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The Preparation of $B_{10}CH_{13}^-$ Derivatives by Carbon Atom Insertion with Alkyl Isocyanides[1]

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Decaborane-14 reacts with alkyl isocyanides to produce an unusual 1:1 adduct. Infrared, nmr, and mass spectral data as well as chemical evidence are presented which suggest that the product has the zwitterionic structure, R^+NH_2-[$-CB_{10}H_{12}^-$]. Bis(ethyl isocyanide)decaborane is obtained by a ligand-exchange reaction and its chemical and physical properties are discussed.

Introduction

There have been several recent reports concerning the novel reactions of alkyl and aryl isocyanides with diborane-6[3] and trialkylboranes.[4-7]

We have studied the reaction of alkyl isocyanides with decaborane-14 and wish to report some of the physical and chemical properties of the unusual products from these reactions.

Experimental Section

Apparatus and Materials.—Mass spectra were obtained with an Atlas CH-4 mass spectrometer using an ionizing voltage of 70 ev and a heated inlet system. Infrared spectra were recorded as Nujol or hexachlorobutadiene mulls using a Beckman IR-7 instrument. Intensities of absorptions are recorded as strong (s), medium (m), or weak (w). Proton nmr spectra were obtained with a Varian A-60 spectrometer and ^{11}B nmrs pectra with a Varian HA 100 spectrometer operating at 32.1 Mc. Molecular weight determinations were made in acetone solution employing a Mechrolab Model 301A osmometer. Melting points were obtained in evacuated capillaries and are uncorrected.

The alkyl isocyanides were prepared by the method of Jackson and McKusick[8] and distilled immediately before use. The decaborane was doubly sublimed. All reactions were carried out under an atmosphere of prepurified argon.

$C_2H_5NH_2CB_{10}H_{12}$.—To a stirred solution of decaborane-14 (1.22 g, 0.01 mole) in 20 ml of benzene was added at room temperature ethyl isocyanide (0.55 g, 0.01 mole). A dark purple color developed within 15 min with mild evolution of heat. The color faded in 1 hr, leaving a white precipitate. The solid was filtered, dried, and recrystallized from hot water, giving 1.24 g (70% yield based on decaborane-14 used) of the desired compound.

The infrared spectrum of $C_2H_5NH_2CB_{10}H_{12}$ showed λ_{max} at 3228 (m), 3203 (m), 3180 (m), 3125 (m), 3000 (w), 2960 (w), 2555 (s, br), 2510 (m), 1975 (w), 1575 (m), 1469 (m), 1453 (m), 1401 (m), 1339 (m), 1031 (m), and 1005 (m) cm^{-1}.

The proton nmr spectrum (acetone-d_6) showed signals at τ 2.49 (broad singlet, 2H), 6.59 (quartet, J = 7.5 cps, 2H), and 8.66 (triplet, 3H).

In a separate experiment, hydrogen evolved during this reaction was collected by a Toepler pump. This yielded 0.026 mmole of H_2 for each mmole of decaborane-14 used.

The analytical and molecular weight data for $C_2H_5NH_2CB_{10}H_{12}$ are recorded in Table I. Three other alkyl isocyanide–decaborane derivatives were obtained by the procedure indicated above and their analytical data are also included in Table I.

$(CH_3)_3NCB_{10}H_{12}$.—To a suspension of NaH (0.48 g, 0.02 mole) in 50 ml of THF was added $CH_3NH_2CB_{10}H_{12}$ (0.32 g, 0.002 mole). The mixture was stirred for 18 hr at room temperature until gas evolution had stopped. The mixture was filtered under argon to remove excess NaH. Dimethyl sulfate (0.5 g, 0.004 mole) was added to the filtrate. The solid products which formed were filtered, dried, and recrystallized from acetone–methanol, giving 0.19 g of $(CH_3)_3NCB_{10}H_{12}$ (50% yield based on the quantity of $CH_3NH_2CB_{10}H_{12}$ used).

