

Table IV. Bond Angles (Deg) for $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{O}_2\text{CH}^a$

atom 1	atom 2	atom 3	angle ^b
O3	Fe	C1	96.6 (1)
O3	Fe	C2	94.4 (1)
O3	Fe	Cp1	86.1 (1)
O3	Fe	Cp2	106.3 (1)
O3	Fe	Cp3	146.1 (1)
O3	Fe	Cp4	143.3 (1)
O3	Fe	Cp5	103.6 (1)
C1	Fe	C2	93.6 (1)
Cp1	Fe	Cp2	38.8 (1)
Cp1	Fe	Cp5	38.6 (1)
Cp2	Fe	Cp3	39.8 (1)
Cp3	Fe	Cp4	39.3 (1)
Cp4	Fe	Cp5	39.8 (1)
Cp1	Fe	Cp3	65.7 (1)
Cp2	Fe	Cp4	66.2 (1)
Cp3	Fe	Cp5	66.2 (1)
Cp4	Fe	Cp1	65.6 (1)
Cp5	Fe	Cp2	65.6 (1)
Fe	O3	C3	123.1 (2)
Fe	C1	O1	173.1 (3)
Fe	C2	O2	176.1 (3)
O3	C3	O4	128.4 (3)
O3	C3	H3	110 (2)
O4	C3	H3	121 (2)
Cp5	Cp1	Cp2	109.0 (3)
Cp2	Cp1	Hp1	125 (2)
Cp5	Cp1	Hp1	126 (2)
Cp1	Cp2	Cp3	107.3 (3)
Cp1	Cp2	Hp2	127 (2)
Cp3	Cp2	Hp2	126 (2)
Cp2	Cp3	Cp4	108.1 (3)
Cp2	Cp3	Hp3	126 (2)
Cp4	Cp3	Hp3	125 (2)
Cp3	Cp4	Cp5	108.2 (3)
Cp3	Cp4	Hp4	124 (2)
Cp5	Cp4	Hp4	127 (2)
Cp4	Cp5	Cp1	107.5 (3)
Cp4	Cp5	Hp5	124 (2)
Cp1	Cp5	Hp5	128 (2)

^a The atoms are labeled in agreement with Figure 2. ^b The figures in parentheses are the estimated standard deviation in the last significant digit.

final atomic coordinates and thermal parameters are collected in Tables I and II. Figure 2 presents a perspective view of the structure and defines the atomic numbering scheme employed. Interatomic distances and angles are provided in Tables III and IV.

It is clear from Figure 2 that the complex contains a monodentate formate ligand which is oriented such as to place its uncoordinated oxygen atom in the direction of the carbonyl ligands and 3.172 Å away from the iron center. This distal oxygen of the formate ligand to iron distance is considerably longer than the sum of their van der Waals radii (2.67 Å).¹⁵ On the other hand, the formate's distal oxygen is tilted toward C1, having a nonbonding distance of 2.702 (3) Å (van der Waals contact = 3.00 Å) as compared with the distance to C2 to 3.246 (3) Å. This observation is suggestive of a nonbonding interaction analogous to intermolecular nucleophilic addition to a carbonyl carbon atom. The formate carbon-oxygen bond distances are consistent with the conventional description for the M—OC(O)H linkage, i.e., (Fe)O—C and C=O. The average Fe—C and C—O bond lengths in the metal carbonyl fragment are 1.783 (3) and 1.134 (4) Å, respectively. The cyclopentadienyl ring, inclusive of hydrogen atoms, is fairly planar (see Table V) with the Fe—C bond distances displaying only slight variations (range 2.071 (3)–2.125 (3) Å) with an average value of 2.096 (3) Å.

Table V. Best Least-Squares Plane for the Cyclopentadienyl Group^a

atom	dev from plane, Å	atom	dev from plane, Å
Cp1	-0.0032	Hp1	0.0237
Cp2	0.0019	Hp2	-0.0028
Cp3	0.0001	Hp3	0.0544
Cp4	-0.0020	Hp4	0.0623
Cp5	0.0032	Hp5	0.0074

^a Defined by $-0.8749X + 0.4820Y + -0.0475Z = -0.3427$, where X, Y, and Z are orthogonal coordinates measured along \vec{a} , \vec{b} , and \vec{c}^* of the unit cell, respectively.

Bonding parameters within the cyclopentadienyl ring are normal.

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Registry No. $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{O}_2\text{CH}$, 42870-99-5; $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{THF})][\text{BF}_4]$, 63313-71-3.

