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Preliminary communication

ISOLATION AND REACTIONS OF 6-H_3N-6-CB_9H_{11}

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Summary

An efficient route leading to the isolation of *nido*-6-H_3N-6-CB_9H_{11} and its reactions leading to other 6-L-6-CB_9H_{11} species (L = H, Me_2C=NH or Me_2S) are reported along with the formation of [2-L-1-C_5H_5-2,1-$CCoB_9H_9$] (L = H_3N, H_2N^- or Me_2NH) *closo*-metallacarboranes. The structures are suggested on the basis of ^1H and ^{11}B NMR data.

The carborane *nido*-6-H_3N-6-CB_9H_{11} is an important starting point for the synthesis of a relatively large number of ten and nine-vertex carbaboranes [1,2] including their metallacarborane analogues [1,3—5]. Surprisingly, the compound has not previously been isolated pure or characterized. We outline here a convenient and simple method for its isolation and present some preliminary results of a study of its reactions.

The 6-H_3N-6-CB_9H_{11} species (I), (Fig. 1) is known to be formed along with 7-H_3N-7-$CB_{10}H_{12}$ (II) on treatment of the $[B_{10}H_{13}CN]^{2-}$ dianion with hydrochloric acid as a result of a degradation insertion of the carbon atom into the decaboron cage; the I/II ratio is typically in the range 1/4—1/2. The mixture is usually methylated in an alkaline medium [1, 2, 5] to give a mixture of the *N*-trimethyl derivatives, 6-Me_3N-6-CB_9H_{11}, (III) and 7-Me_3N-7-$CB_{10}H_{12}$, (IV), which can be separated by tedious chromatographic procedures. Thus compound I has not previously been isolated in a pure state.

In seeking an efficient procedure for obtaining pure I, we found that on treatment of the I/II mixture with acetone (Scheme 1) in the presence of hydrochloric acid compound I reacts more rapidly than II, to form the isopropylidene derivative, 6-Me_2C=NH-6-CB_9H_{11} (V), which, being insoluble in aqueous medium, can be readily separated from the unchanged II. In a series of experiments 35—40% yields of I (based on decaborane used) were attained after removal of the isopropylidene group in alkaline solution.

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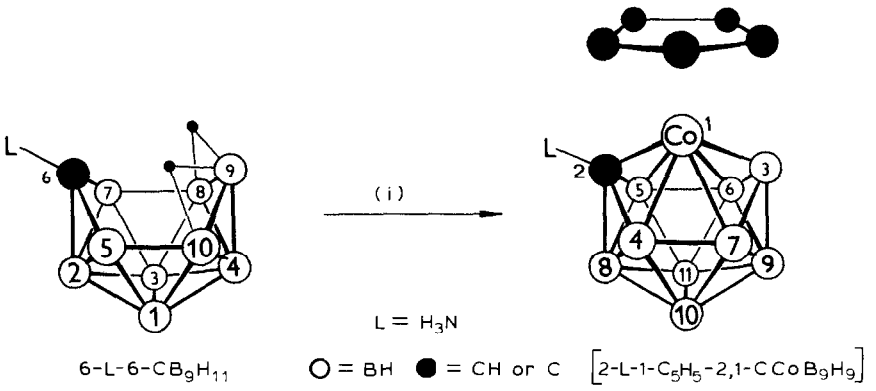
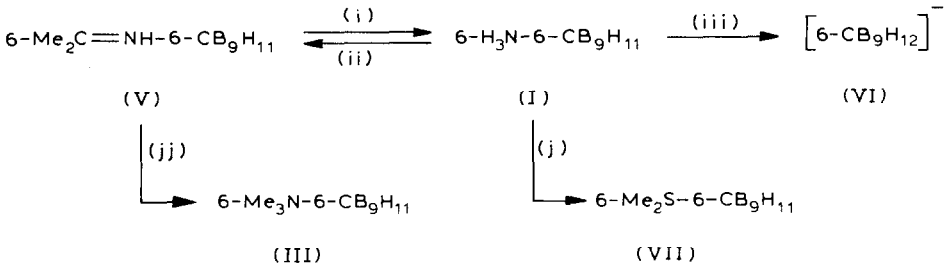


Fig. 1. Formation of the *closo*-[2-H_3N-1-C_5H_5-2,1-$CCoB_9H_9$] complex; (i) $CoCl_2 \cdot 6H_2O$, cyclopentadiene, concentrated ethanolic KOH, 50°C (60% yield).



SCHEME 1. Monocarbaboranes from 6-Me_2C=NH-6-CB_9H_{11}; (i) heating with 5% KOH in vacuo, then diluted HCl (> 95% yield); (ii) acetone, diluted HCl, 25°C; (iii) Na/NH_3 (l), reflux, isolated after solvolysis as $[NMe_4]^+$salt (81% yield); (j) $NaNO_2$, Me_2S, diluted HCl, 0°C (91% yield); (jj) Me_2SO_4, diluted KOH (> 95% yield).

