

300-nm light are employed, the same photostationary state is reached. This results in a decrease of the CD absorptions at 232 and 262 nm to 33% of the original values for **M-cis 1a**. Alternating irradiation at two wavelengths, $\lambda_1 = 250$ nm and $\lambda_2 = 300$ nm, results in a modulated CD signal at 232 and 262 nm. A typical example using a switching time of 3 s is shown in Figure 1. Similar cycles were found using switching times between 0.5 and 60 s. The cycle between the two photostationary states could be repeated at least 10 times without racemization or changes in UV and CD spectra.

Several features should be emphasized that were essential for the successful demonstration of this new principle of a chiroptical molecular switch: the remarkable thermal stability, the photoisomerization between two "pseudoeantiomeric"⁹ helical systems without racemization, the stability toward photodegradation, and the large chiroptical effects that arise from the inherently dissymmetric structure.

Approaches to optimize the structure-property relations are currently under investigation.

Acknowledgment. Discussions with Professor N. Harada, Institute of Non-Aqueous Solutions, Tohoku University, Sendai, on circular dichroism are gratefully acknowledged.

Supplementary Material Available: Synthetic scheme and spectroscopic and analytical data for **1**, **2**, and precursors and details of HPLC separations (5 pages). Ordering information is given on any current masthead page.

Lithium Cyanocuprates, $\text{RCu}(\text{CN})\text{Li}$: First Observation of Two-Bond ^{13}C - ^{13}C NMR Couplings in Organocuprates¹

Steven H. Bertz

AT&T Bell Laboratories
Murray Hill, New Jersey 07974

Received November 1, 1990

NMR coupling constants have proven to be a rich source of structural information on organic and organometallic compounds.²⁻⁵ For example, ^6Li - ^{13}C J -coupling has allowed the structures of many organolithium compounds to be elucidated.^{4,5} Unfortunately, ^6Li - ^{13}C and ^7Li - ^{13}C couplings are generally not observed for organocuprates,⁶ making the determination of their solution structures a difficult problem. Consequently, investigations were undertaken to find other coupling constants that would provide structural information on organocuprates. It can now be reported that under appropriate conditions two-bond ^{13}C - ^{13}C couplings ² J can be observed for some types of organocuprates.

When 1 equiv of $\text{CH}_3\text{CH}_2^6\text{Li}$ is added to Cu^{13}CN in tetrahydrofuran- d_8 (THF- d_8), the ^1H -decoupled ^{13}C NMR spectrum obtained at -78 °C shows singlets at δ 149.1 and 15.54 ppm for the ^{13}CN and ethyl C2 resonances and a doublet ($J = 22$ Hz) for the ethyl C1 resonance at 1.64 ppm (Table I). In contrast, the

use of natural abundance CuCN results in a singlet for C1 at 1.68 ppm. These results establish that both the Et and the CN are bonded to the same Cu, which is consistent with the designation of this reagent as $[\text{EtCuCN}]\text{Li}^+$ or, more commonly, $\text{EtCu}(\text{CN})\text{Li}$.

For $\text{EtCu}^{13}\text{CN}\text{Li}$ in ether- d_{10} at -78 °C, C1 is a singlet at δ 1.85 ppm (Table I). Upon cooling to -100 °C, C1 is a doublet ($J = 21$ Hz). Alternatively, if hexamethylphosphoramide (HMPA, ~ 10 % by volume) is added to the ether solution at -78 °C, C1 is a doublet at 2.04 ppm ($J = 22$ Hz). Apparently, some exchange mechanism removes the coupling at -78 °C in ether. The effect of HMPA suggests that Li^+ is involved in the exchange process, since its complexation by HMPA slows the exchange sufficiently to allow the coupling to be observed.

Upon the addition of a second equivalent of Et^6Li to the THF- d_8 solution of $\text{EtCu}^{13}\text{CN}^6\text{Li}$, and ^{13}C NMR spectrum at -100 °C contains three singlets at 158.7, 17.35, and 4.76 ppm for the CN, C2 and C1, respectively. Even in the presence of HMPA (~ 10 vol %, -78 °C) or HMPA and 12-crown-4 (12-C-4, 2 equiv, -78 °C and -100 °C), the CN-C1 coupling is absent in the 2:1 reagent, which we represent as $\text{Et}_2\text{CuLi}\cdot\text{LiCN}$.

The addition of $^{13}\text{CH}_3^6\text{Li}$ to Cu^{13}CN in THF- d_8 yields $^{13}\text{CH}_3\text{Cu}^{13}\text{CN}\text{Li}$, which must be cooled to -110 °C in order for a ^1H -decoupled ^{13}C NMR spectrum comprising two doublets ($J = 21$ Hz) at 149.0 ppm (CN) and -12.46 ppm (Me) to be observed. At -78 °C and -100 °C the spectrum is a pair of singlets; however, upon the addition of HMPA (~ 10 vol %) to the solution, coupling ($J = 22$ Hz) is observed at -78 °C as well as at -100 °C.

