

Synthesis and Characterization of (THF)₃Li(NC)Cu(C₆H₃-2,6-Mes₂) and Br(THF)₂Mg(C₆H₃-2,6-Trip₂) (Mes = C₆H₂-2,4,6-Me₃; Trip = C₆H₂-2,4,6-*i*-Pr₃): The Structures of a Monomeric Lower-Order Lithium Organocyanocuprate and a Bulky Terphenyl Grignard Reagent in the Solid State

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Received January 24, 2003

The lower-order lithium organocyanocuprate compound, (THF)₃Li(NC)Cu(C₆H₃-2,6-Mes₂) (**1**), and the bulky terphenyl Grignard reagent, Br(THF)₂Mg(C₆H₃-2,6-Trip₂) (**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.¹ 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.² 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[CuR₂].³ This adaptation was based on earlier work⁴ 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 reported⁵ to give a new type of highly reactive organocyanocuprate reagent of the proposed formula Li₂[Cu(CN)R₂] in which the two R groups and CN⁻ ligand were assumed to be bound directly to copper to give a "higher-order" cyanocuprate.⁶ The structures of these interesting species have been the focus of intensive study. Initial investigation by ¹³C NMR spectroscopy seemed that the CN⁻ group was bound to copper.⁷ However, subsequent ¹³C NMR studies⁸ indicated that the chemical 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 EXAFS⁹ and IR¹⁰ data as well as by

theoretical calculations.^{11,12} 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)₂Cu{Li(THF)(pmteda)₂CN}]_n¹³ and [(2-(Me₂NCH₂C₆H₄CH₂)₂CuLi₂(CN)(THF)₄)_n]¹⁴ which were structurally characterized by X-ray crystallography. These structures have clearly shown that the CN⁻ 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)₂{Cu(CN)(C₆H₃-2,6-Trip₂)}]₂,¹⁵ in which the CN⁻ 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 Li₂N₂ four-membered ring. More recently, Eaborn *et al.*¹⁶ reported that they had prepared a monomeric cyanocuprate of the formula [(Me₂PhSi)₃CCu(CN)Li(THF)₃] 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)₃Li(NC)Cu(C₆H₃-2,6-Mes₂) 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.¹⁷ Subsequent interpretations of their structural and spectroscopic data cast considerable doubt on their formulation, however.¹⁸ In addition, further experimental works on $[\text{Li}(\text{THF})_4][\text{Ag}(\text{Triph})_2]\cdot\text{THF}$ ($\text{Triph} = \text{C}_6\text{H}_2\text{-2,4,6-Ph}_3$), $[\text{Li}(\text{THF})_4][\text{Ag}(\text{C}_6\text{H}_3\text{-2,6-Mes}_2)_2]\cdot 1/8 \text{Et}_2\text{O}$,¹⁹ and $(\text{CuC}_6\text{H}_3\text{-2,6-Ph}_2)_3$,²⁰ organosilver and copper species with identical or almost identically sized substituents suggested that the $\text{C}_6\text{H}_2\text{-2,4,6-Ph}_3$ (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. CuCN and MgBr_2 were purchased (Aldrich) and were used as received. ^1H , ^7Li and ^{13}C NMR spectra were recorded on a Bruker 300MHz instrument and referenced to the deuterated solvents.

2,6-Mes₂C₆H₂Cu(CN)Li(THF)₃ (1). $[\text{2,6-Mes}_2\text{C}_6\text{H}_3\text{Li}]_2$ (1.60 g, 5.0 mmol) in Et_2O (20 mL) was added dropwise (over ca. 1 h) to a suspension of CuCN (0.46 g, 5.0 mmol) in Et_2O (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°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). ^1H NMR (THF-D_8 , 25°C): δ 1.79 (quintet, THF-D_8), 2.08 (s, 12H, *o*-Me(Mes)), 2.27 (s, 6H, *p*-Me(Mes)), 3.64 (quintet, THF-D_8), 6.65 (d, 2H, $J = 7.5$ Hz, *m*-C₆H₃), 6.78 (s, 4H, *m*-Mes), 6.98 (t, 1H, $J = 7.5$ Hz, *p*-C₆H₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF-D_8 , 25°C): δ 22.51 (*p*-Me(Mes)), 22.97 (*o*-Me(Mes)), 26.47 (quintet, THF-D_8), 68.59 (quintet, THF-D_8), 125.09 (*p*-C₆H₃), 125.35 (*m*-C₆H₃), 129.12 (*m*-Mes), 134.92 (*o*-Mes), 137.25 (*p*-Mes), 148.94 (*i*-Mes), 151.20 (CN), 152.99 (*o*-C₆H₃), 170.92 (*i*-C₆H₃). ^7Li NMR (THF-D_8 , 25°C , LiCl in D_2O was used as reference): δ -1.01 ppm (s). IR (Nujol mull): 2120 cm^{-1} (CN); (neat THF): 2136 cm^{-1} (CN).

