A Model Structure for the Resting State of Cyanocuprate Reagents $R_2Cu(CN)Li_2$. The X-ray Crystal Structure of $[Ar_2Cu(CN)Li_2(THF)_4]_\infty$[1]

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Among organocopper reagents, cyanocuprates are members of a versatile class of reagents that find useful application in organic synthesis.[2,3] Depending on the synthetic route, two different types can be distinguished: (i) 1:1 cyanocuprates, formulated as RCu(CN)Li, obtained from the reaction of equimolar amounts of an organolithium with CuCN, and (ii) 2:1 cyanocuprates with $R_2Cu(CN)Li_2$ stoichiometry, a 2:1 molar mixture of an organolithium with CuCN. Initially, it has been proposed that 2:1 cyanocuprates exist in solution as Cu(I) dianionic species, $[R_2Cu(CN)]^{2-}2[Li]^+$ and 1:1 species as monoanions, $[RCu(CN)]^-$.[4] In both of these cyanocuprates, the CN^- anion is thought to act simply as a nontransferable ligand during reactivity. Despite their widespread use in organic synthesis, there has been little success in obtaining reliable structural (solid-state or solution) data about cyanocuprates. This has led to considerable debate among academic researchers concerning the proposed structural motifs of these compounds.

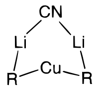
Four different models have been put forward to describe the structure of 2:1 cyanocuprates: (**a**) a dianionic species with a three-coordinate Cu(I) center,[4] (**b**) a monoanionic copper species with a lithiumcyanide cationic counterion,[5,25] (**c**) a neutral trinuclear structure with a diagonally coordinated Cu(I) center and LiCN incorporated in the overall structure,[6] and (**d**) a mixture of the neutral cuprate and LiCN.[7]

$[R_2Cu(CN)]^{2-}\ 2[Li]^+$

a

$[R_2Cu]^-\ [Li_2(CN)]^+$

b



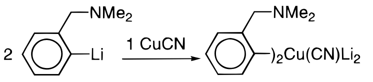
c

$R_2CuLi + LiCN$

d

Extensive spectroscopic studies have been performed (EXAFS,[8] NMR[5,9,26] and IR[10]) to elucidate the structure of dialkylcyanocuprates. One of these studies prefers structure **a**[9] but the others point to a preference for structure **c**[10,26] or **d**.[5,8] Molecular weight determinations by cryoscopy (THF) strongly indicated that this type of cyanocuprate exists as a discrete monomeric species: $[R_2Cu(CN)Li_2]$.[6b] At this point, it should be emphasized that the composition of organocopper (and aryllithium) aggregates are strongly solvent dependent (vide infra).[6,11] Our earlier investigations have shown that the use of the C,N-chelating aminoaryl anion $[C_6H_4CH_2NMe_2\text{-}2]^-$,[12] instead of the simple parent phenyl anions has a stabilizing effect on a variety of copper complexes including organocopper(I) species.[13,14] This has allowed the isolation of well-defined compounds that have been unequivocally characterized both in the solid state and in solution.

We now report on the synthesis, isolation, and structural characterization (X-ray) of $[Ar_2Cu(CN)Li_2(THF)_4]_\infty$ (**1**, Ar = $[C_6H_4CH_2NMe_2\text{-}2]^-$), which represents the first fully elucidated example of a cyanocuprate of the general stoichiometry $R_2Cu(CN)Li_2$. Compound **1** is obtained as the only reaction product when 2 equiv of ArLi is treated with 1 equiv of CuCN in THF at low temperature (−78 °C; eq 1). Crystals suitable for single-crystal X-ray diffraction were obtained from a solution of **1** in THF at −30 °C.



(1)

1

The molecular structure in the solid state of **1** reveals a linear (zigzag) polymeric chain, consisting of alternating $[Ar_2Cu]^-$

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(1) Ar = $[C_6H_4CH_2NMe_2\text{-}2]^-$: the structure of the title compound in the solid state is represented by $(\mu^2{}_{Li2}\text{-}C,N\text{-}CN)Li_2\cdot(THF)_4(\mu^2{}_{Cu,Li}\text{-}C_{Cu},N_{Li}\text{-}2\text{-}Me_2NCH_2C_6H_4)_2Cu$.

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(12) The CH_2NMe_2 substituent in $[C_6H_4CH_2NMe_2\text{-}2]^-$ (abbreviated as Ar^-) can be considered as a well-positioned intramolecular "solvent" molecule, viz. the similar structural features of $Ph_4Li_4(OEt_2)_4$[11d] and Ar_4Li_4 as well as of $Ph_4Cu_2Li_2(OEt_2)_2$[11e] and $Ar_4Cu_2Li_2$.

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(15) X-ray data for **1** are available as Supporting Information.

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(18) Cyanocuprate **1** contains a two center-two electron (2c-2e) Cu−C bond whereas in $Ar_4Cu_2Li_2$ each aryl group is 3c-2e bonded to a CuLi atomic pair.

