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NMR Studies of (Amido)cuprates

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A series of MeLi/Et_2NCu ratios in THF and Et_2O were examined by ^7Li and ^1H NMR spectroscopy. MeLi/$CuNEt_2$ ratios between 0.5 and 1.0 appear to afford a series of species with composition $[MeCu_2(NEt_2)_2]Li$ (**5**), $[Me_2Cu_3(NEt_2)_3]Li_2$ (**6**), and $(MeCuNEt_2)Li$ (**8**) analogous to Me_3Cu_2Li (**2**), Clive's reagent $Me_5Cu_3Li_2$ (**1**), and Me_2CuLi observed in the homocuprate series. Addition of 0.5 equiv of $LiNEt_2$ to MeCu appears to form Me_2CuLi and $(Me_2Cu_2NEt_2)Li$ (**7**). Addition of 2.0 equiv of MeLi to Et_2NCu affords a solution that may contain Me_2CuLi, $[Me_4Cu_2NEt_2]Li_3$ (**13**), or a mixture of the two species depending upon the mode of preparation. No new species are formed for 1.0–2.0 MeLi:Et_2NCu ratios. Possible structures for **5**–**7** are suggested by analogy with reported X-ray structures for organocopper compounds with varying Li:Cu ratios in the metal cluster.

Introduction

The mechanism(s) of organocopper reactions and the structure and composition of the reagents remain largely undetermined despite the enormous synthetic utility of organocopper reagents.[1] In large measure this is a reflection of the air sensitivity, the thermal instability,[2] and the dynamic equilibrium exhibited by these reagents in solution. The term "higher order" cuprate was originally introduced by Lipshutz[1a] to describe stoichiometric mixtures with Li:Cu ratios greater than 1.0 consistent with the presence of an additional negatively charged ligand in the copper cluster and formally corresponding to a Cu(I) dianionic species. The term "higher order" cuprate, however, has been used in the literature to describe cuprate compositions with Li:Cu ratios either greater than or less than 1.0. Although various compositions of "higher order" cuprates (e.g. Me_3CuLi_2,[3] Me_3Cu_2Li,[3a,b,4] $Me_5Cu_3Li_2$,[3-5], Ph_3CuLi_2,[6] $Ph_5Cu_2Li_3$,[7] $R_2Cu(CN)Li_2$,[8,9] and $[(Ph_6Cu_3Li_2)^-]$[10]) have been suggested, they have largely (with the exception of $Ph_5Cu_3Li_2$ and $[Ph_6Cu_3Li_2]^-$ for which X-ray structures have been determined) represented the stoichiometry of balanced equations with little supporting experimental evidence other than chemical reactivity differences. It should be noted that Me_3Cu_2Li, $Me_5Cu_3Li_2$ and $[Ph_6Cu_3Li_2]^-$ have Li:Cu ratios less than 1.0 and that the latter species is the anion portion of the crystalline salt. In recent years, NMR studies[3,4,6,8b,9,11] and X-ray structure determinations[7,10,12] have begun to provide structural insight into various cuprate compositions.

The pioneering work of Lipshutz,[4] with a combination of ^1H and ^7Li, NMR showed that Me_3CuLi_2 and Clive's reagent [$Me_5Cu_3Li_2$ (**1**)] apparently do not exist as discrete species in THF but as mixtures of the Gilman reagent (Me_2CuLi) and Me_3Cu_2Li (**2**). In the absence of LiI in THF an equilibrium is established between Gilman's reagent and MeLi plus Me_3Cu_2Li. This equilibrium does not occur in the presence of LiI or in Et_2O solutions. Clive's reagent **1** is a discrete species in Et_2O. Chemical and spectroscopic evidence[6] supports the proposed existence of Ph_3CuLi_2 although crystals produced from the solution afford an X-ray structure[7] of $Ph_5Cu_2Li_3$ (**3**). In Me_2S several crystalline higher order cuprates have been obtained and their X-ray structures solved.[7] These include **3** and $Ph_5Cu_4Li_5$ (**4**), which exist as combinations of $CuPh_3^{2-}$ and $CuPh_2^-$ units held together by bridging Li atoms. Two recent reports provided evidence for[9a] and against[9b] the existence of "higher order" cyanocuprates [i.e. $(R_2CuCN)Li_2$], illustrating the difficulty in probing these systems in an informative manner.

In connection with our studies on asymmetric induction in organocopper conjugate addition reactions, we undertook an NMR investigation of (amido)cuprate compositions. The complexity of the chiral reagents coupled with the dynamic equilibrium led us to investigate simple (amido)cuprates as a probe of cuprate composition. This represents the first reported NMR study of mixed heterocuprates where the nontransferable ligand on copper is a heteroatom, although an NMR study of "lower order" and "higher order" silylcyanocuprates has been reported.[11g]

Results

The ^7Li and ^1H NMR spectra of various (amido)cuprate compositions (eqs 1–6) have been examined in both THF and Et_2O. The compositions were achieved by the addition

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† Clemson University.

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(1) (a) For a review of HO cuprates see: Lipshutz, B. H. *Synthesis* **1987**, 325. (b) Lipshutz, B. H.; Whilhelm, R. S.; Kozlowski, J. A. *Tetrahedron* **1984**, *40*, 5005.

(2) (a) Bertz, S. H.; Dabbagh, G. *J. Org. Chem.* **1984**, *49*, 1119. (b) Bertz, S. H.; Dabbagh, G. *J. Chem. Soc., Chem. Commun.* **1982**, 1030.

(3) (a) Ashby, E. C.; Watkins, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 5312. (b) *Idem. J. Chem. Soc., Chem. Commun.* **1976**, 784. (c) Ashby, E. C.; Lin, J. J. *J. Org. Chem.* **1977**, *42*, 2805. (d) Ashby, E. C.; Lin, J. J.; Watkins, J. J. *Ibid.* **1977**, *42*, 1099.

(4) Lipshutz, B. H.; Kozlowski, J. A.; Breneman, C. M. *J. Am. Chem. Soc.* **1985**, *107*, 3197 and references cited therein.

(5) Clive, D. L. J.; Farina, V.; Beaulieu, P. L. *J. Org. Chem.* **1982**, *47*, 2572.

(6) Bertz, S. H.; Dabbagh, G. *J. Am. Chem. Soc.* **1988**, *110*, 3668.

(7) (a) Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1990**, *112*, 8008. (b) *Ibid.* **1989**, *111*, 4135.