As in the ethyl case, exchange in $\text{CH}_3\text{Cu}^{13}\text{CN}\text{Li}$ is more facile in ether- d_{10} than in THF- d_8 : the methyl singlet at -78 °C broadens at -100 °C and splits into a partially resolved doublet ($J = 12$ Hz) at -110 °C and finally into a doublet ($J = 22$ Hz) at -120 °C. The addition of HMPA (~ 10 vol %) allows the doublet ($J = 22$ Hz) to be observed at -78 °C.⁷ Apparently, exchange is more facile in $\text{MeCu}(\text{CN})\text{Li}$ than in $\text{EtCu}(\text{CN})\text{Li}$ in both THF- d_8 and ether- d_{10} .

At -100 °C in THF- d_8 , $(^{13}\text{CH}_3)_2\text{CuLi}\cdot\text{Li}^{13}\text{CN}$ has a spectrum that consists of two singlets (158.8 ppm, CN; -9.20 ppm, CH_3) that are not split into doublets by the addition of HMPA (~ 10 vol %, -78 °C and -100 °C) or HMPA and 12-crown-4 (2 equiv, -78 °C), as is also true for $\text{Et}_2\text{CuLi}\cdot\text{Li}^{13}\text{CN}$ (above).

In the case of $\text{PhCu}^{13}\text{CN}\text{Li}$ in THF- d_8 , C1 is a singlet (δ 166.0 ppm) at -78 °C, a broad doublet (166.0 ppm, $J = 13$ Hz) at -100 °C, and a sharp doublet (δ 165.9 ppm, $J = 23$ Hz) at -110 °C. In contrast to the alkyl cases, exchange in $\text{PhCu}^{13}\text{CN}\text{Li}$ is slower in ether- d_{10} than in THF- d_8 and the full coupling is observed at -100 °C. The addition of HMPA at -78 °C results in a doublet ($J = 24$ Hz) in both THF- d_8 and ether- d_{10} .

In analogy with both $(^{13}\text{CH}_3)_2\text{CuLi}\cdot\text{Li}^{13}\text{CN}$ and $\text{Et}_2\text{CuLi}\cdot\text{Li}^{13}\text{CN}$, $\text{Ph}_2\text{CuLi}\cdot\text{Li}^{13}\text{CN}$ has a singlet for C1 at -100 °C in THF- d_8 or ether- d_{10} . Addition of HMPA (~ 10 vol %, -78 °C) or HMPA and 12-crown-4 (2 equiv, -78 °C) did not cause coupling to be observed.

As may be seen in Table I, the addition of 12-crown-4 to the solutions of $\text{RCu}^{13}\text{CN}\text{Li}$ in THF- d_8 or ether- d_{10} containing HMPA does not significantly change the coupling constants.⁸ The addition of HMPA to $\text{RCu}(\text{CN})\text{Li}$ causes an upfield shift of the CN resonance due to increased back-bonding into CN π^* orbitals, which decreases the multiple-bond character.

This study establishes that the reagents prepared from 1 equiv of RLi and CuCN are indeed cyanocuprates $\text{RCu}(\text{CN})\text{Li}$ in which R and CN are both bonded to Cu. This is important because in the case of the so-called "higher order" cyanocuprates, which have been represented as $\text{R}_2\text{Cu}(\text{CN})\text{Li}_2$, evidence has been presented that the CN is not bonded to Cu;⁹ consequently, we represent them

(1) New Copper Chemistry. 20. Part 19; Bertz, S. H.; Dabbagh, G.; Mujica, A. M. *J. Am. Chem. Soc.* 1991, 113, 631.

(2) Maciel, G. E. *Nuclear Magnetic Resonance Spectroscopy of Nuclei Other Than Protons*; Axenrod, T., Webb, G. A., Eds.; Wiley: New York, 1974; p 187.

(3) Marshall, J. L. *Carbon-Carbon and Carbon-Proton NMR Couplings*; Verlag Chemie International: Deerfield Beach, FL.

(4) Fraenkel, G.; Hsu, H.; Su, B. M. *Lithium*; Bach, R. O., Ed.; Wiley: New York, 1985; p 273.

(5) Seebach, D.; Hässig, R.; Gabriel, J. *Helv. Chim. Acta* 1983, 66, 308.

(6) One example of ^7Li - ^{13}C coupling has been reported: van Koten, G.; Noltes, J. G. *J. Am. Chem. Soc.* 1979, 101, 6593.

