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MONOCARBON CARBORANES
II*. SYNTHESES OF CARBORANE DERIVATIVES BY REACTION OF GROUP IV HALIDES WITH CYANOBORON HYDRIDES

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SUMMARY

Reaction of the $B_{10}H_{13}CN^{2-}$ ion with alkyl iodides in tetrahydrofuran/water produces a mixture of $B_{10}H_{12}CN(H)_nR_{3-n}$ carboranes. The unsubstituted molecule, $B_{10}H_{12}CNH_3$ is obtained by treatment of $B_{10}H_{13}CN^{2-}$ with either trimethylsilyl or trimethyltin chloride followed by base hydrolysis. Methylation of $B_{10}H_{12}CN[S(CH_3)_2]^-$ in tetrahydrofuran/methanol gives a single isomer of the composition $B_{10}H_{11}(OCH_3)CN(CH_3)_3$. Observations which suggest that carborane formation may proceed thru a $B_{10}H_{13}CNR^-$ intermediate are presented.

INTRODUCTION

The synthesis and chemistry of alkyl isocyanide complexes of transition metals has been actively studied for many years[1]. Alkylation of coordination compounds containing cyanide ligands with alkyl iodide or dialkyl sulfate is a general method for obtaining alkyl isocyanide–metal complexes. Recently this type of reaction has been broadened in scope with the discovery by King[2] that cyanopentacarbonylmetalates react with trimethylsilyl and trimethyltin chlorides to form the corresponding isocyanide–metal complexes (eqn. 1). Of even greater interest was the finding that $[M(CO)_5CN]^-$ reacted with hydrochloric acid to form $HNCM(CO)_5$, (M=Cr, Mo, W) the first metal complexes of hydrogen isocyanide.

$$Na[M(CO)_5CN] + (CH_3)_3M'Cl \rightarrow (CH_3)_3M'NCM(CO)_5 \qquad (1)$$
$$(M' = Sn;\ M = Cr, Mo, W)$$
$$(M' = Si;\ M = Mo)$$

Alkyl isocyanide complexes of boron and aluminum compounds have been studied only in the last few years. Some of these complexes undergo facile rearrangement reactions. Thus decaborane-14 presumably forms a complex with an alkyl isocyanide which rearranges to produce a one-carbon carborane, $B_{10}H_{12}CNH_2R$[3]. Recently it was reported that treatment of the $B_{10}H_{13}CN^{2-}$ ion with concentrated

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hydrochloric acid produces $B_{10}H_{12}CNH_3$[4]. This process also may involve initial formation of a hydrogen isocyanide–borane complex followed by rearrangement.

The subject of this paper is a study of the reaction of the $B_{10}H_{13}CN^{2-}$ and related cyanoboron hydride ions with monohalides of carbon, silicon and tin to form monocarbon carborane derivatives.

RESULTS AND DISCUSSION

Treatment of $Cs_2B_{10}H_{13}CN$ with a slight excess of methyl iodide in tetrahydrofuran/water at reflux produced $B_{10}H_{12}CN(CH_3)_3$ in 45% yield (eqn. 2). The

$$Cs_2B_{10}H_{13}CN+3\,CH_3I \rightarrow B_{10}H_{12}CN(CH_3)_3+2\,CsI+C_4H_8OHI \qquad (2)$$

carborane product of this reaction and $B_{10}H_{12}CN(CH_3)_3$ obtained earlier via the alkyl isocyanide/decaborane route[3] and from the $B_{10}H_{13}CN^{2-}$/HCl process[4] had infrared, proton NMR and ^{11}B NMR spectra which were identical in all respects. Initially we had expected to obtain only $B_{10}H_{12}CNH(CH_3)_2$ from this reaction. However the tetrahydrofuran appears to be basic enough to remove the remaining proton on the nitrogen atom and aid methylation to the *N*-trimethyl derivative. The overall yield of the *N*-trimethyl derivative can be greatly improved (increased to 71%) if the initial reaction products are treated with aqueous sodium hydroxide and then dimethyl sulfate. This result suggests that some $B_{10}H_{12}CNH_2CH_3$ and/or the *N*-dimethyl derivative are probably present in the initial product mixture*. This view is supported by the fact that $B_{10}H_{12}CNH(C_2H_5)_2$ has been isolated and characterized from the reaction of the $B_{10}H_{13}CN^{2-}$ ion with ethyl iodide.

