GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

Date: JANUARY 27, 1977

Project Title: AN EVALUATION OF NEW AND UNUSUAL SIMPLE AND METAL COMPLEX HYDRIDES OF THE MAIN GROUP ELEMENTS AS STEREO-SELECTIVE AND REGIOSELECTIVE REDUCING AGENTS

Project No: G-33-621

Project Director: DR. E. C. ASHBY

Sponsor: AMERICAN CHEMICAL SOCIETY/PETROLEUM RESEARCH FUND

Agreement Period: From 9/1/77 Until 8/31/80

Type Agreement: PRF GRANT #9728-AC1, 4-C

Amount: $24,000 AMERICAN CHEMICAL SOCIETY
1,400 GIT (G-33-390)
22,400 TOTAL

Reports Required: AS REQUESTED

Sponsor Contact Person(s):

Technical Matters

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Contractual Matters

(thru OCA)

Defense Priority Rating:

Assigned to: CHEMISTRY (School/Laboratory)

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Project File (OCA)
Project Code (GTRI)
Other
SPONSORED PROJECT TERMINATION SHEET

Date 10/7/83

Project Title: "An Evaluation of New and Unusual Simple and Metal Complex Hydrides of the Main Group Elements as Stereo-Selectivc and Regioselective Reducing Agents"

Project No: G-33-621

Project Director: Dr. E.C. Ashby

Sponsor: American Chemical Society/Petroleum Research Fund.

Effective Termination Date: 8/31/80

Clearance of Accounting Charges: 8/31/80

Grant/Contract Closeout Actions Remaining:

- Final Invoice and Closing Documents
- Final Fiscal Report
- Final Report of Inventions
- Govt. Property Inventory & Related Certificate
- Classified Material Certificate
- Other

NONE: Discussed PPC's request for review with Cindy Arnold who had no objections to closing.

Assigned to: Chem. (School/Department)

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FORM OCA 10:781
Please refer to instructions.
Fill in information requested above for each page.
The report heading, narrative, and all drawings must be prepared within the box.
Make copy (Xerox, carbon, etc).
The new organocuprates, LiCu₂(CH₃)₃ and Li₂Cu(CH₃)₃ in THF and Li₂Cu₃(CH₃)₅ in Et₂O, react with enones in a similar manner compared to LiCu(CH₃)₂. Except in the cases of disubstituted enones, Li₂Cu(CH₃)₃ gives quantitative conjugate methylation of the enones studied at a comparable or greater rate than LiCu(CH₃)₂ provided that the reaction is carried out in THF. On the other hand, poor regioselectivity was observed in diethyl ether. LiCu₂(CH₃)₃ gave quantitative regioselectivity in THF and reacted in general more slowly than LiCu(CH₃)₂. Since LiCu₂(CH₃)₃ is insoluble in diethyl ether, studies were not carried out in this solvent. Li₂Cu₃(CH₃)₅ in ether gave excellent results with all of the enones and appeared to react somewhat more rapidly compared to LiCu(CH₃)₂.
9728-AC1 An Evaluation of New and Unusual Simple and Complex Metal Hydrides of the Main Group Elements as Stereoselective and Regioselective Reducing Agents

E. C. Ashby, Georgia Institute of Technology

Recently we reported the preparation of lithium alkylcuprates other than LiCuR₂ compounds. These compounds were prepared by the addition of CH₃Li to CH₃Cu in Me₂O, Et₂O and THF and the integrity established by variable temperature 'H NMR and DTA-TGA.

We have now allowed a series of ate complexes to react with LiAlH₄ to form the corresponding lithium copper hydrides (eqs. 1-5). LiCuH₂ and Li₄CuH₅ have

