heteroenyne-allenes in which other $CH_n$ groups are replaced by hetero units (e.g., B = NH in **2**).

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# X-Ray Absorption Spectroscopy of Dimethylcuprates: Evidence for Solvent-Dependent Aggregation**

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Organocopper reagents are widely used in organic synthesis. Although their properties depend on experimental conditions, with solvent often a key factor,[1] only limited information is available on the solvent dependence of organocopper structures.[2, 3] Vapor pressure depression and X-ray scattering measurements have suggested that lithium dimethylcuprate derived from cuprous halide is dimeric $(Me_2CuLi)_2$ in $Et_2O$;[4a] this structure is supported by theoretical calculations.[4b, 5] In contrast, recent cryoscopic measurements suggest that monomeric lithium dimethylcuprate is the major species in THF.[3] Dimethylcuprates derived from cuprous halide give different $^1$H and $^7$Li NMR signals in THF and $Et_2O$,[2b] consistent with a solvent-dependent difference in structure. However, to date there have been no direct data

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comparing the copper structures as a function of solvent. Here we describe the use of X-ray absorption spectroscopy (XAS) to determine the structure of dimethylcuprates in $Et_2O$, THF, and dimethyl sulfide (DMS).

The XANES spectra (XANES = X-ray absorption near edge structure) for all of the dimethylcuprates are characterized by an intense 1s→4p transition at 8982–8983 eV, consistent with two-coordinate $Cu^I$ (Figure 1).[6] However, in contrast with dimethylcuprates prepared from CuCN,[7] there is a noticeable solvent dependence for the spectra of a mixture of CuI and two equivalents of MeLi.

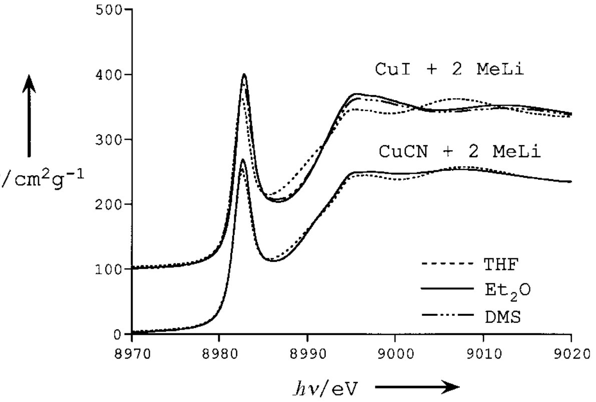


Figure 1. Normalized XANES spectra for CuI+2MeLi and CuCN+2MeLi.

Although all of the EXAFS data (EXAFS = extended X-ray absorption fine structure; Figure 2, Table 1) are dominated by a first-shell peak at $R+\alpha \approx 1.5$ Å ($R$ = absorber–scatterer distance, $\alpha$ = phase shift, typically ≈ −0.4 Å, $R_{\text{Cu-C}} = 1.95$ Å), typical of digonal Cu,[6, 8] the outer-shell scattering is solvent-dependent. Samples prepared in $Et_2O$ or DMS show peaks at $R+\alpha \approx 2.3$ and 2.7 Å, respectively, which can be modeled as Cu–Cu interactions at 2.82 and 3.12 Å. The observation of a strong Cu–Cu feature demonstrates that a substantial fraction of the Cu atoms are present in dimers or higher aggregates in $Et_2O$ and DMS. There may also be outer-shell peaks for the sample in THF; however, they are much weaker and shifted to longer distances.

