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New ^{1}H and ^{13}C NMR Spectral Data on "Higher Order" Cyanocuprates. If the Cyano Ligand Is Not on Copper, Then Where Is It?

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Summary: Using literature procedures for the *in situ* generation of LiCN in THF, it has been shown that this salt, in the presence of Me_2CuLi, combines to form a different species commonly referred to as a "higher order cyanocuprate". A new proposal to account for the location of the nitrile ligand is suggested.

Back in 1990, the claim was made that cuprates derived from the 2RLi + CuCN combination are not correctly represented as "$R_2Cu(CN)Li_2$" (*i.e.*, "higher order" (H.O.) cyanocuprates, **1**), but rather exist as modified Gilman-like species $R_2CuLi{\cdot}LiCN$ (**2**), with the nitrile ligand *unbound* to copper in an undefined location (Scheme 1).[1]

Our initial response to this seemingly cogent picture was to show how there are too many data points (both of the IR and NMR type) which do not fit the strictly ^{13}C NMR argument offered.[2] Furthermore, we subsequently documented how the presence of HMPA in THF solutions of "$R_2Cu(CN)Li_2$" used by others could dramatically influence the interpretation of the ^{13}C NMR observations made.[3] Of late, there has been renewed interest in this topic, with both EXAFS[4] and theoretical studies[5] supporting the notion that the nitrile ligand is not copper bound. Irrespective of the merits of these two approaches, we have set out to address by spectral means the possibility that "LiCN" could be present in *non*-HMPA-containing solutions of *either* "$R_2Cu(CN)Li_2$" *or* R_2CuLi. We now describe recently completed ^{1}H and ^{13}C NMR studies that shed new light on this current issue.

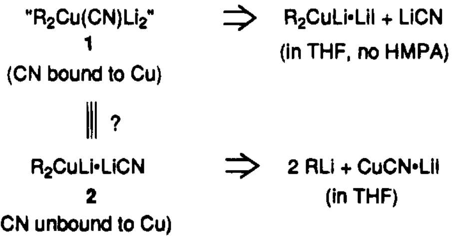
The experiments described below grew out of our study on the interactions which exist between Me_2CuLi and TMS−CN at low temperatures (<−60 °C) where consumption of reagents (to give, *e.g.*, Me_4Si) does not occur (eq 1).[6] At higher temperatures these components do

$$Me_2CuLi{\cdot}LiI + TMS{-}CN \xrightarrow[<-60\ ^\circ C]{THF} [Me_2CuLi \leftarrow NC{-}TMS] \xrightarrow{warm} Me_4Si + LiCN \quad (1)$$

$$MeLi + TMS{-}CN \xrightarrow[rt]{THF} Me_4Si + 1/n(LiCN)_n \quad (2)$$

react to give Me_4Si, along with copious quantities of solids presumed to be polymeric MeCu [$(MeCu)_n$] and LiCN [$(LiCN)_n$]. A more commonly used literature route to $(LiCN)_n$ calls for admixture of TMS−CN with MeLi in THF at low temperatures (eq 2).[7]

Scheme 1



Armed with this information on LiCN generation, $Me_2CuLi{\cdot}LiI$ was exposed to TMS−CN at −60 °C to which was added MeLi (1 equiv). The signals for TMS−CN (δ 0.29) and MeLi (δ −2.05) were completely lost while new peaks for Me_4Si (δ 0.00) and "$Me_2Cu(CN)Li_2$" appeared (Me: δ −1.52 in the ^{1}H NMR, δ −9.95 in the ^{13}C NMR; CN: δ 159 in the ^{13}C NMR; Scheme 2, experiment 1). The ^{13}C NMR spectrum of LiCN at +50 °C in THF,[8] generated initially at room temperature according to eq 2, showed a signal at δ 162.