(7) The further addition of 12-crown-4 (2 equiv) also results in a doublet ($J = 22.0$ Hz, -11.93 ppm) at -78 °C, which begins to collapse ($J = 17.0$ Hz, -12.74 ppm) at -30 °C and becomes a broad singlet (-12.98 ppm) at -20 °C.

(8) The 12-crown-4 salts are not soluble without the HMPA present as a cosolvent.

Table I. ^{13}C NMR Spectra of Lithium Cyanocuprates

cuprates ^a	solvent ^b	temp. °C	C1 ^c	C2	C3	C4	CN
PhCu(^{13}C N)Li	THF- d_8	-78	166.05, s	140.94	126.08	123.87	148.50
	THF- d_8 /HMPA	-78	168.40, d ($J = 24.2$ Hz)	141.22	125.80	123.18	145.41
	THF- d_8 /HMPA/12-C-4	-78	168.38, d ($J = 24.2$ Hz)	141.21	125.80	123.19	145.43
	THF- d_8	-100	165.97, d ($J = 12.7$ Hz)	140.92	126.10	123.90	148.33
	THF- d_8 /HMPA	-100	168.33, d ($J = 23.7$ Hz)	141.19	125.83	123.23	145.38
	THF- d_8	-110	165.93, d ($J = 23.3$ Hz)	140.91	126.18	123.93	148.25
	ether- d_{10}	-78	166.03 (br s)	140.88	125.87	123.61	149.70
	ether- d_{10} /HMPA	-78	168.70, d ($J = 24.2$ Hz)	141.18	125.60	122.90	145.60
	ether- d_{10} /HMPA/12-C-4	-78	168.66, d ($J = 23.7$ Hz)	141.17	125.60	122.89	145.61
	ether- d_{10}	-100	165.99, d ($J = 24.2$ Hz)	140.82	125.85	123.57	149.42
$\text{CH}_3\text{CH}_2\text{Cu}(^{13}\text{C}\text{N})\text{Li}$	THF- d_8	-78	1.64, d ($J = 21.6$ Hz)	15.54			149.11
	THF- d_8 /HMPA/12-C-4	-78	1.92, d ($J = 22.0$ Hz)	16.05			146.47
	THF- d_8	-100	1.74, d ($J = 22.0$ Hz)	15.65			148.96
	ether- d_{10}	-78	1.85, s	15.32			150.86
	ether- d_{10} /HMPA	-78	2.04, d ($J = 22.0$ Hz)	15.92			146.76
	ether- d_{10} /HMPA/12-C-4	-78	2.05, d ($J = 21.6$ Hz)	15.93			146.76
	ether- d_{10}	-100	1.89, d ($J = 20.8$ Hz)	15.47			150.10
	ether- d_{10} /HMPA	-100	2.17, d ($J = 21.6$ Hz)	16.04			146.69
	ether- d_{10} /HMPA/12-C-4	-100	2.17, d ($J = 21.6$ Hz)	16.03			146.67
	ether- d_{10}	-78	-12.85, s				149.34
$^{13}\text{CH}_3\text{Cu}(^{13}\text{C}\text{N})\text{Li}$	THF- d_8 /HMPA	-78	-12.36, d ($J = 22.0$ Hz)				146.48, d
	THF- d_8 /HMPA/12-C-4	-78	-12.42, d ($J = 21.6$ Hz)				146.56, d
	THF- d_8	-100	-12.60 (br s)				149.13
	THF- d_8 /HMPA	-100	-12.04, d ($J = 21.6$ Hz)				146.36, d
	THF- d_8	-110	-12.46, d ($J = 20.8$ Hz)				148.97, d
$\text{CH}_3\text{Cu}(^{13}\text{C}\text{N})\text{Li}$	ether- d_{10}	-78	-12.58, s				151.01
	ether- d_{10} /HMPA	-78	-11.97, d ($J = 21.6$ Hz)				146.76
	ether- d_{10} /HMPA/12-C-4	-78	-11.93, d ($J = 21.6$ Hz)				146.77
	ether- d_{10}	-100	-12.25 (br s)				150.20
	ether- d_{10}	-110	-12.10, d ($J = 12.3$ Hz)				149.95
	ether- d_{10}	-120	-11.93, d ($J = 21.6$ Hz)				149.78

^aIn the cases of EtCu(CN)Li and of MeCu(CN)Li in THF- d_8 , the Li is ^6Li . ^bTo 3 mL of THF- d_8 or ether- d_{10} were added 312 μL of HMPA and 100 μL of 12-C-4. ^cChemical shifts are referenced to the δ 67.391 line in the spectrum of THF- d_8 and the 14.707 ppm line in the spectrum of ether- d_{10} . J values are ± 0.04 Hz. The spectra were obtained on a Bruker AM360 NMR spectrometer.

as $\text{R}_2\text{CuLi}\cdot\text{LiCN}$. The lack of coupling between ^{13}CN and C1 in $\text{R}_2\text{CuLi}\cdot\text{Li}^{13}\text{CN}$ also mitigates against the higher order formulation, although exchange may be responsible for the lack of coupling in these cases.

