

## Observations on Copper(I) Borohydride

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### Abstract

The solution usually described as 'copper borohydride' contains chloride which continues to be associated with the copper, even through thermal decomposition or complexation.

### Introduction

Copper(I) borohydride,  $\text{CuBH}_4$ , was first reported by Wiberg and Henle in 1952, as a thermally unstable compound arising from the reaction of an ether solution of  $\text{LiBH}_4$  at  $-20^\circ\text{C}$  with an excess of cuprous chloride suspended in tetrahydrofuran (THF) [1]. Analytical data supporting the formulation as  $\text{CuBH}_4$ , however, were not given but the significant properties of the compound appeared to be: its high solubility in 1:1 ether-THF, decomposition at  $0^\circ\text{C}$  into copper(I) hydride and either diborane or boron and hydrogen and, finally, the formation of a stable bright green product by interaction with pyridine. Later, Kligen reported the formation of colorless  $\text{CuBH}_4$  which precipitated from ether in the reaction of cupric chloride and  $\text{LiBH}_4$  at  $-45^\circ\text{C}$ . Although reliable analytical data this time were presented for the precipitated solid, lithium chloride appeared to be present in it. Again, the compound was reported to be thermally unstable, decomposing above  $-12^\circ\text{C}$ , but no other properties were reported [2].

Apart from these sparse results, copper borohydride is much more familiar in a number of thermally stable complexes with phosphine ligands. In fact the most well-known: bis(triphenylphosphine)-copper(I) borohydride,  $(\phi_3\text{P})_2\text{CuBH}_4$ , is now marketed commercially as a useful reducing agent for a number of organic functional groups [3–7].

Since  $\text{CuBH}_4$  itself could prove to be a reactive and reducing molecule despite its thermal instability, we were prompted to investigate it further. That copper borohydride is not necessarily a simple spe-

cies – indeed that it appears from two somewhat disparate lines of evidence to be quite strongly interacting with the reaction by-product – is the basis of this report.

### Experimental

#### (i) Reagents and Handling

Cuprous chloride was prepared via the method of Keller and Wycoff [8] and stored in a vacuum desiccator. Lithium borohydride (B.D.H.) was recrystallized from diethyl ether prior to use. Other reagents used were good commercial quality and employed without further purification. Tetrahydrofuran and diethyl ether were distilled (under nitrogen) from calcium hydride pellets. All reactions were routinely performed in inert atmosphere ( $\text{N}_2$  or Ar) using Schlenk-ware, a synthetic high-vacuum line or a nitrogen-filled glovebox, as convenient.

#### (ii) 'Copper Borohydride' Solutions

Lithium borohydride (0.15 g, 6.89 mmol) dissolved in tetrahydrofuran (*ca.*  $15\text{ cm}^3$ ) was added slowly to a suspension of cuprous chloride (0.68 g, 6.89 mmol) in tetrahydrofuran (*ca.*  $20\text{ cm}^3$ ) maintained at  $-45^\circ\text{C}$ . All the  $\text{CuCl}$  went into solution. Dry diethyl ether (*ca.*  $35\text{ cm}^3$ ) was then added. A very small amount of white solid may separate at this stage, depending on exact temperature and volume of ether employed.

#### (iii) Decomposition

The 'copper borohydride' solution obtained in (ii) above was allowed to warm to room temperature under  $\text{N}_2$ . As decomposition occurred, the solution turned a red-brown color and deposited a similar-colored precipitate together with a copper mirror on the walls of the flask. Quite rapidly (minutes) the red color blackened, leaving a black precipitate and a clear, colorless solution. Hydrogen (identified by mass spectrometry) was evolved as darkening proceeded. The black precipitate appeared stable under nitrogen, but turned green on prolonged exposure to air.

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*(iv) Complexation by Ligand Addition*

To the 'copper borohydride' solution obtained in (ii) above, the appropriate number of mole equivalents of the various ligands (L) required to give  $L_nCuBH_4$  were added directly with vigorous stirring. For example, 2 mol of solid triphenylphosphine were added under  $N_2$  per mole of  $CuCl$  initially employed ( $L_2CuBH_4$ ). In all cases, precipitates were obtained which were filtered off and washed with a small amount of dry ether.

