

Lithium Cyanocuprates: Structural Studies of a Phosphane Adduct of a “Lower-Order” Lithium Cyanocuprate

Robert P. Davies*^[a] and Stefan Hornauer^[a]

Keywords: Cuprates / Lithium / Reaction intermediates / Michael addition

Addition of PPh₃ to the “lower-order” cyanocuprate PhCuCNLi results in a significant increase in reactivity in 1,4-Michael addition reactions. This is explained by a marked structural change in the cyanocuprate reagent, observed in both THF solution and the solid state, to

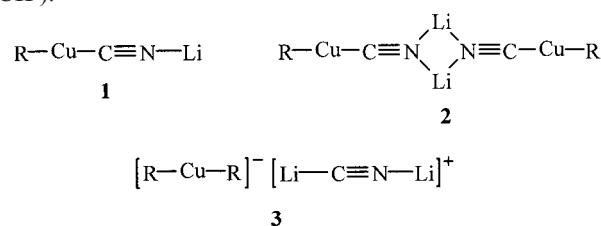
give [Ph₂Cu][−] cuprate anions and a [Cu₂Li₄(CN)₄(PPh₃)₄(THF)₁₀]²⁺ dication.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2005)

Introduction

Lithium cyanocuprates are commonly used in the regioselective formation of new carbon–carbon bonds, and have been shown to have significant advantages for certain reactions over classical Gilman reagents prepared from copper(I) halides.^[1,2] Cyanocuprates can conveniently be divided into two distinct groups based upon their composition and reactivity: “lower order” cyanocuprates formed from the 1:1 reaction of CuCN and LiR (R = organo group) to give species of the general formula RCu(CN)Li; and “higher order” species from the 1:2 reaction of CuCN and LiR and hence with the formulation R₂Cu(CN)Li₂. Spectroscopic studies of lower-order cyanocuprates both in solution^[3] and the solid state^[4–7] have shown **1**, or aggregates of **1** such as **2**, to be the most likely structural motif for these species (Scheme 1). Hence [(Me₂PhSi)₃C–Cu(CN)Li(THF)₃]^[4] is a monomer (**1**) in the solid state, whilst [(Me₂PhSi)₃CCu(CN)Li(THF)₂]₂^[4] [(C₆H₃–2,6-Trip)₂Cu(CN)Li(THF)₂]₂^[5] (Trip = –C₆H₂–2,4,6-*i*Pr₃), [Me₃SiCH₂CuCNLi(OEt)₂]₂^[6] and [*t*BuCu(CN)Li(Et₂O)₂]_∞^[7] are all dimers (**2**). However, the structure of higher-order cyanocuprates has been the subject of much more controversy with arguments centering on whether the cyanide group remains bound to the copper or not. Again recent crystallographic studies have played a major part in this discussion with structural characterization of the higher order cyanocuprates [*t*Bu₂Cu{Li(THF)(pmdeta)}₂CN]^[7] and [(2-C₆H₄CH₂NMe₂)₂Cu{Li(THF)₂}₂CN]_∞^[8] both revealing ionic compounds consisting of [R₂Cu][−] cuprate anions and [Li–CN–Li]⁺ cations (**3**). In contrast, infrared spectroscopic,^[9] NMR spectroscopic,^[10–13] cryoscopic,^[14] and kinetic reactiv-

ity^[15,16] studies of these higher-order cuprates have been less conclusive predicting several possible solution structures. However, the current consensus as laid out by Krause in a recent review,^[17] is that the reactive solution species consists of a cuprate anion [R₂Cu][−] and a [Li–CN–Li]⁺ cation, either as a solvent-separated ion pair (SSIP), such as **3**, and similar to the structures observed in the solid-state characterizations, or possibly as some form of contact-ion pair (CIP).