Monocarbon carboranes can also be prepared by reaction of trimethylsilyl or trimethyltin chloride with $B_{10}H_{13}CN^{2-}$ (eqn. 3). The intermediate silicon and tin

$$Na_2B_{10}H_{13}CN+(CH_3)_3MCl \rightarrow \xrightarrow{H_2O} \underset{(M = Si\ or\ Sn)}{B_{10}H_{12}CNH_3} \qquad (3)$$

derivatives, which are hydrolytically unstable, are easily hydrolyzed under basic conditions to give $B_{10}H_{12}CNH_3$. This product and the amino derivative prepared by the $B_{10}H_{13}CN^{2-}$/HCl method[4] had identical infrared and ^{11}B NMR spectra.

It is possible that $B_{10}H_{13}CNR^-$ is formed initially (eqn. 4) and that the remaining reaction sequence to the carborane is similar to the decaborane/alkyl isocyanide process. In agreement with this postulate we have found that methylation

$$Na_2B_{10}H_{13}CN+RX \rightarrow NaB_{10}H_{13}CNR+NaX \qquad (4)$$

of $2\text{-}BrB_{10}H_{12}CN^{2-}$ gave $BrB_{10}H_{11}CN(CH_3)_3$ which had identical infrared and ^{11}B NMR spectra to the single isomer obtained earlier by reaction of $2\text{-}Br\text{-}B_{10}H_{13}$ with methyl isocyanide followed by methylation of the nitrogen atom[5].

Alkylation of $CsB_{10}H_{12}CNL$, where $L = S(CH_3)_2$ or pyridine, in tetrahydrofuran/water solution with methyl iodide gave $B_{10}H_{11}(OH)CN(CH_3)_3$[4] in low yield.

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* Treatment of $Cs_2B_{10}H_{13}CN$ with several portions of sodium hydroxide and dimethyl sulfate did not produce $B_{10}H_{12}CN(CH_3)_3$.

A methoxy derivative, $B_{10}H_{11}(OCH_3)CN(CH_3)_3$ was obtained when the solvent medium in the above reaction was changed to tetrahydrofuran/methanol.

The 32 MHz ^{11}B NMR spectrum of $B_{10}H_{11}(OCH_3)CN(CH_3)_3$ is given in Fig. 1. The low field singlet at +11.5 ppm [$B(OCH_3)_3 = 0$ ppm] was assigned to the methoxy-substituted boron atom. The boron NMR spectrum of the hydroxy-substituted derivative was quite similar to Fig. 1 and contained a low field singlet at +12.5 ppm. Other studies have shown[8] that there is a low field shift of the resonance of a hydroxyl-substituted boron atom. The relative areas of the singlet to the remainder of the spectrum were 1/9.15 and 1/9.05 for the methoxy and hydroxy derivative respectively. The integration values suggest that each of these substituted derivatives is mainly a single isomer. The proton NMR spectra at 100 MHz are also in accord with this view. The proton spectrum of $B_{10}H_{11}(OCH_3)CN(CH_3)_3$ contains two singlets at τ 6.6 (N-CH_3) and 6.45 (O-CH_3) with relative areas 3.1/1. Similarly the proton NMR of $B_{10}H_{11}(OH)CN(CH_3)_3$ contains two singlets at τ 6.55 (N-CH_3) and 4.9 (O-H) with relative areas 9/1.