Addition of triphenylarsine caused a white precipitate to settle out at  $-45^\circ C$ , but this decomposed quite quickly at room temperature. While this precipitate appeared to contain  $(\phi_3As)_2CuBH_4$ , its decomposition appears to be quite consistent with the earlier observations of Lippard and Ucko [9].

**Results and Discussion**

The reaction of cuprous chloride with an equimolar quantity of  $LiBH_4$  in THF at  $-45^\circ C$  indeed produces a thermally unstable solution as reported originally by Wiberg. Usually a clear solution with a hint of a red-brown coloration is obtained in this preparation. The color is consistent with the presence of a slight amount of copper hydride arising from decomposition and, at lower temperatures, such color is not generally observed. If diethyl ether is included in the solvent (*cf.* ref. 1) and the reaction is performed at low temperature, the precipitation of some white solid is observed. This observation appears to support those of Klingen whose product precipitated directly from the ether solvent. Low temperature  $^{11}B$  NMR spectra of these solutions reveals only the presence of some  $LiBH_4$  as a characteristic 1:4:6:4:1 quintet [ $^1J(^{11}B-^1H) = 83.0$  Hz,  $-63.96$  ppm *vs.* 0.5 M  $H_3BO_3/D_2O$  (for THF solution)]\* [10]. It is unfortunate that no signal which can be attributed to  $CuBH_4$  itself is evident, possibly because of broadening due to interaction with the quadrupolar copper nuclei ( $^{63}Cu$ , 69.09%;  $I = 3/2$ ;  $^{65}Cu$ , 30.91%;  $I = 3/2$ ).

When the THF/ether solution containing a 1:1 ratio of  $LiBH_4:CuCl$  is allowed to warm to room temperature, decomposition occurs, apparently in two stages. First, a brown-red precipitate separates from a dark red solution, accompanied by evolution of hydrogen. On standing (*ca.* 1/2 h) the precipitate blackens and the solution becomes clear and colorless. The red-brown color so evident probably is due to the formation of copper hydride, although all our attempts to isolate it proved unsuccessful.

Accordingly, copper metal also may be identified by X-ray powder diffraction as a major constituent of the final black precipitate.

In view of suggestions that interaction of transition-metal salts with alkali-metal borohydrides may yield dark-colored borides [11-13] this black precipitate was examined further. Elemental analyses were attempted on this decomposition product (Table I) but it is difficult to come to any firm conclusions from the figures obtained. It is evident, however, that a consistent product is not achieved. Around 3% boron is generally found, together with variable amounts of carbon, hydrogen, chlorine and (apparently) oxygen. Lithium analysis via atomic absorption reveals virtually none of this metal in the black product. This is an interesting result which suggests that the significant amount of chlorine which is present in the product remains associated with the copper rather than with the lithium.

TABLE I. Analyses of the Dark Solid and Clear Solution Arising from the Decomposition of 'Copper Borohydride' Solution

	Li <sup>a</sup>	Cu <sup>a</sup>	B	Cl	C	H	O
Solid <sup>b</sup>	<1	72.08 <sup>c</sup>	3.9	1.9	1.70	0.73	10.1
	<1	77.77 <sup>d</sup>	3.5	4.6	0.55	0.33	16.5
Solution <sup>b</sup>	96.48 <sup>e</sup>	0 <sup>e</sup>					
	91.57 <sup>e</sup>	0 <sup>e</sup>					

<sup>a</sup>Obtained via atomic absorption spectrophotometry; remaining elements via microanalytical methods. <sup>b</sup>Two separate determinations. <sup>c</sup>Cu:B = 3.14:1. <sup>d</sup>Cu:B = 3.78:1. <sup>e</sup>Percentages of the starting quantities which were finally present in the solution.

