

# Synthesis and Characterization of (THF)<sub>3</sub>Li(NC)Cu(C<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub>) and Br(THF)<sub>2</sub>Mg(C<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub>) (Mes = C<sub>6</sub>H<sub>2</sub>-2,4,6-Me<sub>3</sub>; Trip = C<sub>6</sub>H<sub>2</sub>-2,4,6-*i*-Pr<sub>3</sub>): The Structures of a Monomeric Lower-Order Lithium Organocyanocuprate and a Bulky Terphenyl Grignard Reagent in the Solid State

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The lower-order lithium organocyanocuprate compound, (THF)<sub>3</sub>Li(NC)Cu(C<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub>) (**1**), and the bulky terphenyl Grignard reagent, Br(THF)<sub>2</sub>Mg(C<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub>) (**2**), have been synthesized and structurally characterized both in the solid state by single crystal x-ray crystallography and in solution by multi-nuclear NMR and IR spectroscopy. The compound (**1**) was isolated as a monomeric contact ion-pair in which the C (organic ipso)-Cu-CN-Li atoms are coordinated linearly. The lithium has a tetrahedral geometry as a result of solvation by three THF molecules. The compound (**1**) is the first example of fully characterized monomeric lower order lithium organocyanocuprate. The bulky Grignard reagent (**2**) was also isolated as a monomer in which the magnesium, solvated by two THF molecules, has a distorted tetrahedral geometry. The crystals of (**1**) possess triclinic symmetry with the space group  $P\bar{1}$ ,  $Z = 2$ , with  $a = 12.456(3)$  Å,  $b = 12.508(3)$  Å,  $c = 13.904(3)$  Å,  $\alpha = 99.81^\circ$ ,  $\beta = 103.72(3)^\circ$ , and  $\gamma = 119.44(3)^\circ$ . The crystals (**2**) have a monoclinic symmetry of space group  $P2_1/c$ ,  $Z = 4$ , with  $a = 13.071(3)$  Å,  $b = 14.967(3)$  Å,  $c = 22.070(4)$  Å, and  $\beta = 98.95(3)^\circ$ .

**Key Words** : Cyanocuprate, Organocopper, Grignard reagent, Terphenyl ligand

## Introduction

Both organocopper and Grignard reagents are among the most widely used organometallic reagents in organic synthesis.<sup>1</sup> One route for the preparation of organocopper reagents was by the treatment of copper halides with Grignard reagents although organolithium reagents are now more commonly used for this purpose.<sup>2</sup> Among organocopper reagents, lower-order lithium organocyanocuprates, whose formula is represented as Li[Cu(CN)R], were originally introduced into organocopper chemistry as alternative synthetic reagents to the lithium diorganocuprates Li[CuR<sub>2</sub>].<sup>3</sup> This adaptation was based on earlier work<sup>4</sup> involving related mixed lithium cuprate 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 alkylation agent. Subsequently, the addition of 2 equivs of an organolithium reagent LiR to CuCN was reported<sup>5</sup> to give a new type of highly reactive organocyanocuprate reagent of the proposed formula Li<sub>2</sub>[Cu(CN)R<sub>2</sub>] in which the two R groups and CN<sup>-</sup> ligand were assumed to be bound directly to copper to give a "higher-order" cyanocuprate.<sup>6</sup> The structures of these interesting species have been the focus of intensive study. Initial investigation by <sup>13</sup>C NMR spectroscopy seemed that the CN<sup>-</sup> group was bound to copper.<sup>7</sup> However, subsequent <sup>13</sup>C NMR studies<sup>8</sup> indicated that the chemical shift of the CN<sup>-</sup> carbon was unaffected by the changes in the R group, implying that CN<sup>-</sup> was not bound to copper. These findings were later corroborated by EXAFS<sup>9</sup> and IR<sup>10</sup> data as well as by

theoretical calculations.<sup>11,12</sup> Consequently, it was suggested that there was no such higher-order cyanocuprate species formed. The claim for the non-existence of higher-order cyanocuprates was strengthened by the independent isolation of two polymeric lithium cyanocuprate compounds: [(*t*-Bu)<sub>2</sub>Cu{Li(THF)(pmteda)<sub>2</sub>CN}]<sub>n</sub><sup>13</sup> and [(2-(Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)<sub>2</sub>CuLi<sub>2</sub>(CN)(THF)<sub>4</sub>)<sub>n</sub>]<sup>14</sup> which were structurally characterized by X-ray crystallography. These structures have clearly shown that the CN<sup>-</sup> ion is not directly attached to the copper center.

