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Analyses of *Anionic* Cu(I) Complexes *via* Electrospray Mass Spectrometry

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The preparation of organocopper reagents has traditionally relied on the combination of a copper(I) salt and 2 equiv of an organolithium reagent, thereby affording Gilman (or lower order) cuprates R_2CuLi.[2] Solubilization of cuprate precursors, such as CuBr, CuI, and, in particular, CuCN, in ethereal media is usually effected with lithium salts (*e.g.*, nLiCl, $n = 1, 2$) which obviates potentially damaging increases in reagent temperature usually required to generate homogeneous solutions of organocuprates. Such mixtures of salts are oftentimes designated "CuX·nLiX" (*e.g.*, CuCN·2LiCl),[3] a shorthand accounting of stoichiometry which imparts little information about composition or structure (*vide infra*). Similar descriptors have been used for cuprates (*e.g.*, "RCu(CN)Li·LiX")[4] and have recently served as a focal point of controversy surrounding the existence[5] of "higher order" (HO) cyanocuprates.[6] We now describe our preliminary results on the use of electrospray ionization mass spectrometry (ESIMS)[7] to characterize commonly used cuprate precursor Cu(I) salts infused as THF solutions. To the best of our knowledge, this study represents the first of its kind on *negative* ion copper(I) complexes.

While applications of ESIMS have grown steadily of late,[8] the vast majority involve solutions containing cationic species. Observations by negative ion ESIMS are far less frequent, and studies on anionic organometallics are very few in number[9] owing to recognized complications associated with electric (corona) discharge at the tip of the instrument's probe.[10] However, we have found that by employing the nonprotic medium THF and low source voltages (among other parameters),[11] a constant signal is realized during standard direct infusion of the sample *via* syringe pump.

Table 1

salt	species [M/Z][b,c]
CuI + 2LiCl	$\mathrm{CuCl_2}$ [133], Cu(I)Cl [225], $\mathrm{CuI_2}$ [317], $\mathrm{I_3}$ [381]
CuI + 2LiBr	$\mathrm{CuBr_2}$ [221], Cu(I)Br [269], $\mathrm{CuI_2}$ [317], $\mathrm{I_3}$ [381]
CuI + 2LiI	$\mathrm{CuI_2}$ [317], $\mathrm{I_3}$ [381]
CuCN + 2LiCl	Cu(CN)Cl [124], **$\mathrm{LiCu(CN)Cl_2}$ [166]**, $\mathrm{Cu_2(CN)_2Cl}$ [213], $\mathrm{Cu_2CN(Cl_2}$ [222], $\mathrm{LiCu_2(CN)_2Cl_2}$ [255], $\mathrm{Cu_3(CN)_2Cl_2}$ [311], $\mathrm{LiCu_3(CN)_3Cl_2}$ [344], $\mathrm{Cu_4(CN)_3Cl_2}$ [400]
CuCN + 2LiBr	Cu(CN)Br [168], $\mathrm{CuBr_2}$ [221], **$\mathrm{LiCu(CN)Br_2}$ [254]**, $\mathrm{Cu_2(CN)_2Br}$ [257], $\mathrm{Cu_2(CN)Br_2}$ [310], $\mathrm{LiCu_2(CN)_2Br_2}$ [343], $\mathrm{Cu_3(CN)_2Br_2}$ [399]
CuCN + 2LiI	I [127], Cu(CN)I [216], $\mathrm{CuI_2}$ [317], **$\mathrm{LiCu(CN)I_2}$ [350]**, $\mathrm{I_3}$ [381]

[a] M/Z ratio given for the most abundant isotopic values, not by peak intensities. [b] Monoanionic species. [c] No structural information is implied by these data, beyond those which are in bold (see text).

