Isolation and Structural Characterization of the Lithium Cyanoorganocuprate Salt $[Li(THF)_2\{Cu(CN)C_6H_3\text{-}2,6\text{-}Trip_2\}]_2$ (Trip = $-C_6H_2\text{-}2,4,6\text{-}i\text{-}Pr_3$)

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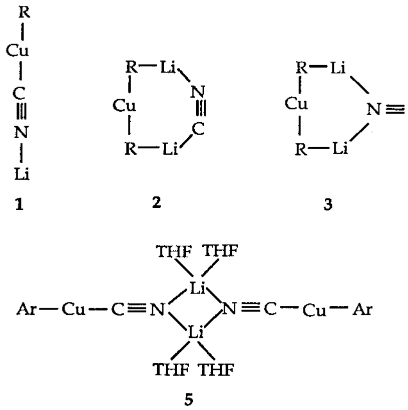
The unsymmetrical lithium cyanoorganocuprates Li[Cu(CN)R] (**1**) were originally introduced into organocopper chemistry as alternative synthetic reagents to the symmetrical lithium diorganocuprates $Li[CuR_2]$.[1] This adaptation was based on earlier work[2] involving related unsymmetrical lithium cuprates of the type Li[Cu(C≡C−R′)R], which showed that the R group was preferentially transferred, thereby conserving an equivalent of the potentially valuable R group in forming the alkylating agent. Subsequently, the addition of 2 equiv of an organolithium reagent LiR to CuCN was reported[3] to give a new type of highly reactive cyanoorganocuprate reagent of the proposed formula $Li_2[Cu(CN)R_2]$ in which the two R groups and CN^- ligand were assumed to be bound directly to copper to give, in effect, a "higher-order" cyanocuprate.[4] The structures of these interesting species have been the focus of intense study. Initial investigations with ^{13}C NMR spectroscopy indicated that the CN^- group was bound to copper.[5] However, subsequent ^{13}C NMR studies[6] indicated that the shift of the CN^- carbon was unaffected by the changes in the R group implying that CN^- was not bound to copper. These findings were later corroborated by EXAFS[7] and IR[8] data as well as by calculations.[9,10] This work favored the non-higher-order formulas **2**−**4** as probable structures. The most recent ^{15}N, ^{6}Li, and ^{13}C NMR data also strongly favor structure **2**.[11]

In contrast, somewhat less attention has been given to the "lower-order" cyanocuprates; ^{13}C NMR[12] and EXAFS[7] data indicate that CN^- is directly bound to the copper, and that the copper coordination is probably linear as shown in **1**. Evidence for dimer formation was adduced,[12] but the interaction (if any) between the Li^+ ion and the $[Cu(CN)R]^-$ anion is not well defined. Such interactions are obviously crucial to the structures of **1**−**4**. Heretofore, no X-ray structures of cyanoorganocuprate species of type **1** have appeared in the literature and EXAFS data[7] have not thrown light on the disposition of the Li^+ ion. Such compounds have, in fact, proved elusive to crystallize or purify.[13] In this paper the synthesis and spectroscopic and structural characterization of the compound $[Li(THF)_2\{Cu(CN)C_6H_3\text{-}2,6\text{-}Trip_2\}]_2$ (**5**), which is the THF-solvated lithium salt of the $\{Cu(CN)C_6H_3\text{-}2,6\text{-}Trip_2\}^-$ ion, are now reported.

Chart 1



Compound **5** was synthesized[14] under anaerobic and anhydrous conditions by the reaction of $(Et_2O)LiC_6H_3\text{-}2,6\text{-}Trip_2$[14] with a CuCN suspension in Et_2O/THF (20:1) solution. It was obtained as colorless, air-sensitive crystals which displayed relatively high thermal stability. Its X-ray crystal structure[16] is illustrated in Figure 1. It crystallizes as well-separated centrosymmetric dimers. Dimerization occurs through the bridging interactions of the two Li^+ ions with nitrogens from the cyanide ligands and is thus very different from the type of dimerization seen in the Gilman dimer **6**. The Li^+ ions in **5** are each further solvated by two THF donors. The coppers, which have almost linear coordination (C(1)−Cu(1)−C(37) = 175.6(2)°), are bound to the cyanide ligands through the carbons and also to the ipso-carbon of the central ring of the aryl ligand. The cyanide carbon also has an essentially linear geometry, N(1)−C(37)−Cu(1) = 179.3(5)°, but there is an angle of 13.3° between the CN bond and the Li_2N_2 plane. The Cu(1)−C(1) distance is 1.906(4) Å, which is marginally longer than the 1.894(4) Å observed in the structure of $(Me_2S)CuC_6H_3\text{-}2,6\text{-}Trip_2$.[15] However, it is the shortest Cu−C(organo) distance known for an organocuprate ion.[17] The Cu−C(37) distance to the cyanide carbon is 1.858(5) Å. A short Cu−CN distance is to be expected