Next, freshly made LiCN in THF[8] was quickly added to pre-formed $Me_2CuLi{\cdot}LiI$ at 0 °C in THF (experiment 2). This homogeneous sample was then cooled to −60 °C and its ^{1}H and ^{13}NMR spectra recorded. Results: identical spectra as observed in experiment 1.

Finally, both LiCN and $Me_2CuLi{\bullet}LiI$ were generated in the same flask by mixing CuI with TMS−CN in THF, to which was introduced MeLi (3 equiv) at −60 °C (experiment 3). This homogeneous mixture was then examined by ^{1}H and ^{13}C NMR at this temperature. Results: the same spectral data as seen above. *Not* coincidentally, "$Me_2Cu(CN)Li_2$", formed from CuCN + 2MeLi, displays the same chemical shift data (*cf.* Scheme 2).

Although the implication from these experiments is that the nitrile ligand must be incorporated somehow within the cuprate cluster,[9] there is no guarantee that either $L_nCu{-}CN$ or $L_nCu{-}NC$ covalent bonding exists between the metal and "ligand". What is clear is that "LiCN", as $(LiCN)_n$ or as the solvent separated salt,[1] is *not* present. So how then, is the CN "ligand" present in **1**? An intriguing possibility that would seem to accom-

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(1) Bertz, S. H. *J. Am. Chem. Soc.* **1990**, *112*, 4031; **1991**, *113*, 5470.

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

(3) Lipshutz, B. H. Recent Progress in Higher Order Cyanocuprate Chemistry. In *Advances in Metal−Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: London, in press.

(4) Stemmler, T.; Penner-Hahn, J. E.; Knochel, P. *J. Am. Chem. Soc.* **1993**, *115*, 348.

(5) Snyder, J. P.; Spangler, D. P.; Behling, J. R.; Rossiter, B. E. *J. Org. Chem.* **1994**, *59*, 2665.

(6) Lipshutz, B. H.; James, B. *Tetrahedron Lett.* **1993**, *34*, 6689.

(7) Mai, K.; Patil, G. *J. Org. Chem.* **1986**, *51*, 3545.

(8) The elevated temperature for this experiment was needed to maintain the solubility of LiCN in THF at a level such that the CN absorption in the ^{13}C NMR spectrum could be seen.

(9) A separate ^{13}C NMR experiment at room temperature where an extra equivalent of LiCN was generated in the presence of [$Me_2CuLi{\cdot}LiI$ + LiCN; *i.e.*, experiment (3) but using CuI + 2TMS-CN + 4MeLi] led to a significantly broadened signal for the CN centered at 158 ppm. Likewise, the ^{13}C NMR spectrum for $Me_2Cu(CN)Li_2$ (from CuCN + 2MeLi) in the presence of n-Bu_4NCN in THF at −60 °C displays a broadened CN signal (158 ppm). These data suggest that the nitrile ligand is undergoing an exchange phenomenon within the cuprate cluster. Further lowering of the sample temperature in each case unfortunately resulted in salt precipitation.

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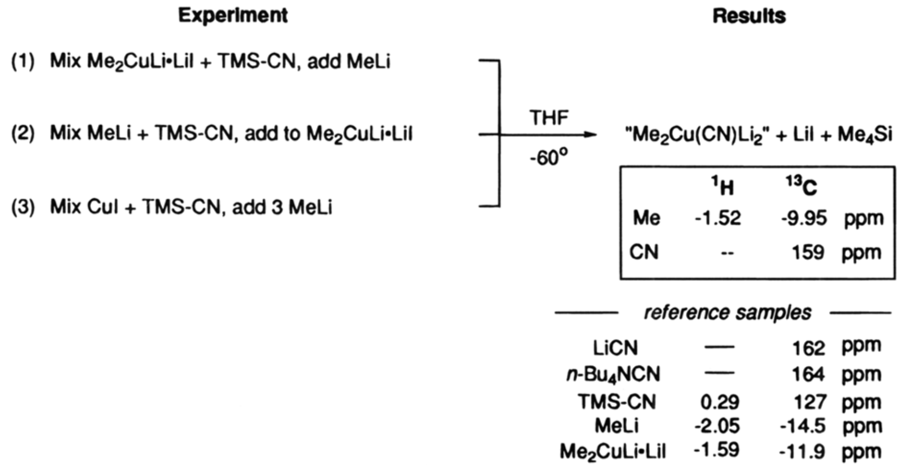
Scheme 2



