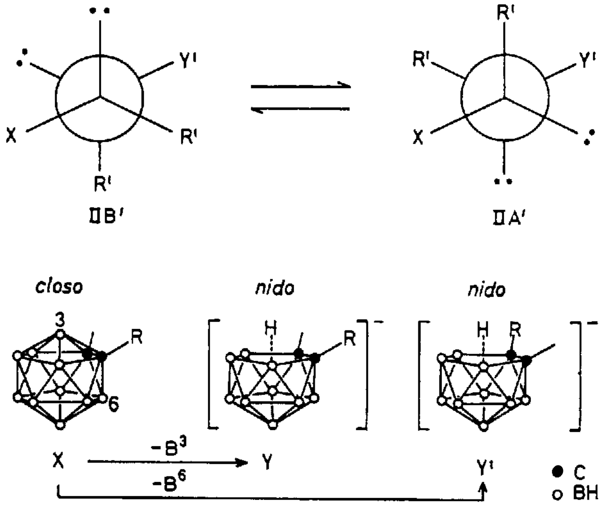

FIGURE 5 Possible interconvertible diastereoisomers of *closo-nido*-hydrazocarbaboranes (R′ = H or Me). The upper set (IIA, IIB) and lower set (IIA′, IIB′) are enantiomeric to one another but are not interconvertible because of the rigid configuration of the *nido* ions

signals would be observable in the n.m.r. spectrum, therefore this is not the case. In addition, none of the *closo-nido* derivatives has an absorption maximum above 200 nm, which suggests little mesomeric electron delocalization through the C(*closo*)–N–N–C(*nido*) linkage, caused by geometrical isomers such as *cis,trans* types.

Unlike *NN′*-dimethyl derivatives, the ^1H n.m.r. spectra of unsubstituted compounds $RCB_{10}H_{10}CNHNH$-$CB_9H_{10}CR^-$ (5a—c) did not show any isomeric signals in various solvents or down to −40 °C for (5b) in [$^2H_5$]-pyridine solution. The results presumably suggest a considerably lower energy barrier to the interconversion described above in these compounds.

EXPERIMENTAL

All reactions were carried out under an atmosphere of nitrogen. *closo-closo*-Azocarbaboranes were prepared by the method described previously.[2] Alkyl- and aryl-lithium compounds were prepared by literature methods.[12] Solvents used were dried and purified by standard methods. Hydrogen-1 n.m.r. spectra were obtained with Varian EM-360L, T-60, or Varian XL-100-12A spectrometers equipped with a variable-temperature accessory. Infrared spectra were recorded on a Japan Spectroscopic Co. DS-402G spectrometer.

Preparation of N-*Monosubstituted Hydrazocarbaboranes* (3) *by Reaction of Azocarbaborane* (1) *with Alkyl- and Aryl-lithium*.—$HCB_{10}H_{10}CNHNMeCB_{10}H_{10}CH$, (3a). To a solution of $HCB_{10}H_{10}CN{=}NCB_{10}H_{10}CH$ (1a) (314 mg, 1 mmol) in dry benzene (30 cm^3) was added a diethyl ether solution of methyl-lithium (5 mmol) dropwise for 5 min at room temperature. The resulting yellow solution was continuously stirred for 1 h and was cooled on an ice-bath. To the cooled solution was added saturated aqueous [NH_4]Cl (2 cm^3); the resulting mixture was stirred vigorously until the yellow colour vanished. The organic layer was decanted, dried over $Na_2[SO_4]$, and concentrated to near dryness. The residue was chromatographed on silica gel using dichloromethane–hexane (1 : 3) as eluant and recrystallized from hexane to afford colourless crystals of (3a) (315 mg, 95%). Subsequent elution with dichloromethane, followed by evaporation of the solvent, gave colourless crystals (3 mg) whose melting point and i.r. spectrum were identical to that of hydrazocarbaborane $HCB_{10}H_{10}CNHNHCB_{10}H_{10}CH$ prepared by the reduction of (1a). Similar reactions of (1a) with ethyl- and phenyl-lithium afforded $HCB_{10}H_{10}CNHNEtCB_{10}H_{10}CH$ (3b) and $HCB_{10}H_{10}CNHNPhCB_{10}H_{10}CH$ (3c) respectively, along with (2a), while reactions of $MeCB_{10}H_{10}CN{=}NCB_{10}H_{10}CMe$ (1b) with methyl-, ethyl-, n-butyl-, phenyl-, *p*-chlorophenyl-, and *p*-dimethylaminophenyl-lithium afforded $MeCB_{10}H_{10}$-$CNHNMeCB_{10}H_{10}CMe$ (3d), $MeCB_{10}H_{10}CNHNEtCB_{10}H_{10}$-$CMe$ (3e), $MeCB_{10}H_{10}CNHNBu^nCB_{10}H_{10}CMe$ (3f), $MeCB_{10}$-$H_{10}CNHNPhCB_{10}H_{10}CMe$ (3g), $MeCB_{10}H_{10}CNHN(C_6H_4Cl$-*p*$)CB_{10}H_{10}CMe$ (3h), and $MeCB_{10}H_{10}NHN(C_6H_4NMe_2$-*p*$)$-$CB_{10}H_{10}CMe$ (3i) respectively, along with $MeCB_{10}H_{10}CNHN$-$HCB_{10}H_{10}CMe$ (2b). Reaction of $PhCB_{10}H_{10}CN{=}NCB_{10}H_{10}$-$CPh$ (1c) with methyl- and phenyl-lithium afforded $PhCB_{10}$-$H_{10}CNHNMeCB_{10}H_{10}CPh$ (3j) and $PhCB_{10}H_{10}CNHNPh$-$CB_{10}H_{10}CPh$ (3k) respectively, along with $PhCB_{10}H_{10}CN$-$HNHCB_{10}H_{10}CPh$ (2c).