Supplementary Material Available: A listing of the observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

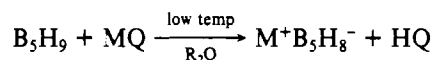
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Deprotonation of Pentaborane(9) with Solid Potassium Hydroxide

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Since the preparation of octahydro-pentaborate(1-) was reported by Gaines¹ and by Shore² in 1967, the anion has been used for the syntheses of various B_5H_8^- derivatives.³ Furthermore, a variety of novel metallaborane and metallacarborane compounds have been prepared by the reactions involving the B_5H_8^- ion.⁴ The anion has usually been prepared by deprotonating pentaborane(9) with alkali metal hydrides or alkyls.^{1,2}



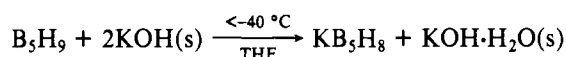
Earlier, Jolly employed solid potassium hydroxide to deprotonate extremely weak acids and, at the same time, to dehydrate the reaction mixtures.⁵ The task of preparing compounds such as $\text{CH}_3\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$, ferrocene, and methylphosphines has become less laborious by incorporating the KOH method in the procedures of the syntheses. In this note we report the deprotonation of pentaborane(9) with potassium hydroxide powder in tetrahydrofuran. The resulting solution of KB_5H_8^- would be of use for various syntheses as the source of the B_5H_8^- anion.

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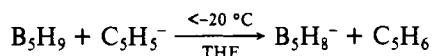
Results and Discussion

When pentaborane(9) was treated with excess potassium hydroxide powder at $-80\text{ }^{\circ}\text{C}$ in tetrahydrofuran, the B_5H_8^- anion was produced slowly in the solution. The rate of the B_5H_8^- formation was fast at $-40\text{ }^{\circ}\text{C}$, and the reaction was complete in 15 min. At $-20\text{ }^{\circ}\text{C}$ further reactions and/or the decomposition of the B_5H_8^- anion was observed. These secondary reactions appeared to proceed only very slowly at $-40\text{ }^{\circ}\text{C}$. The above observation was made on the boron-11 NMR spectra of the reaction mixture. The sample was prepared by mixing B_5H_9 , KOH powder (ca. 0.37 g per mmol of B_5H_9), and tetrahydrofuran at $-80\text{ }^{\circ}\text{C}$ in a 10-mm o.d. sample tube. This experiment confirmed the formation of the B_5H_8^- ion and the stability of the B_5H_8^- solution below $-40\text{ }^{\circ}\text{C}$ in the presence of solid potassium hydroxide. An appropriate equation for the reaction would be



The extent of the KB_5H_8 dissociation in the solution phase and the synthetic utility of the B_5H_8^- solution thus prepared were examined by performing two established reactions of the B_5H_8^- ions.⁶ The deprotonation reaction of B_5H_9 was performed at $-45\text{ }^{\circ}\text{C}$ in a larger reaction vessel with use of a larger excess of potassium hydroxide (0.7-1.5 g per mmol of B_5H_9). The solid in the resulting reaction mixture was filtered quickly and washed briefly with tetrahydrofuran in the cold. The volatile components were removed from the filtrate, and then the residue was treated with anhydrous hydrogen chloride for the conversion of the B_5H_8^- ion to B_5H_9 . The pentaborane(9) recovery was 95% or higher. Very small amounts of hydrogen gas and tetraborane(10) were produced during the process of the HCl treatment. In another experiment, the KB_5H_8 solution was filtered directly into a flask containing mercuric chloride. The reaction gave $\mu, \mu'-(\text{B}_5\text{H}_8)_2\text{Hg}$ in a 74% yield on the basis of the amount of mercuric chloride used.

Pentaborane(9) is a stronger Brønsted acid than cyclopentadiene as demonstrated by the reaction



which was used by Grimes and his co-workers to generate the B_5H_8^- ion in situ for the preparations of certain metalboranes.^{4a} Thus, the deprotonation of pentaborane(9) with solid potassium hydroxide was not an unexpected reaction, but the stability of the B_5H_8^- ion in the presence of solid KOH had been unknown. The observations described in this note suggest that the Jolly's method^{5a} can be adapted to the metallaborane and metallacarborane syntheses for which B_5H_8^- anion is utilized.

Experimental Section

General Data. Conventional vacuum-line techniques were used for the handling of volatile compounds. Potassium hydroxide powder was prepared by pulverizing KOH pellets (approximately 85%, ACS reagent grade) with use of a Waring Blender.^{5a} Pentaborane(9) (Callery Chemical Co.) and hydrogen chloride (Matheson Gas Products) were purified by fractional condensation on the vacuum line. Laboratory stock tetrahydrofuran, which had been stored over LiAlH_4 , was condensed directly in the reaction vessels from the solvent container. Commercially obtained reagent grade mercuric chloride was used as received.