(1) Mix $Me_2CuLi{\cdot}LiI$ + TMS-CN, add MeLi

(2) Mix MeLi + TMS-CN, add to $Me_2CuLi{\cdot}LiI$

(3) Mix CuI + TMS-CN, add 3 MeLi

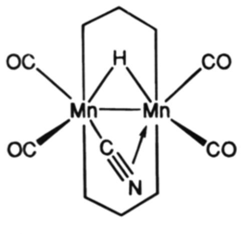
"$Me_2Cu(CN)Li_2$" + LiI + Me_4Si

	^1H	^{13}C	
Me	-1.52	-9.95	ppm
CN	--	159	ppm

reference samples

LiCN	—	162	ppm
n-Bu_4NCN	—	164	ppm
TMS-CN	0.29	127	ppm
MeLi	-2.05	-14.5	ppm
$Me_2CuLi{\cdot}LiI$	-1.59	-11.9	ppm

modate both schools of thought (*i.e.*, no formal σ Cu−CN bond, yet no uncomplexed LiCN), is that the nitrile ligand is *both* σ-bound to Li^+ and π-bound to copper (Figure 1). The former mode of bonding for nitriles is usually stronger[10] than the latter which, together with the dianionic nature of the cluster, would explain the shift to higher frequency in the IR for ν_{CN} (*e.g.*, $Me_2Cu(CN)Li_2$ in THF, 2128 cm^{-1}) relative to free cyanide (*e.g.*, LiCN, 2095 cm^{-1} (KBr); Bu_4NCN, 2070 cm^{-1} (KBr); 2080 cm^{-1} in THF).[11] The η^2 dπ^*-copper-bound (−C≡N−) is akin to that proposed for the initial step in 1,4-additions of cuprates to enones.[12] Moreover, bridging cyanide groups in the σ,π-domain (*cf.* Figure 1) are well-precedented in manganese,[13a] rhodium,[13b] and molybdenum[13c] chemistry (**3**−**5**, respectively).[14] Such an orientation might explain the seemingly contrasting phenomena of H.O. cuprate stability and yet oftentimes greater reactivity (due to the increase in negative charge in the cyanocuprate) relative to monoanionic R_2CuLi.[15] Furthermore, positioning the nitrile ligand in this fashion does little to upset the overall gross features of the reagent which remain "Gilman-like".[16]



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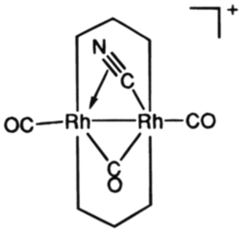

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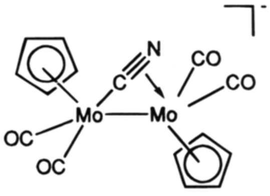

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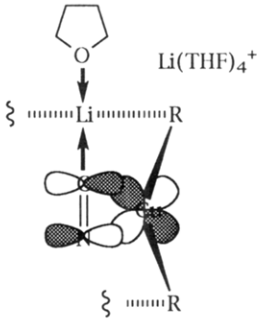

Figure 1.

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(10) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1986; pp 272−282. Fehlhammer, W. P.; Fritz, M. *Chem. Rev.* **1993**, *93*, 1243.

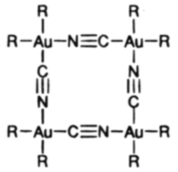
(11) The υ_{CN} for a THF solution of LiCN + LiI appears at 2110 cm^{-1}. This band is absent from the IR of H.O. cyanocuprates prepared from CuCN or CuCN·LiI, again in line with the claim that neither free LiCN nor free "Li_2CN^{+}"[1] is present as part of the H.O. cuprate formulation.

