

## PREPARATION, PROPERTIES AND APPLICATIONS OF SOME NEW

COMPLEX METAL HYDRIDES OF COPPER,  $\text{Li}_n\text{Cu}_m\text{H}_{(n+m)}$ 

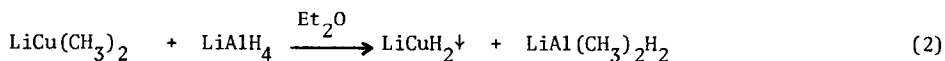
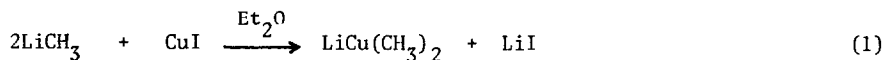
E. C. Ashby\*, A. B. Goel and J. J. Lin

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

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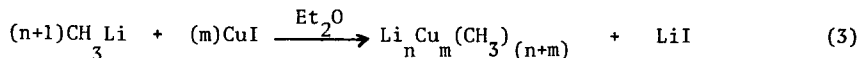
The chemistry of organocuprates ( $\text{LiCuR}_2$ ) and copper hydride ( $\text{CuH}$ ) has been the subject of considerable current interest because of the many synthetic applications<sup>1-3</sup> of these interesting reagents. Although most organocuprates have reasonable stability in the range  $-20^\circ\text{C}$  to  $+20^\circ\text{C}$ , the greatest limitation of  $\text{CuH}$  as a reagent is the poor thermal stability of this compound even at temperatures as low as  $-80^\circ\text{C}$ .<sup>4</sup> The ability of  $\text{CuH}$  to form more thermally stable complexes with pyridine<sup>2</sup> and  $\text{PPh}_3$ <sup>3</sup> provides insight into the possible synthesis of thermally stable complex metal hydrides of copper. Recently we have demonstrated the existence of some new organocuprates, namely  $\text{LiCu}_2(\text{CH}_3)_3$  and  $\text{Li}_2\text{Cu}(\text{CH}_3)_3$ <sup>5</sup> by variable temperature NMR studies and have also shown that these reagents are valuable for the methylation of enones and alkyl halides.<sup>6,7</sup> In view of the unusual chemistry of these reagents, we have been interested in the conversion of the alkylcuprates to the corresponding hydrides in order to study their usefulness as reducing agents in organic chemistry.

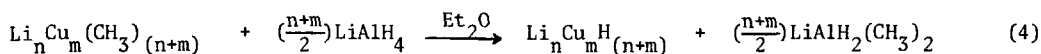
We have recently reported the preparation of the first stable complex metal hydride of copper ( $\text{LiCuH}_2$ ) by the reaction of  $\text{LiCu}(\text{CH}_3)_2$  with  $\text{LiAlH}_4$  (eq. 1-2)<sup>8</sup>. Later the preparation of complexes of the type,  $\text{LiCuHR}$  (where  $\text{R} = \text{alkyl, OBu}^t$  and  $\text{SR}_2$ ), with organic



substrates were reported by several workers.<sup>9,10</sup> However, the limitations of these reagents is that they are not stable at room temperature and are difficult to prepare.

In the present investigation, we have prepared a series of stable complex metal hydrides of copper with the empirical formula  $\text{Li}_n\text{Cu}_m\text{H}_{(n+m)}$  by the reaction of  $\text{LiAlH}_4$  with the corresponding lithium alkylcuprate (eqs. 3-4) in ether solvent. The reactions were carried out simply by adding  $\text{CH}_3\text{Li}$  to  $\text{CuI}$  in the appropriate ratios in ether at  $-78^\circ\text{C}$  (eq. 3).





In each case a clear colorless solution resulted in just a few minutes after which time a solution of  $\text{LiAlH}_4$  in ether was added and the solution allowed to warm to room temperature with stirring. A white precipitate formed during the warming process which was stable in ether solution at room temperature (for  $\text{LiCuH}_2$ ,  $\text{Li}_2\text{CuH}_3$ ,  $\text{Li}_3\text{CuH}_4$ ,  $\text{Li}_4\text{CuH}_5$  and  $\text{Li}_5\text{CuH}_6$ ) for an indefinite period of time or stable at  $0^\circ\text{C}$  (for  $\text{LiCu}_2\text{H}_3$  and  $\text{Li}_2\text{Cu}_3\text{H}_5$ ) for several hours. The white solids were filtered, washed with ether, analyzed for lithium, copper and hydrogen (gas evolution), x-ray powder patterns were obtained and DTA-TGA recorded (Table I). In this way the following compounds were characterized:  $\text{LiCu}_2\text{H}_3$ ,  $\text{Li}_2\text{Cu}_3\text{H}_5$ ,  $\text{LiCuH}_2$ ,  $\text{Li}_2\text{CuH}_3$ ,  $\text{Li}_3\text{CuH}_4$ ,  $\text{Li}_4\text{CuH}_5$  and  $\text{Li}_5\text{CuH}_6$  with their thermal stabilities ranging from  $0^\circ$  to  $140^\circ\text{C}$  (Table I).