The structures of lower-order lithium organocyanocuprates, [RCu(CN)Li], have received relatively less attention than that of higher-order species. Previously, we have isolated a bulky lower-order lithium organocyanocuprate compound, [Li(THF)<sub>2</sub>{Cu(CN)(C<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub>)}]<sub>2</sub>,<sup>15</sup> in which the CN<sup>-</sup> is directly bound to the copper. The compound was isolated as a centro symmetric dimer where the two lithium ions bridged the nitrogen atoms of the cyanide ligands to form a Li<sub>2</sub>N<sub>2</sub> four-membered ring. More recently, Eaborn *et al.*<sup>16</sup> reported that they had prepared a monomeric cyanocuprate of the formula [(Me<sub>2</sub>PhSi)<sub>3</sub>CCu(CN)Li(THF)<sub>3</sub>] in THF solvent. However, they were not able to present a detailed structure in the paper due to the high *R* value in the crystal refinement data. In this paper, the first fully characterized lithium organocyanocuprate structure of (THF)<sub>3</sub>Li(NC)Cu(C<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub>) is described.

The bulky terphenyl Grignard reagent (**2**) has been investigated as a useful precursor to synthesize an unusual organometallic species. Especially, we have long been interested in the synthesis of a monomeric, one-coordinate organocopper

compound. The controversial compound  $\text{Cu}(\text{C}_6\text{H}_2\text{-2,4,6-Ph}_3)$  and its silver analogue  $\text{Ag}(\text{C}_6\text{H}_2\text{-2,4,6-Ph}_3)$  were claimed as the first example of one coordinate metals in the solid state.<sup>17</sup> Subsequent interpretations of their structural and spectroscopic data cast considerable doubt on their formulation, however.<sup>18</sup> In addition, further experimental works on  $[\text{Li}(\text{THF})_4][\text{Ag}(\text{Triph})_2]\cdot\text{THF}$  ( $\text{Triph} = \text{C}_6\text{H}_2\text{-2,4,6-Ph}_3$ ),  $[\text{Li}(\text{THF})_4][\text{Ag}(\text{C}_6\text{H}_3\text{-2,6-Mes}_2)_2]\cdot 1/8 \text{Et}_2\text{O}$ ,<sup>19</sup> and  $(\text{CuC}_6\text{H}_3\text{-2,6-Ph}_2)_3$ ,<sup>20</sup> organosilver and copper species with identical or almost identically sized substituents suggested that the  $\text{C}_6\text{H}_2\text{-2,4,6-Ph}_3$  ( $\text{Triph}$ ) ligand would not be a suitable one to form the target species in the solid state. Alternatively the bulky Grignard reagent (**2**) was regarded as a potential candidate to synthesize such species in our group. It is interesting to note that a monomeric, one-coordinate organoindium compound  $[\text{In}(\text{C}_6\text{H}_3\text{-2,6-Trip}_2)]^{21}$  was successfully isolated and characterized by using the same terphenyl ligand in (**2**).

### Experimental Section

**General procedures.** All manipulations were carried out using modified Schlenk techniques under an atmosphere of nitrogen or in a vacuum atmosphere HE-43 dry box. All solvents were distilled from Na/K alloy and degassed immediately before use. The compounds  $[\text{Li}(\text{C}_6\text{H}_3\text{-2,6-Mes}_2)_2]^{22}$  and  $(\text{Et}_2\text{O})\text{Li}(\text{C}_6\text{H}_3\text{-2,6-Trip}_2)^{23}$  were synthesized by literature procedures.  $\text{CuCN}$  and  $\text{MgBr}_2$  were purchased (Aldrich) and were used as received.  $^1\text{H}$ ,  $^7\text{Li}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker 300MHz instrument and referenced to the deuterated solvents.