(12) Smith, R. A. J.; Vellekoop, A. S. In *Advances in Detailed Reaction Mechanisms*; Coxon, J., Ed.; JAI Press: London, 1994; Vol. 3, pp 79−130.

(13) (a) Aspinall, H. C.; Deeming, A. J.; Donovan-Mtunzi, S. *J. Chem. Soc., Dalton Trans.* **1983**, 2669. (b) Deraniyagala, S. P.; Grundy, K. R. *Inorg. Chim. Acta* **1984**, *84*, 205. (c) Curtis, M. D.; Klinger, R. J. *J. Organomet. Chem.* **1978**, *161*, 23. Curtis, M. D.; Han, K. R.; Butler, W. M. *Inorg. Chem.* **1980**, *19*, 2096.

(14) It should be noted, however, that compounds **3**−**5** involve a nitrile ligand acting as a π-*base* rather than as a π-acid (in a dπ^* sense) as shown in Figure 1.

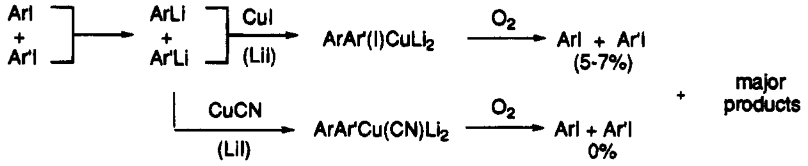
(15) (a) Lipshutz, B. H.; Sengupta, S. *Org. React.* (*N.Y.*) **1992**, *41*, 135. Lipshutz, B. H. *Synlett* **1990**, *3*, 119. (b) On the other hand, it is difficult to escape the likelihood of an extremely prevalent linear bridging nitrile ligand, where for example, the analogous Au(III) complex **i** is known[15c] and might well resemble the corresponding Cu(I) dianion. Although such a complex would not be in line with either EXAFS[4] data or theory,[5] we note that the former technique has not been rigorously proven for tri- and tetracoordinate Cu(I) species, while the latter arguments invoke monomeric complexes which are not supported by well-established NMR observations of either RR'CuLi or RR'Cu(CN)Li_2.[15d] (c) Stocco, F.; Stocco, G. C.; Scovell, W. M.; Tobias, R. S. *Inorg. Chem.* **1971**, *10*, 2639. (d) Lipshutz, B. H.; Kozlowski, J. A.; Wilhelm, R. S. *J. Org. Chem.* **1984**, *49*, 3943. Lipshutz, B. H.; Kozlowski, J. A.; Breneman, C. M. *Tetrahedron Lett.* **1985**, *26*, 5911.



i, R = CH_3 or n-C_3H_7

(16) This view would also account for results obtained from oxidations of mixed diaryl Gilman (ArAr'CuLi·LiI) *vs* cyanocuprates (ArAr'Cu(CN)Li_2), where halide ion (I^-) was shown to be present on Cu (at least to some extent). This conclusion was necessary so as to rationalize regeneration of ArI and Ar'I in lower order reagents, while the H.O. species in the presence or absence of I^- led to *none* of the starting iodides (or ArCN/Ar'CN, Scheme 3); *cf.* Lipshutz, B. H.; Kayser, F.; Siegmann, K. *Tetrahedron Lett.* **1993**, *34*, 6693.

Scheme 3



In summary, NMR experiments have shown that various combinations of non-cyano-ligand-containing cuprates accept *in situ* generated LiCN into the cluster to afford the identical species arrived at *via* 2RLi addition to originally nitrile-bound CuCN. A new proposal which accounts for both prior literature data and the results herein is offered where the nitrile ligand is datively coordinated to lithium and π-bound to copper.

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