Br(THF)₂MgC₆H₃-2,6-Trip₂ (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 MgBr_2 (0.33 g, 1.78 mmol) in THF (20 mL) at ca. -78°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°C) ca. 3 weeks to afford colorless crystals of (**2**). Yield: 0.16 g (12%). mp: $158\text{-}160^\circ\text{C}$. ^1H NMR (C_6D_6 , 25°C): δ 7.28 (t, 1H, $J = 9.0$ Hz, *p*-C₆H₃), 7.21 (br s, 4H, *m*-Trip), 7.15 (s, C_6D_6), 7.12 (d, 2H, $J = 9.0$ Hz, *m*-C₆H₃), 3.46 (sept., 4H, $J = 7.0$ Hz, *o*-CH(CH₃)₂), 3.15 (s, THF), 2.84 (sept., 2H, $J = 7.0$ Hz, *p*-CH(CH₃)₂), 1.44 (d, 12H, $J = 7.0$ Hz, *o*-CH(CH₃)₂), 1.26 (d, 12H, $J = 7.0$ Hz, *o*-CH(CH₃)₂), 1.19 (d, 12H, $J = 7.0$ Hz, *p*-CH(CH₃)₂). 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 (C_6D_6 , 25°C): δ 166.85 (*i*-C₆H₃), 150.61 (*i*-Trip), 147.76 (*o*-Trip), 146.96 (*p*-Trip), 145.64 (*o*-C₆H₃), 128.00 (t, C_6D_6), 127.34 (*m*-C₆H₃), 124.36 (*p*-C₆H₃), 120.74 (*m*-Trip), 69.24 (THF), 34.77 (*p*-CH(CH₃)₂), 30.48 (*o*-CH(CH₃)₂), 26.11 (*p*-CH(CH₃)₂), 25.02 (THF), 24.55 (*o*-CH(CH₃)₂), 24.05 (*o*-CH(CH₃)₂). 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.²⁴ Data for (**1**) and (**2**) were collected at 130 K with Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$) on a Syntex P2₁ 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.²⁵ 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> , \AA	12.456(3)	13.071(3)
<i>b</i> , \AA	12.508(3)	14.967(3)
<i>c</i> , \AA	13.904(3)	22.070(4)
α , Deg.	99.81(3)	90
β , Deg.	103.72(3)	98.95(3)
γ , Deg.	119.44(3)	90
<i>V</i> , \AA^3	1724.0(6)	4265(2)
<i>Z</i>	2	4
<i>d</i> , g cm^{-3}	1.206	1.198
Crystal Dimensions, mm	$0.33 \times 0.28 \times 0.20$	$0.42 \times 0.30 \times 0.12$
μ , 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> ₂ , All Data	0.1382	0.2484

was applied using the XABS2 program.²⁶ 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).

