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Activation of Methane and Benzene during Reactions of 1,10-$B_{10}H_8(N_2)_2$[†,‡]

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Summary: The reactions of 1,10-$B_{10}H_8(N_2)_2$ with carbon monoxide/methane mixtures and with carbon monoxide in benzene at 130 °C give $B_{10}H_8(CO)_2$ substituted with methyl and phenyl groups, respectively. Reaction of 1,10-$B_{10}H_8(N_2)_2$ with methane in the absence of carbon monoxide also gives a product containing carbon.

Interest in C–H bond activation has been increasing steadily over the past few years. The activation of methane is of particular interest because of its availability and because the C–H bond in methane is one of the strongest known. Several systems, all involving metals or organometallic reagents, have been described which activate methane under relatively mild conditions.[1-3] This paper reports the first activation of methane by a boron hydride derivative.

1,10-$B_{10}H_8(N_2)_2$ is known to react with carbon monoxide at 130 °C to form 1,10-$B_{10}H_8(CO)_2$.[4] We have now found that if methane is present during this reaction, $CH_3B_{10}H_7(CO)_2$ and $(CH_3)_2B_{10}(H_6(CO)_2$ are formed. These have been identified by elemental analysis, ^1H and ^{13}C NMR, infrared, and GC/MS.[5] The last shows the absence of $B_{10}H_8(CO)_2$ and the presence of two isomers of $CH_3B_{10}H_7(CO)_2$ (parent ion mass 188, Cd 188) and one isomer of $(CH_3)_2B_{10}H_6(CO)_2$ (parent ion mass 202, Cd 202). In common with 1,10-$B_{10}H_8(CO)_2$, these methylated species are sublimable, readily soluble in organic solvents and in water, and have the hydrolytic and oxidative stability typical of $B_{10}H_{10}^{2-}$ derivatives.[6,7] No methylated derivatives are formed when 1,10-$B_{10}H_8(N_2)_2$ is reacted with carbon monoxide in the absence of methane; the methyl groups therefore are not formed by reduction of carbon monoxide. Additionally, carbon-containing products are formed from 1,10-$B_{10}H_8(N_2)_2$ and methane at 130 °C in the absence of carbon monoxide. Unfortunately, these products are intractable, are hydrolytically unstable, and do not sublime. However, analysis estalishes the presence of carbon (Fd 5.66, 5.79), and ^1H NMR in dimethyl sulfoxide, in which the product is partially soluble, exhibits a sharp singlet at +0.04 ppm superimposed on a very broad multiplet, consistent with CH_3 on boron in a boron hydride. Despite the unsatisfactory nature of these carbonyl-free products and their characterization, they provide conclusive evidence for methane activation because methane was the only carbon source present during their preparation.

Two isomers of $C_6H_5B_{10}H_7(CO)_2$ (parent ion mass 250, Cd 250) and a minor amount of $B_{10}H_8(CO)_2$ are formed when 1,10-$B_{10}H_8(N_2)_2$ and carbon monoxide are reacted in benzene as shown by GC/MS analysis of the sublimed product.[8]

This work is an extension of an earlier report from this laboratory that 1,10-$B_{10}H_8(N_2)_2$ and carbon monoxide react in cyclohexane to give $C_6H_{11}B_{10}H_7(CO)_2$ and $(C_6H_{11})_2B_{10}H_6(CO)_2$.[4]

The mechanism of C–H activation in this reaction is not known. The first step is undoubtedly thermal dissociation of dinitrogen from 1,10-$B_{10}H_8(N_2)_2$ because the reaction does not occur below about 125 °C, which is the decomposition temperature of the dinitrogen complex. The intermediate fragment thus formed, by loss of either one or both dinitrogen molecules, must react with the hydrocarbon substrate before reaction with carbon monoxide to form $B_{10}H_8(CO)_2$ because the latter does not react with benzene or methane. Loss of a dinitrogen from 1,10-$B_{10}H_8(N_2)_2$ would temporarily leave an electron-deficient site that could act as an exceedingly strong acid or form radical sites by rearrangement of electrons in the B_{10} cage structure. The stereochemistry of the $RB_{10}H_7(CO)_2$ and $R_2B_{10}H_6(CO)_2$ products will be of interest in this connection; attempts to determine the stereochemistry are in progress. In the meantime, the existence of two isomers of both $CH_3B_{10}H_7(CO)_2$ and $C_6H_5B_{10}H_7(CO)_2$ is itself informative. The infrared spectra of these products are sufficiently close to those of 1,10-$B_{10}H_8(N_2)_2$ and 1,10-$B_{10}H_8(CO)_2$ to infer that no gross structural change of the *closo*-$B_{10}H_{10}^{2-}$ skeleton has occurred. While the 1,10 stereochemistry of $B_{10}H_8(N_2)_2$ is retained during its conversion to $B_{10}H_8(CO)_2$,[4] the carbonyl groups in the $RB_{10}H_7(CO)_2$ isomer pairs cannot all be apical because only one isomer of 1,10-$(OC)_2RB_{10}H_7$ is possible. Therefore, at