Scheme 1. Solid-state structural motifs for lower-order (**1**, **2**) and higher-order (**3**) lithium cyanocuprates

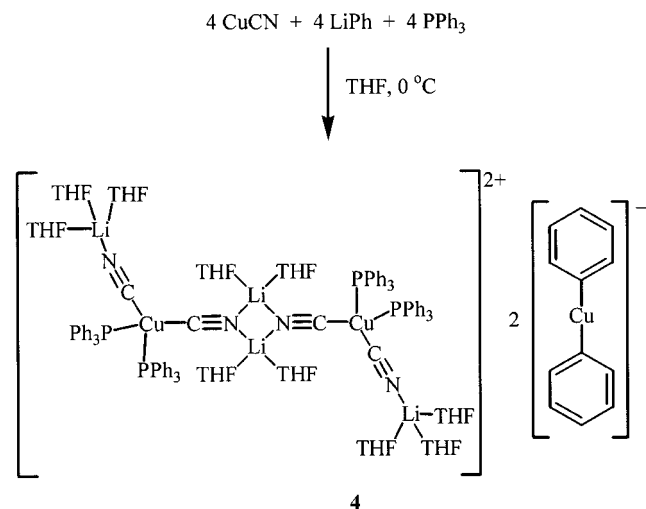
Despite these recent advances, there are still many gaps in our knowledge of cyanocuprates, and this is particularly true when we consider the use of additives. Boron trifluoride, alkali-metal halides and phosphanes amongst others have all been employed as additives for lithium cyanocuprates in order to enhance the stability, selectivity and/or reactivity of these species.^[1] Despite their reported success in this field, little is known about their mode of operation and the effect they have upon the molecular structure of the organocopper reagents. This paper reports on the first structural characterization of a phosphane adduct of a lithium cyanocuprate and discusses its reactivity in Michael addition reactions.

Results and Discussion

Addition of triphenylphosphane to a THF/toluene solution of the lower-order cyanocuprate PhCuCNLi (formed

^[a] Dept. of Chemistry, Imperial College London, South Kensington, London, SW7 2AZ, UK
Fax: (internat.) +44-870-1300438
E-mail: r.davies@imperial.ac.uk

from the 1:1 reaction of CuCN and LiPh at 0 °C gave a clear yellow solution from which crystals of **4** were grown at –30 °C (Scheme 2). X-ray structural studies show **4** to be an ionic species comprising a centrosymmetric $[\text{Cu}_2\text{Li}_4(\text{CN})_4(\text{PPh}_3)_4(\text{THF})_{10}]^{2+}$ dication and two symmetry-related $[\text{CuPh}_2]^-$ cuprate anions (Figure 1).



Scheme 2. Synthesis of **4**

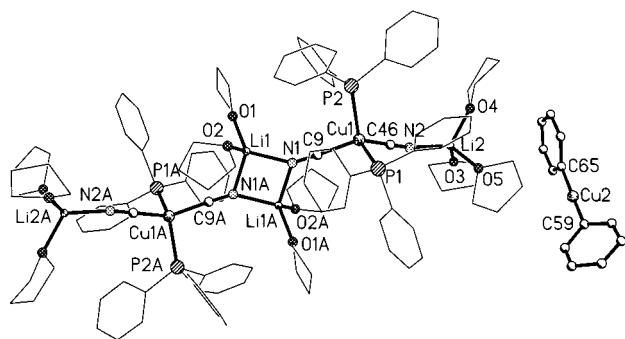


Figure 1. Molecular structure of **4**; only one of the two symmetry-related $[\text{CuPh}_2]^-$ cuprate anions is shown for clarity

The dication in **4** is unprecedented, containing both Li^+ and Cu^I ions linked together through cyanide groups, and can perhaps best be thought of as two PPh_3 -complexed $[\text{Cu}(\text{CN})_2]^-$ anions aggregated with four THF-solvated Li^+ cations. The copper atoms in the dication are approximately tetrahedral, and bond to two PPh_3 groups [$\text{Cu}(1)-\text{P}(1)$ 2.294(2) Å; $\text{Cu}(1)-\text{P}(2)$ 2.299(2) Å] and to the carbon atoms of two cyanide groups [$\text{Cu}(1)-\text{C}(9)$ 1.944(6) Å; $\text{Cu}(1)-\text{C}(46)$ 1.952(9) Å]. These Cu–CN distances are therefore longer than those observed in previously reported lower-order cyanocuprates (mean, 1.906 Å),^[4–7] but are similar to the Cu–CN distances of 1.964(4) and 1.948(5) Å reported for $[\text{Cu}_2(\text{CN})_2(\text{PPh}_3)_4(\text{hppH})]$ (hppH = 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-*a*]pyrimidine), which also contains a $\text{Cu}^I(\text{CN})_2(\text{PPh}_3)_2$ metal center.^[18] Two different lithium ions are observed in the asymmetric

