Reactivity of Metal Boronhydride Derivatives with Amines and Ethanolamines

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Abstract. Reducing agents LiBH₄, NaBH₄, NaBH(CO₂CH₃)₃, NaBH(OCH₃)₃ and NaBH₃CN are widely applied in organic synthesis, biochemistry and medical chemistry. In this paper, the structure and the reactivity of metal boronhydride derivatives with amines were studied and the coordination of amines and ethanolamines towards metalboronhydride derivatives was investigated.

1. Introduction
LiBH₄, NaBH₄, NaBH(CO₂CH₃)₃, NaBH(OCH₃)₃ and NaBH₃CN are all reducing agents. Particularly LiBH₄, NaBH₄ are commercially produced [1] and have a wide applicability in organic synthesis [2]. NaBH(CO₂CH₃)₃, NaBH(OCH₃)₃ and NaBH₃CN are also used very popular in biochemistry and medical chemistry [3, 4, 5]. For example, NaBH(OCH₃)₃ can be used in reductive amination [6, 7]; NaBH(OCH₃)₃ is an effective hydride source in selective reductive displacement of halides [8]; In reductive decyanation with NaBH₃CN excises the cyano group and furnishes unadorned quinolizidines in excellent yield [9].

We are interested in the study of the structure and the reactivity of metal boronhydride derivatives (M = Li, Na, K) with amines. In particular, we investigated the coordination of amines and ethanolamines towards metalboronhydride derivatives.

In this study, we used the following amines: isopropyl amine, N, N, N’, N’-tetramethylethyldiamine, 2-picolyamine, (N-methyl) ethanolamine, isoquinoline and pyridine.

2. Results and Discussion

2.1. Lone pairs ligands
There are six reactions in this group. The reactions and their results are described in Table 1. The aim of this research was to prepare metalboronhydrides complexes in order to study their reactivity and structural properties by X-ray diffraction. So N, N, N’, N’-tetramethylethyldiamine, isopropyl amine and 2-picolyamine were chosen as the ligands because of they have lone pairs.
Table 1. Preparation of Metalboronhydrides Complexes.

| Number | Reagent 1   | Reagent 2 | NMR-$^{11}$B (ppm) | Results        |
|--------|-------------|-----------|---------------------|----------------|
| 1      | $\text{NH}_2$ | NaBH$_4$  | -42.5              | no reaction    |
| 2      | $\text{NH}_2$ | KBH$_4$   | -----              | compound was insoluble |
| 3      | $\text{N}$$\text{N}$ | NaBH$_4$  | -42.9 -9.5         | reaction       |
| 4      | $\text{N}$$\text{N}$ | LiBH$_4$  | -40.7 -9.5         | reaction       |
| 5      | $\text{H}$ $\text{N}$$\text{N}$ | NaBH$_4$  | -40.4 -40.6 -40.7 | reaction       |
| 6      | $\text{N}$$\text{N}$ | LiBH$_4$  | -39.2              | reaction       |

The reactions 1 - 6 of MBH$_4$ (M=Li, Na, K) with an excess of amine were performed, its $^{11}$B NMR spectra showed a quintet assigned to the BH$_4^{-}$ group. Also, in the reactions 3 and 4, a minor signal (quartet) was observed at -9.5 ppm, indicating the formation of N→BH$_3$ adduct. The reaction 2 did not proceed because of the scarce solubility of KBH$_4$ in isopropyl amine, the same was observed in the reaction 1.

The used crystallization method was the slow diffusion method. Pentane (5 mL) was diffused into the solution of the corresponding amine and MBH$_4$ (M=Li, Na, K). From the reaction 1, single crystals suitable for X-ray structure analysis were obtained after one week. The X-ray structure showed the lack of the reaction of NaBH$_4$ with isopropyl amine and also showed how the molecule NaBH$_4$ forms an infinite chain in the lattice by the presence of Na-H intermolecular bonds.

2.2. Aliphatic and Aromatic Amines

There are nine reactions in this group. The reactions and their results are described in Table 2. The aim of this research was to prepare the coordination compounds derived from NaBH$_2$CN, NaBH(OMe)$_3$ and NaBH(OAc)$_3$ with aliphatic and aromatic amines, to get single crystals suitable for X-ray diffraction in order to study their structural properties.
Table 2. Preparation of Coordination Compounds.

| Number | Reagent 1      | Reagent 2     | NMR $^{11}$B (ppm) | Results         |
|--------|----------------|---------------|---------------------|-----------------|
| 7      | $\text{NH}_2$  | NaBH(OAc)$_3$| 0.1 (borate)        | reaction        |
|        |                |               | 19.8 (B(OR)$_3$)   |                 |
|        |                |               | 25.8               |                 |
| 8      | $\text{NH}_2$  | NaBH$_3$CN    | -43.5 (NaBH$_3$CN complex) | reaction |
|        |                |               | -22.0 (N→BH$_3$)   |                 |
| 9      | $\text{NH}_2$  | NaBH(OMe)$_3$| -42.0 (NaBH(OMe)$_3$ complex) | reaction |
|        |                |               | 2.1, 6.6 (borate)  |                 |
| 10     | $\text{N}$     | NaBH(OAc)$_3$| 1.1 (borate)        | reaction        |
|        | $\text{N}$     |               | 2.7 (borate)        |                 |
| 11     | $\text{N}$     | NaBH$_3$CN    | -42.4 (NaBH$_3$CN complex) | reaction |
|        | $\text{N}$     |               | -12.1 (N→BH$_3$)   |                 |
| 12     | $\text{N}$     | NaBH(OMe)$_3$| -41.0 (NaBH(OMe)$_3$ complex) | reaction |
|        | $\text{N}$     |               | 2.6, 7.3 (borate)  |                 |
| 13     | $\text{N}$     | NaBH$_3$CN    | -41.1 (NaBH$_3$CN complex) | reaction |
| 14     | $\text{N}$     | NaBH(OMe)$_3$| -39.6 (NaBH(OMe)$_3$ complex) | reaction |
|        | $\text{N}$     |               | 3.1 (borate)        |                 |
| 15     | $\text{N}$     | NaBH(OAc)$_3$| -----               | compound was insoluble |