The apparently high oxygen content is surprising. The carbon, hydrogen and some of the oxygen probably arise from small quantities of bonded or entrained solvent. It is possible that some copper oxides or borates could be formed or that the finely-divided material is extremely sensitive to oxidation and is attacked even under normally inert conditions. Regardless of this, however, the oxygen analyses themselves could be subject to a considerable degree of error. While the analytical method employed commercially yields essentially correct values when applied to cuprous oxide (%O = 11.18) it is claimed to be unreliable in the presence of boron and lithium\*\*.

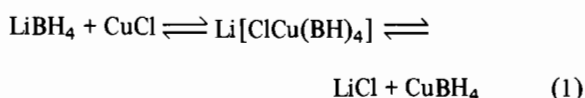
Analysis of the solution remaining after the decomposition has taken place shows that all the

\*Signal at  $-63.27$  ppm with 1:1 ether/THF solvent.  $^{11}B$  NMR spectra obtained on a JEOL FX-200 instrument operating at 63.98 MHz.

\*\*H. Malissa and G. Reuter, Engelskirchen, F.R.G., private communication. All microanalytical data were obtained from their laboratory or from the Australian Microanalytical Service Division of AMDEL, Melbourne.

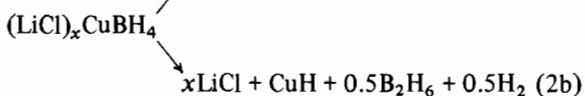
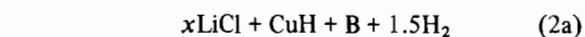
copper is precipitated and that the lithium concentrates in this phase. A  $^{11}\text{B}$  NMR spectrum obtained in the initial stages of the decomposition reveals the presence of  $\text{THF}:\text{BH}_3$  (1:3:3:1 quartet,  $^1J(^{11}\text{B}-^1\text{H}) = 105$  Hz [10] together with the characteristic pattern of  $\text{LiBH}_4$ .

Since cuprous chloride is virtually insoluble in THF at low temperature, the analytical data alone strongly suggest that the 'copper borohydride' which forms is significantly complexed with the  $\text{LiCl}$  by-product (also *vide infra*). One possibility might be that a 'double salt' type of intermediate could exist (at least in part) in the 'copper borohydride' solution (eqn. (1)), similar to those observed for zinc [14], aluminum [15] and zirconium [16].



Another possible intermediate might be a copper cluster similar to those generated at low temperatures in ethereal solvents by the interaction of phenyllithium and copper(I) halides (or pseudohalides) [17, 18]. It is significant that a recent attempt to prepare  $[\phi_3\text{PCuH}]_6$  from  $[\phi_3\text{PCuCl}]_4$  and potassium 'selectride' in THF yielded the cluster molecule in which chloride was incompletely replaced by hydride [19].

Whatever the nature of the intermediate (which may be represented by  $(\text{LiCl})_x\text{CuBH}_4$ ), it is possible to visualize its decomposition involving the elimination of  $\text{LiCl}$  while its 'copper borohydride' component decomposes to  $\text{CuH}$  (and thence to copper) and either  $\text{B}_2\text{H}_6$  or elemental boron according to the original suggestion of Wiberg:



The  $\text{LiBH}_4$  and  $\text{THF}:\text{BH}_3$  observed in the NMR spectra thus arise from the processes described in eqns. (1) and (2). Since the  $\text{Cu}:\text{B}$  ratio in the solid decomposition product is between 3 and 4 to one, clearly the process in eqn. (2b) predominates over that in (2a). The issue of possible boride formation is still unresolved, although it should be pointed out that genuine borides of copper,  $\text{Cu}_x\text{B}_y$ , are not known when  $x$  and  $y$  are small integers and, further, genuine metal borides are synthesized by high temperature reactions [20–22].