(8) (a) Lipshutz, B. H.; Wilhelm, R. S.; Floyd, D. M. *J. Am. Chem. Soc.* **1981**, *103*, 7672. (b) Lipshutz, B. H.; Kozlowski, J. A.; Wilhelm, R. S. *J. Org. Chem.* **1984**, *49*, 3943.

(9) (a) Lipshutz, B. H.; Sharma, S.; Ellsworth, E. L. *J. Am. Chem. Soc.* **1990**, *112*, 4032. (b) Bertz, S. H. *Ibid.* **1990**, *112*, 4031.

(10) Hope, H.; Oram, D.; Power, P. P. *J. Am. Chem. Soc.* **1984**, *106*, 1149.

(11) (a) Lipshutz, B. H.; Kozlowski, J. A.; Breneman, C. M. *Tetrahedron Lett.* **1985**, *26*, 5911. (b) Christenson, B.; Olsson, T.; Ullenius, C. *Tetrahedron* **1989**, *45*, 523. (c) Hallnemo, G.; Olsson, T.; Ullenius, C. *J. Organomet. Chem.* **1984**, *265*, C22. (d) Hallnemo, G.; Olsson, T.; Ullenius, C. *J. Organomet. Chem.* **1985**, *282*, 133. (e) Van Koten, G.; Noltes, J. G. *Ibid.* **1979**, *174*, 367. (f) Filippo, J. S., Jr. *Inorg. Chem.* **1978**, *17*, 275. (g) Sharma, S.; Oehlschlager, A. C. *Tetrahedron* **1989**, *45*, 557.

(12) (a) van Koten, G.; Jastrzebski, J. T. B. H. *J. Am. Chem. Soc.* **1985**, *107*, 697. (b) Martin, S. F.; Fishpaugh, J. R.; Power, J. M.; Giolando, D. M.; Jones, R. A.; Nunn, C. M.; Cowley, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 7226. (c) Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C. *J. Organomet. Chem.* **1984**, *263*, C23. (d) Hope, H.; Olmstead, M. M.; Power, P. P.; Sandell, J.; Xiaojie, X. *J. Am. Chem. Soc.* **1985**, *107*, 4337. (e) Lorenzen, N. P.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 300.

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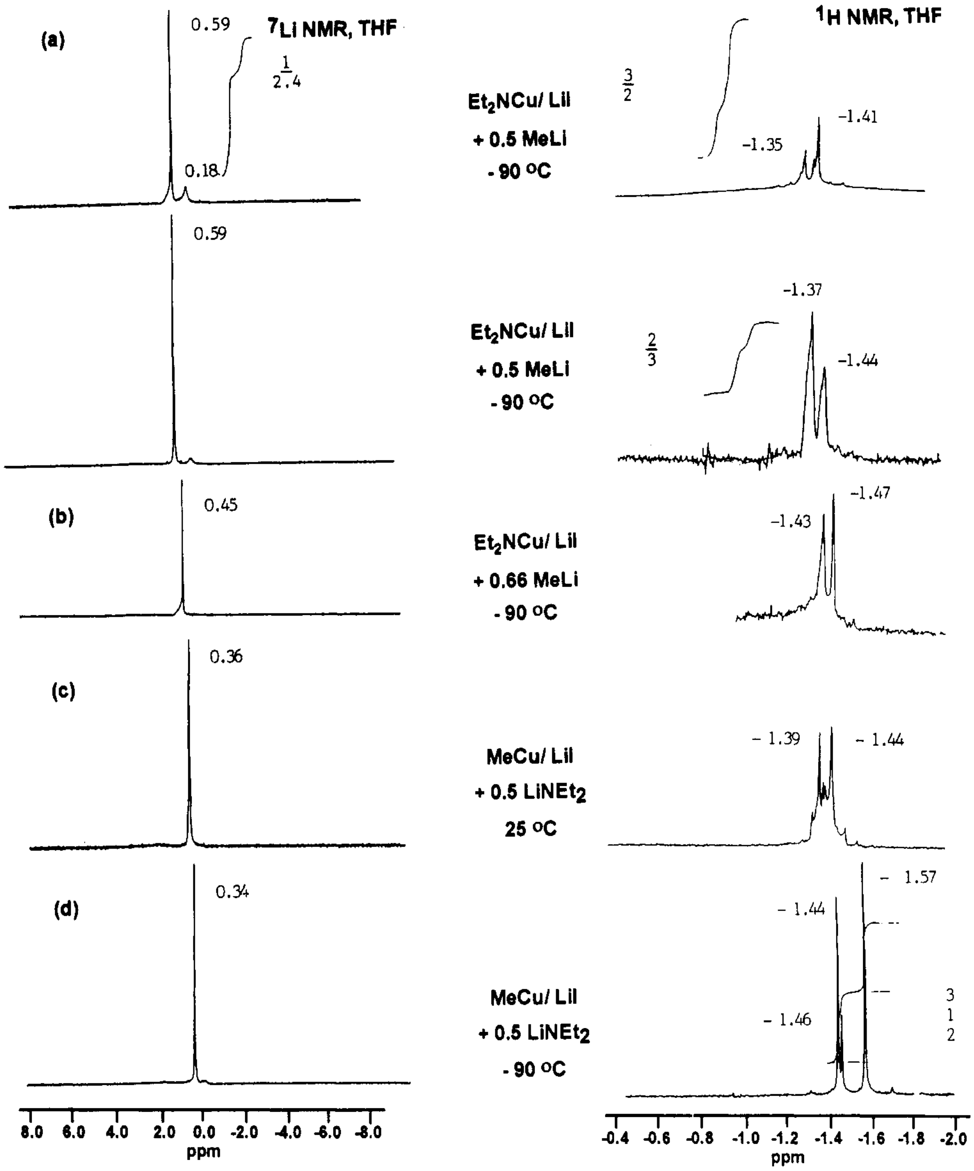


Figure 1. ^{7}Li and ^{1}H NMR spectra for various $\mathrm{Et_2NCu{:}MeLi}$ ratios between 1:0.5 and 1:1 and a 1.0:0.5 $\mathrm{MeCu{:}LiNEt_2}$ ratio in $\mathrm{THF/Et_2O}$ at −60 to −90 °C and 25 °C: (a) $[\mathrm{MeCu_2(NEt_2)_2}]\mathrm{Li}$ (**5**) for two different experiments; (b) $[\mathrm{Me_2Cu_3(NEt_2)_3}]\mathrm{Li_2}$ (**6**); (c) $[\mathrm{Me_2Cu_2NEt_2}]\mathrm{Li}$ (**7**) at 25 °C; (d) $[\mathrm{Me_2Cu_2NEt_2}]\mathrm{Li}$ (**7**) at −90 °C. Legend descriptions refer to stoichiometric ratios (eqs 1–3).