The infrared spectrum of $(CH_3)_3NCB_{10}H_{12}$ showed λ_{max} at 3000 (w), 2550 (s, br), 1975 (w), 1485 (m), 1462 (m), 1407 (m), 1130 (m, br), 1027 (m), and 922 (m) cm^{-1}. The proton nmr spectrum (acetone-d_6) showed one signal at τ 6.69 (singlet).

In a separate experiment hydrogen evolved during reaction with excess NaH was collected; this gave 2 mmoles of hydrogen for each mmole of $CH_3NH_2CB_{10}H_{12}$ used.

The analytical data for $(CH_3)_3NCB_{10}H_{12}$ and three other N-trialkyl derivatives prepared by the same procedure are recorded in Table I.

Proton Exchange of $RNH_2CB_{10}H_{12}$ in D_2O.—In a typical experiment, 0.25 g of $C_2H_5NH_2CB_{10}H_{12}$ in 10 ml of D_2O (99.8 atom % pure) was refluxed for 17 hr. The material which crystallized upon cooling was filtered under argon and vacuum dried. The infrared spectrum of the product contained new bands at λ_{max} 2410 (m), 2360 (m), 2320 (w), 1897 (w, br), and 1080 (m) cm^{-1}. The peak of highest mass in the mass spectrum appeared at m/e 183.

A similar exchange experiment was performed with $CH_3NH_2CB_{10}H_{12}$. The peak of highest mass in the mass spectrum after 47 and 158 hr reflux appeared at m/e 170 and 171, respectively. The proton nmr of these products did not contain a peak in the τ 1.5–2.5 region (NH_2).

$B_{10}H_{12}(C_2H_5NC)_2$.—To a solution of bis(diethyl sulfide)decaborane (4.30 g, 0.014 mole) in 50 ml of benzene was added ethyl isocyanide (1.65 g, 0.030 mole), and the mixture was heated at reflux for 4 hr. The solid which formed was filtered, dried, and recrystallized from CH_2Cl_2–pentane, mp 215° dec.

Anal. Calcd for $C_6H_{22}B_{10}N_2$: C, 31.30; H, 9.56; N, 12.18. Found: C, 31.40; H, 9.45; N, 12.02.

The infrared spectrum of $B_{10}H_{12}(C_2H_5NC)_2$ showed λ_{max} at 2990 (w), 2520 (s, br), 2265 (s), 1440 (w), 1380 (w), and 1343 (m) cm^{-1}. The proton nmr spectrum (acetone-d_6) showed signals at τ 6.00 (quartet, broad, J = 6.5 cps, 4H) and 8.55 (triplet of triplets, J_{NH} = 3 cps, 6H).

Results and Discussion

Several years ago Schaeffer discovered[9] that decaborane-14 reacts with acetonitrile in the manner illustrated below

$$B_{10}H_{14} + 2CH_3CN \longrightarrow B_{10}H_{12}(N{\equiv}CCH_3)_2 + H_2$$

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[1] Presented in part at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

[2] National Science Foundation Predoctoral Fellow, summer 1965.

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[5] J. Casanova, Jr., and R. E. Schuster, *ibid.*, **8**, 405 (1964).

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TABLE I

ANALYTICAL DATA FOR $R(R')_2NCB_{10}H_{12}$

			C, %		H, %		N, %		B, %		Mol wt	
R	R'	Mp, °C	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
CH_3	H	292–293	14.70	14.81	10.48	10.55	8.56	8.56				
C_2H_5	H	234–235 dec	20.31	20.10	10.80	10.74	7.90	7.54	60.99	60.2	177	181
n-C_3H_7	H	220–222	25.11	25.24	11.05	10.74	7.31	7.40	56.52	56.3	191	183
t-C_4H_9	H	237–238 dec	29.23	29.77	11.28	11.25	6.81	6.87	52.67	51.2	205	218
CH_3	CH_3	344–345 dec	25.09	25.30	11.06	10.83	7.31	7.15				
C_2H_5	CH_3	310–311	29.23	29.40	11.22	11.40	6.81	6.66				
n-C_3H_7	CH_3	185–187	32.82	32.80	11.47	11.13	6.38	6.24				
t-C_4H_9	CH_3	202–204	36.06	35.82	10.03	10.35	4.90	4.80				