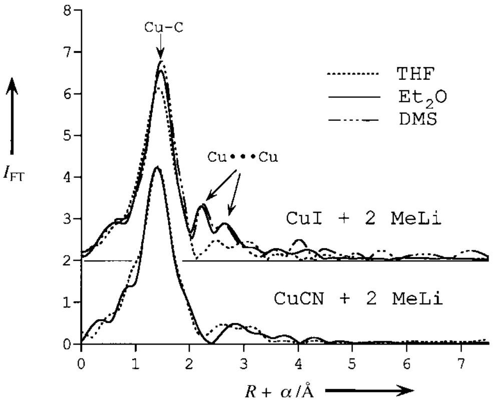


Figure 2. Fourier-transformed EXAFS spectra for CuI+2MeLi and CuCN+2MeLi. $I$ = intensity.

The Cu–Cu distances in crystallographically characterized $[Me_2Cu]_n$ aggregates are 2.67–3.38 Å.[8, 9] The Cu–Cu distance of 2.82 Å determined by EXAFS is very similar to that in a $[Ph_2Cu]Li_2$ dimer crystallized from $Et_2O$ (2.87 Å).[10] The other distance of 3.12 Å determined by EXAFS may reflect a different dinuclear structure or indicate formation of a cluster with higher nuclearity. Neither of the Cu–Cu distances found by EXAFS is close to the value of 4.4 ± 0.7 Å reported from X-ray solution scattering measurements.[4a]

The presence of only weak outer-shell features for the sample in THF suggests that most of the cuprates are present either as the monomeric $CuMe_2^-$ ion or as weakly associated $[CuMe_2]^-Li^+$ ion pairs (**2**), which is consistent with cryoscopic results.[3] The EXAFS spectrum for a mixture of CuI and two equivalents of MeLi in THF/$Et_2O$ (50/50) is identical to that in a 86/14 mixture, demonstrating that 50% THF is sufficient to break apart the dimeric structure seen in $Et_2O$.

The solvent-dependent structural changes may be due to the differences in solvent polarity and dielectric constant ($\varepsilon$). The higher value of $\varepsilon$ for THF leads to the stabilization of $[CuMe_2]^-$ and $Li^+$ ions, while neutral $[CuMe_2Li]_2$ dimers are favored in $Et_2O$. As a soft base, DMS might be expected to coordinate to the soft $Cu^I$ ion, thus favoring formation of mononuclear cuprates. However, DMS and $Et_2O$ give nearly identical spectra, with no evidence for Cu–S ligation in DMS. Evidently, two methyl ligands are sufficiently strong donors to prevent any significant coordination by solvent, resulting in retention of the dimeric structure in DMS.

We reported previously that dimethylcuprates formed from CuCN and CuI have identical structures in THF.[6a] In contrast, the Cu source does affect the dimethylcuprate structure in $Et_2O$. With CuCN, only weak outer-shell peaks are seen, suggesting a monomeric structure. There are small changes in $\tilde{\nu}_{CN}$ (from 2115 cm$^{-1}$ in THF to 2104/2115 cm$^{-1}$ in $Et_2O$), but no change in the total IR intensity, indicating only

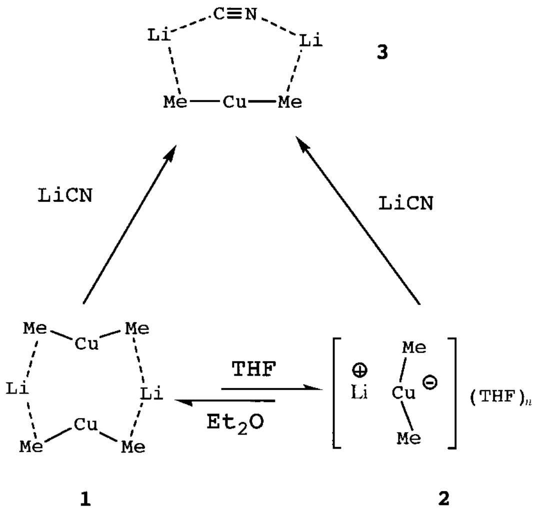
Table 1. Results of the EXAFS curve fitting.[a]

