

Metal Tetrahydroborates and Tetrahydroborato Metallates, 30 [1].

Alkoxo-Substituted Alkali Metal Tetrahydroborates:

Studies in Solution and Structures in the Solid State

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Dedicated to Professor Kurt Dehnicke on the occasion of his 70th birthday

Reactions of MBH₄ (M = Li, Na, K) with *t*BuOH, Ph₃COH, PhOH, F₅C₆OH, and 2,4-*t*Bu₂C₆H₃OH in THF in a 1 : 1 ratio were followed by ¹¹B NMR spectroscopy. No M[H₂B(OR)₂] species could be detected, but minor amounts of M[H₃BOR] and larger amounts of M[HB(OR)₃]. In the reaction of LiBH₄ with 2,4-*t*Bu₂C₆H₃OH also a fair proportion of (RO)₂BH was generated. The perfluorophenolato borane (F₅C₆O)₂BH·THF was prepared from the phenol and BH₃·THF in THF solution. It is unstable to disproportionation. Compound (C₆F₅O)₃B·THF was isolated and its crystal structure determined. Reaction of LiBH₄ with F₅C₆OH in hexane generated a solid that proved to be Li[H₂B(OC₆F₅)₂]. It is unstable in THF. On the other hand, 2,2'-dihydroxydiphenyl in the presence of secondary amines reacts to give Li[C₁₂H₈O₂B(NR₂)₂] (**3**–**5**). Li[B(O₂C₁₂H₈)₂], **2**, is formed when HN(*t*Bu)Ph is used as a secondary amine.

The unstable phthalatoborane H{C₆H₄[C(O)O]₂}BH·THF (**7**), is stabilized as its pyridine adduct (phth)BH·py (**8**). **7** reacts with 3 equivalents of Li*t*Bu to give [Li(HB*t*Bu)₃] (**11**), isolated as its tris(THF) solvate. Analogously, **7** reacts with LiNMePh to produce compound Li[HB(NMePh)₃] (**10**). Similarly, **7** and Na*Or*Bu (molar ratio 1 : 3) give access to Na[HB(*Or*Bu)₃] (**9**). In attempts to grow single crystals, specimens resulting from a hexane solution showed that partial hydrolysis has occurred to give Na[HB(*Or*Bu)₃]·Na[(*t*BuO)₂BO]·Na[*t*BuOB(O)H], which crystallizes as a centrosymmetric dimer.

While catecholborane when treated with Li*t*Bu in THF and DME gave access to (dme)₂Li[catB-*t*Bu]₂], **12** (dme)₂, several compounds were observed when Li piperidide was used as nucleophile. Amongst these, the most interesting one was (dme)(THF)Li₂(cat)(catBH), **13** (dme)THF, the crystal structure of which was determined. In all cases where the borate species carried OR groups the O atoms of the RO or PhO group coordinate with the alkali metal cation.

DFT calculations for the series of anions H_{4-n}BX_n[–] showed that HBX₃[–] is the most stable species for X = F, OH, NH₂. This confirms experimental results.

Key words: Hydridoborates, Catecholohydridoborates, Aminohydridoborates, Alkali Metals, DFT Calculations