unit of **4**: Li(1) bridges two cyanide groups at their nitrogen ends [$\text{Li}(1)-\text{N}(1)$ 2.036(12) Å; $\text{Li}(1)-\text{N}(1\text{A})$ 2.095(12) Å] and is solvated by two THF molecules [mean Li–O, 1.919 Å], whereas Li(2) is terminally bound to just one cyanide group [$\text{Li}(2)-\text{N}(2)$ 1.90(4) Å] and has its quadruplet completed by three THF molecules [mean Li–O, 1.87 Å]. In keeping with all previously reported lithium cyanocuprates,^[4–7] the cyanide carbon atoms in **4** are essentially linear [$\text{Cu}(1)-\text{C}(9)-\text{N}(1)$, 175.5(6); $\text{Cu}(1)-\text{C}(46)-\text{N}(2)$, 176.2(8)°] and the CN unit is bent out of the plane of the central Li_2N_2 ring (by 12.6°).

The $[\text{Ph}_2\text{Cu}]^-$ cuprate anions in **4** contain close to linear Cu^I centers [$\text{C}(59)-\text{Cu}(2)-\text{C}(65)$, 174.8(4)°] with C–Cu bond lengths of 1.900(11) Å [$\text{Cu}(2)-\text{C}(59)$] and 1.931(11) Å [$\text{Cu}(2)-\text{C}(65)$]. The dihedral angle between the phenyl rings is 59.1°. These units are therefore structurally very similar to the $[\text{R}_2\text{Cu}]^-$ cuprate anions observed in the higher-order cyanocuprates $[\text{tBu}_2\text{CuLi}_2(\text{CN})(\text{THF})_2(\text{pmdeta})_2]^{[7]}$ and $[(2\text{-C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_2\text{Cu}\{\text{Li}(\text{THF})_2\}_2\text{-CN}]_{\infty}^{[8]}$.

Low temperature (–100 °C) ^1H -decoupled ^{13}C NMR spectroscopy carried out on an aliquot of the CuCN + PhLi + PPh_3 reaction mix after stirring for 10 min at 0 °C in toluene/THF solution shows singlets at $\delta = 174.20$ and 144.27 ppm for the phenyl *ipso* carbon and the cyanide carbon resonances, respectively. The chemical shift of the *ipso* carbon is therefore downfield from the value observed for PhCuCNLi in the absence of phosphane ($\delta = 166.05$ ppm),^[3] indicating some structural change has occurred. Bertz has previously reported the chemical shifts of the *ipso* carbon atoms of the higher-order cyanocuprate formed from CuCN + 2 PhLi and also of the Gilman reagent from CuI + 2 PhLi as 174.33 and 174.13 ppm, respectively (in $[\text{D}_8]\text{THF}$ at –78 °C).^[10] Based on these almost identical NMR shifts, he was able to argue that $[\text{CuPh}_2]^-$ cuprate subunits were present in each case. The fact that we observe the *ipso* carbon shift to be of an almost identical value to those observed by Bertz confirms that diphenylcuprate anions are present in solution for **4** as well as in the solid state. The cyanide ^{13}C NMR resonance ($\delta = 144.27$ ppm) differs from that observed for PhCuCNLi in the absence of PPh_3 ($\delta = 148.50$ ppm)^[3] and is significantly upfield from the $[\text{Li}_2\text{CN}]^+$ cation cyanide resonance reported for higher-order cyanocuprates (mean, $\delta = 158.80$ ppm).^[10] However, the resonance is close to the range of reported values for lower-order cyanocuprates ($\delta = 45.51\text{--}151.20$ ppm),^[3–7] suggesting that “CuCNLi” units, similar or identical to those observed in the cation of **4**, are present in solution.

