Communications

Structural Characterization of Organocopper Complexes by EXAFS and XANES: Evidence That Cyanide Does Not Coordinate to Cu in Dimethyl Cuprate Solutions

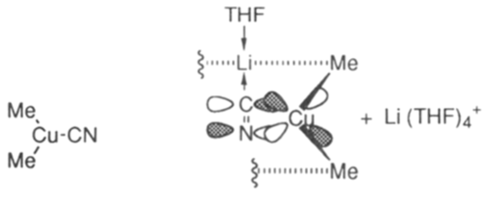
Terence M. Barnhart, Hui Huang, and
James E. Penner-Hahn*

Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109

Received March 14, 1995

The addition of cyanide ion to dialkyl cuprate solutions (e.g. Me_2CuLi) leads to altered reactivity compared to cuprate solutions prepared without cyanide. This effect has been used in hundreds of syntheses and has been ascribed to formation of a three-coordinate Cu−cyanide complex[1,2] known as a "higher-order" cuprate, **1** (see Figure 1). Recently, the existence of a σ-coordinated cyanide in **1** has been questioned.[3−5] NMR data have not shown the ^{13}C chemical shift differences expected for a coordinated cyanide complex.[3] Three-coordinate Cu complexes do not represent energetic minima in ab initio structure calculations of organocyanocuprates.[4] Consistent with these findings, extended X-ray absorption fine structure (EXAFS) spectra of CuCN + 2BuLi showed no second shell Cu···N (CuC≡N) backscattering.[5] Moreover, the Cu−C bond length and apparent coordination number from the EXAFS of CuCN + 2BuLi were consistent with a two-coordinate complex, but inconsistent with a three coordinate complex. These data suggested that the dominant species in solutions of CuCN + 2BuLi was best formulated as $Bu_2CuLi{\cdot}LiCN$, where the precise nature of "LiCN" is not specified.

Recently, Lipschutz and James[6] have addressed these inconsistencies by suggesting that "higher-order" cuprate effects may be due to a π-complexed, rather than a σ-complexed cyanide ligand, **2** (Figure 1). While there are no crystallographically characterized examples of π-only coordinated cyanides, such a species would lack the second shell EXAFS from Cu···N (CuC≡N) scattering and thus might be consistent with published data. Lipschutz and James further suggest that EXAFS "has not been rigorously proven for tri- and tetracoordinate Cu(I) species" which, while not true in general,[7] *is* true for organocuprate reagents. In this communication, we provide a direct test of cyanide π-coordination to R_2CuLi.



1 2

Figure 1. Proposed structures for "higher-order" cyanocuprates. **1**: σ-Bound structure.[1,2] **2**: π-Bound structure.[6]

X-ray absorption near edge structure (XANES) spectra were measured for dimethyl cuprate prepared from CuI or from CuCN, and for the complex formed between Me_2CuLi and methyl *trans*-cinnamate.[8] The sensitivity of XANES spectra to both coordination number and geometry for 2-, 3-, and 4-coordinate Cu(I) complexes is well established.[7] Linear, two-coordinate Cu(I) complexes display a prominent 1s → 4p transition at 8983 eV. The intensity of this transition decreases markedly on addition of a third and fourth ligand.

The XANES spectrum of a THF solution of Me_2CuLi made from CuI displays an intense 1s → 4p transition at 8983 eV, characteristic[7] of a linear, two-coordinate complex (Figure 2). The XANES spectrum of a THF solution of Me_2CuLi made from CuCN + 2 MeLi is virtually indistinguishable from that of Me_2CuLi made from CuI. Both the preedge intensity and energy (8983 eV) are identical and are consistent with formulation of this complex as a linear, two-coordinate Cu(I) complex. These spectra are inconsistent with higher coordination numbers at Cu.[7] Similarly, the EXAFS (Table 1) show no detectable dependence on the presence of cyanide. The observation of identical EXAFS and XANES spectra, independent of the Cu(I) source, demonstrates that the presence of cyanide does not cause any significant change in the Cu structure.

In order to determine the sensitivity of XANES spectroscopy for detection of Cu(I) π-bonded ligands, an

---

* Author to whom correspondence should be addressed.

[1] For reviews of cyanocuprate chemistry, see: (a) Lishutz, B. H.; Sengupta, S. *Org. React.* **1992**, *41*, 135. (b) Lipshutz, B. H. *Synlett* **1990**, *3*, 119.

[2] Lipshutz, B. H.; Sharma, S.; Ellsworth, E. L. *J. Am. Chem. Soc.* **1990**, *112*, 4032.

[3] (a) Bertz, S. H. *J. Am. Chem. Soc.* **1991**, *113*, 5470. (b) Bertz, S. H. *J. Am. Chem. Soc.* **1990**, *112*, 4031. (c) Bertz, S. H.; Dabbagh, G. *J. Am. Chem. Soc.* **1988**, *110*, 3668.