Alkylation of Hydroazocarbaboranes.—$MeCB_{10}H_{10}CNHN$-$Bu^nCB_{10}H_{10}CMe$, (3f). To a stirred solution of (2b) (160 mg, 0.47 mmol) in tetrahydrofuran (3 cm^3), was added n-butyl-lithium (0.25 cm^3 of 2 mol dm^{-3} hexane solution) at 20 °C. After 5 min, freshly distilled n-butyl iodide (1 cm^3) was added. The mixture was refluxed for 20 h. After cooling, benzene (7 cm^3) and saturated aqueous [NH_4]Cl (1 cm^3) were added. The benzene layer was separated, washed with water, dried over $Na_2[SO_4]$, and concentrated to give an oily residue. The residue was recrystallized from hexane to afford colourless crystals of (3f) (102 mg, 53%).

Preparation of NN′-*Disubstituted Hydrazocarbaboranes* (4).—Several typical preparative procedures are given below.

$HCB_{10}H_{10}CNMeNMeCB_{10}H_{10}CH$, (4a). To a stirred solution of (3a) (165 mg, 0.5 mmol) in tetrahydrofuran (3 cm^3) was added NaH (0.5 mmol, 24 mg of 50% oil-coated dispersion) in small portions, at 0—5 °C under nitrogen. The mixture was stirred until the evolution of H_2 ceased, then freshly distilled methyl iodide (0.5 cm^3) was added. The mixture was stirred at room temperature for 6 h. To the resulting mixture was added benzene (10 cm^3) and the mixture filtered. The filtrate was evaporated using a rotary evaporator. The residue was chromatographed on silica gel using dichloromethane–hexane (1 : 9) as the eluant and recrystallized from hexane to afford colourless crystals of (4a) (88 mg, 51%). Infrared (Nujol mull): 3 060m, 2 650(sh), 2 600(sh), 2 570vs, 2 540(sh), 1 260w, 1 255w, 1 190m, 1 153m, 1 120w, 1 095w, 1 070m, 1 010s, 935w, 885m, 860w, 820w, 730(sh), 720 cm^{-1}.

$HCB_{10}H_{10}CNEtNEtCB_{10}H_{10}CH$, (4b). To a stirred solution of (3b) (80 mg, 0.23 mmol) in tetrahydrofuran (2 cm^3) was added NaH (0.24 mmol) at 0—5 °C under nitrogen. After H_2 evolution had ceased, ethyl iodide (0.25 cm^3) was added. The mixture was heated at 65 °C for 12 h and cooled. To the resulting mixture was added benzene (5 cm^3) and the mixture filtered. The filtrate was evaporated. The oily residue was chromatographed on silica gel using hexane as eluant and recrystallized from pentane to afford colourless crystals of (4b) (40 mg, 47%).

$MeCB_{10}H_{10}CNBu^nNMeCB_{10}H_{10}CMe$, (4d). To a tetrahydrofuran solution (1.5 cm^3) prepared from (3d) (72 mg, 0.2 mmol) and NaH (0.21 mmol), was added n-butyl iodide (0.2 cm^3) in essentially the same manner as described above. The mixture was refluxed for 36 h under nitrogen. After cooling, benzene (5 cm^3) was added and the resulting mixture filtered. The filtrate was evaporated and the residue was crystallized from pentane to afford colourless crystals of (4d) (41 mg, 50%).