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[14] $(Et_2O)LiC_6H_3\text{-}2,6\text{-}Trip_2$[15] (1.00 g, 1.78 mmol) in Et_2O (20 mL) was added dropwise (over ca. 1 h) to a suspension of CuCN (0.08 g, 0.89 mmol) in Et_2O (20 mL) with cooling in a dry ice bath. The solution was stirred ca. 2 h and was then allowed to come to room temperature; THF (2 mL) was added and stirring was continued for 5 h. The solution was filtered and the dark yellow filtrate was placed in a freezer (−20 °C) for 3 days to afford the product as colorless crystals. Yield 0.218 g, 34%; mp 205−210 °C dec (became a brown gray powder). ^1H NMR (THF-d_8, 25 °C): δ 1.00 (d, 12H, J = 8.9 Hz, p-$CH(CH_3)_2$); 1.81 (d, 12H, J = 8.9 Hz, o-$CH(CH_3)_2$; 1.93 (d, 12H, J = 8.9 Hz, o-$CH(CH_3)_2$); 2.44 (br, THF-d_8); 3.52 (sept, 2H, J = 8.3 Hz p-$CH(CH_3)_2$); 3.74 (sept, 4H, J = 8.2 Hz, o-$CH(CH_3)_2$); 4.28 (br, THF-d_8); 7.39 (d, 2H, J = 8.0 Hz, m-C_6H_3); 7.58 (s, 4H, m-Trip); 7.72 (t, 1H, J = 8.0 Hz, p-C_6H_3). $^{13}C\{^1H\}$ NMR (THF-d_8 25 °C): δ 24.38 (o-$CH(CH_3)_2$); 24.91 (THF-d_8, J = 20.7 Hz, quintet); 25.96 (p-$CH(CH_3)_2$); 30.27 (o-$CH(CH_3)_2$); 34.88 (p-$CH(CH_3)_2$); 66.99 (THF-d_8, J = 24.8 Hz, quintet); 119.67 (m-Trip); 122.82 (m-C_6H_3); 124.09 (p-C_6H_3); 145.34 (i-Trip); 145.78 (o-Trip); 146.65 (p-Trip); 148.31 (CN); 150.09 (o-C_6H_3); 171.66 (i-C_6H_3). ^7Li NMR (THF-d_8, 25 °C; LiCl in D_2O was used as reference): δ −1.23 ppm (s). IR (Nujol mull) 2123 cm^{-1} (C≡N).

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[16] Crystallographic data at 130 K with Cu Kα (λ = 1.54178 Å) radiation (Siemens Rotating Cu Anode): a = 12.842(2) Å, b = 18.788(3) Å, c = 17.285(3) Å, β = 108.93(1)°, V = 4071.2(14) Å^3, Z = 4, space group $P2_1/c$, $R_1 = 0.0592$, $wR_2 = 0.153$ for $3613 > 2(\sigma)I$ data. Attempted refinement of the data with the positions of N(1) and C(37) interchanged led to a decrease in U_{eq} from 48 to 33 for N(1) and an increase in U_{eq} from 34 to 64 for C(37); the R value also increased slightly.

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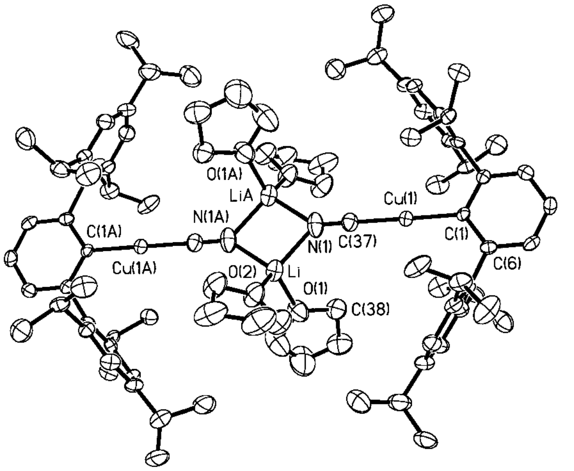

Figure 1. Thermal ellipsoid plot of **5** with H atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Cu(1)−C(1) = 1.906(4), Cu(1)−C(37) = 1.858(5), N(1)−C(37) = 1.144(6), Li−N(1) = 2.046(11), Li−N(1)′ = 2.051(10), Li−O(1) = 1.934(10), Li−O(2) = 1.920(10), C(1)−Cu(1)−C(37) = 175.6(2), Cu(1)−C(37)−N(1) = 179.3(5), N(1)−Li−N(1)′ = 97.5(5), Li−N(1)−Li′ = 82.5(5), O(1)−Li(1)−O(2) = 109.4(5), Li−N(1)−C(37) = 136.0(5), Li′−N(1)−C(37), 138.7(5), C(2)−C(1)−C(6) = 116.6(4).

as a result of the carbon sp-hybridization and the small size of the CN$^-$ ligand.