\[ \text{LiCu(CH}_3\text{)}_2 + \text{LiAlH}_4 \rightarrow \text{LiCuH}_2 + \text{LiAl(CH}_3\text{)}_2 \text{H}_2 \]  
\[ \text{Li}_2\text{Cu(CH}_3\text{)}_3 + \frac{3}{2}\text{LiAlH}_4 \rightarrow \text{Li}_2\text{CuH}_3 + \frac{3}{2}\text{LiAl(CH}_3\text{)}_2 \text{H}_2 \]  
\[ \text{Li}_3\text{Cu(CH}_3\text{)}_4 + 2\text{LiAlH}_4 \rightarrow \text{Li}_3\text{CuH}_4 + 2\text{LiAl(CH}_3\text{)}_2 \text{H}_2 \]  
\[ \text{Li}_4\text{Cu(CH}_3\text{)}_5 + \frac{5}{2}\text{LiAlH}_4 \rightarrow \text{Li}_4\text{CuH}_5 + \frac{5}{2}\text{LiAl(CH}_3\text{)}_2 \text{H}_2 \]  
\[ \text{Li}_5\text{Cu(CH}_3\text{)}_6 + 3\text{LiAlH}_4 \rightarrow \text{Li}_5\text{CuH}_6 + 3\text{LiAl(CH}_3\text{)}_2 \text{H}_2 \]

appreciable solubility in THF.

We have now studied the reactions of these new hydrides of copper with alkyl halides, enones and cyclic ketones. It has been shown that the different hydrides exhibit different regioselectivities toward enones and different stereoselectivities toward cyclic ketones. These data support the integrity of each hydride as a single compound rather than a physical mixture. Tetrahydrofuran-soluble Li₄CuH₅ has been shown to be the most reactive of the complex metal hydrides of copper toward alkyl halides in that this hydride reduced 1-iodo-, 1-bromo-, and 1-chlorodecane in
100, 100, and 99% yields, respectively. The complex metal hydrides of copper reduce enones predominantly 1,4(Li₂CuH₃, 96%) or 1,2(Li₄CuH₅, 95%), depending on the hydride. In most cases, the complex metal hydrides of copper reduce 4-tert-butylcyclohexanone predominantly from the axial side, as in the case of LiAlH₄. Other cyclohexanones are reduced by the complex metal hydrides of copper similarly to LiAlH₄, except with less selectivity.
A series of stable complex metal hydrides of copper of composition $\text{Li}_{n} \text{CuH}_{n+1}$ ($n=1-5$) prepared by the reaction of $\text{LiAlH}_{4}$ with the corresponding lithium methylcuprates in diethyl ether, has been allowed to react with selected alkyl halides, enones, and cyclic ketones in both diethyl ether and THF. It has been shown that the different hydrides exhibit different regioselectivities toward enones and different stereoselectivities toward cyclic ketones. These data support the integrity of each hydride as a single compound rather than a physical mixture. Tetrahydrofuran-soluble $\text{Li}_{4} \text{CuH}_{5}$ has been shown to be the most reactive of the complex metal hydrides of copper toward alkyl halides in that his hydride reduced 1-iodo-, 1-bromo-, and 1-chlorodecane in 100, 100, and 99% yield, respectively. The complex metal hydrides of copper reduce enones predominantly 1,4-($\text{Li}_{2} \text{CuH}_{3}$, 96%) or 1,2($\text{Li}_{4} \text{CuH}_{5}$, 95%), depending on the hydride. In most cases, the complex metal hydrides of copper reduce 4-tert-butylcyclohexanone predominantly from the axial side, as in the case of $\text{LiAlH}_{4}$. Other cyclohexanones are reduced by the complex metal hydrides of copper similarly to $\text{LiAlH}_{4}$, except with less selectivity.
We have been studying the hydromagnesiation of olefins by the reaction of \( R_2Mg, RMgH, \) and \( RMgX \) compounds (where \( X = \text{Cl, Br, or I} \)). The reaction is catalyzed by \( Cp_2TiCl_2 \) and is carried out in THF at room temperature. For these studies: \( \text{MeMgH, EtMgH, n-BuMgH, } \), \( t\text{-BuMgH, CpMgH, and PhMgH have been prepared in addition to the } \text{R}_2\text{Mg and RMgX compounds possessing the same R groups as shown above for the RMgH compounds. It appears that all of the RMgH, } \text{R}_2\text{Mg and RMgX compounds hydromagnesiate terminal olefins, although the rate and yield are more a function of the nature of the R group rather than the nature of the magnesium compound (RMgH, } \text{R}_2\text{Mg or RMgX). For convenience it appears that Grignard compounds are best used for this reaction and particularly } t\text{-BuMgBr.} \)