of MeLi to either $\mathrm{CuNEt_2}$ or $(\mathrm{MeCuNEt_2})\mathrm{Li}$ and by the addition of $\mathrm{LiNEt_2}$ to MeCu or $\mathrm{Me_2CuLi}$. Equations 1–6 show possible compositions based upon simple stoichiometric considerations.

$$\mathrm{CuNEt_2} + 0.5\mathrm{MeLi} \rightarrow 0.5\underset{\mathbf{5}}{[\mathrm{MeCu_2(NEt_2)_2}]\mathrm{Li}} \tag{1}$$

$$\mathrm{CuNEt_2} + 0.66\mathrm{MeLi} \rightarrow 0.33\underset{\mathbf{6}}{[\mathrm{Me_2Cu_3(NEt_2)_3}]\mathrm{Li_2}} \tag{2}$$

$$\mathrm{CuMe} + 0.5\mathrm{Et_2NLi} \rightarrow 0.5\underset{\mathbf{7}}{[\mathrm{Me_2Cu_2NEt_2}]\mathrm{Li}} \tag{3}$$

$$\mathrm{CuNEt_2} + 1.0\mathrm{MeLi} \rightarrow \underset{\mathbf{8}}{[\mathrm{MeCuNEt_2}]\mathrm{Li}} \tag{4}$$

$$\mathrm{CuNEt_2} + 1.5\mathrm{MeLi} \rightarrow 0.5\underset{\mathbf{9}}{[\mathrm{Me_3Cu_2(NEt_2)_2}]\mathrm{Li_3}} \tag{5}$$

$$\mathrm{CuNEt_2} + 2.0\mathrm{MeLi} \rightarrow \underset{\mathbf{10}}{[\mathrm{Me_2CuNEt_2}]\mathrm{Li_2}} \tag{6}$$

$\mathrm{CuNEt_2}$ + 0.5MeLi and 0.66MeLi and MeCu + 0.5$\mathrm{LiNEt_2}$. These compositions were initially investigated as THF solutions. Addition of 0.5 equiv of MeLi to $\mathrm{CuNEt_2}$ in THF (eq 1) affords a single sharp peak (Δppm + 0.07, +25 to −90 °C, δ 0.59) in the ^{7}Li NMR (Figure 1a) with a small broad absorption at δ 0.18. The ^{1}H NMR spectrum displays two absorptions at δ −1.37 and −1.44 (Figure 1a), the integration of which varied from 3:2 to 2:3 for two different experiments. Addition of 0.66 equiv of MeLi to $\mathrm{CuNEt_2}$ (eq 2) shifted the ^{7}Li absorption upfield to δ 0.45 and gave two methyl absorptions at δ −1.43 and −1.47 (Figure 1b). Minimization of the amide content by adding 0.5 equiv of $\mathrm{LiNEt_2}$ to MeCu (eq 3) affords a ^{7}Li absorption whose chemical shift is constant over a 115 °C (δ 0.34, Δppm = 0.01) temperature range and three sharp, clean singlets (Figure 1c,d) in the ^{1}H NMR spectrum (δ −1.44, −1.46, and −1.57, 2:1:3).

$\mathrm{CuNEt_2}$ + 1.0MeLi. The 1.0 $\mathrm{MeLi{:}CuNEt_2}$ ratio gave rise to a discrete species in THF (eq 4). In THF the ^{7}Li NMR spectra at −60 to −80 °C exhibits a single sharp absorption at δ 0.68–0.70 for $(\mathrm{MeCuNEt_2})\mathrm{Li}$ both in the absence and presence (Figure 2a,b) of LiI and regardless of the sequence of addition of the lithium reagents to CuI (compare Figure 2a with Figure 2b). The LiI-free MeCu experiment displayed a Δppm +0.16 between +25 and −90 °C with broading at −20 °C and appearance of a small broad peak at δ −0.12, although this experiment could not be cleanly reproduced. Similar behavior was observed for

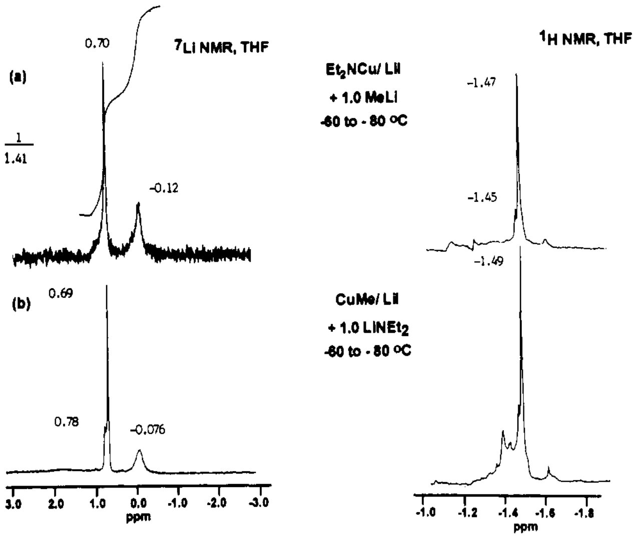


Figure 2. Spectra of $(MeCuNEt_2)Li$ (8): (a) by addition of MeLi to $CuNEt_2$; (b) by addition of $LiNEt_2$ to MeCu.