Scheme 1 also depicts further reactions of V leading to other compounds of the ten-vertex *nido*-family of carboranes. The ^1H and ^{11}B NMR data of the compounds isolated (Table 1) agree well with the *nido*-6-L-6-CB_9H_{11} structure [1]. Assignments of individual ^{11}B NMR signals were based on the recent two-dimensional ^{11}B—^{11}B NMR study [6] of the parent $[6\text{-}CB_9H_{12}]^-$ anion (VI). The new, high-yield preparation of the anion VI and the isolation of the still uncharacterized 6-Me_2S-6-CB_9H_{11} (VII) derivative may be of interest.

Insertion of the $Co(C_5H_5)$ unit into the cage of I gives rise to a blue complex whose elemental analysis and NMR data suggest the *closo*-[H_3N-1-C_5H_5-2,1-$CCoB_9H_9$] (VII) geometry (Fig. 1, Table 2). An identical product is obtained in 60% yield under the same conditions when the isopropylidene derivative V is used in place of I. Complex VIII behaves as a weak *N*-acid (pK_a 8.58 in 50% ethanol) in aqueous KOH to form the $(2\text{-}H_2N\text{-}1\text{-}C_5H_5CCoB_9H_9]^-$ anion (IX), which was characterized as the tetramethylammonium salt. Complex VIII is isomeric with the red-brown *closo*-[2-Me_3N-5-C_5H_5-2,5-$CCoB_9H_9$] species [5] in which the bulk of the Me_3N and $[C_5H_5]^-$ groups prevents the cobalt atom entering the favoured 1-position, as is the case of VIII. Methylation of VIII with an

TABLE 1

SIGNAL ASSIGNMENTS IN THE ^1H (200 MHz) AND ^{11}B (64.18 MHz) NMR SPECTRA OF 6-L-6-CB_9H_{11} COMPOUNDS IN $(CD_3)_2CO$

L	^1H NMR [a]	^{11}B NMR [b]					
		B(5,7)	B(9)	B(1,3)	B(8.10)	B(2)	B(4)
H^-	5.47(1H, $CH_{skel.}$)	2.01	−2.63	−4.22	−12.45	−30.33	−37.86
	−3.71(2H, μH)	(137)	(152)	(128)	(143)	(147)	(141)
H_3N	8.33(3H, H_3N)	0.40	0.40	−4.47	−11.63	−30.33	−38.98
	−3.44(2H, μH)	(137)		(137)	(145)	(154)	(146)
Me_3N	3.36(9H, Me)	−1.11	1.88	−5.31	−11.53	−29.32	−37.49
	−3.33(2H, μH)	(139)		(137)	(150/35)	(157)	(147)
Me_2S	3.01(3H, μH)	3.75	5.05	−1.98	−11.73	−31.02	−34.80
	−3.25(1H, μH)	(142)		(143)	(143)	(157)	(147)
$Me_2CH{=}NH$	2.60(3H, Me)	1.90	ca.2.10	−3.75	−11.33	−29.05	−37.49
	−3.22(1H, μH)	(141)		(137)	(151)	(156)	(147)

[a] δ values in ppm, relative to internal TMS. [b] δ values in ppm relative to external $BF_3{\cdot}OEt_2$, with positive values downfield; all the signals are doublets; values of J(B—H) (Hz) are given in parentheses.

TABLE 2

^1H (200 MHz) AND ^{11}B (64.18 MHz) NMR SPECTRA OF *closo*-[2-L-1-C_5H_5-2,1-$CCoB_9H_9$] COMPLEXES IN $(CD_3)_2CO$

L	^1H NMR[a]	^{11}B NMR[b]		
H_3N	5.16(5H, C_5H_5)	53.29(1B, ca.130)[c]	11.90(1B, 126)	−6.08(2B, 132)
		−10.71(1B, 147)	−21.11(2B, 137)	−23.65(2B, 130)
$[H_2N]^-$	4.77(5H, C_5H_5)	46.14(1B, ca. 130)	8.78(1B, 133)	−4.76(1B, ca. 130)
	3.42(12H, NMe_4^+)	−7.30(2B, 139)	−22.48(2B)	−26.23(2B, 133)
Me_2NH	5.19(5H, C_5H_5)	53.14(1B)[c]	13.41(1B, 136)	−6.93(2B, 136)
	3.54(6H, Me)	−14.01(1B, 144)	−22.82(4B)	

[a] δ in ppm relative to internal TMS standard, all singlets. [b] δ in ppm relative to $BF_3{\cdot}OEt_2$; all the signals are doublets; intensities and J(B—H) (in Hz) in parentheses. [c] Broad doublets.

excess of dimethyl sulphate gave the *N*-dimethyl derivative, [2-Me_2NH-1-C_5H_5-2,1-$CCoB_9H_9$], (IX) as the highest methylated product, which reflects the steric hindrance between the $[C_5H_5]^-$ ligand and the 2-H_3N group in VIII.

We are presently attempting the isolation of other monocarbaborane derivatives arising from reactions of I and related species.

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