

Communications to the Editor

"Higher-Order" Cyanocuprates: Are They Real?¹

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Gilman reported in 1952 that lithium dimethylcuprate(I) can be prepared from 2 equiv of MeLi and 1 equiv of CuI.² Following his lead, House et al.,^{3a} Whitesides et al.,^{3b} and Corey and Posner^{3c} also used cuprates prepared from CuI in their pioneering work on the synthetic applications of organocuprates. Beginning in 1981, Lipshutz et al. published a series of papers entitled "Chemistry of Higher Order, Mixed Organocuprates" about the cuprates prepared from 2 equiv of lithium reagent (RLi) and 1 equiv of CuCN, symbolized as R₂Cu(CN)Li₂.⁴ On the basis of improved yields and (where relevant) different stereochemical outcomes,⁴⁻⁶ it was claimed that "these species are differentiated from 'lower order' or Gilman-like cuprates, R₂CuLi, in that the Cu-cluster contains an additional ligand (originally negatively charged). Hence, they are formally Cu(I) dianionic salts".^{4b}

It can now be reported that the reagents prepared from 2 equiv of RLi (R = alkyl or aryl) and 1 equiv of CuCN may not be truly higher order *ate* complexes of Cu. ¹³C NMR spectral evidence suggests that they are, in fact, Gilman-like cuprates, in tetrahydrofuran (THF) where the reagents prepared from CuCN are usually used. Except for a CN resonance that is independent of R, their ¹³C NMR spectra are virtually identical with those of the corresponding reagents prepared from CuI, both before and after the addition of hexamethylphosphoramide (HMPA) and 12-crown-4 (12-C-4).

Ph₂CuLi was chosen as a typical aryl cuprate, and Et₂CuLi and Me₂CuLi were chosen for study as typical alkyl cuprates. The corresponding lithium reagents used in this study were obtained as crystalline solids that are accurately weighable in a drybox.⁷ The ¹³C NMR chemical shifts at -78 °C of these cuprates, prepared from CuI and CuCN in THF (0.1 M), are summarized in Table I. Within ±0.1 ppm for each measurement, all four lines in the ¹³C NMR spectrum of Ph₂CuLi prepared from CuI, which we symbolize as Ph₂CuLi·LiI, have the same chemical shifts in THF as the corresponding lines in the spectrum of Ph₂CuLi prepared from CuCN, which we denote as Ph₂CuLi·LiCN. Likewise, Et₂CuLi·LiI and Et₂CuLi·LiCN have virtually identical ¹³C NMR spectra, and the same is true of Me₂CuLi·LiI and Me₂CuLi·LiCN. We have proposed the dot formalism to indicate some sort of interaction between the components which may or may not be understood in detail.⁶

Table I. ¹³C Nuclear Magnetic Resonance Chemical Shifts of Organocuprates^a

reagent	C1	C2	C3	C4	CN
Ph ₂ CuLi·LiCN	174.33	141.44	125.38	121.95	158.72
(+HMPA + 12-C-4) ^b	(174.75)	(141.61)	(125.35)	(121.83)	(166.32)
Ph ₂ CuLi·LiI	174.13	141.38	125.44	122.07	
(+HMPA + 12-C-4)	(174.74)	(141.60)	(125.36)	(121.84)	
Et ₂ CuLi·LiCN	4.64	17.24			158.81
(+HMPA + 12-C-4)	(5.00)	(17.48)			(166.06)
Et ₂ CuLi·LiI	4.63	17.14			
(+HMPA + 12-C-4)	(5.01)	(17.48)			
Me ₂ CuLi·LiCN	-9.51				158.88
(+HMPA + 12-C-4)	(-8.72)				(166.10)
Me ₂ CuLi·LiI	-9.62				
(+HMPA + 12-C-4)	(-8.66)				

^a Measured at -78 °C in THF-*d*₆ (0.1 M). ^b HMPA (312 μL) and 200 μL of 12-C-4 were added to 3.0 mL of THF-*d*₆. The 12-C-4 salts are insoluble in THF without the HMPA.

Iodide and cyanide are very different in their electronic properties as ligands for metal ions; e.g., they are at opposite ends of the spectrochemical series⁸ and have significantly different nephelauxetic^{8a} and trans effects.^{8b} These phenomena have been correlated with changes in the NMR spectra of transition-metal complexes;⁹ in fact, NMR has been reported to be more sensitive than optical spectroscopy for locating ligands in the spectrochemical series.^{9a} The sizable influence of the CN ligands in organomercuric cyanides on the chemical shifts was attributed to back-bonding.¹⁰ Even if back-bonding were not involved in a cyanocuprate, an inductive effect would be expected to operate via the σ-bonds.

