

^1H Nuclear Magnetic Resonance Evidence for the Existence of LiCu_2Me_3 and Li_2CuMe_3

By E. C. ASHBY* and JOHN J. WATKINS

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

Summary Low-temperature n.m.r. spectra of the system MeLi–MeCu at various ratios in dimethyl ether show the presence of three cuprate complexes: LiCuMe_2 , LiCu_2Me_3 , and Li_2CuMe_3 .

LITHIUM DIALKYL-CUPRATES have proven to be very versatile reagents in organic synthesis.¹ Several recent reports, however, have been concerned with unusual reactivity of

reagents prepared by mixing lithium dialkyl- or diaryl-cuprates with the corresponding organolithium compounds. For example, the reagent having the stoichiometry $\text{LiCuPh}_2\text{-PhLi}$ appears to be more reactive than LiCuPh_2 in metal-halogen exchange reactions and coupling with aryl bromides.² Also it has been recently found³ that a 3:2 mixture of LiCuMe_2 and MeLi is more stereoselective toward 4-t-butylcyclohexanone than either LiCuMe_2 or MeLi. These reports suggest that lithium diorganocuprates and organolithium compounds are capable of reacting to form complexes of the type Li_2CuMe_3 and Li_3CuMe_4 . However, previous ^1H and natural abundance ^{13}C n.m.r. studies on the system MeLi and LiCuMe_2 in diethyl ether at -60°C have failed to show the existence of any complexes.⁴ In view of the interest in this area and the possibility of the existence of other cuprates in addition to LiCuMe_2 , we studied the ^1H n.m.r. spectra of MeLi–MeCu mixtures further. Dimethyl ether was chosen as solvent since exchange rates should be considerably slower than in diethyl ether because of its greater basicity compared to diethyl ether and because considerably lower solution temperatures can be reached (-136 vs. -90°C).

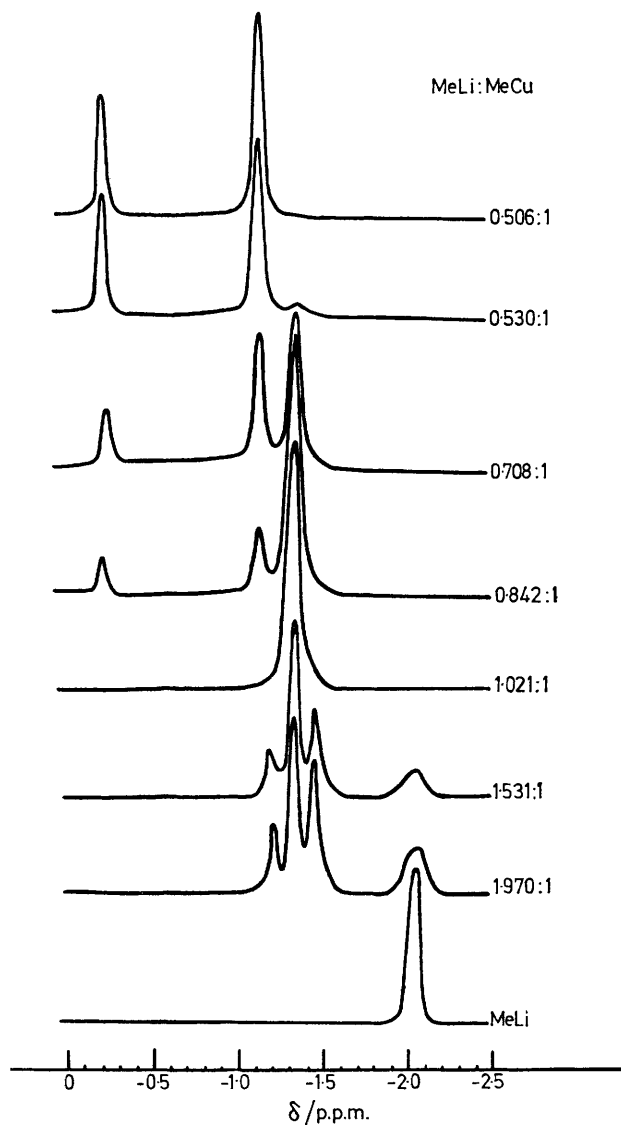
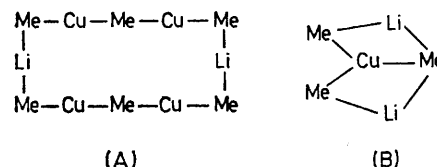


FIGURE. 60 MHz ^1H n.m.r. spectra of solutions of various ratios of MeLi to MeCu in Me_2O at -136°C .