Data were initially obtained[12] at room temperature on homogeneous solutions prepared by combining copper iodide and lithium halide salts[13] [CuI + 2LiX], where X = I, Br, Cl. Notwithstanding initial concentrations of 10^{-4} M in THF, several monoanionic clusters were observed, each containing from one to five copper atoms[14] (Table 1 and Figure 1). Dissimilar halides of copper and lithium (*e.g.*, CuBr + 2LiCl) afforded both homo- and mixed halocuprate anions. Assignments of the various species are unequivocal, as they rest on direct comparison of isotopic fingerprints with computer-generated theoretical plots that were a perfect match in each case.

Still more intriguing are results garnered from related studies using CuCN, together with either LiCl, LiBr, or LiI (two equiv, in THF). Each of the three permutations, including the well-known combination CuCN·2LiCl[3] (*i.e.*, the precursor to functionalized zinc−copper reagents FG···$CH_2Cu(CN)ZnX$, FG = ester, nitrile, etc.),[15] gives rise to the same types of homo- and, now, mixed halocyanocuprate anions. Thus, this routinely used mix of individually THF-insoluble salts may well exist as several discrete species prior to transmetalation (Table 1 and Figure 2). Most noteworthy, however, is the presence of $[\mathrm{CuCN{\cdot}LiX_2}]^-$, found for all cases of CuCN + 2LiX, X = Cl, Br, I, where Li^+ is part of the anionic complex (Table 1). The relatively low intensities observed for these aggregates do not allow a precise role to be assigned to them as yet. Nonetheless, the species can be conceived to arise by either adding X^- or removing Li^+ from neutral parents XCu(CN)Li or Cu(CN)·2LiX, respectively. The identical monoanions can likewise be observed by ESIMS starting from a copper halide to which has been added LiCN and LiX (1 equiv of each). Significantly, no such equivalent unit $[\mathrm{CuX{\cdot}Li\ X_2}]^-$ is detected from admixture of a copper halide + 2LiX ($X \neq CN$; *cf.* Table 1), attesting to the unique role of cyanide for drawing Li^+ into these anionic aggregates[5b,c,16]

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[12] Standard conditions: VG Platform II ESI mass spectrometer; direct infusion *via* Harvard Apparatus syringe pump at 30 μL/min. Voltages: capillary (4.8 KV), HV lens (0.5 KV), cone (20 V), multiplier (650). Gases: drying (N_2), nebulizing (N_2). Temperature: 30 °C.

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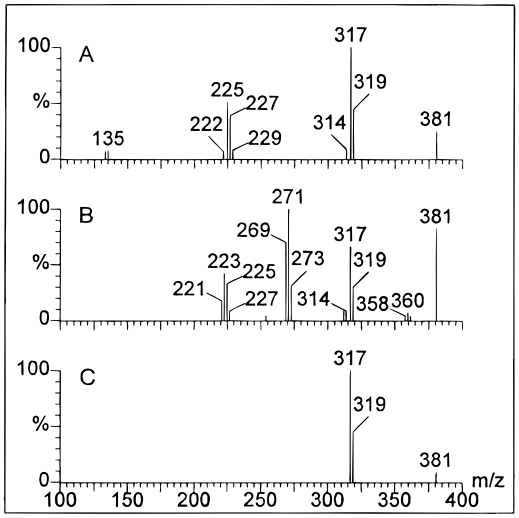

Figure 1. CuI + 2LiX; A, X = Cl; B, X = Br; C, X = I.

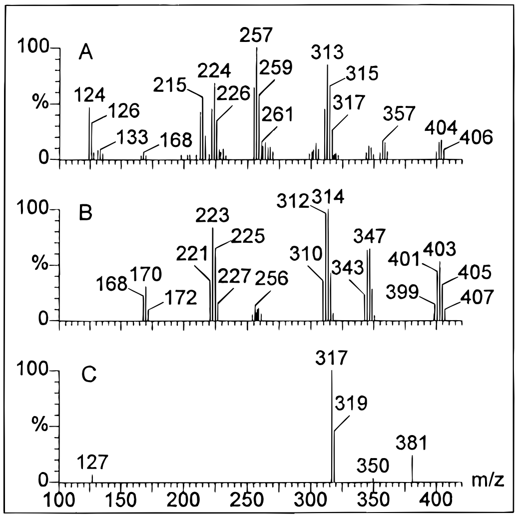

Figure 2. CuCN + 2LiX; A, X = Cl; B, X = Br; C, X = I.