Consequently, if CN were coordinated to Cu in an organocuprate, a significant difference in chemical shifts would be expected between such a cyanocuprate and the corresponding cuprates with or without a coordinating I. As detailed above, we do not see significant differences between the ¹³C NMR chemical shifts for R in R₂CuLi·LiI and the corresponding R₂CuLi·LiCN (R = Me, Et, Ph). Furthermore, it is significant that the CN resonances for Ph₂CuLi·LiCN (158.7 ppm), Et₂CuLi·LiCN (158.8 ppm), and Me₂CuLi·LiCN (158.9 ppm) are essentially identical. In light of the different σ-donor properties of Ph and Me or Et, this is additional evidence that CN is not bonded to Cu. The role of CN in these reagents is illuminated by the observation that the ¹³C NMR chemical shift of ⁶Li¹³CN in THF-*d*₆ (0.1 M) at -78 °C is shifted upfield from 160.3 to 158.9 ppm by the addition of 1 equiv of LiClO₄, which suggests that R₂CuLi·LiCN may be R₂Cu⁻Li⁺CN⁻. In the presence of HMPA and 12-C-4 (see Table I, footnote b), the ¹³C NMR peak is at 164.9 ppm.

In the methyl case ¹H NMR chemical shifts^{4d} show somewhat larger differences between corresponding iodocuprates and cyanocuprates, since the H atoms are farther from the Cu atom and its associated electronic effects and closer to other species in solution. In contrast, our ethyl and phenyl cuprates have virtually superimposable ¹H NMR spectra. For example, the chemical shifts for Et₂CuLi·LiI are -0.531 (*J* = 8.0 Hz) and 1.08 ppm (*J* = 8.0 Hz) and those for Et₂CuLi·LiCN are -0.538 (*J* = 8.0 Hz) and 1.08 ppm (*J* = 8.0 Hz).

The ⁶Li NMR peaks for Ph₂CuLi·LiI and Ph₂CuLi·LiCN measured under the same conditions as the ¹³C NMR spectra are at -0.08 and -1.07 ppm (1 M ⁶LiCl/MeOH internal capillary reference at 0 ppm), respectively. The ⁶Li NMR peaks for Et₂CuLi·LiI and Et₂CuLi·LiCN are at 0.06 and -1.01 ppm, and

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the peaks for $\text{Me}_2\text{CuLi}\cdot\text{LiI}$ and $\text{Me}_2\text{CuLi}\cdot\text{LiCN}$ are at 0.03 and -1.03 ppm, respectively. These results are consistent with either our formulation or Lipshutz's, both of which feature a different counterion for Li in the case of the corresponding cuprates prepared from CuI and CuCN. The ^6Li NMR peak for $^6\text{Li}^{13}\text{CN}$ under the same conditions is at -1.38 ppm, and in the presence of equimolar LiClO_4 it is at -0.87 ppm. It is interesting to note that the shifts for $\text{R}_2\text{CuLi}\cdot\text{LiCN}$ are in this range.

The cuprates prepared from CuCN and 1 equiv of RLi have different CN chemical shifts for R = Ph (148.51 ppm) and R = Et (149.11 ppm) or Me (149.33 ppm). Upon addition of Li-complexing agents HMPA and 12-C-4, these chemical shifts move *upfield* to 145.44 and 146.47 or 146.55 ppm, respectively. Increased back-bonding is expected to result in an upfield shift of the CN resonance.¹¹ These observations are evidence that CN is indeed bonded to Cu in these 1:1 reagents.

In the presence of HMPA and 12-C-4, the corresponding cuprates $\text{R}_2\text{CuLi}\cdot\text{LiI}$ and $\text{R}_2\text{CuLi}\cdot\text{LiCN}$ (R = Ph, Et, Me) have the same spectra (Table I) for the organic groups, to within ± 0.01 ppm (digital resolution) for Et and Ph and ± 0.05 ppm for Me. Furthermore, the chemical shifts for R in the presence of HMPA and 12-C-4 are only modestly downfield from the values measured without them. For comparison LiCN in THF in the presence of HMPA and 12-C-4 has a chemical shift of 165.2 ppm at -78 °C.

Power and co-workers have reported that mononuclear cuprates can be prepared as $\text{Li}(12\text{-C-4})_2^+$ salts and characterized by X-ray crystallography.¹² The similarity of our results with and without Li-complexing agents strongly suggests that these cuprates are essentially $[\text{RCuR}]^-$ anions or their aggregates (vide infra) in THF solution. The additives may serve to convert aggregates or contact ion pairs to solvent-separated ion pairs,^{13,14} or to convert one solvent-separated ion pair into another.