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)₂{Cu(CN)(C₆H₃-2,6-Trip₂)}]₂,¹⁵ but shorter than 1.933(3) Å in the structure of [(Me₂PhSi)₃CCu(CN)Li(THF)₂]₂¹⁶ which has a sp³-hybridized carbon. The Cu-C distance is also longer than the 1.894(4) Å observed in the structure of (Me₂S)Cu(C₆H₃-2,6-Trip₂).²³ The C(1)-Cu(1)-CN angle 173.46(14)° is close to that for [(Me₂PhSi)₃CCu(CN)Li(THF)₂]₂ (173.68(16)°), but smaller than that in the [Li(THF)₂{Cu(CN)(C₆H₃-2,6-Trip₂)}]₂ (175.6(2)°). In addition, the

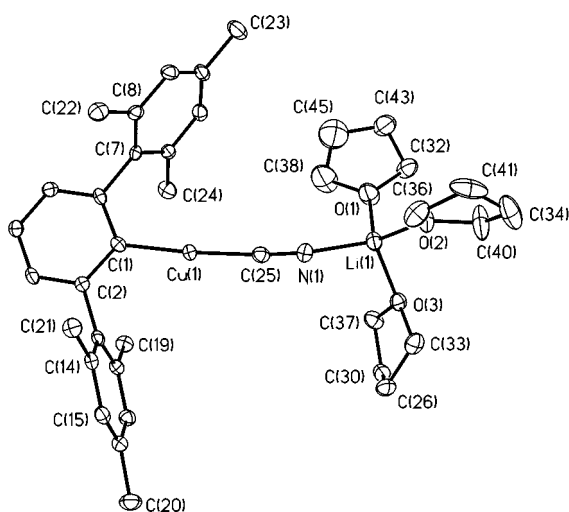


Figure 1. Crystal structure of (1). Thermal ellipsoids are drawn at 30% probability level. H atoms are not shown for clarity. Selected bond lengths (Å) and angles (deg): Cu(1)-C(1) 1.916(3), Cu(1)-C(25) 1.869(4), C(25)-N(1) 1.159(5), N(1)-Li(1) 1.972(7), C(1)-Cu(1)-C(25) 173.46(14), Cu(1)-C(25)-N(1)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

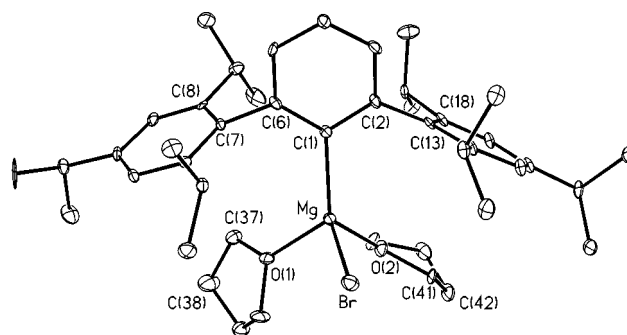


Figure 2. Crystal structure of (2). Thermal ellipsoids are drawn at 30% probability level. H atoms are not shown for clarity. Selected bond lengths (Å) and angles (deg): C(1)-Mg 2.147(6), Mg-Br 2.478(2), Mg-O(1) 2.059(5), Mg-O(2) 2.034(5), C(1)-Mg-Br 116.0(2), O(1)-Mg-Br 101.89(14), O(1)-Mg-O(2) 90.4(2).

Cu-C-N angle at the cyanide (174.4(3)°) is very close to [(Me₂PhSi)₃CCu(CN)Li(THF)₂]₂ (174.9(4)°) but more bent relative to [Li(THF)₂{Cu(CN)(C₆H₃-2,6-Trip₂)}]₂ (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⁻ ligand. The structures of (1) can be compared to [*t*-BuCu(CN)Li(OEt₂)₂]_n, [*t*-Bu₂Cu{Li(THF)(pmdeta)₂(CN)}]₁₃ and [(2-(Me₂NCH₂)C₆H₄CH₂)₂CuLi₂(CN)(THF)₄]_n.¹⁴ The former species [*t*-BuCu(CN)Li(OEt₂)₂]_n 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⁻ 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 (sp² for (1); sp³ 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 (C₆H₃-2,6-Mes₂) and *tert*-Butyl ligands. The compounds [*t*-Bu₂Cu{Li(THF)(pmdeta)₂(CN)}]₁₃ and [(2-(Me₂NCH₂)C₆H₄CH₂)₂CuLi₂(CN)(THF)₄]_n¹⁴ were suggested as models for the controversial Lipschutz's "higher-order" cyanocuprate which he formulated as R₂Cu(CN)Li₂.⁸ The compound [(*t*-Bu)₂Cu{Li(THF)(pmdeta)₂(CN)}]₁₃ has a well-separated ion-pair structure which consists of [Cu(*t*-Bu)₂]⁻ and [(pmdeta)(THF)Li(CN)Li(THF)(pmdeta)]⁺ 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-(Me₂NCH₂)C₆H₄CH₂)₂CuLi₂(CN)(THF)₄]_n¹⁴ has a contact ion-pair structure consisted of [(2-(Me₂NCH₂)C₆H₄CH₂)₂Cu]⁻ and [(THF)Li(CN)Li(THF)]⁺ ions, which are connected through the 2-(Me₂NCH₂) 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, (Et₂O)₂Li{ICu(C₆H₃-2,6-Trip₂)}.²⁷ This compound has a [R-