[4] (a) Snyder, J. P.; Spangler, D. P.; Behling, J. R.; Rossiter, B. E. *J. Org. Chem.* **1994**, *59*, 2665. (b) Snyder, J. P; Tipsword, G. E.; Spangler, D. P. *J. Am. Chem. Soc.* **1992**, *114*, 1507. (c) Snyder, J. P.; Bertz, S. H., *J. Org. Chem.* **1995**, *60*, 4312.

[5] Stemmler, T.; Penner-Hahn, J. E.; Knochel, P. *J. Am. Chem. Soc.* **1993**, *59*, 348.

[6] Lipshutz, B. H. and James, B. *J. Org. Chem.* **1994**, *59*, 7585.

[7] (a) Kau, L.-S.; Spira-Solomon, D. J.; Penner-Hahn, J. E.; Hodgeson, K. O.; Solomon, E. I. *J. Am. Chem. Soc.* **1987**, *109*, 6433. (b) Kau, L.-S.; Hodgson, K. O.; Solomon, E. I. *J. Am. Chem. Soc.* **1989**, *111*, 7103.

[8] X-ray absorption spectra were measured in transmission mode at the Stanford Synchrotron Radiation Laboratory, beamlines 2-3 and 4-3, and at the National Synchrotron Light Source, beamline X-19A. Samples were held at 10 K (SSRL) or 77K (NSLS) throughout data acquisition. Data were analyzed using standard procedures[9] and fit using ab initio models calculated with FEFF 6.1.[10] The amplitude and phase parameters were calibrated by fitting data for compounds of known structure. Unfiltered k^3 weighted data were fit by allowing R_{Cu-C} and σ^2 factor to vary. The apparent coordination number was fixed and systematically increased in units of 0.2 to find the best fit. Monochromator energy was calibrated by reference to the first inflection point (8980.3 eV) of a copper foil internal standard. Solutions of Me_2CuLi were prepared using standard schlenk-line techniques. A solution of MeLi (0.71 mL, 1.0 mmol) was added dropwise to a slurry of either 99.999% purity CuI (0.095 g, 0.5 mmol, Aldrich) or CuCN (0.0448 g, 0.5 mmol, Aldrich) in dry, degassed THF at −78 °C. The solution was warmed to room temperature for 5 min yielding a clear, colorless solution of Me_2CuLi. This solution was then cooled to −78 °C and injected into a pre-cooled, septum-sealed, high-purity aluminum EXAFS cell via Teflon cannula. Samples of Me_2CuLi containing methyl *trans*-cinnamate ester were prepared by making solutions of Me_2CuLi as above. A 0.5 mmol (0.0811g) amount of methyl *trans*-cinnamate (Aldrich) was then added to the solutions under positive N_2 pressure. The cold solutions immediately turned bright yellow, indicating the formation of the π-complex. The solutions were transferred to precooled sample cells at −78 °C via Teflon cannula.

0022-3263/95/1960-4310$09.00/0

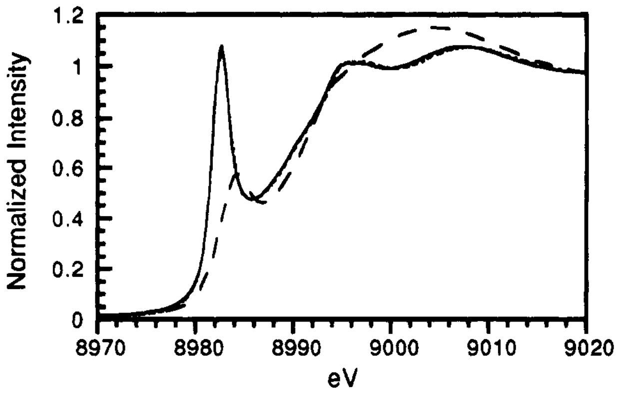


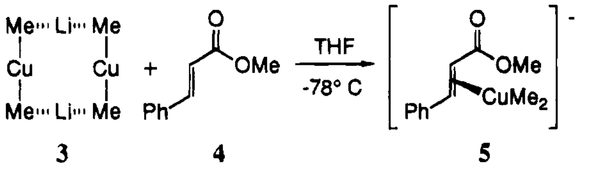
Figure 2. Normalized XANES spectra for organocopper solutions. (a) Solid line: CuI + 2MeLi. (b) Dotted line: CuCN + 2MeLi. (c) Dashed line: CuI + 2MeLi + methyl *trans*-cinnamate ester. Spectra are normalized to an edge jump of 1.0 per Cu.

Table 1. EXAFS Fitting Parameters

complex	R^a	$\sigma^{2,b}$	scatterers[c]
Me_2CuLi	1.95	4.2	2
Me_2CuLi + cyanide	1.95	3.6	2
Bu_2CuLi + cyanide	1.95	3.4	2
Me_2CuLi + enoate	1.99	3.4	4

[a] Cu−C nearest neighbor distance in Å. [b] Debye−Waller factor, in $Å^2 \times 10^3$. [c] Best integer number of scatterers.