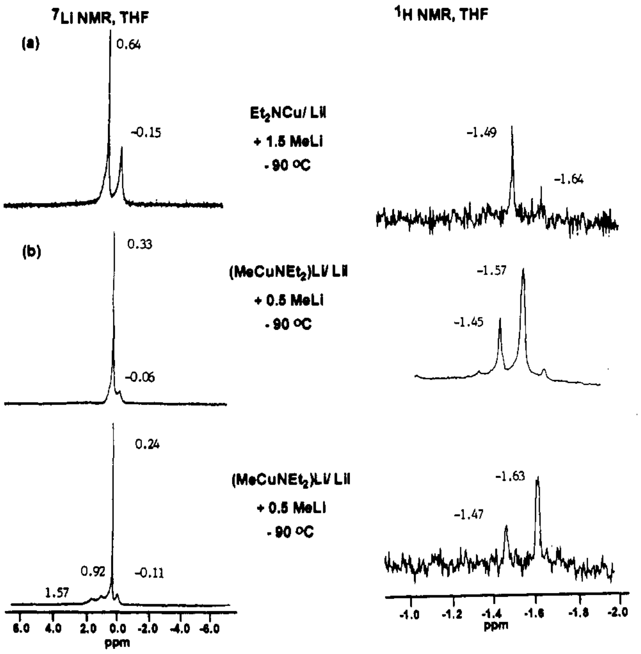


Figure 3. ^{7}Li and ^{1}H NMR spectra of $[Me_3Cu_2(NEt_2)_2]Li_3$ (9) for a Et_2NCu:MeLi ratio of 1:1.5 in THF/Et_2O at -90 °C: (a) by addition of MeLi to Et_2NCu; (b) by addition of MeLi to $(MeCuNEt_2)Li$ for two different experiments. The legend description refers to the stoichiometric ratio (eq 5).

the experiment with LiI present which gave a greater chemical shift difference (Δppm +0.25) as expected. In THF, the ^{1}H NMR spectrum displays a sharp singlet at δ -1.47 with a small shoulder at δ -1.45 (Figure 2a) in the presence of LiI and two broad absorptions centered at δ -1.39 and -1.44 in the absence of LiI.

$CuNEt_2$ + 1.5MeLi or $(MeCuNEt_2)Li$ + 0.5MeLi. The addition of 1.5 equiv of MeLi (eq 5) to $CuNEt_2$ (Figure 3a) or 0.5 equiv of MeLi to $MeCuNEt_2$ (Figure 3b) affords comparable spectra. For three experiments, the ^{7}Li absorptions appeared at δ 0.64, 0.33, and 0.24 and the ^{1}H NMR spectra displayed two absorptions: A (δ -1.45 to -1.49) and B (δ -1.57 to -1.64). The integration ratios or peak heights of the ^{1}H absorptions correlated with the observed ^{7}Li chemical shift with the ^{7}Li absorption moving upfield proportionately with the increase in the ^{1}H signal at δ -1.57 to -1.64. Using ^{7}Li chemical shift values of δ 0.70 for $(MeCuNEt_2)Li$ and δ 0.095 for $[(MeCuNEt_2) + MeLi]$ gave calculated ^{7}Li [$\delta = 2A(0.70) + B(0.095)/2A + B$, where A and B equal the corresponding peak heights or integration ratios for species A and B] values of δ 0.60, 0.41, and 0.37 for the three experiments.

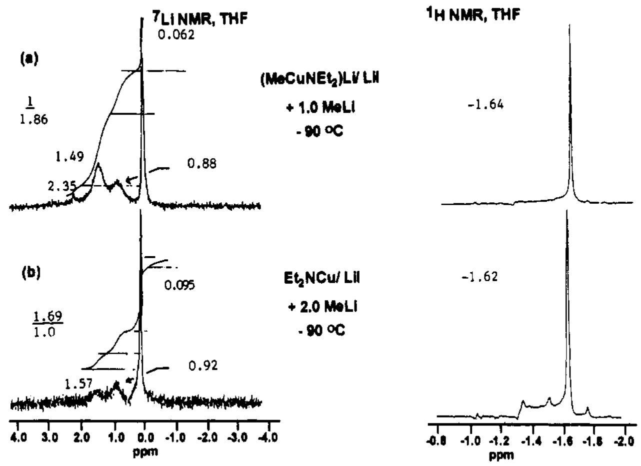


Figure 4. Spectra of $[Me_2CuNEt_2]Li_2$ (10): (a) by addition of MeLi (1.0 equiv) to $(MeCuNEt_2)Li$; (b) by addition of MeLi (2.0 equiv) to Et_2NCu. The legend description refers to the stoichiometric ratio (eq 6).

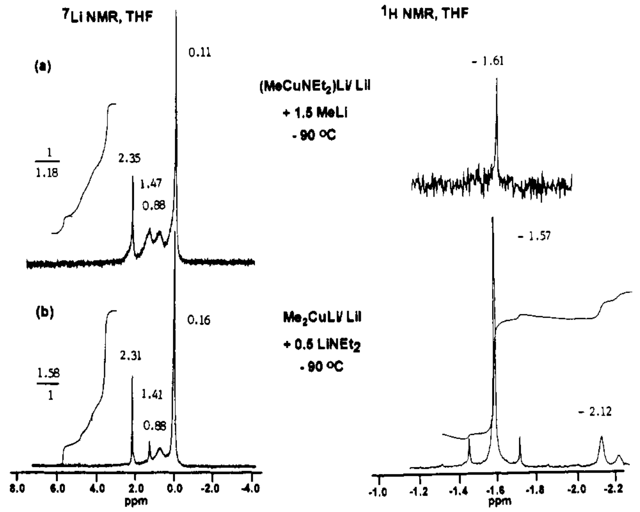


Figure 5. ^{7}Li and ^{1}H NMR spectra at -90 °C in THF/Et_2O for (a) $(MeCuNEt_2)Li$ (8)/LiI + 1.5MeLi and (b) Me_2CuLi/LiI + 0.5$LiNEt_2$.

$(MeCuNEt_2)Li$ + MeLi or $CuNEt_2$ + 2.0MeLi. Addition of MeLi to $(MeCuNEt_2)Li$ (Figure 4a) or 2.0 equiv of MeLi to $CuNEt_2$ (eq 6, Figure 4b) affords the same ^{7}Li NMR spectrum with a strong sharp peak at δ 0.062 and 0.095, respectively, and broad minor peaks at δ 1.49/1.57 ($LiNEt_2$) and δ 0.88/0.92, respectively. The large chemical shift differences over the 115 °C temperature range (Δppm -0.62 and -0.74, respectively) is consistent with an equilibrium between the major and minor components. The peaks at δ 1.49/1.57 and δ 0.88/0.92 have the same appearance as $LiNEt_2$/LiI and MeLi/LiI/$LiNEt_2$ equilibrium mixtures, respectively, measured with control samples of these species. A small amount of free MeLi (δ 2.31) can be seen in the sample with LiI. Integration indicates considerable Li content for the broad downfield peaks with the ratios of the δ 0.062 peak/downfield peaks varying between 1.69 and 0.54. The latter value was obtained for the LiI free experiment consistent with possible over addition of MeLi and $LiNEt_2$.