**2,6-Mes<sub>2</sub>C<sub>6</sub>H<sub>2</sub>Cu(CN)Li(THF)<sub>3</sub> (1).**  $[\text{2,6-Mes}_2\text{C}_6\text{H}_3\text{Li}]_2$  (1.60 g, 5.0 mmol) in  $\text{Et}_2\text{O}$  (20 mL) was added dropwise (over ca. 1 h) to a suspension of  $\text{CuCN}$  (0.46 g, 5.0 mmol) in  $\text{Et}_2\text{O}$  (20 mL) cooled in a dry-ice bath. The solution was stirred for ca. 2 h, and was then allowed to warm to room temperature: THF (2 mL) was added and stirring was continued 5 h. The solution was filtered through Celite and the dark yellow filtrate was placed in a freezer (ca.  $-20^\circ\text{C}$ ) for 5 days to afford the product (**1**) as colorless crystals. Yield 1.37 g (43.8%). mp  $152\text{-}156^\circ\text{C}$  dec (black powder).  $^1\text{H}$  NMR ( $\text{THF-D}_8$ ,  $25^\circ\text{C}$ ):  $\delta$  1.79 (quintet,  $\text{THF-D}_8$ ), 2.08 (s, 12H, *o*-Me(Mes)), 2.27 (s, 6H, *p*-Me(Mes)), 3.64 (quintet,  $\text{THF-D}_8$ ), 6.65 (d, 2H,  $J = 7.5$  Hz, *m*-C<sub>6</sub>H<sub>3</sub>), 6.78 (s, 4H, *m*-Mes), 6.98 (t, 1H,  $J = 7.5$  Hz, *p*-C<sub>6</sub>H<sub>3</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{THF-D}_8$ ,  $25^\circ\text{C}$ ):  $\delta$  22.51 (*p*-Me(Mes)), 22.97 (*o*-Me(Mes)), 26.47 (quintet,  $\text{THF-D}_8$ ), 68.59 (quintet,  $\text{THF-D}_8$ ), 125.09 (*p*-C<sub>6</sub>H<sub>3</sub>), 125.35 (*m*-C<sub>6</sub>H<sub>3</sub>), 129.12 (*m*-Mes), 134.92 (*o*-Mes), 137.25 (*p*-Mes), 148.94 (*i*-Mes), 151.20 (CN), 152.99 (*o*-C<sub>6</sub>H<sub>3</sub>), 170.92 (*i*-C<sub>6</sub>H<sub>3</sub>).  $^7\text{Li}$  NMR ( $\text{THF-D}_8$ ,  $25^\circ\text{C}$ ,  $\text{LiCl}$  in  $\text{D}_2\text{O}$  was used as reference):  $\delta$   $-1.01$  ppm (s). IR (Nujol mull):  $2120\text{ cm}^{-1}$  (CN); (neat THF):  $2136\text{ cm}^{-1}$  (CN).

**Br(THF)<sub>2</sub>MgC<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub> (2).** A solution of  $(\text{Et}_2\text{O})\text{Li}(\text{C}_6\text{H}_3\text{-2,6-Trip}_2)$  (1.0 g, 1.78 mmol) in dry ether (20 mL) was added to a suspension of  $\text{MgBr}_2$  (0.33 g, 1.78 mmol) in THF (20 mL) at ca.  $-78^\circ\text{C}$ . The mixture was allowed to warm to room temperature, and the stirring was continued overnight, which afforded a pale yellow homogeneous