Scheme 1



authentic cuprate-π-complex was studied. NMR studies[11] have indicated that addition of methyl *trans*-cinnamate to solutions of Me_2CuLi at low temperature causes formation of a stable intermediate arising from π-complexation of the enoate to the copper center (Scheme 1). The XANES spectrum of this solution is dramatically different (Figure 2) from that of either Me_2CuLi or $Me_2CuLi + CN^-$. The 1s → 4p transition is significantly reduced in intensity on formation of the π-complex. This observation indicates an increase in the copper coordination sphere[7] from two to three,[12] consistent with π-complexation of the enoate substrate to the Cu(I) center. EXAFS measurements (see Table 1) also show an increase in the average Cu−C bond length from 1.95 Å in Me_2CuLi to 1.99 Å in the π-complex, as predicted in ab initio calculations[4b,c] In addition, the apparent number of first shell scatterers increases from 2 to 4, as expected for a π complex. These results demonstrate that authentic π-complexes of Cu(I) are readily observed by XANES and EXAFS spectroscopy and are easily distinguishable from linear, two-coordinate Cu(I) complexes.

The XANES and EXAFS data both demonstrate that the addition of cyanide to a dialkyl cuprate does not cause a detectable change at the copper center. The strength of X-ray spectroscopy arises from its ability to probe the copper center *directly*. In contrast, NMR and IR spectroscopies cannot observe the copper center directly and thus rely on information about the ligand environment to infer the coordination site of the metal. In previous work, the NMR and IR spectral differences between cyanide "free" in solution and cyanide in solutions containing organocuprates have been used to support the existence of three coordinate "higher-order" cuprates.[2,6,13] However, these differences are of nearly the same magnitude as those caused by changes in solvent or counterion. The NMR and IR data demonstrate that the local environment of the cyanide is sensitive to the presence of Me_2Cu^- in solution, but they do not demonstrate direct coordination of the cyanide to Cu(I). In spite of several attempts to demonstrate the contrary, there remains *no direct NMR, IR, or x-ray spectroscopic evidence* for coordination of the cyanide ion to the copper center.

We stress that our data in no way preclude a role for the cyanide in organocuprate chemistry. For example, it is possible that cyanide alters the *long-range* characteristics of the organocuprate solution. There is evidence that Me_2CuLi exists as a dimer in solution (**3**, Scheme 1).[4b,14−16] Cyanide may disrupt this long-range structure. Alternatively, cyanide may act at some point further along the reaction path of 1,4-addition or substitution. Experiments are under way to study these and other possibilities.

Acknowledgment. SSRL and NSLS are supported by the U. S. Department of Energy. SSRL is supported by an NIH Research Resource grant and beamline X-19A was supported in part by the University of Michigan Office of the Vice President for Research. J.P.H. was supported in part by a grant from the A. P. Sloan Foundation and T.M.B. by a fellowship from the Herman and Margaret Sokol Foundation.

JO950491J

---

(9) See, for example: *X-ray Absorption: Principles, Applications, and Techniques of EXAFS, SEXAFS and XANES*; Prins, R., Koningsberger, D., Eds.; Wiley: New York, 1988.

(10) (a) Rehr, J. J.; Zabinsky, S. I.; Albers, R. C. *Phys. Rev. Lett.* **1992**, *69*, 3397. (b) Rehr, J. J.; Mustre de Leon, J.; Zabinsky, S. I.; Albers, R. C. *J. Am. Chem. Soc.* **1991**, *113*, 5135.

(11) Ullenius, C.; Christenson, B. *Pure Appl. Chem.* **1988**, *60*, 57, and references therein.

(12) In this nomenclature, the π-complexed structure, **5**, is described as three-coordinate, in analogy with common usage in the organometallic literature. The η^2-alkene ligand provides two carbon nearest neighbors, giving a total of four Cu nearest neighbors (see Table 1).

(13) (a) Lipshutz, B. H.; Wilhelm, R. S.; Kozlowski, J. A. *Tetrahdron* **1984**, *40*, 5005. (b) Lipshutz, B. H.; Kozlowski, J. A.; Wilhelm, R. S. *J. Org. Chem.* **1984**, *49*, 3943.

(14) For a review of organocuprate structures, see: Power, P. P. *Prog. Inorg. Chem.* **1991**, *39*, 75.

(15) (a) Ashby, E. C.; Watkins, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 5312. (b) Krauss, S. R.; Smith, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 141.

(16) (a) House, H. O. *Acc. Chem. Res.* **1976**, *9*, 59. (b) Pearson, R. G.; Gregory, G. D. *J. Am. Chem. Soc.* **1976**, *98*, 4098. (c) Lipshutz, B. H.; Kozlowski, J. A.; Breneman, C. M. *Tetrahedron Lett.* **1985**, *26*, 5911.