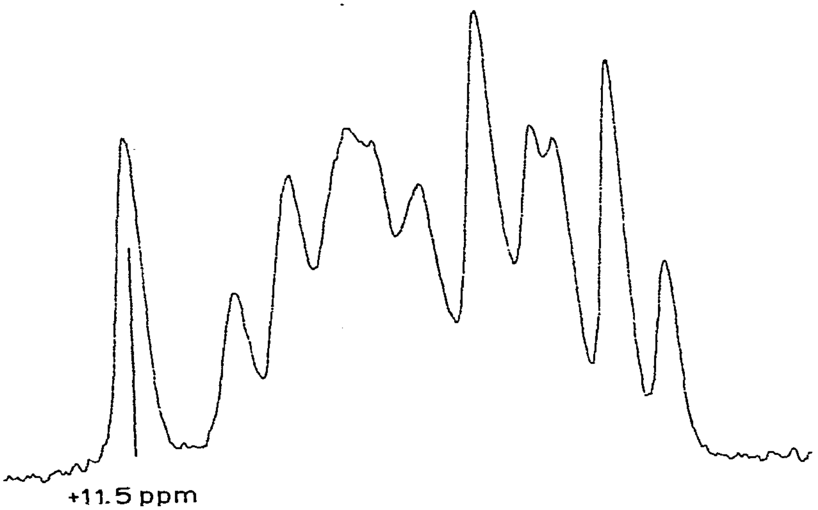

Fig. 1. ^{11}B NMR spectrum (32.1 MHz) of $B_{10}H_{11}(OCH_3)CN(CH_3)_3$ in acetone externally referenced to trimethyl borate.

Further study may show that alkylation of cyanoboron hydrides is applicable to many more systems and has distinct advantages over the previously reported methods. Thus the malodorous alkyl isocyanides have been observed to polymerize in the presence of certain neutral boranes. The most apparent limitation of the acid ion exchange method is that many cyanoboron hydrides are rapidly degraded to borates in strong aqueous acid.

EXPERIMENTAL

General comments

All reactions were carried out under an atmosphere of prepurified argon. Analyses were performed by Mr. J. Nemeth, University of Illinois Microanalytical

Laboratory. Infrared spectra were recorded as KBr disks using a Perkin–Elmer 521 instrument. Proton NMR spectra were obtained with a Varian A-60A or HA-100 spectrometer and the boron (^{11}B) NMR spectra with a Varian HA-100 spectrometer operating at 32.1 MHz.

Starting materials

The trimethylchlorosilane was a gift from Dow Corning Corp. and was distilled before use. The trimethyltin chloride was a gift from M and T Chemicals Co. The $Na_2B_{10}H_{13}CN$ and $NaB_{10}H_{12}CN[S(CH_3)_2]$ were prepared by the method of Knoth and Muetterties[6].

Reaction of $Cs_2B_{10}H_{13}CN$ with methyl iodide

To a slurry of $Cs_2B_{10}H_{13}CN$ (0.01 mole, 4.11 g) in a 60/40 mixture of tetrahydrofuran and water was added methyl iodide (0.03 mole, 4.26 g). The reaction mixture was stirred at reflux for 5 h and then additional 0.03 mole of methyl iodide added. After refluxing for a total of 12 h, the solution was cooled and the tetrahydrofuran removed *in vacuo*. A white crystalline solid, 0.85 g, was removed by filtration. The aqueous filtrate was treated with sodium hydroxide (0.02 mole, 0.80 g) and then dimethyl sulfate (0.02 mole, 2.52 g). After stirring for 5 h, 0.94 g of solids were removed by filtration. Crystallization of the combined solids from methanol/acetone gave 1.35 g (70% yield) of $B_{10}H_{12}CN(CH_3)_3$, m.p. 345–346°. The infrared and ^{11}B NMR spectra of this product were identical to the authentic compound reported earlier[3]. (Found: C, 24.81; H, 10.95; N, 7.20. $C_4H_{21}B_{10}N$ calcd.: C, 25.09; H, 11.06; N, 7.31%.)