Increasing the amount of MeLi to 2.5 (Figure 5a) and 3.0 equiv affords the same ^{7}Li NMR pattern with a slight downfield shift of the major peak and an increase in the integration ratio for the broad downfield peaks. The same spectrum can be obtained by adding 0.5 equiv of $LiNEt_2$ to Me_2CuLi (Figure 5b).

Results in Et_2O. The spectra obtained for these compositions (eqs 1–6) in Et_2O are consistent with the THF results but not as clean and generally more ambiguous. The $(MeCuNEt_2)Li$ (**8**) composition (eq 4) gave small broad peaks at δ 2.40 (MeLi), 1.79, and 0.90–0.98 and strong sharp peaks at δ 0.36/0.42, respectively, in the ^7Li NMR. The ^1H NMR spectra were more varied with one showing a strong absorption at δ −1.28 and weak absorptions at δ −1.20 and δ −1.35, while these three absorptions were of equal intensity in the composition displaying the δ 0.42 absorption in the ^7Li NMR spectrum. Interestingly, LiI-free MeCu prepared in THF and then reacted with $LiNEt_2$ in Et_2O gave absorptions at δ −1.56 for cuprate composition **8** comparable to the values obtained for this species in THF. The $CuNEt_2$ + 2.0MeLi composition displays strong absorptions for ^7Li between δ 0.32 and 0.39 with smaller absorptions at δ 2.40, 1.86, and 1.04. The ^1H NMR spectra gave strong absorptions between δ −1.22 and −1.27. The reaction of Me_2CuLi with $LiNEt_2$ gave an extremely clean ^1H NMR spectrum with a single absorption at δ −1.26 significantly different than the δ −1.17 recorded for Me_2CuLi. Utilization of 3.0 equiv of MeLi shows a 1:1 ratio of downfield Li absorptions to that at δ 0.32, while the ^1H NMR spectrum shows a single peak at δ −1.27 and small peaks at δ −2.10 for free MeLi.

Discussion

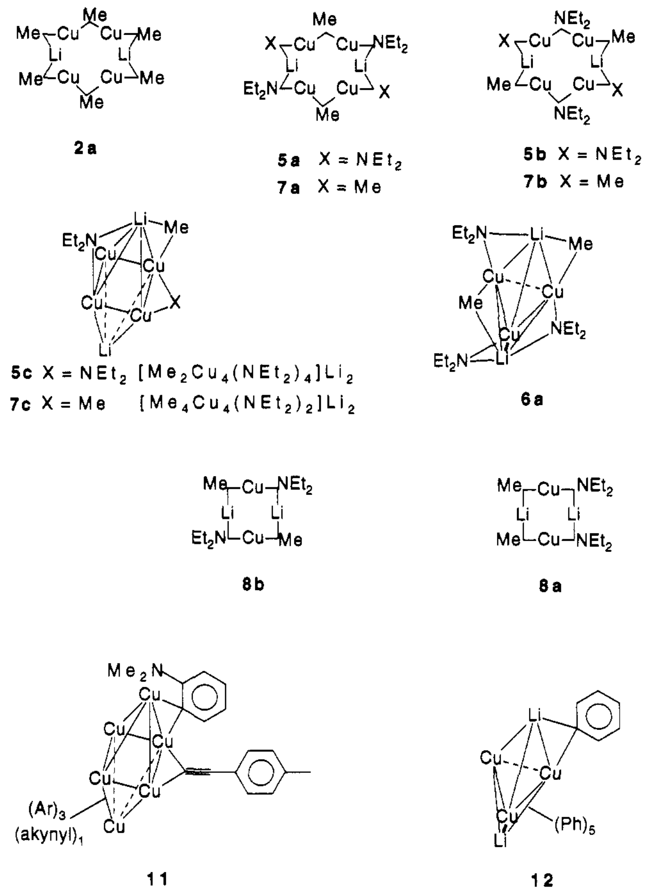
$CuNEt_2$ + 1.0MeLi. The addition of 1.0 equiv of MeLi to $CuNEt_2$ in THF gives rise to a clear solution displaying single absorptions in the ^7Li (δ 0.69) and ^1H NMR spectra consistent with the formation of a discrete species. This species is formulated as the dimer $[(Et_2N)_2Cu_2Me_2]Li_2$ (**8**) by analogy with X-ray structures[12] obtained for several $R_4Cu_2Li_2$ compounds. This dimer can, in principle, exist as a mixture of geometrical isomers with the like ligands (i.e. the two methyls) either cis (**8a**) or trans (**8b**) (Chart I) to each other. A small shoulder at δ −1.45 in the ^1H NMR spectrum could be consistent with the minor, and presumably cis, geometrical isomer. The broad absorption at δ −0.12 in the ^7Li NMR occurs at the same chemical shift as that of LiI, but the broadness of the absorption in comparison to control samples of LiI is suggestive of additional complexation. It is noteworthy that both the ^7Li and ^1H NMR spectra of **8** are much cleaner in THF then in Et_2O with the ether solutions showing broad downfield absorptions that appear identical to those obtained for a $MeLi/Et_2NLi/LiI$ mixture in a control experiment.

$CuNEt_2$ + 0.5MeLi. The addition of less than 1.0 equiv of MeLi to $CuNEt_2$ affords solutions that give rise to two signals in the ^1H NMR between δ −1.37 and −1.47 and a single absorption in the ^7Li NMR. As the MeLi content is increased, the absorptions in both the ^1H and ^7Li NMR move upfield. Consideration of stoichiometry gives rise to eqs 1 and 7 for the $0.5MeLi/CuNEt_2$ composition. Both

$$CuNEt_2/LiI + 0.5MeLi \rightarrow 0.25\underset{\mathbf{5}}{[MeCu_2(NEt_2)_2]Li} + 0.125\underset{\mathbf{6}}{[Me_2Cu_3(NEt_2)_3]Li_2} + 0.125Et_2NCu \quad (7)$$

