**Table IV.** Bond Angles (Deg) for $(\eta^5\text{-}C_5H_5)Fe(CO)_2O_2CH)$[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. Bonding parameters within the cyclopentadienyl ring are normal.

**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.

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**Registry No.** $(\eta^5\text{-}C_5H_5)Fe(CO)_2O_2CH$, 42870-99-5; $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(THF)][BF_4]$, 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 octahydropentaborate(1−) was reported by Gaines[1] and by Shore[2] 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]

$$B_5H_9 + MQ \xrightarrow[R_2O]{\text{low temp}} M^+B_5H_8^- + HQ$$

$$MQ = \text{Li alkyls, NaH, KH}$$

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 $CH_3Mo(CO)_3C_5H_5$, 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 °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 °C, and the reaction was complete in 15 min. At −20 °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 °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 °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 °C in the presence of solid potassium hydroxide. An appropriate equation for the reaction would be

$$B_5H_9 + 2KOH(s) \xrightarrow[\text{THF}]{<-40\ ^\circ C} KB_5H_8 + KOH{\cdot}H_2O(s)$$

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 °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 $\mu,\mu'$-$(B_5H_8)_2Hg$ 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

$$B_5H_9 + C_5H_5^- \xrightarrow[\text{THF}]{<-20\ ^\circ C} B_5H_8^- + C_5H_6$$

which was used by Grimes and his co-workers to generate the $B_5H_8^-$ ion in situ for the preparations of certain metallaboranes.[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 Blendor.[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. × 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 °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 °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 °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 °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 °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 °C, and then the volatile components were pumped out at −45 °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 °C for 11 h. The yield of the sublimed product $Hg(B_5H_8)_2$ 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 $Hg(B_5H_8)_2$, indicating the sublimation was incomplete.

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**Registry No.** $B_5H_9$, 19624-22-7; KOH, 1310-58-3; $Hg(B_5H_8)_2$, 70850-80-5.

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(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.

(7) A yield of 90% was reported for the synthesis of $Hg(B_5H_8)_2$ 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

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