The thermally unstable 'copper borohydride' solution in THF/ether yields the known stable complexes of formula  $\text{L}_n\text{CuBH}_4$  when ligands  $\text{L}$  such as triphenylphosphine or tris(*p*-methoxyphenyl)phosphine (both  $n = 2$ ) and methyldiphenylphosphine ( $n = 3$ ) or the bidentates 'neocuproine' (2,9-dimethyl-1,10-phenanthroline) or 1,2-bis(diphenylphosphino)ethane ('DIPHOS') (both  $n = 1$ ) are added, (Table II) [9, 23–25].

TABLE II. Analytical Data for Copper Borohydride Complexes

	C	H	B	Cl	Li
$(\phi_3\text{P})_2\text{CuBH}_4$	70.52	6.38	1.56	0.43	0.016
Calculated	71.70	5.64	1.71		
$[(p\text{-MeOC}_6\text{H}_4)_3\text{P}]_2\text{CuBH}_4$	62.34	6.34	1.04	1.3	0.19
Calculated	64.42	5.92	1.38		
2,9-DMPCuBH <sub>4</sub>	61.68	5.41	3.0	6.83	1.07
Calculated	58.66	5.43	3.77		
(DIPHOS)CuBH <sub>4</sub>	62.15	5.24	1.16	1.5	0.19
Calculated	65.22	6.32	2.26		
$(\text{MeP}\phi_2)_3\text{CuBH}_4$	67.65	6.14	1.54	1.78	0.032
Calculated	68.98	6.38	1.59		

While infrared spectra of these stabilized products display the characteristic terminal and bridging B–H stretching and deformation modes expected for each of the likely borohydride compounds (see Fig 1) analyses performed on them however reveal once again that both lithium and chloride are present in

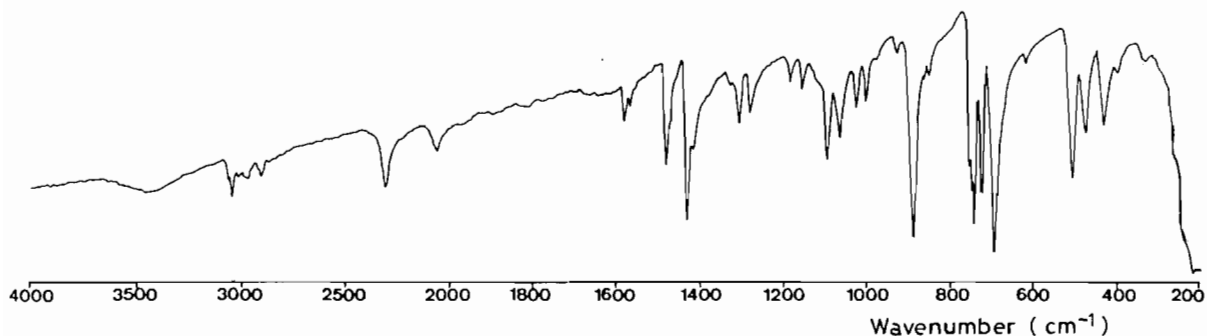


Fig. 1. Infrared spectrum of the product obtained by addition of methyldiphenylphosphine to a solution of copper borohydride.

the samples. Assuming that the very small amounts of lithium found are due to LiCl there still remain substantial amounts of chloride which are not accounted for (Table II). This situation parallels that obtaining for the black solid arising from the thermal decomposition and shows that the results are again consistent with the presence of a chloride-containing intermediate, with copper bound to both  $\text{Cl}^-$  and  $\text{BH}_4^-$  moieties. Addition of other ligands, then, produces not only a copper borohydride complex but also some concomitant copper chloride analog.

Corroboration of this can be obtained from X-ray powder diffraction data. The pattern obtained from the product mixture which was precipitated by addi-

tion of methyldiphenylphosphine to the solution of 'copper borohydride' is shown in Fig 2a and this may be compared with the patterns obtained for authentic samples of the borohydride and the chloride (Figs 2b 2c)\*. Despite the relatively complex nature of all the patterns, it is quite clear that in Fig. 2a. it is the chloride pattern which predomi-

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\*X-ray powder diffraction data were obtained by Dr. D. G. Hay at C.S.I.R.O. Division of Materials Science, Clayton, Victoria, using a Siemens D500 Diffractometer which employed Ni filtered  $\text{Cu K}\alpha$  radiation. A pulse height analyzer was fitted to the instrument.