solution. The solvent was removed under reduced pressure, and the off-white residue was extracted with *n*-hexane/toluene mixture (20 mL). After filtration through Celite, the solution was placed in a freezer ( $-20^\circ\text{C}$ ) ca. 3 weeks to afford colorless crystals of (**2**). Yield: 0.16 g (12%). mp:  $158\text{-}160^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta$  7.28 (t, 1H,  $J = 9.0$  Hz, *p*-C<sub>6</sub>H<sub>3</sub>), 7.21 (br s, 4H, *m*-Triph), 7.15 (s,  $\text{C}_6\text{D}_6$ ), 7.12 (d, 2H,  $J = 9.0$  Hz, *m*-C<sub>6</sub>H<sub>3</sub>), 3.46 (sept., 4H,  $J = 7.0$  Hz, *o*-CH(CH<sub>3</sub>)<sub>2</sub>), 3.15 (s, THF), 2.84 (sept., 2H,  $J = 7.0$  Hz, *p*-CH(CH<sub>3</sub>)<sub>2</sub>), 1.44 (d, 12H,  $J = 7.0$  Hz, *o*-CH(CH<sub>3</sub>)<sub>2</sub>), 1.26 (d, 12H,  $J = 7.0$  Hz, *o*-CH(CH<sub>3</sub>)<sub>2</sub>), 1.19 (d, 12H,  $J = 7.0$  Hz, *p*-CH(CH<sub>3</sub>)<sub>2</sub>). Small peaks at 7.05-7.10 (m) and 2.11 (s) ppm were assigned as toluene (solvent).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta$  166.85 (*i*-C<sub>6</sub>H<sub>3</sub>), 150.61 (*i*-Triph), 147.76 (*o*-Triph), 146.96 (*p*-Triph), 145.64 (*o*-C<sub>6</sub>H<sub>3</sub>), 128.00 (t,  $\text{C}_6\text{D}_6$ ), 127.34 (*m*-C<sub>6</sub>H<sub>3</sub>), 124.36 (*p*-C<sub>6</sub>H<sub>3</sub>), 120.74 (*m*-Triph), 69.24 (THF), 34.77 (*p*-CH(CH<sub>3</sub>)<sub>2</sub>), 30.48 (*o*-CH(CH<sub>3</sub>)<sub>2</sub>), 26.11 (*p*-CH(CH<sub>3</sub>)<sub>2</sub>), 25.02 (THF), 24.55 (*o*-CH(CH<sub>3</sub>)<sub>2</sub>), 24.05 (*o*-CH(CH<sub>3</sub>)<sub>2</sub>). Small peaks at 128.52-120.06 and 22.41 ppm were assigned as toluene (solvent).

**X-ray crystallography data collection and refinement for (1) and (2).** Crystals of (**1**) and (**2**) were coated with hydrocarbon oil, mounted on a glass fiber, and quickly placed in the nitrogen cold stream on the diffractometer.<sup>24</sup> Data for (**1**) and (**2**) were collected at 130 K with Cu K $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ) on a Syntex P2<sub>1</sub> diffractometer. The diffractometer was equipped with a low-temperature device, and the radiation was monochromated with graphite filter. Calculations were carried out with the SHELXTL-plus program system.<sup>25</sup> Scattering factors and the correction for anomalous scattering were taken from common sources. The structures were solved by direct methods and refined by full matrix least-squares refinement. An absorption correction