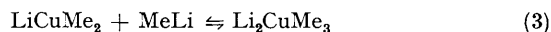
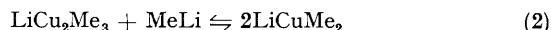
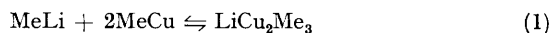
† Several other equilibrium mixtures were assumed, but none matched the data as well as MeLi, LiCuMe_2 , and Li_2CuMe_3 .

‡ Molecular weight measurements on LiCu_2Me_3 show the compounds to be dimeric in tetrahydrofuran and LiCu_2Me_3 to be monomeric in both diethyl ether and tetrahydrofuran.



We report that ^1H n.m.r. signals due to Li_2CuMe_3 , LiCuMe_2 , and LiCu_2Me_3 can be observed for the system MeLi–MeCu at -136°C in dimethyl ether solvent (Figure). When the ratio of MeLi:MeCu is less than 1, three signals are observed ($\delta -0.22$, -1.17 , and -1.38). The signal at $\delta -1.38$ (due to LiCuMe_2) increases as the MeLi:MeCu ratio increases from 0.530 to 1.021 and is the only signal observed at the latter ratio. The integration of the signals at $\delta -0.22$ and -1.17 is always in the ratio 1:2 and is due to LiCu_2Me_3 , since these signals are the only ones observed at a MeLi:MeCu ratio of 0.506. When the ratio of MeLi:MeCu is greater than 1, four signals are observed ($\delta -1.25$, -1.38 , -1.49 , and -2.03). The signal at $\delta -2.03$ is due to MeLi and the signal at $\delta -1.38$ is due to LiCuMe_2 . The integration of the signals at $\delta -1.25$ and -1.49 is always in a 1:2 ratio and is due to Li_2CuMe_3 , since a calculation of the amount of Li_2CuMe_3 correlated well with that predicted by integration of the n.m.r. spectrum.† The 1:2 integration of the two methyl signals observed for LiCu_2Me_3 and Li_2CuMe_3 can be accounted for on the basis of structures (A) and (B).‡

The data presented suggested the following equilibria (1)–(3) at -136°C . Equilibria (1) and (2) lie very much to the right whereas equilibrium (3) had $K_{\text{eq}} = 0.36$ at -136°C .



Although LiCu_2Me_3 and Li_2CuMe_3 are observed at -136°C , a question arises as to the existence of these species at 0°C , the temperature at which these reagents are normally allowed to react with organic substrates. Equilibrium (3) would not be expected to shift to the left as the temperature is increased based on the observation that the equilibrium constant for the formation of Li_3ZnMe_5 from Li_2ZnMe_4 and MeLi increases with increasing temperature.⁵ As the temperature is raised, for $\text{MeLi}:\text{MeCu}$ ratios greater than 1, the three signals at $\delta -1.25$, -1.38 , and -1.49 collapse

into a single peak at $\delta 1.38$ owing to intermolecular exchange between Li_2CuMe_3 and LiCuMe_2 . However, the ratio between this signal and that at $\delta -2.03$ for MeLi remains constant to temperatures as high as -40°C . (Higher temperatures were not attempted because of the high volatility of dimethyl ether). This ratio is the same as that between $\text{Li}_2\text{CuMe}_3 + \text{LiCuMe}_2$ and MeLi when the temperature is -136°C .

Low temperature n.m.r. studies of the system $\text{MeLi}-\text{MeCu}$ at temperatures as high as 0° in tetrahydrofuran reveal the presence of the same three 'ate' complexes as observed in dimethyl ether, *i.e.* LiCu_2Me_3 , LiCuMe_2 , and Li_2CuMe_3 . In diethyl ether, separate n.m.r. signals for Li_2CuMe_3 are not observed at temperatures as low as -110°C . However, the ratio of the LiCuMe_2 signal to the MeLi signal is greater than that predicted by analysis of the mixture and can be accounted for by a compound such as Li_2CuMe_3 .

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¹ For recent reviews of organocopper chemistry, see G. H. Posner, *Org. Reactions*, 1972, **19**, 1; J. Normant, *Synthesis*, 1972, **63**; A. E. Jukes, *Adv. Organometallic Chem.*, 1974, **12**, 215; H. O. House, *Accounts Chem. Res.*, 1976, **9**, 59.

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