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## Communications

### The Structure of "R<sub>2</sub>Cu(CN)Li<sub>2</sub>" 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 (CH<sub>3</sub>)<sub>2</sub>Cu(CN)·Li<sub>2</sub> strongly suggests that the compounds are best described as lower-order Gilman cuprates complexed by ring formation with 1 mol of either CH<sub>3</sub>Li 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 "R<sub>2</sub>Cu(CN)Li<sub>2</sub>" to effect substitution reactions on secondary halides.<sup>1</sup> The replacement of a single carbon ligand in the previously described R<sub>3</sub>CuLi<sub>2</sub> cuprates<sup>2–5</sup> with a "dummy" cyano ligand thereby spawned an impressive literature of novel and practical synthetic reagents.<sup>6–8</sup> While no unambiguous structure determinations have been carried out, the higher order species have been designated as Cu(I) dianions ("R<sub>2</sub>Cu(CN)<sup>2-</sup> 2Li<sup>+</sup>").<sup>6–9</sup> It has been unequivocally asserted

that the cyano group is bonded to copper<sup>10</sup> by means of a Cu–C(N) bond.<sup>10</sup> The "higher order" claim has been strongly challenged<sup>11</sup> and subsequently defended.<sup>12</sup> In the present work we describe a computational analysis of the Me<sub>2</sub>Cu(CN)Li<sub>2</sub> 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  $\zeta$  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).<sup>13,14</sup> Less elaborate basis sets have been effectively applied to the stereoselective nucleophilic addition of organocupper reagents to acroleins and cyclopropenes.<sup>15,16</sup> The rather long Cu–C(H<sub>3</sub>) 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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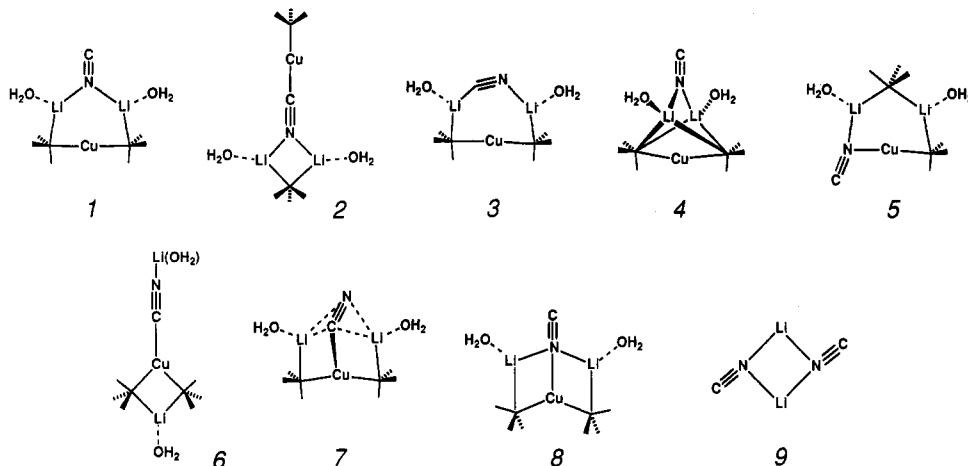
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Table 1. Relative Energies and Partial Geometries ( $\text{\AA}$ , deg) for LANL2DZ-Optimized Isomers of  $\text{Li}_2\text{Cu}(\text{CN})\text{Me}_2\cdot(\text{H}_2\text{O})_2$ 

$r(\text{Cu}-\cdots-\text{X})^c$	$r(\text{Cu}-\text{CH}_3)$	$\theta(\text{C}-\text{Cu}-\text{C})$	LANL2DZ	$\Delta E_{\text{rel.}}^{a,b}$ kcal/mol			LANL2DZ SCRF <sup>d</sup>
				6-31+G*/ECP-2(DZ)	LANL2DZ/MP2		
1	3.365	2.068	178.1	0.0	0.0	0.0	0.0
2	2.024	2.000	180.0	1.3	4.6	1.6	0.4
3	3.254 (C) 3.303 (N)	2.097 2.091	161.4	3.6	3.9	0.7	3.6
4	3.561	2.046	154.8	9.0	11.2	7.3	9.6
5	3.806	2.028	178.4	11.9	14.3	12.9	11.8
6	2.082	2.261	114.3	23.3	26.1	24.9	22.7
7	2.540 <sup>e</sup>	2.146	156.0	20.6	16.1	20.4	16.6
8	2.100 <sup>e</sup>	2.196	141.8	15.6	14.4	17.6	13.7

<sup>a</sup> LANL2DZ as implemented in Gaussian 92 employs the Los Alamos 10-electron effective core potential (ECP-2) plus double  $\zeta$  (DZ) basis for copper ((8s2p5d)/[3s2p2d] contraction with (341/311/41) splitting)<sup>13b</sup> and utilizes the D95V basis<sup>6b</sup> for atoms from H to Ne. The 6-31+G\*/ECP-2(DZ) prescription uses a standard 6-31G\* basis supplemented by diffuse orbitals<sup>6b</sup> on carbon, nitrogen, and oxygen. Electron correlation effects were calculated with Møller-Plesset theory<sup>57</sup> carried out to second order (MP2). <sup>b</sup> All calculations used the Gaussian 92 program.<sup>14</sup> Absolute energies for LANL2DZ-optimized 1 (au): LANL2DZ, -533.543 47; 6-31+G\*/ECP-2(DZ), -533.595 03; LANL2DZ/MP2, -534.394 58; LANL2DZ/SCRF, -533.544 98. <sup>c</sup> X = CN, NC, or CH<sub>3</sub> depending on structure. Apart from methyl C-H bonds, structures 1-3, 5, 6, 8, and 9 are planar. Selected geometric variables for 1 (LANL2DZ//LANL2DZ) include the following:  $r\text{CN}$ , 1.183;  $r\text{LiN}$ , 2.014;  $r\text{LiC}$ , 2.214;  $r\text{CuC}$ , 2.068  $\text{\AA}$ ;  $\theta(\text{CCuC})$ , 178.1°;  $\theta(\text{ClLiN})$  140.4°. <sup>d</sup> Onsager reaction field<sup>25</sup> with  $\epsilon$  = 7.58 (dielectric constant, THF). <sup>e</sup> Cu- $\cdots$ -NC distance constrained at the PRDDO optimized value.