Infrared spectroscopic characterization of the addition product of PhLi and CuCN (PhCuCNLi) gave a cyanide stretch in THF solution at 2137 cm^{-1} (cf. 2133 cm^{-1} previously reported for MeCuCNLi).^[9] On addition of PPh_3 , this peak decreases significantly in size and a new peak is observed at 2120 cm^{-1} . This new absorption differs in frequency from the cyanide stretch reported for the higher-order cyanocuprate formed from CuCN + 2 MeLi (2115 cm^{-1}), attributable to $[\text{Li}-\text{CN}-\text{Li}]^+$,^[9] and instead can be

assigned to a cyanide stretch in a $[\text{Cu}(\text{PPh}_3)_2\text{CNLi}]^+$ unit, which is also in agreement with the ^{13}C NMR spectroscopic and X-ray crystallographic observations (vide supra).

^{31}P NMR spectroscopy on the reaction mixture in THF containing excess triphenylphosphane ($\text{CuCN} + \text{PhLi} + 1.5 \text{ PPh}_3$) reveals one peak ($\delta = -2.54$ ppm) at room temperature. On cooling to -100 °C, this peak splits into two new resonances: a broad peak at $\delta = 0.04$ ppm and a sharp peak at $\delta = -7.76$ ppm. These resonances can be assigned to $[\text{Cu}(\text{CN})_2]^-$ -complexed PPh_3 and free PPh_3 , respectively, and interchange of the two types of PPh_3 occurs at room temperature on the NMR time scale. ^7Li NMR spectroscopy on the same reaction mixture reveals two resonances ($\delta = -2.44$ and -3.37 ppm), consistent with the bridging and terminal lithium atoms present in the cation of **4**.

The addition of the phosphane therefore results in a considerably different structural motif for **4** relative to all previously reported lower-order cyanocuprates (**1**, **2**), and the most significant difference, in terms of its effect on the reactivity, undoubtedly is the generation of $[\text{Ph}_2\text{Cu}]^-$ cuprate anions. The observed increased reactivity of higher- than lower order cyanocuprates has previously been attributed to the presence of such $[\text{R}_2\text{Cu}]^-$ cuprate units,^[17] and it seems likely that any increase in reactivity for PhCuCNLi on addition of PPh_3 is due to the generation of these anions. However, although it has previously been suggested that addition of PPh_3 to cuprates does indeed increase their reactivity,^[1] no systematic studies have been reported. We therefore obtained logarithmic reactivity profiles (LRPs)^[15] to compare the rates of reaction of (a) PhCuCNLi , (b) $\text{PhCuCNLi} + \text{PPh}_3$ (**4**), and (c) $\text{Ph}_2\text{CuCNLi}_2$ in Michael addition reactions with 2-cyclohexanone (Table 1). The LRP was generated by quenching the reaction after a series of times spanning several orders of magnitude, and measuring the yields of 3-phenylcyclohexanone using GLC and the internal standard method.^[15] The lower order cyanocuprate PhCuCNLi is very unreactive under these conditions with no product formation observed even after 1 h. However, addition of PPh_3 increases the yields significantly to 29% after 1 h. The yields are larger still for the higher order cyanocuprate and this can be explained by double the concentration of cuprate anions in solution for $\text{Ph}_2\text{CuCNLi}_2$ than **4**, and also by the differing nature of the cations in the two reagents, with the larger more sterically hindered cations in

4 likely to favor the formation of SSIPs rather than the more reactive CIP species.^[16]

Conclusion

Addition of PPh_3 to the “lower-order” cyanocuprate PhCuCNLi drastically alters its structure by promoting the formation of $[\text{CuPh}_2]^-$ cuprate units both in THF solution (observed using multi-nuclear and variable temperature NMR spectroscopy) and in the solid state (observed using single-crystal X-ray diffraction). Such cuprate units have been previously reported in “higher-order” cyanocuprates and Gilman cuprates, but this is the first time they have been observed in a formally “lower-order” cyanocuprate. The addition of PPh_3 is also shown to increase the reactivity of PhCuCNLi in Michael addition reactions with 2-cyclohexanone, and this increase in reactivity can be explained by the observed structural changes in the reagent on addition of phosphane, in particular the generation of the anionic $[\text{R}_2\text{Cu}]^-$ cuprate units.