**Table 1.** Crystallographic data summary for compounds (**1**) and (**2**)

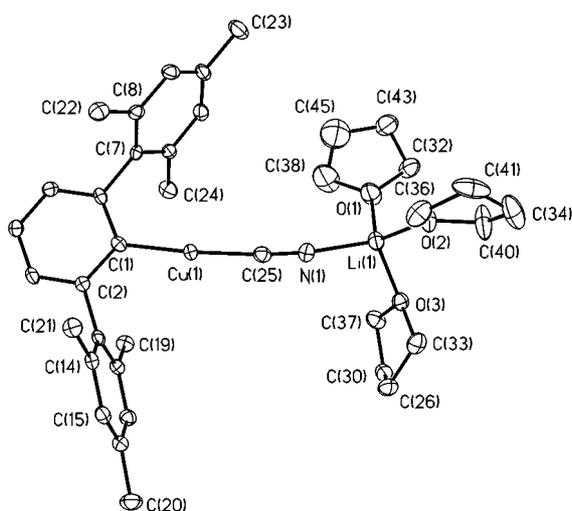
	(1)	(2)
Formula	$\text{C}_{37}\text{H}_{49}\text{CuLiNO}_3$	$\text{C}_{47}\text{H}_{68}\text{BrMgO}_2$
Formula Weight	626.25	769.23
Color, Habit	Colorless, Block	Colorless
Crystal System	Triclinic	Monoclinic
Space Group	$P\bar{1}$	$P2_1/c$
<i>a</i> , $\text{\AA}$	12.456(3)	13.071(3)
<i>b</i> , $\text{\AA}$	12.508(3)	14.967(3)
<i>c</i> , $\text{\AA}$	13.904(3)	22.070(4)
$\alpha$ , Deg.	99.81(3)	90
$\beta$ , Deg.	103.72(3)	98.95(3)
$\gamma$ , Deg.	119.44(3)	90
<i>V</i> , $\text{\AA}^3$	1724.0(6)	4265(2)
<i>Z</i>	2	4
<i>d</i> , $\text{g cm}^{-3}$	1.206	1.198
Crystal Dimensions, mm	$0.33 \times 0.28 \times 0.20$	$0.42 \times 0.30 \times 0.12$
$\mu$ , $\text{cm}^{-1}$	11.51	1.72
No. of Unique Data	4657	7048
No. of data with $I > 2\sigma(I)$	4210	6439
<i>R</i> ( $I > 2\sigma(I)$ )	0.0495	0.0856
<i>wR</i> <sub>2</sub> , All Data	0.1382	0.2484

was applied using the XABS2 program.<sup>26</sup> Crystal data for (1) and (2) are provided in Table 1. For (1), attempted refinement of the data with the position of N(1) and C(25) interchanged led to a decrease in  $U_{eq}$  from 42 to 27 for N(1) and an increase in  $U_{eq}$  from 33 to 57 for C(25); the  $R$  value also increased slightly.

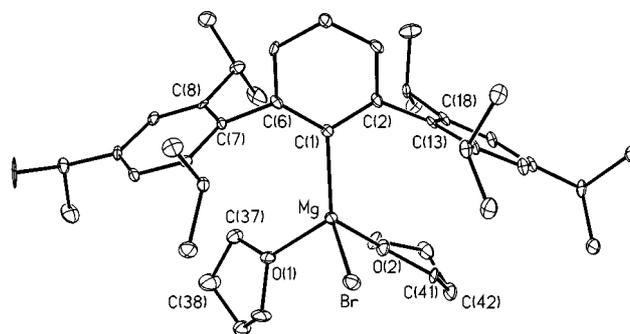
Crystallographic data for the structures reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition Nos. CCDC-202768 (1) and CCDC-202767 (2)). The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/perl/catreq/catreq.cgi> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

## Results and Discussion

The structures of the compounds are illustrated in Figures 1 and 2. Compound (1) crystallizes as a monomeric contact ion-pair. The lithium cation is solvated by three THF molecules. The copper, which has an almost linear coordination (C(1)-Cu(1)-C(25) 173.46(14)°), is bound to the cyanide ligand through the carbon and also to the ipso-carbon of the central ring of the aryl ligand. The cyanide carbon also has an essentially linear geometry, Cu(1)-C(25)-N(1) 174.4(3)°. The copper-(ipso carbon) distance is 1.916(3) Å, which is marginally longer than the 1.906(4) Å observed in [Li(THF)<sub>2</sub>{Cu(CN)(C<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub>)}<sub>2</sub>],<sup>15</sup> but shorter than 1.933(3) Å in the structure of [(Me<sub>2</sub>PhSi)<sub>3</sub>CCu(CN)Li(THF)<sub>2</sub>]<sub>2</sub><sup>16</sup> which has a sp<sup>3</sup>-hybridized carbon. The Cu-C distance is also longer than the 1.894(4) Å observed in the structure of (Me<sub>2</sub>S)Cu(C<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub>).<sup>23</sup> The C(1)-Cu(1)-CN angle (173.46(14)°) is close to that for [(Me<sub>2</sub>PhSi)<sub>3</sub>CCu(CN)Li(THF)<sub>2</sub>]<sub>2</sub> (173.68(16)°), but smaller than that in the [Li(THF)<sub>2</sub>{Cu(CN)(C<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub>)}<sub>2</sub>] (175.6(2)°). In addition, the