Table I. Properties of  $\text{Li}_m\text{Cu}_n\text{H}_{(m+n)}$  Compounds

Hydride	Analysis	X-Ray Pattern	DTA-TGA
	Li : Cu : H		(decomp. temp. $0^\circ\text{C}$ )
$\text{LiCu}_2\text{H}_3$	1.00:1.95:2.97	-	-
$\text{Li}_2\text{Cu}_3\text{H}_5$	1.00:1.45:2.42	-	-
$\text{LiCuH}_2$	1.03:1.00:2.97	-	70, 300, 400
$\text{Li}_2\text{CuH}_3$	2.07:1.00:2.97	4.00w, 3.50m, 2.25d	90, 110, 120, 145 290, 440
$\text{Li}_3\text{CuH}_4$	3.05:1.00:4.01	4.05m, 3.51s, 2.47m 2.13w, 2.02w, 1.57w	110, 120, 140, 308 410, 450
$\text{Li}_4\text{CuH}_5$	3.97:1.00:4.95	4.05m, 3.51s, 2.47m 2.12w, 2.02w, 1.57w	120, 145, 300, 365 430, 480, above 500
$\text{Li}_5\text{CuH}_6$	5.05:1.00:5.92	4.05m, 3.51s, 2.47m, 2.12w, 2.02w, 1.57w	140, 305, 440, 480, above 500

The question, of course, is whether these products of reported empirical formula are truly single compounds or are they mixtures of  $\text{LiCuH}_2$  and  $\text{CuH}$  (as in the case of  $\text{LiCu}_2\text{H}_3$  and  $\text{Li}_2\text{Cu}_3\text{H}_5$ ) or  $\text{LiCuH}_2$  and  $\text{LiH}$  (as in the case of  $\text{Li}_2\text{CuH}_3$ ,  $\text{Li}_3\text{CuH}_4$ ,  $\text{Li}_4\text{CuH}_5$  and  $\text{Li}_5\text{CuH}_6$ ) or a mixture of some other lithium copper hydride and either  $\text{CuH}$  or  $\text{LiH}$ . Unfortunately, the x-ray powder patterns are not conclusive because the x-rays caused some of the compounds to decompose; however, there are several pieces of evidence that indicate strongly that the products are single compounds. First, if  $\text{CuH}$  were in admixture with any of these compounds, the compounds would not have been stable above  $-80^\circ\text{C}$  since  $\text{CuH}$  decomposes above this temperature. DTA-TGA is also quite conclusive in that each hydride decomposes at a different temperature:  $\text{LiCu}_2\text{H}_3$  and  $\text{Li}_2\text{Cu}_3\text{H}_5$  ( $\sim 0^\circ$ ),  $\text{LiCuH}_2$  ( $70^\circ$ ),  $\text{Li}_2\text{CuH}_3$  ( $90^\circ$ ),  $\text{Li}_3\text{CuH}_4$

(110°),  $\text{Li}_4\text{CuH}_5$  (120°), and  $\text{Li}_5\text{CuH}_6$  (140°). If LiH were in admixture with any of the hydrides, x-ray analysis would have easily uncovered this fact. X-ray powder diffraction analysis showed that no LiH was present in the samples. Furthermore,  $\text{LiCuH}_2$  and  $\text{Li}_4\text{CuH}_5$  were found to be very soluble in THF. Since CuH and LiH show no solubility in THF it is clear that these hydrides cannot be mixtures of another complex metal hydride of copper containing either LiH or CuH.

The reducing ability of these hydrides towards alkyl halides and tosylates have been demonstrated by carrying out reactions with decyl iodide, bromide, chloride, fluoride and octyl tosylate (Table II). Each lithium copper hydride reduces decyl iodide to yield

Table II. Reduction of Decyl Halides and Octyl Tosylate by  $\text{Li}_n\text{Cu}_m\text{H}_{(n+m)}$

Hydride	$\text{C}_{10}\text{H}_{21}\text{I}$	$\text{C}_{10}\text{H}_{21}\text{Br}$	$\text{C}_{10}\text{H}_{21}\text{Cl}$	$\text{C}_{10}\text{H}_{21}\text{F}$	$\text{C}_8\text{H}_{17}\text{OTs}$
$\text{LiCuH}_2$	100	85	37	0	65
$\text{Li}_2\text{CuH}_3$	100	100	35	0	80
$\text{Li}_3\text{CuH}_4$	100	90	34	0	39
$\text{Li}_4\text{CuH}_5$	100	100	99	10	99
$\text{Li}_5\text{CuH}_6$	100	100	80	0	69

\* Yields of  $\text{C}_{10}\text{H}_{22}$  or  $\text{C}_8\text{H}_{18}$  were determined by glc using an internal standard. All reactions were carried out over a 24 hr. period in THF at room temperature.

n-decane quantitatively and the yield decreases in the order:  $\text{I} > \text{Br} > \text{OTs} > \text{Cl} > \text{F}$ . It is important to note that the THF soluble lithium copper hydride,  $\text{Li}_4\text{CuH}_5$ , reduced primary iodide, bromide, chloride and tosylate compounds in quantitative yields and even fluoride in 10% yield. These are very unusual results. The difference in behavior of the various hydrides towards alkyl halides and tosylates is further evidence that the hydrides are all different and not mixtures of  $\text{LiCuH}_2$  and LiH or CuH. We are presently studying the stereoselectivity of these new hydrides toward cyclohexanones and their regioselectivity towards enones and are obtaining interesting results that will be reported in more detail later.

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  4. Although numerous efforts have been made by ourselves and others to prepare pure CuH by several different routes, the product always decomposed at  $-80^{\circ}$  (the temperature of the reaction mixture) to  $\text{Cu}^{\circ} + \text{H}_2$ .
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