Experimental Section

General Remarks: CuCN (Fluka > 99%), PPh_3 (Aldrich 99%) and 2-cyclohexene-1-one (Lancaster Synthesis 97%) were used without further purification. Pure, halogen-free PhLi was synthesized prior to use by reaction of equimolar amounts of PhI with $n\text{BuLi}$ in hexane at 0 °C.^[19] THF and diethyl ether were distilled from over sodium wire/benzophenone. Unless otherwise stated, all manipulations were carried out under nitrogen using either a glove box or double-manifold vacuum line. Dry ice/2-propanol baths were used for reactions at -78 °C. GC analyses were performed with an Agilent GC4890 gas chromatograph equipped with FID detector and a 25-m SGE BPX5 capillary column [0.22 mm i.d., 0.25 micron film, cross-linked 5% phenyl (equiv.) polysilphenylene-siloxane]. The GC was calibrated with authentic product (3-phenylcyclohexanone) and dodecane (Aldrich 99%) as internal standard. NMR spectra were recorded on a Jeol EX270 Delta Upgrade or a Bruker AM-500 spectrometer. External standards used were TMS (^1H , ^{13}C) 85% H_3PO_4 (^{31}P) and $\text{LiCl}/\text{D}_2\text{O}$ (^7Li).

Synthesis of $[\text{Cu}_2\text{Li}_4(\text{CN})_4(\text{PPh}_3)_4(\text{THF})_{10}]\cdot 2[\text{Ph}_2\text{Cu}]$ (4**):** A solution of PhLi (1.8 M in cyclohexane/diethyl ether; 1.1 mL, 2.0 mmol) was added to a suspension of CuCN (0.180 g; 2.0 mmol) in THF (10 mL) at -78 °C followed by dropwise addition of PPh_3 (0.577 g; 2.2 mmol) in THF (5 mL). The resulting clear yellow solution was warmed to 0 °C, filtered through celite and reduced in vacuo to 10 mL. On storage for 72 h at -30 °C, crystals of **4** were obtained in 46% yield (0.57 g). M.p. $118\text{--}122$ °C (dec.). Note that NMR studies on the reaction mix, as detailed in the main text, indicate a near quantitative yield based on PhLi and CuCN consumption. Due to the extreme air and moisture sensitive nature of **4** we were unable to obtain satisfactory elemental analyses. ^1H NMR spectroscopy (270 MHz, $[\text{D}_6]\text{DMSO}$, 298 K): $\delta = 7.09\text{--}7.44$ (m, 70 H, PPh_3 , CuPh_2), 3.58 (m, 20 H, THF), 1.72 (m, 20 H, THF) ppm – note that some THF was lost during the isolation procedure. ^{13}C NMR spectroscopy (101 MHz, THF, 173 K): $\delta = 174.20$ (CN), 141.33 (Cu-*ipso*-Ph), 137.49–124.97 (Cu-*olm*/*p*-Ph, PPh_3), 67.57 (THF), 25.84 (THF) ppm. ^{31}P NMR spectroscopy (109.38 MHz, THF, 298 K): $\delta = -2.54$ ppm. ^7Li NMR spectroscopy

Table 1. LRP data for reactions of (a) PhCuCNLi , (b) **4** and (c) $\text{Ph}_2\text{CuCNLi}_2$ with 2-cyclohexanone in THF, showing the yields (%) of 3-phenylcyclohexanone

Reagent ^[a]	Time [h]			
	0.001	0.01	0.1	1
(a) PhCuCNLi	0	0	0	0
(b) $\text{PhCuCNLi} + \text{PPh}_3$ (4)	1	3	22	29
(c) $\text{Ph}_2\text{CuCNLi}_2$	19	53	66	70

^[a] Reactions were carried out at -78 °C on a 1 mmol scale at 0.1 M in THF. Quench: 6 mL of saturated aqueous ammonium chloride/ammonia (90:10).

(194.31 MHz, THF, 298 K): $\delta = -2.44, -3.36$ ppm. IR (THF, 25 °C): $\tilde{\nu} = 2120$ (s) cm^{-1} ($\text{C}\equiv\text{N}$).