equations contain a species with composition $[MeCu_2(NEt_2)_2]Li$ (**5**) analogous to the Me_3Cu_2Li (**2**) composition reported by Ashby[3a,b] and Lipshutz.[4] Ebullioscopic measurements[3a] on solutions of **2** suggest a dimeric structure in THF and a monomer in $Et_2O/P(n\text{-}Bu)_3$. Ashby[3a] has suggested a monocyclic dimer **2a**, the idea of which can be extended to proposed structures **5a**,**b**. Although no X-ray data are available for **2**, an X-ray structure has been determined[13] for $(2,4,6\text{-}Me_3C_6H_2)_5Cu_5$ showing a ten-membered ring with bridging aryl groups linking the Cu atoms. In solution, however, ebullioscopic measurements show a high order (2.5) of aggregation.[13] X-ray structures have been determined for several compounds of R_6Cu_6 composition $[(R_4Cu_6Br_2)$[14a] and $(R_4R_2Cu_6)$[14b]] revealing a bipyrimidal copper cluster with bridging R groups between the Cu atoms and along the apical edges of the bipyrimidal metal cluster (e.g. **11**). In these structures, the Cu–Cu interactions are long and MO calculations suggest very weak bonding interactions between the Cu atoms.[14b] Given the propensity of Cu and Li to form metal clusters with varying Cu:Li ratios, one can visualize replacement of the apical Cu atoms with Li atoms to afford an alternative structure consistent with the dimeric form of the R_3Cu_2Li composition (i.e. **5c**). X-ray studies[15] on $(Et_2N)_4Cu_4$ reveal a tetrameric eight-membered ring structure with bridging Et_2N ligands. The incorporation of MeLi into this tetrameric structure could lead to either **5a**,**b** or **5c**.

Chart I



Equation 7 suggests a mixture of two copper species with different compositions: namely **5** and $[Me_2Cu_3(NEt_2)_3]Li_2$ (**6**), which is analogous to Clive's reagent $Me_5Cu_3Li_2$ (**1**). Ebullioscopic measurements on solutions of **1** are consistent with a monomeric structure in Et_2O. Although a structure has never been proposed for **1**, an X-ray structure

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[13] Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1983**, 1156.

[14] (a) van Koten, G.; Noltes, J. G. *J. Organomet. Chem.* **1975**, *102*, 551. (b) ten Hoedt, R. W. M.; Noltes, J. G.; van Koten, G.; Spek, A. L. *J. Chem. Soc., Dalton Trans.* **1978**, 1800.

[15] (a) Hope, H.; Power, P. P. *Inorg. Chem.* **1984**, *23*, 936. (b) Gambarotta, S.; Bracci, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1987**, 1883.

has been obtained for the anionic trinuclear Cu cluster **12**, $[Ph_6Cu_3Li_2]^-$, revealing a trigonal bipyrimidal metal cluster[10] with the two Li atoms in the apical positions and the six phenyl groups bridging the Li and Cu atoms along the six edges. Similar trigonal bipyrimidal structures were observed for the $[Ph_6Cu_4Li]^-$ and $[Ph_6Cu_5]^-$ anions indicating the interchangeability of the Li and Cu atoms in the metal cluster.[16] An analogous trigonal bipyrimidal structure can be proposed for **1** and **6** (i.e. **6a**), although in these neutral complexes only five anionic bridging ligands are available and the sixth coordination site may either be occupied by solvent or I^- or be open.

The question remains, however, whether the two absorptions observed in the ^1H NMR result from two species with different compositions (eq 7) or from a single species (eq 1) existing as a mixture of geometrical (e.g. **5c**) or constitutional isomers (e.g. **5a** and **5b**). The integration ratios (2:3) for the methyl absorptions in the ^1H NMR spectrum are not obviously consistent with those predicted (1:1) from eq 7 supporting a tentative conclusion that the 0.5MeLi/Et_2NCu mixture affords the discrete species **5**.

$CuNEt_2$ + 0.66MeLi. Several stoichiometric expressions can be written for the 0.66MeLi/$CuNEt_2$ mixture (eqs 2, 8 and 9), all of which contain the species (**6**)

$$\mathrm{CuNEt_2/LiI + 0.66MeLi \rightarrow 0.165\underset{\textbf{6}}{[Me_2Cu_3(NEt_2)_3]Li_2} + 0.33(MeCuNEt_2)Li + 0.175Et_2NCu} \tag{8}$$

$$\mathrm{CuNEt_2/LiI + 0.66MeLi \rightarrow 0.165\underset{\textbf{6}}{[Me_2Cu_3(NEt_2)_3]Li_2} + 0.165(Me_2CuNEt_2)Li_2 + 0.34CuNEt_2} \tag{9}$$

analogous to the Clive regent (**1**). The upfield shift of the ^7Li absorption (from δ 0.59 to 0.45) upon addition of 0.16 equiv of MeLi to the 0.5 MeLi:$CuNEt_2$ ratio rules out eq 8 since $(MeCuNEt_2)Li$ absorbs at δ 0.69 and a dynamic equilibrium with this species would be expected to afford a downfield chemical shift. Equation 9 contains $(Me_2CuNEt_2)Li_2$ analogous to Me_3CuLi_2 which was not observed by Lipshutz in THF.[4] In addition, the integration ratios for the methyl absorptions in the ^1H spectrum are not consistent with the 1:1 ratio given by eq 9. An alternative possibility is a single discreet species **6** existing as a mixture of stereo- or regioisomers involving the relative disposition of the Me and Et_2N ligands about the trinuclear Cu core (i.e. **6**).

MeCu + 0.5LiNEt$_2$. The 0.5LiNEt$_2$/MeCu mixture, deficient in amide, gave the cleanest spectra of the series displaying three sharp peaks (δ −1.44, −1.46, and −1.57) in the ^1H NMR in a simple 2:1:3 ratio. The downfield absorption at δ −1.57 is consistent with the Me_2CuLi/Me_3Cu_2Li mixture observed by Lipshutz[4] and with the upfield absorption at δ 0.34 in the ^7Li NMR indicative of a dynamic equilibrium with another Li-containing species. Accepting this evidence for the presence of Me_2CuLi/LiI rules out eq 3 but not the species $(Me_2Cu_2NEt_2)Li$ (**7**), which is also generated in eq 10. A second possibility is

$$\mathrm{MeCu/LiI + 0.5Et_2NLi \rightarrow 0.25\underset{\textbf{7}}{(Me_2Cu_2NEt_2)Li} + 0.25Me_2CuLi + 0.25Et_2NCu} \tag{10}$$

$$\mathrm{MeCu/LiI + 0.5Et_2NLi \rightarrow 0.125[Me_4Cu_3(NEt_2)]Li_2 + 0.25Me_2CuLi + 0.375Et_2NCu} \tag{11}$$

shown in eq 11, which also contains Me_2CuLi. The 1:1 integration ratio of the downfield pair of methyl absorptions to the upfield singlet is consistent with eq 10, suggesting a new species $[Me_2Cu_2NEt_2]Li$ (**7**) analogous to **5** but with an inverse ratio of the methyl and amide ligands. The ^7Li absorption at δ 0.36 is midway between the Me_2CuLi/LiI absorption (δ 0.00) reported by Lipshutz[4] and the δ 0.59 absorption observed for cuprates of mixed methyl/amide composition (vide infra) expected for 1:1 mixture of Me_2CuLi with **7**. Structural possibilities include the monocyclic dimer **7a**,**b** or the octahedral cluster **7c**, the 2:1 NMR ratio reflecting geometrical or regioisomers.