Reaction of $Na_2B_{10}H_{13}CN$ with ethyl iodide

To a refluxing solution of $Na_2B_{10}H_{13}CN$ (0.05 mole, 9.65 g) in 100 ml of tetrahydrofuran was added dropwise ethyl iodide (0.10 mole). The addition required 5 h and the mixture was refluxed for a total of 18 h. The tetrahydrofuran was removed under vacuum and the residues washed with several portions of hot water. The water insoluble oil was chromatographed on a silica gel column with pentane and benzene as eluents. This gave a crystalline material, m.p. 180–181°, in low yield. (Found: C, 29.58; H, 11.48; N, 6.82. $C_5H_{23}B_{10}N$ calcd.: C, 29.23; H, 11.22; N, 6.81%.) The infrared spectrum of this compound contains a medium intensity band at 3180 cm^{-1} (N–H stretch). The ^{11}B NMR spectrum of this product is quite similar to that of other $B_{10}H_{12}CR$ derivatives.

Reaction of $Na_2B_{10}H_{13}CN$ with trimethylchlorosilane or trimethyltin chloride

(*A*). To a solution of $Na_2B_{10}H_{13}CN$ (0.01 mole, 1.93 g) in 75 ml of tetrahydrofuran was added trimethylchlorosilane (0.01 mole, 1.08 g). The mixture was refluxed with stirring under an argon atmosphere for 15 h. A white solid (NaCl) was removed with a Schlenk filter[7] and vacuum dried. The solid was treated with basic hydrogen peroxide for 48 h. The resulting mixture was acidified with nitric acid and treated with saturated silver nitrate solution to give 0.70 g (49.1% yield) of silver chloride.

The tetrahydrofuran filtrate was evaporated to dryness under vacuum and then treated with 50 ml of 20% sodium hydroxide for 5 h at 50°. The resulting solution was neutralized to pH 6 and evaporated to dryness. The solid residue was extracted with hot chloroform to give 0.46 g (31% yield) of $B_{10}H_{12}CNH_3$. (Found: C, 8.59;

H, 10.07; N, 9.19. $CH_{15}B_{10}N$ calcd.: C, 8.06; H, 10.13; N, 9.39%.) The infrared and ^{11}B NMR spectra of this compound were identical to a sample prepared by the method of Knoth[4].

(*B*). Using the same procedure as described in part (*A*), $Na_2B_{10}H_{13}CN$ was reacted with trimethyltin chloride in tetrahydrofuran to give a 32.5% yield of silver chloride and a 12% yield of $B_{10}H_{12}CNH_3$. The infrared and ^{11}B NMR spectra of the carborane product were identical to those of an authentic sample of the compound.

Reaction of $NaB_{10}H_{12}CN[S(CH_3)_2]$ with methyl iodide

(*A*). Deoxygenation of a 75% solution of tetrahydrofuran in water was accomplished by bubbling prepurified argon thru the mixture. To this solvent (100 ml) was added $NaB_{10}H_{12}CN[S(CH_3)_2]$ (0.005 mole, 1.15 g) and methyl iodide (0.03 mole, 4.26 g). The mixture was refluxed under argon for 12 h. Vacuum evaporation of the solvent left a white solid which was crystallized from methanol/acetone to give 0.22 g (21% yield) of $B_{10}H_{11}(OH)CN(CH_3)_3$, m.p. greater than 390°. (Found: C, 23.03; H, 9.95; N, 6.40. $C_4H_{21}B_{10}NO$ calcd.: C, 23.15; H, 10.21; N, 6.75%.) The infrared spectrum of this compound contained a sharp band at 3600 cm^{-1} (OH stretch). The proton NMR spectrum (acetone-d_6) showed a broad singlet at τ 4.9 (1 H) and a sharp singlet at τ 6.55 (9 H).

(*B*). To 100 ml of oxygen-free tetrahydrofuran/methanol (1/1) was added $NaB_{10}H_{12}CN[S(CH_3)_2]$ (0.0015 mole, 0.35 g) and methyl iodide (0.0075 mole, 1,06 g). The mixture was refluxed under argon for 24 h and the solvent removed *in vacuo*. The tacky solid residue was crystallized from methanol/acetone to give 0.68 g (26% yield) of $B_{10}H_{11}(OCH_3)CN(CH_3)_3$, m.p. 198–199°. (Found: C, 27.30; H, 10.42; N, 6.31. $C_4H_{23}B_{10}NO$ calcd.: C, 27.11; H, 10.48; H, 6.32%.) The proton NMR spectrum (acetone-d_6) contains singlets at τ 6.45 (3 H) and τ 6.6 (9 H). The infrared spectrum contains bands at 3070 w, 2975 m, 2940 m, 2840 m, 2600 s, 2545 s and 1975 w cm^{-1}.

