

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

Date: JANUARY 27, 1977

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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

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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)
\$25,400 TOTAL

Reports Required:
AS REQUESTED

Sponsor Contact Person (s):

Technical Matters

Contractual Matters

(thru OCA)

DR. JUSTING W. COLLAT
PROGRAM ADMINISTRATOR
PETROLEUM RESEARCH FUND
AMERICAN CHEMICAL SOCIETY
1155 SIXTEENTH STREET, N.W.
WASHINGTON, D. C. 20036

Defense Priority Rating:

Assigned to: CHEMISTRY (School/Laboratory)

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Office of Computing Services
Director, Physical Plant
EES Information Office
Project File (OCA)
Project Code (GTRI)
Other _____

SPONSORED PROJECT TERMINATION SHEETDate 10/7/83

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.

Effective Termination Date: 8/31/80Clearance 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/~~Laboratory~~)COPIES TO:

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RESEARCH PROGRESS REPORT

Page 1 of 1 pages.

Date September 1978

PRF# 9728 - AC1 - 4C

PRINCIPAL INVESTIGATOR(S)

E. C. Ashby

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Fill in information requested
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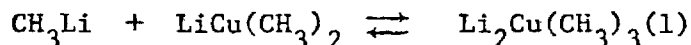
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9728-AC1 An Evaluation of New and Un-⁵⁻⁵⁵¹

usual Simple and Complex Metal Hydrides of
the Main Group Elements as Stereoselective
and Regioselective Reducing Agents

E. C. Ashby, Georgia Institute of Technology

The existence of higher cuprates of LiCuR_2 compounds have been postulated, but never proven. We have recently shown by variable temperature proton NMR that higher ate complexes of LiCuR_2 compounds do exist. These studies were carried out in dimethyl-ether, diethylether and tetrahydrofuran at temperatures as low as -136°C . The NMR studies show that mixtures of CH_3Li and CH_3Cu in 1:2, 1:1 and 2:1 produce $\text{LiCu}_2(\text{CH}_3)_3$, $\text{LiCu}(\text{CH}_3)_2$ and $\text{Li}_2\text{Cu}(\text{CH}_3)_3$ respectively. The ate complex $\text{Li}_2\text{Cu}(\text{CH}_3)_2$ in all solvents is best represented by the equilibrium (eq. 1) whereas the other ate complexes are stable to disproportionation.



The reactions of $\text{LiCu}(\text{CH}_3)_2$, $\text{LiCu}_2(\text{CH}_3)_3$ and $\text{Li}_2\text{Cu}(\text{CH}_3)_3$ with several enones have been studied in both diethyl ether and tetrahydrofuran in an attempt to compare reactivities and regioselectivities of the three cuprates. We have found that in THF, $\text{Li}_2\text{Cu}(\text{CH}_3)_3$ is slightly more reactive and more regioselective than $\text{LiCu}(\text{CH}_3)_2$, although with β -dialkyl substituted enones a significant amount of 1,2-addition product is observed.

BIBLIOGRAPHIC INFORMATION

PRF# 9728 - AC1 - 4C

Please refer to instructions. Fill in information requested on each card. Type (double space) complete reference for one article in space below.

PRINCIPAL INVESTIGATOR(S) E. C. ASHBY, J. J. Lin and J. Watkins,

J. Org. Chem., (1977) 42, 1099.

The new organocuprates, $\text{LiCu}_2(\text{CH}_3)_3$ and $\text{Li}_2\text{Cu}(\text{CH}_3)_3$ in THF and $\text{Li}_2\text{Cu}_3(\text{CH}_3)_5$ in Et_2O , react with enones in a similar manner compared to $\text{LiCu}(\text{CH}_3)_3$. Except in the cases of disubstituted enones, $\text{Li}_2\text{Cu}(\text{CH}_3)_3$ gives quantitative conjugate methylation of the enones studied at a comparable or greater rate than $\text{LiCu}(\text{CH}_3)_2$ provided that the reaction is carried out in THF. On the other hand, poor regioselectivity was observed in diethyl ether. $\text{LiCu}_2(\text{CH}_3)_3$ gave quantitative regioselectivity in THF and reacted in general more slowly than $\text{LiCu}(\text{CH}_3)_2$. Since $\text{LiCu}_2(\text{CH}_3)_3$ is insoluble in diethyl ether, studies were not carried out in this solvent. $\text{Li}_2\text{Cu}_3(\text{CH}_3)_5$ in ether gave excellent results with all of the enones and appeared to react somewhat more rapidly compared to $\text{LiCu}(\text{CH}_3)_2$.