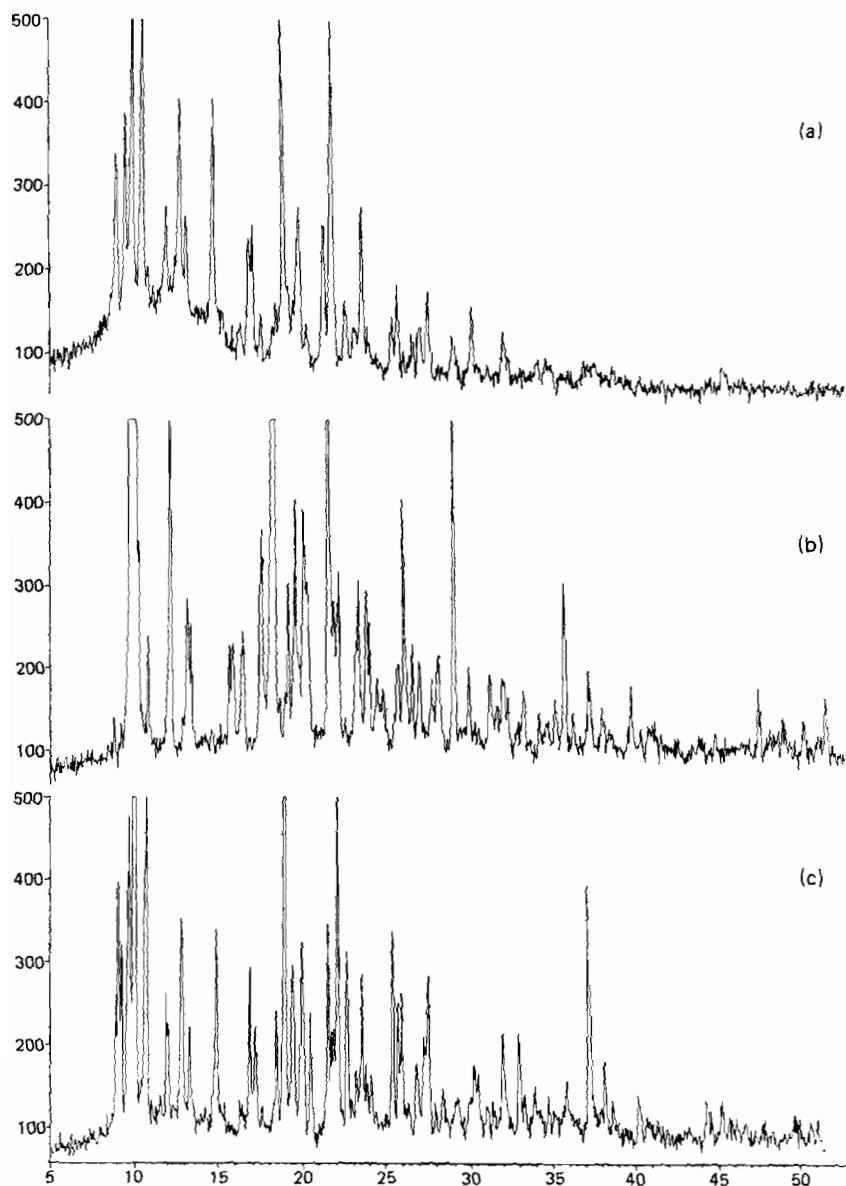


Fig. 2. X-ray powder diffraction patterns. (a) Product from methyldiphenylphosphine addition to a solution of copper borohydride; (b)  $(\text{MeP}\phi_2)_3\text{CuBH}_4$ ; (c)  $(\text{MeP}\phi_2)_2\text{CuCl}$ . Abscissa is  $2\theta$ .