**Figure 1.** Crystal structure of (1). Thermal ellipsoids are drawn at 30% probability level. H atoms are not shown for clarity. Selected bond lengths (Å) and angles (deg): Cu(1)-C(1) 1.916(3), Cu(1)-C(25) 1.869(4), C(25)-N(1) 1.159(5), N(1)-Li(1) 1.972(7), C(1)-Cu(1)-C(25) 173.46(14), Cu(1)-C(25)-N(1) 174.4(3), O(1)-Li(1)-N(1) 107.8(3), O(2)-Li(1)-O(3) 105.3(3).



**Figure 2.** Crystal structure of (2). Thermal ellipsoids are drawn at 30% probability level. H atoms are not shown for clarity. Selected bond lengths (Å) and angles (deg): C(1)-Mg 2.147(6), Mg-Br 2.478(2), Mg-O(1) 2.059(5), Mg-O(2) 2.034(5), C(1)-Mg-Br 116.0(2), O(1)-Mg-Br 101.89(14), O(1)-Mg-O(2) 90.4(2).

Cu-C-N angle at the cyanide (174.4(3)°) is very close to [(Me<sub>2</sub>PhSi)<sub>3</sub>CCu(CN)Li(THF)<sub>2</sub>]<sub>2</sub> (174.9(4)°) but more bent relative to [Li(THF)<sub>2</sub>{Cu(CN)(C<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub>)}<sub>2</sub>] (179.3(5)°). A short Cu-CN distance 1.869(4) Å is to be expected as a result of the carbon sp-hybridization and the small size of the CN<sup>-</sup> ligand. The structures of (1) can be compared to [*t*-BuCu(CN)Li(OEt<sub>2</sub>)<sub>2</sub>]<sub>n</sub>, [*t*-Bu<sub>2</sub>Cu{Li(THF)(pmdeta)<sub>2</sub>(CN)}]<sub>13</sub> and [(2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)<sub>2</sub>CuLi<sub>2</sub>(CN)(THF)<sub>4</sub>]<sub>n</sub>.<sup>14</sup> The former species [*t*-BuCu(CN)Li(OEt<sub>2</sub>)<sub>2</sub>]<sub>n</sub> consists of a contact ion-pair in which the cation moiety is connected to the anion moiety through the lithium atom and the nitrogen atom in the cyanide CN<sup>-</sup> ligand. The distances Cu-C(*t*-Bu) (1.969(7) Å), Cu-C(CN) (1.878 Å), and (CN) (1.159 Å) are slightly longer than those in (1), and the average C-Cu-CN angle 169° is also lower than that in (1). The reason for the longer Cu-C distance could be the different hybridizations (sp<sup>2</sup> for (1); sp<sup>3</sup> for *t*-Bu) of the copper-bound carbons. The difference in aggregation in the solid state between (1) and this compound is probably due to the different steric requirements of the (C<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub>) and *tert*-Butyl ligands. The compounds [*t*-Bu<sub>2</sub>Cu{Li(THF)(pmdeta)<sub>2</sub>(CN)}]<sub>13</sub> and [(2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)<sub>2</sub>CuLi<sub>2</sub>(CN)(THF)<sub>4</sub>]<sub>n</sub><sup>14</sup> were suggested as models for the controversial Lipschutz's "higher-order" cyanocuprate which he formulated as R<sub>2</sub>Cu(CN)Li<sub>2</sub>.<sup>8</sup> The compound [(*t*-Bu)<sub>2</sub>Cu{Li(THF)(pmdeta)<sub>2</sub>(CN)}]<sub>13</sub> has a well-separated ion-pair structure which consists of [Cu(*t*-Bu)<sub>2</sub>]<sup>-</sup> and [(pmdeta)(THF)Li(CN)Li(THF)(pmdeta)]<sup>+</sup> ions. The cation moiety is separated by the N-donor ligand (pmdeta). The copper is bound only to the two organic ligands (*t*-Bu) with a Cu-C distance of 1.957(4) Å and the C-Cu-C angle of 180.0°. The compound [(2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)<sub>2</sub>CuLi<sub>2</sub>(CN)(THF)<sub>4</sub>]<sub>n</sub><sup>14</sup> has a contact ion-pair structure consisted of [(2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)<sub>2</sub>Cu]<sup>-</sup> and [(THF)Li(CN)Li(THF)]<sup>+</sup> ions, which are connected through the 2-(Me<sub>2</sub>NCH<sub>2</sub>) nitrogen atom chelated to the lithium. The Cu-C(organic) distance 1.917(2) Å is very close to that for (1) and the C-Cu-C angle is almost 180.0°. The structures of compound (1) can also be compared to that observed for the monomeric lower-order iodo-mixed cuprate species, (Et<sub>2</sub>O)<sub>2</sub>Li{ICu(C<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub>)}.<sup>27</sup> This compound has a [R-