This has proven to be a general reaction of many types of Lewis bases with decaborane-14.[10] Bis(alkyl isocyanide)decaborane derivatives have been briefly mentioned in the literature.[11] Following the suggestion of Hawthorne,[12] we have prepared bis(ethyl isocyanide)decaborane by a ligand-exchange reaction with bis(diethyl sulfide)decaborane

$$B_{10}H_{12}[S(C_2H_5)_2]_2 + 2C_2H_5N{\equiv}C \longrightarrow B_{10}H_{12}(C{\equiv}NC_2H_5)_2 + 2S(C_2H_5)_2$$

The infrared spectrum of $B_{10}H_{12}(C_2H_5NC)_2$ contains a band at 2265 cm^{-1} which is attributed to the $C{\equiv}N$ stretching frequency. As is expected, this band is at higher frequency (113 cm^{-1}) than the $C{\equiv}N$ frequency observed for ethyl isocyanide. A similar $C{\equiv}N$ frequency shift has been observed in the t-butyl isocyanide–trimethylborane adduct.[5]

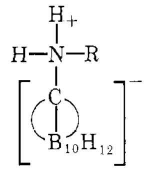
The proton nmr spectra of alkyl isocyanides show long-range $^{14}N-^{1}H$ coupling ($J_{NH} = 3$ cps).[13] This type of coupling is also observed in the nmr spectrum of $B_{10}H_{12}(C_2H_5NC)_2$. This suggests that the symmetry of the electric field in the vicinity of the nitrogen atom is very similar for the free and coordinated alkyl isocyanide.

Treatment of $B_{10}H_{12}(C_2H_5NC)_2$ with triphenylphosphine or pyridine did not result in ligand displacement. The starting materials were recovered quantitatively after heating at 60–80° for 12 hr. Thus ethyl isonitrile is as tightly bound a ligand as triphenylphosphine or pyridine and much more tightly bound than alkyl nitriles.

The product from the direct reaction of ethyl isocyanide with decaborane has the correct analysis and molecular weight for a 1:1 adduct, $B_{10}H_{14}\cdot C_2H_5NC$. This material was obtained in good yield (70%) and only a negligible amount of hydrogen was evolved during the reaction. These observations represent a marked departure from the general reactions of Lewis bases with decaborane and led to a more detailed study of the 1:1 adduct.

Infrared Spectra.—The spectrum of the 1:1 adduct does not exhibit a $C{\equiv}N$ stretching frequency. It does contain a strong terminal B—H stretching frequency at 2550 cm^{-1} and a broad weak absorption at 1975 cm^{-1} which may reflect a B—H—B grouping. A medium intensity band at 1575 cm^{-1} was interpreted *a priori* as a $C{=}N$ stretching frequency. However, the spectrum of the 1:1 adduct recovered after reflux in deuterium oxide indicated that the 1575 cm^{-1} band was nearly eliminated. In addition, several bands in the 3200–3100 cm^{-1} region had apparently shifted to the 2400–2300 cm^{-1} region. This led to a reinterpretation of the 1575 cm^{-1} band as a NH_2 deformation mode. This assignment is consistent with the results of a study of secondary amine salts by Heacock and Marion.[14]

The gross structure of the 1:1 adduct was at this point tentatively written as



When $CH_3NH_2CB_{10}H_{12}$ was treated with excess sodium hydride in THF 2 equiv of hydrogen was evolved based on the quantity of starting boron compound. Subsequent treatment with dimethyl sulfate or methyl iodide produced a trimethyl derivative, $(CH_3)_3NCB_{10}H_{12}$. The infrared spectrum of this product does not contain peaks in the 3200–3100 cm^{-1} region nor at 1575 cm^{-1}, suggesting that the methyl groups have been attached at the nitrogen atom.