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(21) Penner-Hahn et al. reported an $\nu_{(C\equiv N)}$ of 2115 cm^{-1} for $Me_2Cu(CN)Li_2$ in solution which would be in agreement with ab initio calculations of a seven-membered cyclic cyanocuprate.[10] The $\nu_{(C\equiv N)}$ value (2115 cm^{-1}) of $[Ar_2Cu(CN)Li_2]$, **1**, in THF is, however, very similar to that previously reported for the 2:1 cyanocuprates.[10]

(22) It should be noted that the applied methodology (measurements of freezing point depression) presents a value indicative for the amount of *particles* present in solution and not the molecular weight of the individual species. If **1** completely dissociates in THF solution into cationic and anionic species which simultaneously associate to higher aggregates ($Li_2CN \rightarrow (Li_2CN)_n{}^{n+}$; $n \geq 3$), a virtual molecular weight close to the value of a neutral monomeric species will be calculated. Such processes a priori may not be excluded since it has been well established that a combination of Li^+, CN^-, and additional solvent molecules might give rise to highly aggregated species as is exemplified in the solid-state structure of $[LiCN(pyridine)_2]_\infty$.[23]

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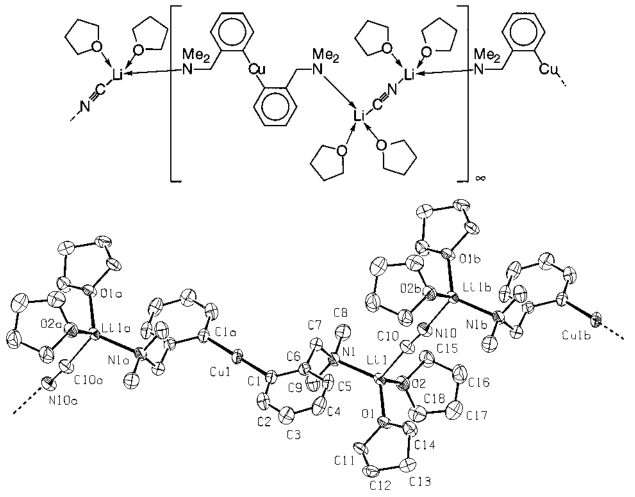

Figure 1. ORTEP drawing (50% probability level) of $[Ar_2Cu(CN)Li_2(THF)_4]_\infty$, **1**. representation of $[Ar_2Cu(CN)Li_2(THF)_4]_\infty$, **1**. Note that the CN orientation is arbitrarily chosen.[15]

anionic and $[Li_2(CN)(THF)_4]^+$ cationic units (see Figure 1). Each $[Li_2(CN)(THF)_4]^+$ unit contains a C≡N anion (1.156 Å) which bridges the two lithium atoms (Li(1)−C(1) and Li(1B)−N(10) 2.045 Å; Li(1)−C(10) 175.6(3)°),[15] while to each lithium atom two additional THF molecules are coordinated. As the cyanide anion is located on a crystallographic inversion center, the cyanide carbon and nitrogen atoms are indistinguishable. The formal $[Ar_2Cu]^-$ and $[Li_2(CN)(THF)_4]^+$ units in the polymeric chain are linked together via coordination of the nitrogen atom of the 2-(dimethylamino)methyl substituent of the Ar anion to the lithium atom of an adjacent $[Li_2(CN)(THF)_4]^+$ cation. The latter N−Li (2.090 Å) interaction renders each lithium atom four coordinate.

The linear C(1a)−Cu−C(1) (180°) arrangement found in the $[Ar_2Cu]^-$ anionic units is in agreement with earlier reported structures that contain free $[R_2Cu]^-$ structural fragments, e.g., $[Cu(dppe)_2][Cu(Mes)_2]$[16] and $[Li(12\text{-crown-}4)_2][CuPh_2]$.[17] The observed Cu−C(1) distance (1.917(2) Å) in **1** is slightly shorter (0.03 Å) than that reported for the neutral cuprate $Ar_4Cu_2Li_2$ pointing to a slight increase in the Cu−C bond order in **1**.[14b,18]

An important question is whether the ionic polymeric structure of **1** is retained in solution. Attempts to dissolve **1** in benzene or toluene results in an immediate disproportionation reaction giving rise to the formation of a solution of the known neutral cuprate $Ar_4Cu_2Li_2$[14] and a precipitate which is assumed to be LiCN.

$$\underset{\mathbf{1}}{[Ar_2Cu(CN)Li_2]_n} \xrightarrow{C_6H_6} {}^{n}/_{2}\, Ar_4Cu_2Li_2 + {}^{1}/_{n}\, [LiCN]_n \downarrow \quad (2)$$