Monitoring of the Reaction. Potassium hydroxide powder (0.5 g) was placed at the bottom of a tube (10-mm o.d. \times 25 cm long, Pyrex, equipped with a stopcock at the upper end), and tetrahydrofuran (ca. 2 mL) and pentaborane(9) (1.35 mmol) were condensed above the powder. The tube was shaken gently in a $-80\text{ }^{\circ}\text{C}$ bath for mixing of the reactants and then placed in the probe of a Varian XL-100-15

NMR spectrometer. The spectra of the sample were recorded at various temperatures beginning at $-80\text{ }^{\circ}\text{C}$. During the measurements, the sample tube was transferred frequently from the probe to cold baths of appropriate temperatures and the reaction mixture was agitated in the bath.

The HCl Reaction. A mixture containing B_5H_9 (2.30 mmol) and KOH powder (3.5 g) in about 30 mL of tetrahydrofuran was stirred in a 100-mL vessel for 45 min at $-45\text{ }^{\circ}\text{C}$. The solution was then filtered into another 100-mL flask through a coarse glass frit, and the solid on the frit was washed twice with cold tetrahydrofuran. Upon removal of the volatile components from the filtrate by pumping at $-45\text{ }^{\circ}\text{C}$, a heavy liquid remained in the flask. An excess of HCl (3.7 mmol) was condensed in the flask, and the flask was warmed to $-45\text{ }^{\circ}\text{C}$. The absorption of the HCl by the residue was evident at this temperature. The flask was eventually warmed to room temperature, and the volatile components were distilled out into the other part of the vacuum line where the mixture was treated with boron trifluoride (to complex tetrahydrofuran) and then fractionated. A 2.28 mmol quantity of pentaborane(9), which was slightly contaminated by tetraborane(10) (identified by IR), was recovered.

The HgCl_2 Reaction. Pentaborane(9) (9.58 mmol) was treated with KOH powder (7.0 g) in about 30 mL of tetrahydrofuran in the same manner as described above. The resulting solution was filtered into a 100-mL flask in which 1.17 g (4.31 mmol) of HgCl_2 had been placed. The washing of the solid on the frit was not performed. The reaction mixture was stirred for 3 h at $-45\text{ }^{\circ}\text{C}$, and then the volatile components were pumped out at $-45\text{ }^{\circ}\text{C}$ and finally at room temperature. The residue was washed with dichloromethane repeatedly by recycling the solvent until nothing could be leached out. The solvent was pumped out from the leachate, and the white solid product was sublimed under vacuum at $100\text{ }^{\circ}\text{C}$ for 11 h. The yield of the sublimed product $\text{Hg}(\text{B}_5\text{H}_8)_2$ was 1.04 g (3.18 mmol) or 73.7% on the basis of the HgCl_2 used.⁷ The product in a dichloromethane solution gave the ^{11}B NMR signals at -8.4 , -9.7 , and 45.1 ppm.⁸ The J_{BH} value for the 45.1 ppm doublet was 176 Hz.⁸ The ^{11}B NMR spectra of the sublimation residue (suspended in CH_2Cl_2) contained strong signals of $\text{Hg}(\text{B}_5\text{H}_8)_2$, indicating the sublimation was incomplete.

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Registry No. B_5H_9 , 19624-22-7; KOH, 1310-58-3; $\text{Hg}(\text{B}_5\text{H}_8)_2$, 70850-80-5.

- (7) A yield of 90% was reported for the synthesis of $\text{Hg}(\text{B}_5\text{H}_8)_2$ which was described in ref 3c.
 (8) The reported values in ref 3c are -7.92 , -9.60 , and -43.85 ppm, the coupling constant for the most shielded doublet being 176 Hz.

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Reaction of Azide Ion with Some Hexafluorides

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This work arose as a part of a study of the complexing of simple anions by binary fluorides.¹ It is known that the azide ion forms weak complexes with sulfur dioxide,² but there is no evidence of interaction with acetonitrile. A compound containing the elements of WF_6 and N_3^- is WF_5N_3 which has been synthesized from trimethylsilyl azide and WF_6 .³ Reactions of some of the title compounds have been found to give

(6) For the reaction of B_5H_8^- with HCl, see ref 1. For the reaction of B_5H_8^- with HgCl_2 , see ref 3c.

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