Cu-I<sup>-</sup> anion moiety with the Cu-C distance of 1.902(5) Å, and the C-Cu-I angle of 171.4(2)°, which is in contact through a Li-I interaction with the counter cation [(Et<sub>2</sub>O)<sub>2</sub>-Li]<sup>+</sup>. In compound (**1**), the lithium has an almost perfect tetrahedral geometry (the average N-Li-O angle is 110.73°) coordinated by three THF molecules and the nitrogen atom in the CN<sup>-</sup> ligand with average Li-O and Li-N distances of 1.930 Å and 1.970 Å. These Li-O distances are relatively short for the four-coordinate lithium cations bound to THF. On the other hand, Li-N distances are relatively long<sup>28</sup> although similar Li-N distances have been observed in lithium imide and certain monomeric amide structures where the nitrogen coordination number is also three.<sup>28b</sup> The structural data may be compared with those obtained from solution EXAFS spectroscopy.<sup>9</sup> The Fourier transform of the EXAFS data for Li[Cu(CN)Me] in THF indicates two-coordinate copper geometry with neighboring atoms at a distance of *ca.* 1.9 and 3.1 Å, which correspond to the two carbons (from CH<sub>3</sub><sup>-</sup> and CN<sup>-</sup>) at the shorter distance and the nitrogen (from CN<sup>-</sup>) at the longer one. Although EXAFS spectroscopy cannot distinguish between carbon and nitrogen coordination,<sup>9</sup> it is clear that the structure deduced for Li[Cu(CN)Me] is quite similar to that of (**1**).

Interestingly, the compound (**1**) was isolated as a monomer with even less bulkier organic ligand than C<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub> in the dimeric [Li(THF)<sub>2</sub>{Cu(CN)(C<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub>)}]<sub>2</sub>.<sup>15</sup> The reason for this is not clear. However, Eaborn *et al.*<sup>16</sup> stated that they obtained a dimeric cyanocuprate, [(Me<sub>2</sub>PhSi)<sub>3</sub>Cu(CN)Li(THF)<sub>2</sub>]<sub>2</sub>, simply by removing the solvent (THF) from the corresponding monomer and then recrystallizing in a different solvent (toluene). Therefore, it was concluded that the concentration of THF could be a key factor for the formation of the monomer in our case. In fact, we have tried the same experiments for the crystal (**1**) to obtain a dimer in toluene or benzene. Unfortunately, we were not able to obtain suitable crystals for X-ray analysis from those solvents. In other literature, it has been also proposed that the types and concentration of the solvent is one of the major factors for formation of a certain structure for organocopper reagents.<sup>29</sup>