Unfortunately, structural data for two-coordinate copper cyanide species are almost nonexistent. The mixed valent compounds $[Cu_4(CN)_6Cu(NH_3)_2]_n$ and $[Cu_3(CN)_5Cu(NH_3)_2(OH_2)]_2$ feature rare examples of two-coordinate Cu$^+$ ions bound to cyanide.[18] In these the cyanides bridge two copper centers in a chainlike structure, and are bound end-on through nitrogen to one copper and through carbon to another, with Cu−C distances that range from 1.8 to 1.86 Å. The Cu−C(37) distance (1.858(5) Å) lies just within this range. These distances are considerably shorter than those found for cyanocopper(I) complexes in which the Cu$^+$ ion is either three-coordinate[19] (Cu−C = ca. 1.90 Å) or four-coordinate[20] (Cu−C = ca. 1.98 Å). The C−N bond length in **5**, 1.144(6) Å, is similar to that found in $NaCu(CN)_2\cdot 2H_2O$,[19b] $K_2Cu(CN)_3\cdot 3H_2O$,[19a] or $KCu(CN)_2$.[21] The Li$^+$ ions, which bridge the two $\{Cu(CN)C_6H_3\text{-}2,6\text{-}Trip_2\}^-$ units, have distorted tetrahedral coordination with average Li−O and Li−N distances of 1.93(1) and 2.05(1) Å. The Li−O distances are at the shorter end of the scale for four-coordinate Li$^+$ ions bound to THF. On the other hand, the Li−N distances are relatively long,[22] but similar Li−N distances have been observed in lithium imide and certain monomeric amide structures where the nitrogen coordination number is also three.[22b]

The structural data may be compared with those obtained from solution EXAFS spectroscopy.[7] The Fourier transform of the EXAFS data for Li[Cu(CN)Me] in THF indicates two-coordinate copper geometry with neighboring atoms at ca. 1.9 and 3.1 Å, which correspond to the two carbons (from Me$^-$ and CN$^-$) at the shorter distance and the nitrogen (from CN$^-$) at the longer one. Although EXAFS spectroscopy cannot distinguish between carbon and nitrogen coordination[7] it is clear that the structure deduced for Li[Cu(CN)Me] is in general agreement with the structure of **5**. In addition, EXAFS spectroscopy showed that the long-range order (with interactions such as Cu−C≡N- - -Cu) in solid CuCN[23] or in solutions of $CuCN\cdot 2LiCl$ was absent in THF solutions of Li[Cu(CN)Me]. This did not rule out association such as that seen in **5**, however, since the Li$^+$ ion is a relatively poor scatterer of X-rays. The structure of **5** is also in agreement with the dimeric formula determined for Li[Cu(CN)Ph] in THF solution by cryoscopy.[24]

Compound **5** was also characterized by ^{1}H and ^{13}C NMR and IR spectroscopy. In the ^{13}C NMR spectrum of **5** (THF-d_8), the $Cu(C_6H_3)$ peak was observed at 171.7 ppm, which is close to the 168.1 ppm value seen for $(Me_2S)CuC_6H_3\text{-}2,6\text{-}Trip_2$[15] and within the 165.99−168.40 ppm range reported[12] for Li[Cu(CN)Ph] in THF-d_8 or $Et_2O\text{-}d_{10}$ at low temperatures. The cyanide carbon resonance was observed at 148.31 ppm, which is also close to the range observed in solution for cuprates of formula Li[Cu(CN)R] (R = Me, Et, or Ph).[12] The IR spectrum of **5** as a Nujol mull or in THF solution displays an absorption at 2123 or 2128 cm^{-1} that is attributable to the C≡N stretching vibration. The solution value is close to the 2133 cm^{-1} observed for Li[Cu(CN)Me] in THF solution.[8] Reactivity studies of **5** are in hand.

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Supporting Information Available: Tables of data collection parameters, atom coordinates, bond distances, angles, anisotropic thermal parameters, and hydrogen coordinates (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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