Positive ion ESIMS was also carried out on all samples. While most of the ions observed are aggregates of solvated lithium, $[Li-n\mathrm{THF}]^+$, solutions originating from copper halides also contained $[Li_2X]^+$ (both with and without *n*THF). With X = CN, however, *no such corresponding cation is observed*. Attempts to maximize formation of this hypothetical ion by admixture of 10 additional equivalents of LiI to CuCN·2LiCl failed to give rise to a detectable species of this makeup.

The absence of Li_2CN^+ and the abundance of cyanide-containing anionic copper clusters in the gas phase can be understood as a consequence of the ion distribution between both the positive and negative ion ensembles. With respect to only the lowest ionic aggregates, admixture of CuCN and LiX most likely yields the following equilibria:

$$[X-Cu-CN-Li-X]^- + [Li-X-Li]^+ \rightleftharpoons [X-Cu-X-Li-X]^- + [Li-CN-Li]^+$$

All-electron B3LYP/6-31+G* calculations were performed for X = Cl, while B3LYP/LANL2DZ effective core potential calculations were carried out on all three halides (X = Cl, Br, I).[17] A variety of topologies and geometries were examined, including HO ligation at copper. The lowest energy forms for both charge types correspond to linear structures characterized by alternating halide ions and metal cations. Cyanide-containing anions were found to be most stable with CN internal in a linear arrangement, *e.g.*, $[X-Cu-CN-Li-X]^-$. In agreement with experiment, the results predict the equilibria to lie uniformly to the left: X = Cl, −13.9 kcal/mol (B3YLP/6-31+G*) and −15.7 kcal/mol (B3YLP/LANL2DZ); X = Br, −11.4 kcal/mol; X = I, −8.4 kcal/mol. An additional set of B3LYP/6-31+G* calculations illustrates an important element determining the equilibrium position. The simple isodesmic $M-CN + Cl^- \rightleftharpoons M-Cl + CN^-$ expresses a metal cation's preference for cyanide vs chloride. For M = Li and Cu, both cations favor CN^- by 2.7 and 12.3 kcal/mol, respectively. The relatively strong Cu−CN interaction would appear to be the dominant driving force localizing Cu, Li, and CN in the same anions.

There are several implications associated with these ESIMS data. They substantiate the view that otherwise insoluble Cu(I) salts become homogeneous in THF in the presence of LiX by forming aggregates. While this has been surmised for years on the basis of entities such as Li_2CuCl_3[18] and Kochi's Cu(II) catalyst Li_2CuCl_4,[19] not previously acknowledged is the possibility for a multitude of complexes at varying concentrations present in these solutions, as is the case for LiX[20a] and LiR.[20b] In a related and very recent example, the extensive multishell fitting required to resolve EXAFS-derived Fourier transform peaks for "CuCN·2LiCl" in THF[21] may be reflective of the unexpected complexity implied by ESIMS. Further studies are needed to determine whether the chemistry of organocopper reagents in an ethereal solvent is characterized by a complex mixture or solvation-selected structures. Curiously, while the HO halocuprate formal constitution might have been reflected by this soft technique, only the monolithiated formulation, $[CuCN{\cdot}LiX_2]^-$, rather than the independent dianionic complex has been observed. The present calculations on these gas phase monoanionic complexes, suggesting a linear array of alternating cations and anions, are in line with recent work that argues against the viability of a high-energy (tricoordinate) copper dianion, $[X_2Cu(CN)^{2-}]$.[5c,21,22] Further studies on organometallics using ESIMS, including all-carbon ligand-containing copper reagents,[23] will be reported in due course.

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