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Communications

The Structure of "R₂Cu(CN)Li₂" Lithium Cuprates: Lower-Order Aggregates of Gilman Reagents and Organolithium Compounds

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Summary: A molecular orbital study of lithium cuprates represented by the constitutional formula (CH₃)₂Cu(CN)-Li₂ strongly suggests that the compounds are best described as lower-order Gilman cuprates complexed by ring formation with 1 mol of either CH₃Li or CNLi rather than as tricoordinate Cu(I) "higher-order" cyanocuprates.

The term "higher order" cuprate first appeared in a 1981 report describing the ability of "R₂Cu(CN)Li₂" to effect substitution reactions on secondary halides.¹ The replacement of a single carbon ligand in the previously described R₃CuLi₂ cuprates²⁻⁵ with a "dummy" cyano ligand thereby spawned an impressive literature of novel and practical synthetic reagents.⁶⁻⁸ While no unambiguous structure determinations have been carried out, the higher order species have been designated as Cu(I) dianions ("R₂Cu(CN)²⁻2Li⁺").⁶⁻⁹ It has been unequivocally asserted

that the cyano group is bonded to copper¹⁰ by means of a Cu-C(N) bond.¹⁰ The "higher order" claim has been strongly challenged¹¹ and subsequently defended.¹² In the present work we describe a computational analysis of the Me₂Cu(CN)Li₂ constitution complemented by two explicit solvent molecules and a THF solvent cavity model. Dianionic trivalent copper does not reside among the lower energy forms; however, the Cu-CN bond is a key element in some of them.

The computational approach employed involves a double ζ quality basis set for the non-metal atoms and a Hay-Wadt effective core potential for the 10 copper inner shell electrons (up to 2p; LANL2DZ, see Table 1).^{13,14} Less elaborate basis sets have been effectively applied to the stereoselective nucleophilic addition of organocopper reagents to acroleins and cyclopropenes.^{15,16} The rather long Cu-C(H₃) bond lengths optimized in the latter work (2.161 and 2.040 Å) can be compared with 2.010 Å obtained here. Inclusion of MP2 correlation shrinks the bond to

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properties of THF. The latter, when applied to the Li-solvated species, models both primary (i.e., LiOR_2) and bulk solvation effects. Results are summarized in Table 1.

The $\text{Me}_2\text{Cu}(\text{CN})\text{Li}_2$ structures fall into two energetically distinct classes with respect to bonding at copper, lower (0–14 kcal/mol, 1–5) and higher order (14–26 kcal/mol, 6–8). Consistent with reactions 1 and 2, the lithium centers prefer association with the CN nitrogen. Although the corresponding NCLi isomers are not depicted, they range from 5 to 10 kcal/mol higher in energy. Polycycles 7 and 8 could be optimized on the LANL2DZ energy surface only by fixing the Cu–N separations at bonding distances of 2.54 and 2.10 Å, respectively. Relaxation of this constraint resulted in a smooth and downhill ring expansion in both cases to monocycle 1, the lowest energy form within the various theoretical regimes (Table 1).

The constitutions of the two lowest energy structures 1 and 2 deserve comment. The former is the cyclic cyano counterpart of the global minimum located for the homocuprate Me_3CuLi_2 .²⁶ The 2,4-dilithio four-membered ring with Li–N bonds (2) is in striking accord with matrix-isolation IR²⁷ and theoretical^{28–30} studies on lithium isocyanide dimers (9). Similarly, the most stable solvated dimer of LiCH_2CN was predicted to be a four-membered N-lithiated ketenimine dimer.³¹ A number of examples have been validated by X-ray crystallography.^{32–34} Many other related LiN containing four rings have been characterized.^{35–37} An important observation supporting structure 1 is the presence of $^{13}\text{C}_1$ – ^{13}CN NMR coupling for lower order $\text{RCu}(\text{CN})\text{Li}$ species and its absence for “higher order” $\text{R}_2\text{Cu}(\text{CN})\text{Li}_2$ compositions.³⁸ Most recently, an EXAFS study of $2\text{BuLi} + \text{CuCN}$ in THF published after the completion of our computational work demonstrated that >90% of the reagent’s Cu(I) is uncoordinated to CN.³⁹

In conclusion, both experiment^{11,38,39} and the present theory argue that trivalent Cu(I) is neither obligatory nor sufficiently stable for describing the structure around

the copper center in $\text{R}_2\text{Cu}(\text{CN})\text{Li}_2$. Viable and general alternatives consist of the well-known dialkyl Gilman reagent spanned by the Li_2CN moiety (1, 3, 4) or the lower order cyano Gilman species complexed to a dilithium alkyl bridge (2, 5). The elegant NMR studies of Bertz drew him to a conceptually similar conclusion.¹¹ The bridging motif portrayed here can be viewed as part of a continuum with the eight-ring lithium-linked Gilman dimers^{5,40–44} at one end and the LiNC (9)^{30–33} and LiNCS ^{45–47} four-ring dimers at the other. This contrasts with crystallographic results for multicopper aggregates able to sustain tricoordination at the metal.⁴⁸ The special role of cyanide in the present context is less to promote the existence of a thermodynamic sink^{8,12,49} than to assist in establishing an equilibrium (e.g., $1 \rightleftharpoons 2 \rightleftharpoons 3 \rightleftharpoons \dots$) potentially dependent on substitution and reaction medium. Other anions and electron pair donors can be expected to exhibit a diverse chemistry by the same principle.

Our final point is that Li^+ rather than $\text{Cu}(\text{I})^+$ appears to be the primary determinant of structure for lithiated cuprates along lines so well established in organolithium chemistry.^{50,51} Near-linear divalent Cu(I) is found in “naked” cuprate anions^{52–54} as well as in complexes^{40–44} (e.g., 1–5). In this context Cu(I) can be viewed as a “passenger” atom. Lithium-containing cuprates with their unique capacity for bridging and cyclization are thus fittingly designated as “lithium cuprates” to emphasize the fundamental structural role of lithium. The term “higher order cyanocuprate” is at best a misleading appellation for structures of the $\text{R}_2\text{CNCuLi}_2$ constitution.

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