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RESEARCH PROGRESS REPORT

Page 1 of 2 pages.

Date September 1979

PRF# 9728 - AC1 - 4C

PRINCIPAL INVESTIGATOR(S)

E. C. Ashby

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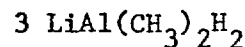
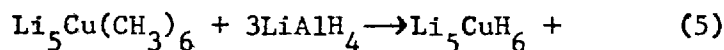
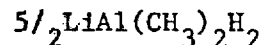
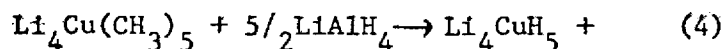
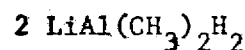
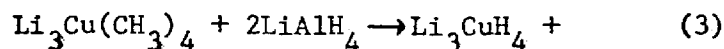
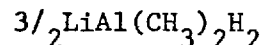
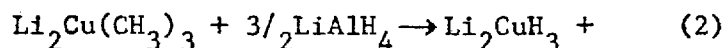
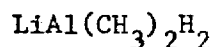
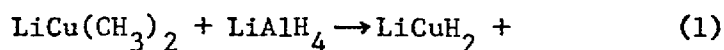
9728-AC1 An Evaluation of New and Un-

usual 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 LiCuR_2 compounds. These compounds were prepared by the addition of CH_3Li to CH_3Cu in Me_2O , Et_2O and THF and the integrity established by variable temperature ^1H NMR and DTA-TGA.

We have now allowed a series of ate complexes to react with LiAlH_4 to form the corresponding lithium copper hydrides (eqs. 1-5). LiCuH_2 and Li_4CuH_5 have



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 Li_4CuH_5 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

RESEARCH PROGRESS REPORT

Page 2 of 2 pages.

Date September 1979

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100, 100, and 99% yields, respectively. The complex metal hydrides of copper reduce enones predominantly 1,4(Li_2CuH_3 , 96%) or 1,2(Li_4CuH_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 LiAlH_4 . Other cyclohexanones are reduced by the complex metal hydrides of copper similarly to LiAlH_4 , except with less selectivity.

PRINCIPAL INVESTIGATOR(S)

E. C. Ashby

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BIBLIOGRAPHIC INFORMATION

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PRINCIPAL INVESTIGATOR(S) E. C. ASHBY, Jiang Jin Lin and Anil B. Goel.

J. Org. Chem., (1978) 43, 183.

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 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 Li_4CuH_5 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% yield, respectively. The complex metal hydrides of copper reduce enones predominantly 1,4- (Li_2CuH_3 , 96%) or 1,2 (Li_4CuH_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 LiAlH_4 . Other cyclohexanones are reduced by the complex metal hydrides of copper similarly to LiAlH_4 , except with less selectivity.

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THE PETROLEUM RESEARCH FUND

REPORT ON ACTIVITY ASSISTED BY

GRANT, PRF # 9728-AC1-4C

Page 1 of 1 pages.

PREPARED BY

E. C. Ashby

Georgia Institute of Technology

Date Oct. 1, 1980

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9728-AC1 An Evaluation of New and Un-

usual Simple and Complex Metal Hydrides of
the Main Group Elements as Stereoselective
and Regioselective Reducing Agents

E. C. Ashby, Georgia Institute of Technology

We have been studying the hydromag-
nesiation of olefins by the reaction of
 R_2Mg , $RMgH$, and $RMgX$ compounds (where $X =$
 Cl , Br , or I). The reaction is catalyzed
by Cp_2TiCl_2 and is carried out in THF at
room temperature. For these studies:
 $MeMgH$, $EtMgH$, $n-BuMgH$, $t-BuMgH$, $CpMgH$, and
 $PhMgH$ have been prepared in addition to the
 R_2Mg and $RMgX$ compounds possessing the same
 R groups as shown above for the $RMgH$ com-
pounds. It appears that all of the $RMgH$,
 R_2Mg and $RMgX$ compounds hydromagnesi-
ate 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 ($RMgH$, R_2Mg or $RMgX$).
For convenience it appears that Grignard
compounds are best used for this reaction
and particularly $i-BuMgBr$.