The reaction 7 - 14 of sodium boron hydride derivatives with an excess of amine were performed, their $^{11}$B NMR spectra showed a mixture of compounds (as we can see in the Table 2), with the exception of the reaction 13, in which it was observed a signal corresponding to the BH$_3$CN complex. In this compound, the $\delta ^{11}$B is not sensitive to the changes in the electronic density of the sodium atom.

On the other side, NaBH(OMe)$_3$ is more reactive than NaBH$_3$CN and NaBH(OAc)$_3$, probably because NaBH(OMe)$_3$ is more soluble than the other two.

The used crystallization method was the slow diffusion method. Pentane (5 mL) was diffused into the solution of the corresponding amine and metalboronhydrides derivatives. From the reaction 10 and 12, single crystals were separated from the reaction mixtures after one week. These single crystals were suitable for X-ray structure analysis.
2.3. High Temperature Conditions

The reaction 16 and 17 were performed in the same way as the reactions 7 - 15 under reflux (Table 3). High temperature is good for the reactions, but we can only see one signal in reaction 17, probably because in these compounds, the δ of $^{11}$B is not sensitive to the electronic environment of the sodium atom.

**Table 3. Reactions under reflux.**

| Number | Reagent 1 | Reagent 2   | NMR-$^{11}$B (ppm) | Results |
|--------|-----------|-------------|---------------------|---------|
| 16     | $\circ$   | NaBH(OMe)$_3$ | -44.1 2.1          | reaction |
| 17     | $\square$ | NaBH(OMe)$_3$ | -40.9              | reaction |

2.4. Function of the Ligand's Mass

There are five reactions in this group. They were performed in different molar ratios (2:1; 1:1; 1:2). Their results are described in Table 4. The aim of this group was to research the function of the ligand's mass in the reaction. At first, ethyl ether was chosen as solvent, but reagent 1 and reagent 2 were not solved on it, so toluene was finally chosen as solvent, although reagent 2 was not solved on it either. After stirring the reaction mixture, it became a suspension. Some minutes later, a kind of white oil-like liquid appeared, it was unsolved in toluene.

**Table 4. Function of the Ligand's Mass.**

| Number | Reagent 1 | Reagent 2 | Solvent   | NMR-$^{11}$B (ppm) | Results |
|--------|-----------|-----------|-----------|---------------------|---------|
| 18     | $\text{N} \text{H} \text{O}$ | NaBH(OMe)$_3$ | $\text{N} \text{H} \text{O}$ | -42.0 1.6          | reaction |
| 19     | $\text{N} \text{H} \text{O}$ | NaBH(OAc)$_3$ | Toluene   | -0.7, 1.6 4.2, 7.5 | reaction |
| 20     | $\text{N} \text{H} \text{O}$ | NaBH(OAc)$_3$ | $\text{N} \text{H} \text{O}$ | 4.3                | reaction |
| 21     | $\text{N} \text{H} \text{O}$ | NaBH$_3$CN   | Toluene   | -----              | reaction |
| 22     | $\text{N} \text{H} \text{O}$ | NaBH$_3$CN   | $\text{N} \text{H} \text{O}$ | -43.6 2.1          | reaction |

From these reactions, we can see that to choose a good solvent is very important. It can make the reagent diffuse well and has more chance to contact with each other. And the NMR spectra showed also the formation of new borate species in all of the reactions. We observed also that the best reaction conditions were when ethanolamine is used as solvent.
2.5. Temperature Effect

There are four reactions in this group. The reactions and their results are described in Table 5. The aim of these reactions was to study how does the reactivity of these boron hydride derivatives in (N-methyl) ethanolamine change with the effect of the temperature.

Table 5. Temperature Effect.

| Number | Reagent 1 | Reagent 2 | NMR-^1^B (ppm) | Results |
|--------|-----------|-----------|----------------|---------|
| 23     |  \( \text{N} \text{H} \text{OH} \) | NaBH(OMe)_3 | 1.8            | reaction |
| 24     |  \( \text{N} \text{H} \text{OH} \) | NaBH(OAc)_3 | 4.2            | reaction |
| 25     |  \( \text{N} \text{H} \text{OH} \) | NaBH_4CN    | -43.7, 2.1     | reaction |
| 26     |  \( \text{N} \text{H} \text{OH} \) | LiBH_4      | -41.4, 1.7     | reaction |

From the results in the table, the following discussion is made. High temperature is good for the reaction. In reaction 24 and 25, there were no starting materials. That means, reagent 2 are all more reactive in high temperature than in room temperature.

Acknowledgments

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