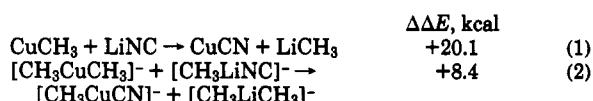
Chart 1



1.957  $\text{\AA}$  in excellent agreement with the triple  $\zeta$  correlated Cu-C(H<sub>3</sub>) value of 1.936  $\text{\AA}$ .<sup>17</sup> In addition, the HF/LANL2DZ and MP2/LANL2DZ calculations produce a linear cuprate anion upon optimization ([CH<sub>3</sub>CuCH<sub>3</sub>]<sup>-</sup>, 160 → 180 °C) with Cu-C bond lengths of 2.061 and 2.004  $\text{\AA}$ , respectively, in reasonable agreement with the X-ray distance of 1.935  $\text{\AA}$  and  $\theta(\text{C}-\text{Cu}-\text{C}) = 180^\circ$ .<sup>18</sup>

With this background, we turn to the “organocuprate” question and first ask whether Cu(I) in unsolvated simple systems prefers CH<sub>3</sub><sup>-</sup> or CN<sup>-</sup> in the presence of Li<sup>+</sup>. The following optimized *ab initio* isodesmic reactions<sup>19</sup> ( $\Delta E$ , 6-31+G\*/LANL2DZ//LANL2DZ<sup>13,14</sup>) are illustrative. Cyanide favors bonding to Li<sup>+</sup> particularly through nitrogen in agreement with the structure of matrix isolated lithium isocyanide.<sup>20</sup>

The operation of these energetic factors for the more complex aggregate Me<sub>2</sub>Cu(CN)Li<sub>2</sub>·(H<sub>2</sub>O)<sub>2</sub> has been ex-



plored for topologies 1-8. Two lithium-bound water molecules were added to approximate explicit and directional solvation by an ether solvent in which cuprates are uniformly generated.<sup>21</sup> Sixteen heteroatom isomers and their conformations were examined. Each was geometry optimized within the approximate *ab initio* PRDDO method.<sup>22</sup> For each topology the lowest energy structure was further optimized with the LANL2DZ basis set (cf. Table 1) and reevaluated for relative energies with 6-31G\*/ECP-2(DZ)//LANL2DZ and MP2/LANL2DZ//RHF//LANL2DZ. The same structures were treated within an Onsager reaction field<sup>25</sup> with  $\epsilon$  = 7.58 to mimic the bulk

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properties of THF. The latter, when applied to the Li-solvated species, models both primary (i.e.,  $\text{LiOR}_2$ ) 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  $\text{NCLi}$  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  $\text{Me}_3\text{CuLi}_2$ .<sup>26</sup> The 2,4-dilithio four-membered ring with Li–N bonds (2) is in striking accord with matrix-isolation IR<sup>27</sup> and theoretical<sup>28–30</sup> studies on lithium isocyanide dimers (9). Similarly, the most stable solvated dimer of  $\text{LiCH}_2\text{CN}$  was predicted to be a four-membered N-lithiated ketenimine dimer.<sup>31</sup> A number of examples have been validated by X-ray crystallography.<sup>32–34</sup> Many other related LiN containing four rings have been characterized.<sup>35–37</sup> An important observation supporting structure 1 is the presence of  $^{13}\text{C}_1-^{13}\text{CN}$  NMR coupling for lower order  $\text{RCu}({}^{13}\text{CN})\text{Li}$  species and its absence for “higher order”  $\text{R}_2\text{Cu}^{13}\text{CNLi}_2$  compositions.<sup>38</sup> 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.<sup>39</sup>

In conclusion, both experiment<sup>11,38,39</sup> and the present theory argue that tricovalent Cu(I) is neither obligatory nor sufficiently stable for describing the structure around

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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  $\text{Li}_2\text{CN}$  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.<sup>11</sup> The bridging motif portrayed here can be viewed as part of a continuum with the eight-ring lithium-linked Gilman dimers<sup>5,40–44</sup> at one end and the  $\text{LiNC}$  (9)<sup>30–33</sup> and  $\text{LiNCS}$ <sup>45–47</sup> four-ring dimers at the other. This contrasts with crystallographic results for multicopper aggregates able to sustain tricoordination at the metal.<sup>48</sup> The special role of cyanide in the present context is less to promote the existence of a thermodynamic sink<sup>8,12,49</sup> 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  $\text{Li}^+$  rather than  $\text{Cu(I)}^+$  appears to be the primary determinant of structure for lithiated cuprates along lines so well established in organolithium chemistry.<sup>50,51</sup> Near-linear divalent Cu(I) is found in “naked” cuprate anions<sup>52–54</sup> as well as in complexes<sup>40–44</sup> (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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