$CuNEt_2$ + 1.5MeLi and 2.0MeLi. The $CuNEt_2$ + 1.5MeLi composition (eq 5) does not appear to be a unique species but rather a mixture of the $(Et_2NCuMe)Li$ (**8**) and the Et_2NCu + 2.0MeLi (eq 6) compositions which are clearly seen at δ −1.47 and −1.60, respectively, in the ^1H NMR spectrum. The ^7Li NMR spectra show a single absorption peak whose chemical shift varies but generally lies about midway between the absorptions observed for **8** (δ 0.70) and that observed for the Et_2NCu + 2.0MeLi composition (δ 0.09) consistent with a dynamic equilibrium between the two species.

The $CuNEt_2$ + 2.0MeLi composition is problematic because of the significant Li content of the broad downfield signals making the stoichometric composition $[Me_2CuNEt_2]Li_2$ (eq 6) unlikely. From control experiments the broad downfield absorptions can be ascribed to various $LiNEt_2$/MeLi/LiI mixtures. The suggestion of Power[7a] that higher order cuprates derived from various PhLi/CuI ratios can be understood as combinations of $CuPh_3^{2-}$ and $CuPh^-$ suggests the possibility of a discrete species having the composition $[Me_4Cu_2NEt_2]Li_3$ (**13**). Formation of this species with the stoichiometry shown in eq 12 requires an equivalent of free or LiI-complexed

$$\mathrm{CuNEt_2 + 2.0MeLi \rightarrow 0.5\underset{\textbf{13}}{[Me_4Cu_2NEt_2]Li_3} + 0.5LiNEt_2} \tag{12}$$

$$\mathrm{(MeCuNEt_2)Li + MeLi \rightarrow Me_2CuLi + LiNEt_2} \tag{13}$$

$$\mathrm{Me_2CuLi + 0.5LiNEt_2 \rightarrow 0.25\underset{\textbf{13}}{[Me_4Cu_2NEt_2]Li_3} + 0.5Me_2CuLi + 0.25LiNEt_2} \tag{14}$$

$LiNEt_2$ which would give a 1:1.5 Li ratio for the broad downfield peaks/δ 0.06 absorption which is close to the 1:1.69 value actually observed. Alternative possibilities are shown in eqs 13 and 14. The observed absorptions in both the ^7Li (δ 0.09) and ^1H (δ −1.60) NMR spectra are quite close to those reported by Lipshutz[4] for the Me_2CuLi/Me_3Cu_2Li mixture suggesting the possibility that MeLi is simply displacing $LiNEt_2$ from the heteroatom mixed cuprate **8** (eq 13). In this case, however, 1:1 integration ratios in the ^7Li NMR would be expected or possibly higher ratios favoring the downfield absorptions involving LiI complexation. An additional observation bears upon the problem. Addition of 0.5 equiv of $LiNEt_2$ to Me_2CuLi gives rise to both ^7Li and ^1H NMR spectra that appear identical to those obtained from the experiments shown in eqs 12 and 13 (Figure 5b).

Equations 12 and 14 both contain $LiNEt_2$ and the higher order cuprate **13** consistent with the NMR spectra. Equation 14 also contains Me_2CuLi and the spectral data would require that **13** and Me_2CuLi or Me_2CuLi/Me_3Cu_2Li have the same chemical shifts in both the ^1H and ^7Li NMR. The data appears to suggest that the Me and amide ligands can readily exchange and that **13** may be formed alone or in equilibrium with Me_2CuLi. The higher order species **13** is most easily envisioned to be formed by addition of $LiNEt_2$ to the Me_2CuLi dimer along the lines

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[16] For the X-ray structure of $[Ph_6Cu_4Li]^-$ see: (a) Khan, S. I.; Edwards, P. G.; Yuan, H. S. H.; Bau, R. *J. Am. Chem. Soc.* **1985**, *107*, 1682. For the X-ray structure of $[Ph_6Cu_5]^-$, see: (b) Edwards, P. G.; Gellert, R. W.; Marks, M. W.; Bau, R. *J. Am. Chem. Soc.* **1982**, *104*, 2072.

suggested by Power[7a] for formation of $Ph_5Cu_2Li_3$ by addition of PhLi to $Ph_4Cu_2Li_2$.

Summary

^7Li and ^1H NMR studies have provided evidence that treatment of $CuNEt_2$ in varying amounts (0.5–1.0 equiv) of MeLi results in the formation of several distinct cuprate reagents in THF. The lower order heteroatom mixed cuprate $(MeCuNEt_2)Li$ (**8**) appears not to form until 1.0 equiv of MeLi has been added. With lower quantities of MeLi the NMR spectra are consistent with discrete species $[MeCu_2(NEt_2)_2]Li$ (**5**), $[Me_2Cu_3(NEt_2)_3]Li_2$ (**6**), and $(Me_2Cu_2NEt_2)Li$ (**7**) although it is not as clear whether the solutions contain a mixture of species of different compositions or whether a single composition gives rise to a mixture of geometrical or regioisomers. These compositions correspond to Me_3Cu_2Li (**2**) or $Me_5Cu_3Li_2$ (**1**) for which spectroscopic data have been obtained.[4] Although it is not possible to distinguish between them on the basis of the current NMR data, monocyclic and bipyrimidal dimers are proposed[17] as possible structures for **5** and **7** while a trigonal bipyrimidal structure is proposed for **6**. Precedence for these structures can be found in a number of reported X-ray structural determinations for a number of organocopper compounds and in the apparent interchangeability of Li and Cu atoms in metal clusters containing varying Li:Cu ratios. Addition of MeLi to $CuNEt_2$ beyond 1.0 equiv leads to a single new species which may be either Me_2CuLi, $[Me_4Cu_2(NEt_2)]Li_3$ (**13**), or a combination of the two. The latter species can be envisioned as the addition of $LiNEt_2$ to Me_2CuLi to afford the higher order species. Although similar ligand exchange and species formation appears to be occurring in ether, the ^7Li and ^1H NMR spectra in this solvent generally show single absorption peaks with similar chemical shifts across the various compositions, thus providing little insight into the formation of species as a function of composition changes. In Et_2O the cuprate **8** appears not to be cleanly formed as evidenced by the smaller downfield absorptions and it is not clear whether this has any implications for the chemistry of this species. Mixed heteroatom cuprates thus appear capable of forming several distinct species varying in Li:Cu ratios and in amide:alkyl ligand ratios, which is entirely analogous to that observed for homocuprates.