The ^{13}C NMR chemical shifts reported by Hallnemo and Ullenius¹⁵ for $\text{Ph}_2\text{CuLi}\cdot\text{LiI}$ in pyridine- d_5 are close to our values in THF- d_8 (Table I). It is also interesting to note that their values for this reagent in dichloromethane- d_2 are very close to our values measured in dimethyl sulfide (DMS),¹⁶ which are significantly different from those in THF- d_8 or pyridine- d_5 . We believe that different species are present in strongly coordinating (THF, pyridine) and weakly coordinating (DMS, dichloromethane) solvents. Power and Olmstead have characterized the crystals grown from DMS solutions of halide-free Ph_2CuLi as dimeric $(\text{Ph}_2\text{CuLi})_2\cdot 3\text{DMS}$.¹⁷ Thus, the ^{13}C NMR chemical shift appears to be useful for elucidating the gross structures of organocuprates, e.g., whether phenyl cuprates are monomeric ($\delta_{\text{ipso}} \approx 175$ ppm for 12-C-4 salt) or dimeric ($\delta_{\text{ipso}} \approx 162$ ppm in DMS). When HMPA and 12-crown-4 are added to $(\text{Ph}_2\text{CuLi})_2$ in DMS, the ^{13}C NMR spectrum changes to that of $\text{Ph}_2\text{Cu}^-\text{Li}(12\text{-C-4})_2^+$.¹⁸

$\text{Ph}_6\text{Cu}_3\text{Li}_2^-$ units in crystals grown from THF solutions of $\text{Ph}_2\text{CuLi}\cdot\text{LiI}$ or $\text{Ph}_2\text{CuLi}\cdot\text{LiCN}$ comprise three nearly linear $[\text{PhCuPh}]^-$ subunits held together by two Li^+ ions.^{17,19} Whether such aggregates are present at equilibrium in our NMR solutions is an open question which does not bear directly upon the question of higher order cuprates. We believe it is significant that neither I nor CN is present in this cluster. If a species with a Cu-CN bond were the "thermodynamic sink", then it should be present in the solid state as well as solution.

The only higher order cuprate that has been confirmed crys-

tallographically is our $\text{Ph}_3\text{CuLi}_2\cdot\text{Ph}_2\text{CuLi}\cdot 4\text{DMS}$ complex,¹⁶ the detailed structure of which was elucidated by Olmstead and Power.²⁰ The $\text{Ph}_3\text{Cu}^{2-}$ subunit appears to be held together by three bridging Li cations; therefore, our higher order cuprate is best viewed as $\text{Ph}_3\text{CuLi}_3^+\text{Ph}_2\text{Cu}^-$. Our NMR study also established that Ph_3CuLi_2 does not exist in ether or THF,¹⁶ presumably because ethereal solvents remove the bridging Li cations and thus destabilize the higher order structure.

In light of the results reported herein, two possibilities are (1) the CN is bonded to Cu in "higher order" cyanocuprates but does not affect the ^{13}C NMR spectra or (2) the CN is not bonded to Cu. We believe the term "higher order" should not be applied to cuprates prepared from CuCN until more positive evidence for such structures is presented.

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"Higher Order" Cyanocuprates $\text{R}_2\text{Cu}(\text{CN})\text{Li}_2$: Discrete Reagents or "Lower Order" LiCN-Modified Gilman Cuprates?

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In late 1981, an initial disclosure was made that addition of 2 equiv of an organolithium to CuCN leads to "higher order, mixed cyanocuprates".¹ These were written as " $\text{R}_2\text{Cu}(\text{CN})\text{Li}_2$ " (1), implying a Cu(I) dianionic species containing three covalently bound ligands on copper, one of which is the cyano group.² Notwithstanding the now extensive use of higher order (HO) cuprates,³ reagents that oftentimes afford considerably different chemical outcomes (e.g., in reactivity,^{4a} yields,^{4b} stability,^{4c} etc.) when compared to other commonly used lower order (LO) analogues [e.g., R_2CuLi , $\text{RCu}(\text{CN})\text{Li}$], the very existence of complexes 1 has recently been challenged.⁵ It has been proposed that cuprates prepared from 2RLi and CuCN are simply Gilman-like species containing LiCN, rather than LiX (X = Br, I), somewhere within the cluster and hence should be more accurately represented as $\text{R}_2\text{CuLi}\cdot\text{LiCN}$. We now describe, using spectroscopic studies, *prima facie* evidence in support of HO cyanocuprates.

Generation of $\text{Me}_2\text{Cu}(\text{CN})\text{Li}_2$ (2) was accomplished in both THF³ and $\text{Me}_2\text{S}/\text{Et}_2\text{O}$ ⁶ from the usual admixture of 2MeLi (in Et_2O) with CuCN. The low-temperature (-80 °C) ^{13}C NMR

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