Reaction of $CsB_{10}H_{12}CN(C_5H_5N)$ with methyl iodide

The pyridine adduct was prepared by reaction of $NaB_{10}H_{12}CN[S(CH_3)_2]$ (0.02 mole, 4.62 g) with pyridine (0.02 mole, 1.58 g) in 50 ml of tetrahydrofuran at ambient temp. for 30 min. The solvent was removed under vacuum and the residues were treated with an oxygen-free saturated solution of cesium chloride. The aqueous solution was heated to boiling under argon and Schlenk-filtered. The yellow product crystallized from the filtrate upon cooling, 5.34 g (67% yield) of $CsB_{10}H_{12}CN(C_5H_5N)$. (Found: C, 20.08; H, 5.45; N, 8.04. $C_6H_{17}B_{10}CsN_2$ calcd.: C, 20.10; H, 4.78; N, 7.76%.)

A mixture of $CsB_{10}H_{12}CN(C_5H_5N)$ (0.007 mole, 2.5 g) and methyl iodide (0.035 mole, 4.97 g) in 50 ml of 4/1 tetrahydrofuran/water was refluxed for 48 h. The solvent was vacuum evaporated and the solid residue recrystallized from methanol/acetone to give 0.47 g (32% yield) of $B_{10}H_{11}(OH)CN(CH_3)_3$. The infrared spectrum of this product was identical to that of an authentic sample.

Reaction of $Cs_2B_{10}H_{12}BrCN$ with methyl iodide

The $Cs_2B_{10}H_{12}BrCN$ was prepared from 2-$BrB_{10}H_{13}$ by the method of Knoth and Muetterties[6], in 16% yield. (Found: C, 2.15; H, 2.36; Br, 15.84; N, 2.50. CH_{12}-

$B_{10}BrCs_2N$ calcd.: C, 2.44; H, 2.45; Br, 16.24; N, 2.85%.) A mixture of $Cs_2B_{10}H_{12}$-BrCN (0.005 mole) and methyl iodide (0.03 mole) in 2/3 water/tetrahydrofuran was refluxed under argon for 24 h. The solvent was evaporated under vacuum and the residue recrystallized from acetone to give 0.323 g (24% yield) of $B_{10}H_{11}BrCN(CH_3)_3$. (Found: C, 18.10; H, 7.65; N, 5.08. $C_4H_{20}B_{10}BrN$ calcd.: C, 17.78; H, 7.42; N, 5.19%.) The infrared and ^{11}B NMR spectra of this compound were identical to 4(6)-$BrB_{10}H_{10}CN(CH_3)_3$ prepared earlier[5].

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REFERENCES

1 L. MALATESTA, *Prog. Inorg. Chem.*, 1 (1959) 283.
2 R. B. KING, *Inorg. Chem.*, 6 (1967) 25.
3 D. E. HYATT, D. A. OWEN AND L. J. TODD, *Inorg. Chem.*, 5 (1966) 1749.
4 W. H. KNOTH, *J. Amer. Chem. Soc.*, 89 (1967) 1274.
5 D. E. HYATT, F. R. SCHOLER, L. J. TODD AND J. L. WARNER, *Inorg. Chem.*, 6 (1967) 2229.
6 W. H. KNOTH AND E. L. MUETTERTIES, *J. Inorg. Nucl. Chem.*, 20 (1961) 66.
7 S. HERZOG AND J. DEHNERT, *Z. Chem.*, in press.
8 W. H. KNOTH, J. C. SAUER, D. C. ENGLAND, W. R. HERTLER AND E. L. MUETTERTIES, *J. Amer. Chem. Soc.*, 86 (1964) 3973.