$MeCB_{10}H_{10}CN(SO_2Me)NMeCB_{10}H_{10}CMe$, (4f). To a stirred tetrahydrofuran solution (2 cm^3) prepared from (3d) (80 mg, 0.22 mmol) and NaH (0.24 mmol) was added methylsulphonyl chloride (60 mg, 0.52 mmol) at 0—5 °C. The mixture was stirred for 20 min at 0—5 °C, then benzene added (10 cm^3). The mixture was filtered at room temperature and the filtrate was evaporated to dryness. The residue was dissolved in dichloromethane–hexane (1 : 1) and chromatographed on silica gel. Recrystallization from dichloromethane–hexane gave colourless crystals of (4f) (43 mg, 45%). Infrared (Nujol mull): 2 570s, 2 460(sh), 1 380s, 1 320w, 1 220w, 1 170s, 1 060w, 1 025(sh), 1 010m, 955m, 940(sh), 740m, 730(sh) cm^{-1}. By chromatography, (3d) was recovered (42 mg, 53% recovery).

$MeCB_{10}H_{10}CNMeNPhCB_{10}H_{10}CMe$, (4g). To a solution of tetrahydrofuran (1.5 cm^3) prepared from (3g) (100 mg, 0.24 mmol) and NaH (0.25 mmol), was added methyl iodide (0.3 cm^3) as described above. The mixture was heated to 60 °C for 4 h. After cooling, benzene (5 cm^3) was added and the mixture filtered. The residue was recrystallized from dichloromethane–hexane to afford colourless crystals of (4g) (99 mg, 95%).

Preparation of closo-nido-*type Monoanions of the Hydrazocarbaborane Derivatives.*—Typical preparative procedures are given below.

$HCB_{10}H_{10}CNHNHCB_9H_{10}CH^-$, (5a). A mixture of (2a) (158 mg, 0.5 mmol), piperidine (426 mg, 5 mmol), and benzene (5 cm^3) was refluxed for 6 h and cooled. The mixture was evaporated under reduced pressure to leave an oily residue. The residue was dissolved in methanol (5 cm^3), and the solution was neutralized with dilute hydrochloric acid. Filtration, addition of water (5 cm^3), followed by slow evaporation of methanol under nitrogen, afforded white crystals of $[C_5H_{10}NH_2][HCB_{10}H_{10}CNHNHCB_9H_{10}CH]$ (140 mg, 71%). Infrared (Nujol mull): 3 306w, 3 171m, 3 050w, 2 496s, 1 576s, 1 406w, 1 295w, 1 272w, 1 244w, 1 154w, 1 072m, 1 012m, 936w, 904w, 855w, 722w cm^{-1}.

$HCB_{10}H_{10}CNMeNMeCB_9H_{10}CH^-$, (6a). A mixture of (4a) (110 mg, 0.32 mmol), piperidine (408 mg, 4.8 mmol), and benzene (3 cm^3) was refluxed for 3 h and cooled. The volume of the mixture was reduced to *ca.* 1 cm^3 under reduced pressure, and hexane (10 cm^3) was added to precipitate a gummy solid of the product. The precipitate was separated by decantation, washed twice with small portions of hexane, and dissolved in acetonitrile–water (1 : 1) (10 cm^3). The solution was passed through a column packed with Amberlite IR-120-(Na) resin. The eluted product, which contained the sodium salt of the monoanion, was concentrated to *ca.* 5 cm^3 and filtered. To the filtrate was added 10% aqueous $[NMe_4]Cl$ (1 cm^3), which precipitated the tetramethylammonium salt. This was recrystallized from dichloromethane–benzene and dried at 80 °C *in vacuo* to afford white crystals of $[NMe_4][HCB_{10}H_{10}CNMeNMeCB_9H_{10}CH]$ (98 mg, 75%). Infrared (Nujol mull): 3 055w, 2 580vs, 2 500vs, 1 280w, 1 240w, 1 170w, 1 092w, 1 063m, 1 009m, 942s, 882w, 720 cm^{-1}. The potassium salt was prepared by passing a solution of the tetramethylammonium salt in acetonitrile–water (1 : 1) through a column packed with Amberlite IR-120-(K) resin rinsed with the same solvent. Concentration of the eluted product left the hydrated crystalline potassium salt. It was dehydrated by drying at 80 °C *in vacuo.*

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