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Preparation of the First Stable Complex Metal Hydride of Copper, LiCuH₂

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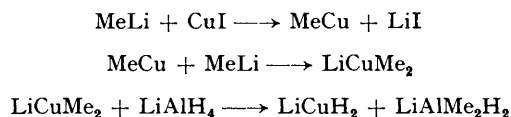
Summary Reaction of LiCuMe₂ at low temperature with LiAlH₄ in diethyl ether results in the formation of a highly pyrophoric solid whose analysis is consistent with the formula LiCuH₂, and which is stable as an etherate.

RECENTLY, there has been considerable interest in copper chemistry, in particular in synthetic applications involving lithium alkylcuprates¹ and copper hydride.^{2,3} In view of the unusual chemistry of these reagents, we have been interested in the preparation of stable complex metal hydrides of copper in order to study their usefulness as reducing agents in organic chemistry.

Copper hydride prepared in ether is not stable at room temperature, decomposing with evolution of hydrogen to form a black solid.⁴ Stable solutions of CuH in pyridine have been prepared by Dilts and Shriver² who have shown that the solubility of CuH is due to its complexation with the Lewis base. Stable complexes of CuH with PPh₃ have also been prepared by Churchill and his co-workers.³ An X-Ray crystal structure determination showed CuH to be hexameric. This ability of CuH to undergo complex formation suggested to us that it should be possible to synthesize complex metal hydrides of copper. Monnier has claimed the preparation of CuAlH₄ at -80° by the reaction of Li₂CuBr₄ with LiAlH₄. However, the CuAlH₄ formed was not stable above -80° and decomposed to Cu, CuH, Al, and H₂.⁵ Our experience with complex metal hydrides of zinc (*e.g.*, LiZnH₃, Li₂ZnH₄, *etc.*) suggest that complex

metal hydrides of copper should be more stable than CuH itself.⁶

We have prepared a complex metal hydride of copper, which is more stable than CuH, by the reaction of lithium dimethylcuprate with LiAlH₄ in Et₂O (Scheme). To a slurry



SCHEME

of CuI (18 mmol) in Et₂O (200 ml) at -78° was added MeLi (36 mmol) in ether. The mixture was stirred for 1 h at -78°, at which time all the CuI had dissolved. LiAlH₄ (18 mmol) in ether was then added. No precipitate formed at -78°; however, while warming the solution to room temperature, a yellow precipitate formed. The mixture was filtered and the yellow solid isolated as an ether slurry. This slurry gave the following analysis. Li:Cu:H:Al; 1.03:1.0:2.06:0.08. The i.r. spectrum of the filtrate corresponded to that of an authentic sample of LiAlH₂Me₂ prepared by the redistribution of LiAlMe₄ and LiAlH₄. The yellow solid was filtered off and dried *in vacuo*.† Differential thermal analysis-thermogravimetric analysis of the solid LiCuH₂ etherate shows violent decomposition at 70° with the evolution of ether. No sharp lines, but two broad diffuse lines were observed in the X-ray powder pattern of the

† Prolonged subjection of the yellow solid (LiCuH₂) to reduced pressure in order to remove the ether of solvation resulted in decomposition. The dry yellow solid was stable at room temperature for at least several days; however, owing to its great sensitivity to O₂ and H₂O, it was generally stored as an ether slurry prior to use.

solid LiCuH_2 . When stored as an ether slurry, LiCuH_2 is stable at room temperature for several days, unlike CuH alone (prepared in diethyl ether) which decomposes immediately on warming to room temperature.⁴ We have studied the preparation of this compound and other stoichiometric complex metal hydrides of copper, e.g., Li_3CuH_4 ,

under a variety of conditions and in different solvents, and we shall report on this study elsewhere.

Reduction of model α,β -unsaturated ketones by LiCuH_2 is in progress.

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