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METAL TETRAHYDROBORATE COMPLEXES: SELECTIVE REDUCING AGENTS FOR ORGANIC SYNTHESIS

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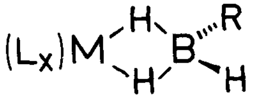
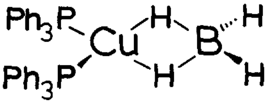
The tetrahydroborate ion and its derivatives have found extensive use as selective reducing agents in both organic[1] and organometallic[2] synthesis. In addition, BH_4^- has been utilized as a ligand to form covalent coordination complexes[3] which are of both theoretical and practical interest because of the unusual bonding modes exhibited by the borohydride moiety,[4] their fluxional behavior,[5] and their catalytic properties.[6] It is our contention that covalent tetrahydroborate complexes, 1, constitute a previously unrecognized class of reducing agents which should be useful for performing selective reductions of organic compounds. The coordinated boron hydride group may possess a reducing capability approaching that of the tetrahydroborate ion itself, however, the reactivity of the B-H bond should be readily varied by a judicious choice of ligands or metal ion.


1


2

Bis(triphenylphosphine)tetrahydroborato copper(I),[7] 2, is an example of one such reagent. We have found that the BH_4 moiety in complex 2 is deactivated to the extent that it will only reduce carboxylic acid chlorides to aldehydes (equation 1). This is in contrast to $NaBH_4$ which results in further reduction to the alcohol.[1] The reaction proceeds in good yields under mild conditions (Table 1), and the reagent appears to tolerate all common functional groups.[8] In no case have we observed reduction past the aldehyde stage.

$$\mathrm{RCOCl} \xrightarrow[\text{acetone, }25^\circ]{(\mathrm{Ph_3P})_2\mathrm{CuBH_4}} \mathrm{RCHO} \tag{1}$$

The tetrahydroborate complex 2 should find applications in synthesis. Unlike many reagents which have been developed to effect reaction (1) including $LiAlH(O\text{-}\underline{t}\text{-}Bu)_3$[9], $Na_2Fe(CO)_4$[10], and $HFe(CO)_4^-$[11], $(Ph_3P)_2CuBH_4$ is readily prepared from inexpensive starting materials[12] and is neither oxygen nor moisture sensitive; furthermore, reductions are carried out at ambient temperatures. The principal drawback of 2 is its high equivalent weight (MW = 603) since only one hydride is active.

The preparation of p-bromobenzaldehyde proceeds as follows. To a stirred solution of p-bromobenzoyl chloride (0.95 g, 4.3 mmol) in 5 mL of acetone was added, in one portion, 2.74 g (4.5 mmol) of 2 followed by 15 mL of acetone. The suspension was stirred for 80 min, filtered, and the residue washed with six 5-mL portions of ether. Evaporation of the combined filtrates

Table 1

Product	Yield[a] (%)
benzaldehyde	85
p-bromobenzaldehyde	100 (75)
p-cyanobenzaldehyde	63
p-methoxybenzaldehyde	66
p-nitrobenzaldehyde	25
3,4-dichlorobenzaldehyde	85 (63)
furfural	82
cinnamaldehyde	77
nonanal	76

[a] Yields were determined by glc using authentic samples of aldehydes and an internal standard. Numbers in parentheses are the yields for isolated products (ref. 13).

followed by bulb-to-bulb distillation gave 606 mg (75%) of *p*-bromobenzaldehyde.[13]

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8. We do not understand the low yield associated with *p*-nitrobenzaldehyde. We find no reduction of the nitro function in any other nitro compounds.
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12. The reagent is prepared as follows. Cuprous chloride (1 g, 0.01 mol) is dissolved in 500 mL of chloroform containing 12 g of triphenylphosphine. A solution of $NaBH_4$ (0.76 g, 0.02 mol) in 100 ml of 95% ethanol is added dropwise. After stirring for an hour, the solution is filtered and concentrated using a rotary evaporator to give white crystalline $(Ph_3P)_2CuBH_4$ which is collected by filtration, and washed with ethanol and ether. The air dried product weighs 6 g (100%), mp 175° (dec.).
13. Isolated compounds had ^{11}H nmr and ir spectra identical with authentic samples.