Logarithmic Reactivity Profiles (LRPs): The three cuprate reagents used were prepared as follows: (a) PhCuCNLi . CuCN (4 mmol, 358 mg) and PhLi (4 mmol, 336 mg) were weighed out into a 250 mL Schlenk flask equipped with a stirrer bar, and cold THF (40 mL, -78 °C) was added, and the flask was maintained at a temperature of -78 °C. The reaction mixture was stirred for 6 min and then warmed up to 0 °C for 6 min to anneal the reagent before it was cooled back to -78 °C; (b) $\text{PhCuCNLi} + \text{PPh}_3$ (**4**). CuCN (4 mmol, 358 mg) and PPh_3 (4 mmol, 336 mg) were weighed out into a 250 mL Schlenk flask equipped with a stirrer bar. PhLi (4 mmol, 336 mg) was weighed out into a separate Schlenk flask equipped with a stirrer bar. Cold THF (20 mL, -78 °C) was added with a syringe into each Schlenk flask, and both solutions were stirred for 10 min at room temperature making sure that the PhLi had completely dissolved. Both Schlenk flasks were then immersed in a cooling bath (-78 °C), and the PhLi solution was transferred with a cannula into the THF suspension of CuCN/PPh_3 . The reaction mixture was stirred for 6 min and then warmed up to 0 °C for 6 min to anneal the reagent before it was cooled back to -78 °C; (c) $\text{Ph}_2\text{CuCNLi}_2$. CuCN (4 mmol, 358 mg) and PhLi (8 mmol, 672 mg) were weighed out into a 250 mL Schlenk flask equipped with a stirrer bar. Cold THF (40 mL, -78 °C) was added, and the flask was maintained at a temperature of -78 °C. The resulting cloudy suspension was stirred at -78 °C for 18 min to give a clear yellow solution.

For all cuprates (a)–(c): After a further 6 min of stirring at -78 °C, 10 mL of the reagent was transferred with a syringe into each of four 25 mL flasks. The flasks were predried overnight in an oven at 120 °C and taken into the glove box where they were equipped with a stirrer bar and a rubber septum. They were kept under a positive nitrogen pressure throughout the experiment. A solution of 2-cyclohexene-1-one (96 mg, 1 mmol) in THF (1 mL) was added to the flask with a syringe. The stopwatch was started when the plunger was pushed. After the appropriate LRP time, a quench solution consisting of 6 mL of saturated aqueous ammonium chloride/ammonia (90:10) was injected. The LRP times used were 1 h = 60 min, 0.1 h = 6 min, 0.01 h = 36 s, 0.001 h = 4 s. After quenching the reaction, the flask was removed from the dry ice/2-propanol bath and warmed in warm water until it reached room temperature. The internal GC standard (dodecane, 227 μL , 1 mmol) was then added. The aqueous layer was removed using a pipette, and the organic layer filtered into a vial. The flask and residue were rinsed with diethyl ether (5 mL), and the combined organic layer and ether extract were dried over MgSO_4 . A sample of the quenched reaction mixture was then run on the GC to ascertain the percentage yield of 3-phenylcyclohexanone. Repeat experiments indicated an experimental error of up to a maximum of $\pm 10\%$ (see reference 15 for a thorough discussion of experimental errors in LRP studies of cuprates).

X-ray Crystallographic Data for 4: $\text{C}_{147}\text{H}_{168}\text{Cu}_4\text{Li}_4\text{N}_4\text{O}_{10}\text{P}_4$, $M_r = 2556.65$, monoclinic, space group $P2_1/c$, $a = 20.240(2)$, $b = 16.112(3)$, $c = 24.575(3)$ Å, $\beta = 113.37(2)^\circ$, $V = 7356.6(18)$ Å³, $Z = 2$ (C_i symmetry), $\rho_{\text{calcd.}} = 1.154$ g·cm⁻³, Mo- K_α radiation, $\lambda = 0.71069$ Å, $\mu = 0.668$ mm⁻¹, $T = 230(2)$ K. 14981 unique data ($R_{\text{int}} = 0.1147$, $\theta < 27.24^\circ$) were collected on a Nonius Kappa CCD diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 values of all data using the SHELXTL and SHELX-97 program systems,^[20] to give $wR2 = 0.3492$, conventional $R = 0.1069$ for 7011 observed

absorption-corrected reflections with $F^2 > 2\sigma(F^2)$, $S = 1.035$, 667 parameters. Residual electron density extrema ± 1.165 e·Å⁻³. Since it proved impossible to differentiate between the cyanide carbon and nitrogen atoms crystallographically, these atoms have been assigned based on previously reported structural characterizations of cyanocuprates, all of which contain the cyanide unit attached to the copper through the carbon end and linear carbon atoms.^[4,7] CCDC-226575 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.): +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

We thank the donors of the American Chemical Society Petroleum Research Fund for support of this research.