TABLE III. B:Cl Ratios in Ligand-stabilized Samples

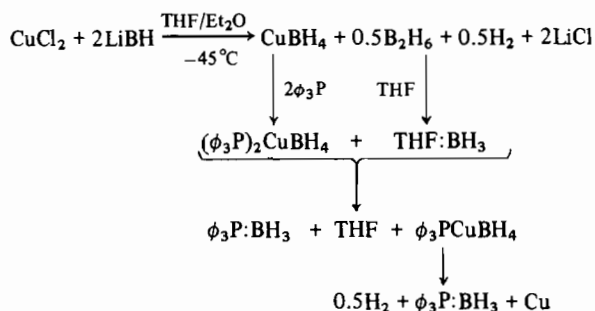
Sample Origin	B:Cl
$\phi_3\text{P}$ (2 mol equivalents)	14.7
( <i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> P (2 mol equivalents)	10.3
Neocuproine (1 mol equivalent)	7.1
MeP $\phi_2$ (3 mol equivalents)	3.1
DIPHOS (1 mol equivalent)	2.5

nates\*. In fact the pattern typical of the borohydride is difficult to discern at all even though the analytical data show that the borohydride is the major constituent. It is possible that in a two-component mixture only one of the constituents may be observed by this method due to sample amorphicity and orientation effects in the crystals because the sample is not rotated in the X-ray beam. Thus, less-intense peaks from one constituent may become obscured in the background from the component which gives the more intense pattern. For example, the intense peak for the borohydride ( $d = 9.037 \text{ \AA}$ ) was obscured in the high background evident between *ca.*  $9.8 \text{ \AA}$  and *ca.*  $5.0 \text{ \AA}$  in the mixture. Another intense reflection ( $d = 4.8551 \text{ \AA}$ ) of the borohydride may possibly be assigned to a low intensity peak at  $4.8613 \text{ \AA}$  in the mixture. The important point is that it is the chloride complex which is clearly identified by this method in a sample which was originally indicated to be the borohydride\*\*.

Recrystallization from chloroform of the product from triphenylphosphine addition causes the B:Cl ratio to decrease markedly, probably because the least soluble product is being favored. After LiCl in the samples is accounted for, the B:Cl ratios of the various products show that the relative amount of chloride complex which is present increases as Table III is descended, with borohydride being favored by triphenylphosphine and neocuproine, whereas chlorides are more evident with the diphosphine and MeP $\phi_2$ . The implication of results such as these is that the solution so long regarded as 'copper borohydride' is an inappropriate one from which to prepare known complexes of CuBH<sub>4</sub>, at least in a pure state.

The preparation of copper borohydride reported by Klingen involves the interaction of cupric chlor-

ide and LiBH<sub>4</sub> in ether. If two moles of triphenylphosphine per mole of copper are added to the 'copper borohydride' solution prepared by this method, ( $\phi_3\text{P}$ )<sub>2</sub>CuBH<sub>4</sub> once again is the major product precipitated. However, in a solvent which is a THF/ether mixture, the  $\phi_3\text{P}$  addition yields a white precipitate at  $-45^\circ\text{C}$ , but then decomposition occurs on warming. We suggest that this difference in behavior between the two different solvents arises because THF:BH<sub>3</sub> formed in solution in the latter case destabilizes the mixture by competing for the added  $\phi_3\text{P}$  ligand. A similar reaction was reported by Shore *et al.* in which ( $\phi_3$ )<sub>2</sub>CuBH<sub>4</sub> lost a phosphine to added diborane leading to  $\phi_3\text{P}:\text{BH}_3$  and the unstable  $\phi_3\text{-PCuBH}_4$  molecule [26]. Thus:



The bidentate ligands 1,2-bis(diphenylphosphino)ethane and neocuproine, however, yield stable complexes from the mixed solvent, as expected.

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\*Slight shifts in *d*-spacing values between the mixture and the authentic samples probably arise from the different solvents employed in the two cases. Some solvent becomes entrained in the voids of the crystal lattice.

\*\*The patterns obtained in the cases for triphenylphosphine, diphosphine and neocuproine addition conversely corresponded to those of the borohydride complexes rather than the chlorides.

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