Experimental Section

Glassware and syringes were dried in an oven overnight at 100 °C, and the glassware was flame dried prior to use. Ethereal solvents were freshly distilled from sodium/benzophenone ketyl. Diethylamine was purchased from Eastman Organic Chemicals and purified by distillation over KOH. Methyllithium was purchased from Aldrich and titrated according to the methods of Lipton[18a] and Kofron.[18b] Cuprous iodide was purchased from Aldrich and purified by the method of House.[19] All reactions were performed under dry nitrogen atmosphere. LiI used in control experiments was purchased from Sigma and used without further purification.

All variable-temperature ^1H and ^7Li NMR experiments were performed on an IBM AF 200 spectrometer at 200.13 and 77.71 MHz, respectively. A 0.8 M LiCl/MeOH (0.00 ppm) solution was used as an external reference for ^7Li NMR experiments, while the middle peak of the triplet for diethyl ether (cosolvent) was assigned at δ 1.07 and was used as the reference for ^1H NMR experiments. Samples were prepared under dry argon or nitrogen and transferred to a 5-mm NMR tube in a Vacuum Atmospheres drybox. The 5-mm tubes were then inserted into a 10-mm NMR tube containing d^6-acetone as a lock solvent and the experiments conducted in a multinuclear 10-mm probe. Resonances due to the THF/ether solvent were suppressed in the ^1H experiments by sequentially irradiating each peak for 0.05 s at low wattage, and this cycle was repeated 75 times prior to each acquisition pulse.

General Procedure for the Preparation of Et_2NLi. THF (2.0 mL) was added to a test tube or round-bottom flask equipped with a magnetic stir bar and septum and under a dry nitrogen atmosphere. The vessel was cooled to −5 °C, and diethylamine (73 mg, 1 mmol) was added followed by the dropwise addition of methyllithium (0.74 mL, 1.0 mmol). The resulting pale yellow solution was stirred for 15 min and used in the flask or transferred via cannular. THF (1.0 mL) was used to rinse the test tube during the transfer process.

General Procedure for the Preparation of $CuNEt_2$. A solution of Et_2NLi, prepared as above, was added via cannular to a suspension of CuI (190 mg, 1.0 mmol) in 2.0 mL of THF at −5 °C in a 25-mL round-bottom flask under a nitrogen atmosphere. A brownish yellow solution was obtained.

General Procedure for the Preparation of MeCu. MeLi (0.74 mL, 1.0 mmol) was added dropwise via syringe to a suspension of CuI (190 mg, 1.0 mmol) in 2.0 mL of THF cooled to 0 °C in a 25-mL round-bottom flask under a nitrogen atmosphere. A bright yellow precipitate was obtained.

General Procedure for the Preparation of LiI-Free MeCu. LiI-free MeCu was prepared according to the procedure of Lipshutz.[4] CuI (190 mg, 1.0 mmol) was placed in a centrifuge tube fitted with a septum and flushed with dry nitrogen. THF (2.0 mL) was injected, and the suspension was cooled to 0 °C whereupon methyllithium (0.74 mL, 1.0 mmol) was added dropwise, and the resulting yellow suspension was warmed to room temperature and spun in a centrifuge. The clear supernatant solution was removed via cannula and replaced with 2.0 mL of THF. The methylcopper was then stirred and the washing procedure repeated three times. THF (2.0 mL) was added to the washed LiI-free MeCu.

Preparation of $(MeCuNEt_2)Li/LiI$. Method A. A solution of Et_2NLi was added via cannular to a suspension of MeCu in THF at −78 °C, and the resulting colorless solution was allowed to warm to room temperature by removing the 2-propanol/liquid-N_2 bath.

Method B. Methyllithium (0.74 mL, 1.0 mmol) was added dropwise to a solution of (diethylamido)copper (1.0 mmol prepared as described above) at −78 °C. The cooling bath was removed, and the colorless solution was allowed to warm to room temperature (over 30 min).

Preparation of LiI-Free $(MeCuNEt_2)Li$. LiI-free MeCu (1.0 mmol in 1.0 mL of THF) was prepared as described above and cooled to −78 °C. (Diethylamido)lithium (1.0 mmol) in THF (2.0 mL) was then added via cannular, and the colorless solution was warmed to room temperature (over 30–40 min).

Preparation of $(Me_4Cu_2NEt_2)Li_3$. Method A. Methyllithium (0.74 mL, 1.0 mmol) was added dropwise at 0 °C to a solution of $(MeCuNEt_2)Li$ (1.0 mmol) prepared as described above. The pale yellow solution was stirred at room temperature for 15 min.

Method B. Methyllithium (1.48 mL, 2.0 mmol) was added dropwise to a solution of (amido)copper (1.0 mmol) in 2.0 mL of THF at 0 °C, and the resulting yellow solution was warmed to room temperature.

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[17] Note added in proof: Although we had entertained the idea of monomeric six-membered ring structures with bridging methyl and amido ligands for **5** and **7** (RX_2Cu_2Li or R_2XCu_2Li), we did not consider these further due to the lack of precedence for these structures in the literature and the suggestion that Me_3Cu_2Li was dimeric in THF (see ref 3a). A reviewer has pointed out a recent computational study [Snyder, J. P.; Tipsward, G. E.; Spangler, D. P. *J. Am. Chem. Soc.* **1992**, *114*, 1507] suggesting that six-membered ring structures are more stable for monomeric R_3CuLi_2 species. The experimental data do not rule out the possibility of similar structures for **5** and **7**.

[18] (a) Lipton, M. F.; Sorensen, C. M.; Sadler, A. C.; Shapiro, R. H. *J. Organomet. Chem.* **1980**, *186*, 155. (b) Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879.

[19] House, H. O.; Chu, C. Y.; Wilkens, J. M.; Umen, M. J. *J. Org. Chem.* **1975**, *40*, 1460.