Cu-I]⁻ 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 [(Et₂O)₂-Li]⁺. 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⁻ 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 long²⁸ although similar Li-N distances have been observed in lithium imide and certain monomeric amide structures where the nitrogen coordination number is also three.^{28b} The structural data may be compared with those obtained from solution EXAFS spectroscopy.⁹ 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 CH₃⁻ 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,⁹ 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 C₆H₃-2,6-Trip₂ in the dimeric [Li(THF)₂{Cu(CN)(C₆H₃-2,6-Trip₂)}]₂.¹⁵ The reason for this is not clear. However, Eaborn *et al.*¹⁶ stated that they obtained a dimeric cyanocuprate, [(Me₂PhSi)₃Cu(CN)Li(THF)₂]₂, 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.²⁹

The compound (**1**) was also characterized by ¹H, ¹³C NMR, and IR spectroscopy. In the ¹³C NMR spectrum (in THF-D₈), 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)₂{Cu(CN)(C₆H₃-2,6-Trip₂)}]₂,¹⁵ (Me₂S)Cu(C₆H₃-2,6-Trip₂),²³ [Li(THF)₄][(2,6-Mes₂H₃C₆-Cu₂I₂),²⁷ (Et₂O)₂Li{ICu(C₆H₃-2,6-Trip₂)},²⁷ and within the 165.99-168.40 ppm range reported³⁰ for Li[Cu(CN)Ph] in THF-D₈ or Et₂O-D₁₀ 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).⁸ The IR data were obtained on a Nujol mull and in neat THF solution. They displayed absorptions at 2120 (Nujol mull) and 2136 cm⁻¹ (neat THF) which are attributable to the CN stretching vibration.⁹⁻¹¹ The value obtained in THF is close to the 2133 cm⁻¹ reported for Li[Cu(CN)Me] in THF solution.¹⁰

The Grignard reagent (**2**) was synthesized by the metal-metal exchange reaction between the lithium precursor and MgBr₂. 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 metal³¹ also failed to produce (**2**). Accordingly, we had to consider an alternative method involving a metal-metal exchange reaction, RLi + MgX₂.³² This method is commonly used for benzylic systems which may have difficulties in homocoupling reactions.³² The crystals of (**2**) were isolated in a poor yield (12%); however, the titration³² 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 = C₆H₂-2,4,6-Ph₃),³³ was synthesized more than 60 years ago, but only one structure of the terphenyl Grignard reagent, {Mg(μ-Br)(C₆H₃-2,6-Mes₂)(THF)}₂,³⁴ has been published so far. The compound was synthesized by the reaction of bromine contaminated I(C₆H₃-2,6-Mes₂) with activated magnesium. The structure of {Mg(μ-Br)(C₆H₃-2,6-Mes₂)(THF)}₂ features a centro symmetric dimer where the two magnesiums are bridged by bromides to form a virtually square planar Mg₂Br₂ 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)(C₆H₃-2,6-Mes₂)(THF)}₂, 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 Mg²⁺ is unusual viewed from the two coordinate Li⁺ in (Et₂O)Li(C₆H₃-2,6-Trip₂)³ because these two cations have similar sizes,³⁵ but may be due to the stronger coordination by the THF donors.

Acknowledgments. HCS thanks the Dankook University Research Fund, 2002, and PPP thanks the National Science Foundation for financial support for this research.

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