- [1] [1a] R. J. K. Taylor, *Organocopper Reagents* (Series Eds.: L. M. Harwood, C. J. Moody), Oxford University Press, **1994**. [1b] J. A. Kozlowski, in *Comprehensive Organic Synthesis* (Eds.: B. M. Trost, I. Fleming), Pergamon, Oxford, **1991**, vol. 4, pp. 169–198. [1c] B. H. Lipshutz, in *Comprehensive Organometallic Chemistry II* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, Oxford, **1995**, vol. 12, pp. 194–213. [1d] N. Krause, A. Gerold, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 186–204. [1e] N. Krause, *Modern Organocopper Chemistry*, Wiley-VCH, Weinheim, **2002**.
- [2] B. H. Lipshutz, *Synlett* **1990**, 119–128.
- [3] S. H. Bertz, *J. Am. Chem. Soc.* **1991**, *113*, 5470–5471.
- [4] C. Eaborn, M. S. Hill, P. B. Hitchcock, J. D. Smith, *Organometallics* **2000**, *19*, 5780–5783.
- [5] C.-S. Hwang, P. P. Power, *J. Am. Chem. Soc.* **1998**, *120*, 6409–6410.
- [6] F. Bosold, M. Marsch, K. Harms, G. Boche, *Z. Kristallogr. New Cryst. Struct.* **2001**, *216*, 143–144.
- [7] G. Boche, F. Bosold, M. Marsch, K. Harms, *Angew. Chem. Int. Ed.* **1998**, *37*, 1684–1685.
- [8] C. M. P. Kronenburg, J. T. B. H. Jastrzebski, A. L. Spek, G. van Koten, *J. Am. Chem. Soc.* **1998**, *120*, 9688–9689.
- [9] H. Huang, K. Alvarez, Q. Lui, T. M. Branhart, J. P. Snyder, J. E. Penner-Hahn, *J. Am. Chem. Soc.* **1996**, *118*, 8808–8816.
- [10] S. H. Bertz, *J. Am. Chem. Soc.* **1990**, *112*, 4031–4032.
- [11] B. H. Lipshutz, B. James, *J. Org. Chem.* **1994**, *59*, 7585–7587.
- [12] S. H. Bertz, G. Miao, M. Eriksson, *Chem. Commun.* **1996**, 815–816.
- [13] X. Xie, C. Auel, W. Henze, R. M. Gschwind, *J. Am. Chem. Soc.* **2003**, *125*, 1595–1601.
- [14] A. Gerold, J. T. B. H. Jastrzebski, C. M. P. Kronenburg, N. Krause, G. van Koten, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 755–757.
- [15] S. H. Bertz, A. Chopra, M. Eriksson, C. A. Ogle, P. Seagle, *Chem. Eur. J.* **1999**, *5*, 2680–2691.
- [16] M. John, C. Auel, C. Behrens, M. Marsch, K. Harms, F. Bosold, R. M. Gschwind, P. R. Rajamohanam, G. Boche, *Chem. Eur. J.* **2000**, *6*, 3060–3068.
- [17] N. Krause, *Angew. Chem. Int. Ed.* **1999**, *38*, 79–81.
- [18] M. P. Coles, P. B. Hitchcock, *Polyhedron* **2001**, *20*, 3027–3032.
- [19] E. Wehman, J. T. B. H. Jastrzebski, J.-M. Ernsting, D. M. Grove, G. van Koten, *J. Organomet. Chem.* **1988**, *353*, 133–143.
- [20] G. Sheldrick, SHELXTL PC version 5.1, Bruker AXS, Madison, WI, **1997** and SHELX-97, Institut Anorg. Chemie, Tammannstr. 4, 37077 Göttingen, Germany, **1998**.

Received August 9, 2004