However, cyanocuprate **1** dissolves readily in THF. The $^{13}C\{^1H\}$ NMR spectrum of **1** (THF), contains a single carbon resonance at 158.1 ppm that has been assigned to the cyanide carbon atom. This chemical shift value is comparable to that found in $[Ph_2Cu(CN)Li_2]$ (158.7 ppm), $[Et_2Cu(CN)Li_2]$ (158.8 ppm), and $[Me_2Cu(CN)Li_2]$ (158.9 ppm).[5] The presence of CN^-, in the form of LiCN, is not observed ($\delta = 162$ ppm) for **1**.[9] Consequently, it must be concluded that the various anions such as Ph^-, Et^-, or Me^- and in our case Ar^-, which have different σ-donor capabilities, do not significantly influence the cyanide carbon chemical shift.[5,25] This is in agreement with the proposal that the CN anion is exclusively part of the LiCNLi cation. In contrast, it is noteworthy that the chemical shift values for the C≡N carbon for the monoorganocyanocuprates, [RCu(CN)Li], do vary with the nature of the R group,[19] thus indicating that in the 1:1 cyanocuprates a Cu−CN bond is present indeed. This has also recently been observed in the X-ray structure determination of [t-BuCu(CN)Li][20a] and of $[Li(THF)_2\{Cu(CN)C_6H_3\text{-}2,6\text{-}Trip_2\}]_2$,[20b] in contrast to the 2:1 cyanocuprates where a direct CN−Cu bond is absent.[21]

Most likely the polymeric solid-state structure of **1** is broken down in THF solution as a result of the consecutive dissociation of the N−Li interactions, which links the anionic and cationic units (e.g., by solvation). In the limiting situation, this would give rise to completely dissociated $[Ar_2Cu]^-$ anionic and $[(THF)_3Li(CN)Li(THF)_3]^+$ cationic species. This conclusion seems to be corroborated by the observation that the ^1H NMR spectrum of **1** in THF-d_8 (RT) shows only one singlet resonance for both the NMe_2 protons ($\delta = 2.20$ ppm) and for the benzylic protons ($\delta = 3.73$ ppm). Moreover, the fact that the ^1H NMR spectra of **1** (THF-d_8) are temperature independent (RT to −78 °C) suggests that no complex equilibria take place on the NMR time scale

Molecular weight determinations (cryoscopy) of **1** (22.5 mM) in THF solution points to the existence of **1** as a nondissociated monomeric, i.e., neutral, species[22] with $Ar_2Cu(CN)Li_2$ stoichiometry, for which a proposed structure **c** is schematically shown (vide supra). To compare the solution structure to the known ionic solid-state structure of **1** its conductivity in THF was measured. The observed molar conductivity of 57.1 Ω^{-1} cm^{-1} for THF solutions of **1** (41.5 mM) is about 500 times larger than that measured for the parent organolithium compound $[Ar_4Li_4]$.[11a] This latter species is known to exist in THF solution as a discrete neutral dimeric complex $[Ar_2Li_2(THF)_4]$.[11b−c] This (somewhat surprising) result strongly suggests that ionic species are present in THF solutions of **1**, which would contradict the earlier proposed neutral trinuclear $CuLi_2$ structure, i.e., **c**.

In conclusion, the solid-state structure of the 2:1 cyanocuprate $[Ar_2Cu(CN)Li_2(THF)_4]$ is comprised of an ionic structure with $[Ar_2Cu]^-$ and $[LiCNLi]^+$ units, whereas according to recent solid-state studies, the 1:1 cyanocuprate $[t\text{-}BuCu(CN)Li(Et_2O)_2]_\infty$ contains a t-BuCu−CN−Li structural motif.[20] Since the lithium-bound carbon atom of the organolithium reagent is a stronger Lewis base than the carbon atom of the cyanide in a 1:1 cyanocuprate, it is not unexpected that the addition of an equimolar amount of RLi to RCu(CN)Li results in the conversion of the cyanide-bridged species into a compound with more stable $[R_2Cu]^-$ and $[Li_2CN]^+$ structural units. The stability of these ions makes the 2:1 cyanocuprate an unique combination. The observed structure (Figure 1) for **1** in the solid state does not conform to any of the previously proposed models **a**, **c**, and **d**[6,8,10] but does correspond to model **b**.[5,25] Especially noteworthy is the unprecedented role of the C≡N ligand as a bridge between the two lithium atoms via coordination of both carbon and nitrogen. The basic role of the C≡N anion in the 2:1 cyanocuprate appears to be as a $[Li_2CN]^+$ counterion for the $[R_2Cu]^-$ anion and this can be a general function of nontransferable anions in cuprate chemistry. Unfortunately, the solid-state structure does not provide any insight into the mechanism of C−C bond formations that are promoted by such reagents, since it is highly unlikely that the observed "resting state" will remain after substrate addition.[24,27]

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Supporting Information Available: X-ray structural data for **1**, and tables of fractional coordinates, thermal parameters, bond distances and angles, and hydrogen coordinates, and ^1H and ^{13}C NMR spectra of **1** (11 pages, print/PDF). An X-ray crystallographic file, in CIF format, is available through the Web only. See any current masthead page for ordering information and Web access instructions.

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(27) The reactivity has been tested in a substitution reaction of **1** with a primary halide. Reaction of 1 equiv of 1-octylbromide with 2 equiv of **1** (THF, −78 °C, 2 h) yields 75% of the substituted product, 2-(octyl)dimethylbenzylamine. Comparing this result with earlier reported data of substitution reactions with species of the form $R_2Cu(CN)Li_2$,[3c] one can say that **1** reacts as a "higher order" or better 2:1 bis(aryl)cyanocuprate.