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[†] This paper is dedicated to the memory of Earl Muetterties in recognition of his interest in and contributions to boron hydride chemistry.

[‡] Contribution No. 3491.

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(5) In a typical reaction, 1,10-$B_{10}H_8(N_2)_2$ (3 g) was heated slowly (1 °C per minute; *this slow heating is important because rapid heat-up can cause vigorous exothermic decomposition*) to 130 °C in an 80-mL platinum-lined pressure vessel under 1:1 CO/CH_4 pressure (700 atm at 130 °C) and then held at this temperature for 3 h. The tube was cooled and vented, and the solid product was removed by dissolution in water. The water was stripped off, and the residue was sublimed at 80 °C (1 torr). A 0.7-g sample of sublimate was collected. This was resublimed at 80–110 °C (1 torr), and several fractions were collected. All had infrared spectra that were slightly perturbed from that of 1,10-$B_{10}H_8(CO)_2$,[7] including the inclusion of a new band (1314 cm^{-1}) assigned to BCH_3. The ^1H NMR spectra in Me_2SO had a very broad featureless multiplet extending from +4 to −3 ppm. Superimposed on this were two sharp singlets (+0.9, +1.2 ppm) that varied in relative intensities in successive sublimation fractions and are assigned to methyl groups on boron. The initial resublimation fraction was analyzed. Anal. Calcd (Found) for $CH_3B_{10}H_7(CO)_2$: C, 19.35 (19.84); H, 5.41 (5.42); B, 58.0 (57.1). The presence of about 14% $(CH_3)_2B_{10}H_6(CO)_2$ in this sample would change the calculated values to the following: C, 20.04; H, 5.50; B, 57.4.

In another experiment, starting with 5 g of 1,10-$B_{10}H_8(N_2)_2$, the yield of a twice-sublimed mixture of $CH_3B_{10}H_7(CO)_2$ and $(CH_3)_2B_{10}H_6(CO)_2$ was 1.6 g; nonvolatile material (2.05 g) was also found. The twice-sublimed material from this preparation was equivalent by infrared to that described above and was used for the GC/MS study described in the text and for determination of the ^{13}C NMR spectrum in benzene. This spectrum (proton-decoupled) displayed quadruplets for carbonyl group carbon atoms at +176.0 and +169.6 ppm and for methyl group carbon atoms at +2.0 and −3.0 ppm.

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(8) 1,10-$B_{10}H_8(N_2)_2$ (5 g) was reacted with benzene (20 mL) and carbon monoxide (800 atm) for 3 h at 130 °C followed by removal of excess benzene and sublimation of the residual solid products. All the sublimation products had infrared spectra exhibiting absorption bands for phenyl groups and otherwise mildly perturbed from that of 1,10-$B_{10}H_8(CO)_2$. The ^1H NMR spectra showed the presence of phenyl groups as well as protons on boron. In one fraction, the ratio of protons on boron to protons on carbon was 1.8:1 (Calcd for $C_6H_5B_{10}H_7(CO)_2$, 1.4:1), the excess of protons on boron is consistent with the presence of $B_{10}H_8(CO)_2$ as shown by the GC/MS results discussed in the text.

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least one carbonyl group in at least one isomer of each pair must be equatorial. The detection of only one isomer of $(CH_3)_2B_{10}H_6(CO)_2$ is intriguing. Several rationales are apparent, but discussion at this point would be premature speculation.

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Registry No. 1,10-$B_{10}H_8(N_2)_2$, 84692-34-2; $CH_3B_{10}H_7(CO)_2$, 92669-30-2; $(CH_3)_2B_{10}H_6(CO)_2$, 92669-31-3; $C_6H_5B_{10}H_7(CO)_2$, 92669-32-4; CO, 630-08-0; CH_4, 74-82-8; benzene, 71-43-2.