The compound (**1**) was also characterized by <sup>1</sup>H, <sup>13</sup>C NMR, and IR spectroscopy. In the <sup>13</sup>C NMR spectrum (in THF-D<sub>8</sub>), the ipso-carbon peak was observed at 170.92 ppm, which is close to the values 171.66, 168.1, 174.16, and 173.74 ppm seen for [Li(THF)<sub>2</sub>{Cu(CN)(C<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub>)}]<sub>2</sub>,<sup>15</sup> (Me<sub>2</sub>S)Cu(C<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub>),<sup>23</sup> [Li(THF)<sub>4</sub>][(2,6-Mes<sub>2</sub>H<sub>3</sub>C<sub>6</sub>-Cu<sub>2</sub>I<sub>2</sub>),<sup>27</sup> (Et<sub>2</sub>O)<sub>2</sub>Li{ICu(C<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub>)},<sup>27</sup> and within the 165.99-168.40 ppm range reported<sup>30</sup> for Li[Cu(CN)Ph] in THF-D<sub>8</sub> or Et<sub>2</sub>O-D<sub>10</sub> at low temperature NMR studies. The cyanide carbon peaks appear at 151.20 ppm, which is also close to the range observed in solution for cuprates of the formula Li[Cu(CN)R] (R = Me, Et, or Ph).<sup>8</sup> The IR data were obtained on a Nujol mull and in neat THF solution. They displayed absorptions at 2120 (Nujol mull) and 2136 cm<sup>-1</sup> (neat THF) which are attributable to the CN stretching vibration.<sup>9-11</sup> The value obtained in THF is close to the 2133 cm<sup>-1</sup> reported for Li[Cu(CN)Me] in THF solution.<sup>10</sup>

The Grignard reagent (**2**) was synthesized by the metal-metal exchange reaction between the lithium precursor and MgBr<sub>2</sub>. The insertion of magnesium into an R-X bond (X = halide), which is the most common synthetic method for a Grignard reagent, was not successful for the synthesis of (**2**). The use of activated magnesium metal<sup>31</sup> also failed to produce (**2**). Accordingly, we had to consider an alternative method involving a metal-metal exchange reaction, RLi + MgX<sub>2</sub>.<sup>32</sup> This method is commonly used for benzylic systems which may have difficulties in homocoupling reactions.<sup>32</sup> The crystals of (**2**) were isolated in a poor yield (12%); however, the titration<sup>32</sup> of the reaction mixture indicated that there was 64% yield formation of the Grignard reagent in the solution. The first terphenyl Grignard compound, (Triph)-MgBr (Triph = C<sub>6</sub>H<sub>2</sub>-2,4,6-Ph<sub>3</sub>),<sup>33</sup> was synthesized more than 60 years ago, but only one structure of the terphenyl Grignard reagent, {Mg(μ-Br)(C<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub>)(THF)}<sub>2</sub>,<sup>34</sup> has been published so far. The compound was synthesized by the reaction of bromine contaminated I(C<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub>) with activated magnesium. The structure of {Mg(μ-Br)(C<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub>)(THF)}<sub>2</sub> features a centro symmetric dimer where the two magnesiums are bridged by bromides to form a virtually square planar Mg<sub>2</sub>Br<sub>2</sub> core. The magnesiums are also coordinated by THF (solvent molecule) to form a distorted tetrahedral geometry at the metal center. In contrast, compound (**2**) was isolated as a monomer, which is probably due to the increased size of the organic ligand. The compound (**2**) has a four-coordinate magnesium (by two THFs, Br, and terphenyl ligand), which features a distorted tetrahedron at the metal center. The Mg-C (ipso) distance, 2.147(6) Å, is very close to that for {Mg(μ-Br)(C<sub>6</sub>H<sub>3</sub>-2,6-Mes<sub>2</sub>)(THF)}<sub>2</sub>, 2.136(6) Å. The Mg-Br bond distance, 2.478(2) Å, is shorter than the average 2.57 Å for the dimer. This is probably due to the terminal nature of Mg-Br bond in **2** in contrast to the bridging Mg-Br-Mg bond in the dimer. The coordination number 4 for Mg<sup>2+</sup> is unusual viewed from the two coordinate Li<sup>+</sup> in (Et<sub>2</sub>O)Li(C<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub>)<sup>3</sup> because these two cations have similar sizes,<sup>35</sup> but may be due to the stronger coordination by the THF donors.

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