Mass Spectra.—We had observed that $C_2H_5NH_2$-$CB_{10}H_{12}$ could be sublimed slowly without decomposition at 180° (10^{-5} mm). This indicated that the mass spectrum could be obtained on an instrument with a heated inlet. A portion of the data obtained is shown in Table II.

In each instance the mass spectrum cuts off sharply at a m/e corresponding to the parent ion ($^{12}C_n{}^{1}H_m{}^{11}B_{10}{}^{14}N_1{}^{+}$). Most spectra also contain a relatively abundant peak which can be assigned to the N-alkyl fragment ($RR'C{=}NR''_2{}^{+}$).

Mass spectra were also obtained of the deuterium oxide exchanged products. The parent ion molecule weight had increased by four to six mass units, depending upon the length of exchange time. The infrared spectra showed substantial N–H to N–D exchange and the appearance of a relatively weak band at 1897 cm^{-1}, suggesting slow B–H terminal exchange. The infrared and mass spectral data roughly indicate that four protons exchange rapidly (less than 17 hr) and that the

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(10) M. F. Hawthorne, *Advan. Inorg. Chem. Radiochem.*, **5**, 307 (1963).

(11) B. M. Graybill and M. F. Hawthorne, *J. Am. Chem. Soc.*, **83**, 2673 (1961).

(12) Private communication.

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TABLE II

SELECTED MASS SPECTRAL DATA FOR $R(R')_2NCB_{10}H_{12}$

Compd	m/e	Intensity	Proposed ion
$CH_3ND_2CB_{10}H_{12-n}D_n$	32	40	$[CH_2{=}ND_2]^+$
$C_2H_5NH_2CB_{10}H_{12}$	44	39	$[CH_3CH{=}NH_2]^+$
	179	*a*	Parent ion molecule
$C_2H_5ND_2CB_{10}H_{12-n}D_n$	46	37	$[CH_3CH{=}ND_2]^+$
n-$C_3H_7NH_2CB_{10}H_{12}$	58	24	$[CH_3CH_2CH{=}NH_2]^+$
	193	*a*	Parent ion molecule
t-$C_4H_9NH_2CB_{10}H_{12}$	56	81[b]	$[(CH_3)_2C{=}CH_2]^+$
	207	2.3	Parent ion molecule
$(CH_3)_3NCB_{10}H_{12}$	58	100	$[CH_2{=}N(CH_3)_2]^+$
	193	30	Parent ion molecule
n-$C_3H_7(CH_3)_2NCB_{10}H_{12}$	221	*a*	Parent ion molecule

[a] In the cases cited, a peak in the parent ion molecule section of the spectrum is of highest intensity and is assigned intensity = 100. [b] In this case m/e 41 = 100.

rate of B–H terminal exchange under these conditions is very slow. We suggest that the N–H and B–H–B hydrogens are the atoms which most rapidly exchange.

Proton Nmr Spectra.—The methylene quartet of $C_2H_5NH_2CB_{10}H_{12}$ has a chemical shift of τ 6.59, which is approximately the value found by others for methylene groups attached to a quaternary nitrogen. The spectrum also contains a broad singlet representing two protons at about τ 2.5. This portion of the spectrum is solvent and concentration dependent, as one might expect for the easily exchangeable protons of the $C_2H_5{}^+NH_2C{<}$ function. Finally, ^{14}N–^1H coupling was not observed with this type of compound, suggesting that the electric field around the nitrogen atom had changed substantially from that experienced in the alkyl isocyanide configuration.