Dimethylmercury is a linear molecule that has a value of $^2J = 22.4$ Hz.¹⁰ The relatively large magnitude of 2J for $\text{RCu}(\text{CN})\text{Li}$ suggests a linear structure as well. The two-bond ^{13}C - ^{13}C couplings between cis carbonyls (bond angle 90°) in a series of pentacarbonyl metal-carbene complexes fall in the range 2.7-5.4 Hz.¹¹ The magnitude of 2J is dependent upon the hybridization of the intervening orbitals;² however, in our case this effect is small, as can be seen by comparing our values for phenyl- and alkylcuprates.

The addition of 12-crown-4 to cuprates has been shown to yield monomeric species,¹² and the addition of HMPA to PhLi aggregates has been shown to yield monomers as well.¹³ Consequently, we presume that $\text{RCu}(\text{CN})\text{Li}$ is monomeric in the presence of HMPA and 12-crown-4. When $\text{RCu}(\text{CN})\text{Li}$ is cooled to a low enough temperature, it is possible to obtain 2J equal to the value in the presence of HMPA and 12-crown-4, where coupling is observed at -78 °C in every case. This observation does not necessarily imply monomers at those temperatures, since the RCuCN units in a dimer might be linear.¹⁴ Nevertheless, it has been shown that Li reagents afford smaller aggregates as the temperature is lowered in coordinating solvents.⁴ Under those conditions where coupling in $\text{RCu}(^{13}\text{C}\text{N})\text{Li}$ is not observed, an

exchange process mediated by Li appears to be involved. This exchange may involve the formation of dimers.

Registry No. PhCu(^{13}C N)Li, 133930-77-5; $\text{CH}_3\text{CH}_2\text{Cu}(^{13}\text{C}\text{N})\text{Li}$, 133930-78-6; $^{13}\text{CH}_3\text{Cu}(^{13}\text{C}\text{N})\text{Li}$, 133930-79-7; $\text{CH}_3\text{Cu}(^{13}\text{C}\text{N})\text{Li}$, 133930-80-0.

Supplementary Material Available: NMR spectra of $[\text{CH}_3\text{CH}_2\text{Cu}^{13}\text{CN}]^{-6}\text{Li}^+$ and $[\text{CH}_3\text{CH}_2\text{CuCN}]^{-6}\text{Li}^+$ (1 page). Ordering information is given on any current masthead page.

Design and Synthesis of New Ferroelectric Liquid Crystals. 14.¹ An Approach to the Stereocontrolled Synthesis of Polar Organic Thin Films for Nonlinear Optical Applications

David M. Walba,* M. Blanca Ros,[†] Noel A. Clark,[‡] Renfan Shao,[‡] Michael G. Robinson,[§] Jian-Yu Liu,[§] Kristina M. Johnson,[§] and David Doroski[§]

Department of Chemistry and Biochemistry and Optoelectronic Computing Systems Center University of Colorado, Boulder, Colorado 80309-0215

Received March 13, 1991

Optical quality thin film materials possessing large $\chi^{(2)}$ (second-order nonlinear optical (NLO) susceptibility) are of clear

(9) Bertz, S. H. *J. Am. Chem. Soc.* **1990**, *112*, 4031. For a rebuttal to this paper, see: Lipshutz, B. H.; Sharma, S.; Ellsworth, E. L. *J. Am. Chem. Soc.* **1990**, *112*, 4032.

(10) Dreeskamp, H.; Hildenbrand, K.; Pfisterer, G. *Mol. Phys.* **1969**, *17*, 429.

(11) Casey, C. P.; Cesa, M. C. *Organometallics* **1982**, *1*, 87.

(12) Hope, H.; Olmstead, M. M.; Power, P. P.; Sandell, J.; Xu, X. *J. Am. Chem. Soc.* **1985**, *107*, 4337.

(13) Reich, H. J.; Green, D. P.; Phillips, N. H. *J. Am. Chem. Soc.* **1989**, *111*, 3444.

(14) Stewart, K. R.; Lever, J. R.; Whangbo, M.-H. *J. Org. Chem.* **1982**, *47*, 1472.

[†] Current address: Quimica Orgánica, Facultad de Ciencias-I.C.M.A., Universidad de Zaragoza-C.S.I.C., 50009-Zaragoza, Spain.

[‡] Department of Physics and Optoelectronic Computing Systems Center, University of Colorado, Boulder, CO 80309-0390.

[§] Department of Electrical and Computer Engineering and Optoelectronic Computing Systems Center, University of Colorado, Boulder, CO 80309-0425.