| Sample | | | Cu–C | | | Cu···Cu | | | Cu···Cu | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | C.N. | $R$ [Å] | $\sigma^2 \times 10^3$ | C.N. | $R$ [Å] | $\sigma^2 \times 10^3$ | C.N. | $R$ [Å] | $\sigma^2 \times 10^3$ |
| CuI+2MeLi | $Et_2O$ | 2.0 | 1.95 | 6.4 | 1.0 | 2.82 | 14.6 | [b] | 3.12 | [b] |
| | THF | 2.0 | 1.94 | 4.5 | | | | | | |
| | DMS | 2.0 | 1.95 | 4.6 | 1.0 | 2.83 | 13.9 | [b] | 3.12 | [b] |
| CuCN+2MeLi | $Et_2O$ | 2.0 | 1.96 | 6.1 | | | | | | |
| | THF | 2.0 | 1.95 | 6.1 | | | | | | |

[a] Results are for best fits using half-integer coordination numbers over $k = 1.5-12.5$ Å$^{-1}$ ($k$ = photoelectron wave vector, $[2m_e(E-E_0)/\hbar^2]^{1/2}$, $m_e$ = electron mass, $E$ = X-ray energy, $E_0$ = threshold energy). Estimated uncertainties are ± 0.02 Å for $R$ and ± 0.25 for C.N. (C.N. = coordination number). [b] C.N. and σ are highly correlated.

1433-7851/98/3711-1565 $ 17.50+.50/0

minor changes in the cyanide environment.[11, 12] The lack of a strong solvent dependence for the IR spectra of cyanocuprates is most likely due to the interaction of $CN^-$, $Li^+$, and $[CuMe_2]^-$ to give **3** (Scheme 1) regardless of solvent. The structure of **3** is supported by IR measurements and theoretical calculations.[11] The present data suggest that, in the absence of cyanide, dimethylcuprate is largely dimeric **1** in $Et_2O$ and monomeric **2** in THF.



Scheme 1. Structural conversion of dimethylcuprates in THF and $Et_2O$ as well as in the presence of cyanide.

In summary, XAS measurements have revealed solvent-dependent effects for the structures of dimethylcuprates derived from CuI. Dimeric $(CuMe_2Li)_2$ species are predominant in $Et_2O$ and DMS, while a monomeric $[CuMe_2]^-$, or at most a weakly associated aggregate, appears to be the main species in THF. The structures of cyanocuprates are less susceptible to solvent, probably due to the association of the cyanide (or the $[Li_2CN]^+$ unit) with the $[CuMe_2]^-$ unit. This may account for the higher yield for cuprate reactions with CuCN as a precursor.

### *Experimental Section*

Organocuprate samples (0.1M) were prepared under dry $N_2$ using Schlenk techniques.[11] CuCN (99%), CuBr (99.999%), and CuI (99.999%) were purchased from Aldrich. Halide-free MeLi (1.4M in $Et_2O$, Aldrich) was titrated with 2-butanol using 1,10-phenanthroline as an indicator. THF was freshly distilled from Na/benzophenone; $Et_2O$ and DMS were freshly distilled from $CaH_2$. The solutions in DMS and THF contain 14% $Et_2O$ from MeLi addition. Sample preparation and data collection and analysis were previously described.[6b] Solutions in THF and $Et_2O$ were measured in the transmission mode, while solutions in DMS were measured in the fluorescence mode. Data for all samples were evaluated in an identical way.

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# Ansa Macrolides as Molecular Workbenches: Stereocontrolled *syn* Additions to *E* olefins

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Stereocontrolled dihydroxylations and epoxidations of acyclic 1,2-disubstituted *E* olefins are in favorable cases carried out catalytically,[1] otherwise with substrate-induced diastereodifferentiation; this method, however, requires allylic or homoallylic hydroxy or amide groups.[2] In general an effective face discrimination is difficult because of the high conformative mobility of the substrate. We herein report a new approach to solving this problem. In this, the acyclic *E*

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