The proton nmr spectrum of the trimethyl derivative, $(CH_3)_3NCB_{10}H_{12}$, exhibited one singlet peak at τ 6.69, thus demonstrating the equivalency of the methyl groups and further confirming the presence of a R^+-$NH_2C{<}$ function in the original 1:1 adduct.

^{11}B Nmr Spectra.—The ^{11}B nmr spectrum of $(CH_3)_3$-$NCB_{10}H_{12}$ is shown in Figure 1.

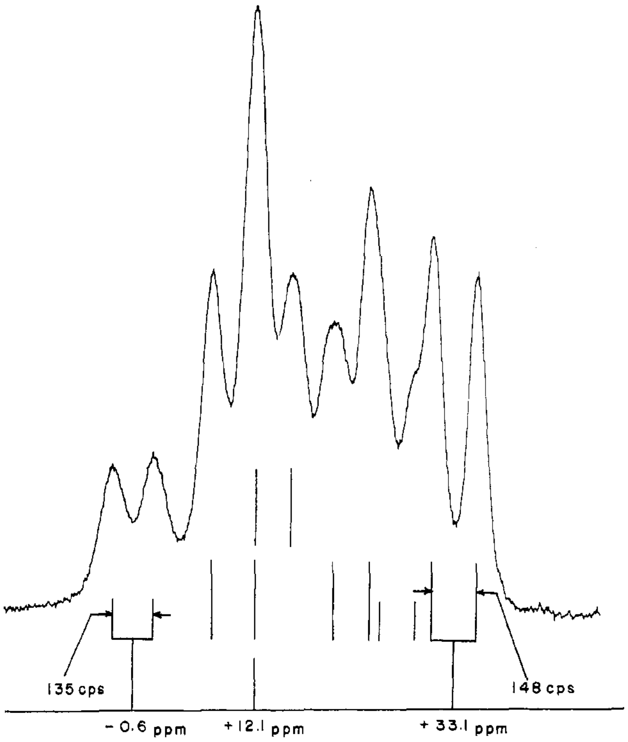

Figure 1.—^{11}B nmr spectrum (32.1 Mc) of $(CH_3)_3NCB_{10}H_{12}$ in dimethylformamide solution externally referenced to $BF_3 \cdot (C_2H_5)_2O$.

The data thus far presented strongly suggest that the basic isocyanide carbon has bonded with its three available orbitals to the boron hydride fragment. The ^{11}B nmr spectrum further indicates that the cage carbon atom cannot be symmetrically disposed in the open face of the decaborane molecule. This configuration requires only four nonequivalent types of boron atoms. The spectrum shown in Figure 1 clearly indicates that there are more than four different types of boron atoms present.

This information prompts us to make the tentative suggestion that the product from the reaction of an alkyl isocyanide with decaborane-14 has the structure shown in Figure 2. Thus $RNH_2CB_{10}H_{12}$ is a zwitterionic derivative of the $B_{10}CH_{13}^-$ ion which is isoelectronic with the known $B_9C_2H_{13}$ and $B_{11}H_{13}^{2-}$ species.[15,16]

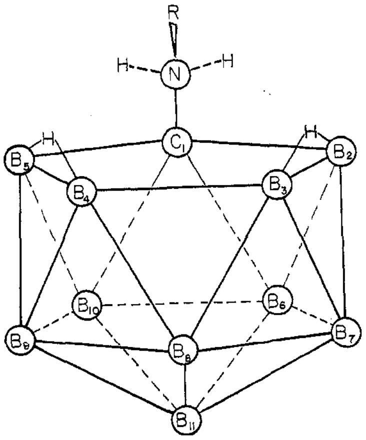

Figure 2.—A proposed structure for $RNH_2CB_{10}H_{12}$.

Although the mechanism of this reaction has not yet been determined, it formally represents an insertion of one carbon atom into a boron hydride molecule to give a new series of carboranes of the type CB_nH_{n+4}.[17]

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