Chemistry, Vol. 6 (Eds.: J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle), Pergamon, Oxford, **1996**, pp. 425–482.

[16] The values for K, ΔH, and ΔS were also determined by the Benesi–Hildebrand method.[14, 15] K values in [D$_6$]acetone: 135 M^{-1} at 21.8 °C, 98.1 M^{-1} at 30.0 °C, 65.6 M^{-1} at 38.0 °C, 46.1 M^{-1} at 46.0 °C, 34.9 M^{-1} at 54.0 °C; $\Delta H = -34.6 \times 10^4$ J mol^{-1}; $\Delta S = -76.2$ J K^{-1} mol^{-1} (Figure 3 b).

[17] The crystal structure of **3c** indicates an open cavity (4.9 × 7.8 Å) which undergoes a small conformational change when it complexes with paraquat.[12a] However, **3d** in the solid state has a collapsed cavity (0.75 × 7.8 Å), perhaps due to crystal packing forces and not intrinsic conformational preferences: Y. Delaviz, J. S. Merola, M. A. G. Berg, H. W. Gibson, *J. Org. Chem.* **1995**, *60*, 516–522.

[18] The values for m/n were calculated by the method specified in ref. [14].

[19] The solution of **5** and **6** in acetone was slowly cooled to −90 °C and then frozen with an acetone/dry ice bath. The solvent was removed under high vacuum to afford an orange solid, pseudopolyrotaxane **7**. The m/n value was calculated from K (4748 M^{-1}), which was estimated from the measured ΔH and ΔS values.

The Use of ^{15}N NMR Spectroscopy To Resolve the "Higher Order Cyanocuprate" Controversy: ^{15}N, ^{6}Li, and ^{13}C NMR Spectroscopic Investigations of CuCN-Derived Butyl Cuprates**

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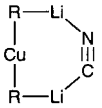
In the modern era of organocopper chemistry,[1] the first cyanocuprate experiments involved the addition of one equivalent of RLi to CuCN to prepare cyanocuprates RCu(CN)Li.[2] Two-bond ^{13}C-^{13}C coupling constants ^2J across copper proved that the R group and the CN group are both bonded to the same Cu in these 1:1 reagents.[3] In 1981 Lipshutz et al. added two equivalents of RLi to CuCN and claimed not only a new class of highly reactive reagents but a new *kind* of organocopper(I) species, the "higher order cyanocuprates."[4] Spectroscopic evidence was not presented, but NMR and IR data were reported later.[5]

Subsequently, Bertz showed that the ^{13}C NMR chemical shifts of the cuprates prepared from two equivalents of RLi and CuCN or CuI were the same and that the shift of the CN carbon atom was independent of the electronic nature of R.[6] In contrast, the chemical shifts of the CN carbon atoms in the "lower order" cyanocuprates RCu(CN)Li vary with R.[3, 6] These observations and the absence of ^2J in the 2:1 compounds cast grave doubt on the higher order formulation R$_2$Cu(CN)Li$_2$.[4, 7] Extended X-ray absorption fine structure (EXAFS)[8, 9] investigations by Penner-Hahn, Knochel, Frenking et al. and IR[10] studies by Penner-Hahn, Snyder et al. supported the conclusions of these NMR studies. Theoretical investigations by Snyder et al.[11] and Penner-Hahn, Knochel, Frenking et al.[9] indicated that higher order structures are 20–30 kcal mol^{-1} higher in energy than lower order alternatives.

Various lower order structures have been proposed for the 2:1 reagents, for example, **1**–**3**. They are related to the Gilman dimer **4** by the substitution of CN$^-$ for R$_2$Cu$^-$ in three archetypal ways : 1) one Li atom is attached to N and one to C, 2) both Li atoms are bonded to N, and 3) both Li atoms are bonded to C. While initial theoretical studies favored variants of **1**–**3**,[11] all of these cyano-Gilman reagents are close enough in energy to be viable candidates. We have now prepared the 1:1 and 2:1 reagents, BuCu(C^{15}N)^{6}Li and Bu$_2$Cu^{6}Li · ^{6}LiC^{15}N, respectively, as well as intermediate stoichiometries from Bu^{6}Li and CuC^{15}N.[12] The results of this ^{15}N NMR study, coupled with theoretical calculations reported herein, strongly support structure **1** over the others.



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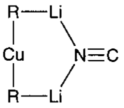

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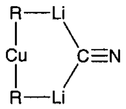

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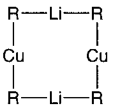

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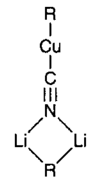

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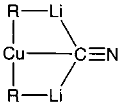

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Figure 1 shows the ^{15}N NMR spectra of solutions in [D$_8$]THF at −80 °C when a) 1.0, b) 1.3, or c) 2.0 equivalents of Bu^{6}Li is added to CuC^{15}N.[12] The 1:1 reagent BuCu(C^{15}N)-^{6}Li is characterized by a singlet at $\delta = -129.3$ (6 Hz width at

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1433-7851/98/3703-0314 $ 17.50+.50/0

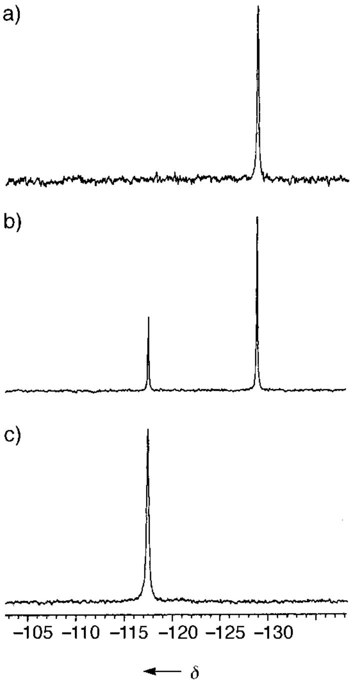

Figure 1. ^{15}N NMR spectra (50.65 MHz) in [D$_8$]THF at $-80\,^\circ$C of the cuprates prepared from various ratios of Bu^{6}Li:CuC^{15}N: a) 1:1, b) 1.3:1, and c) 2:1.

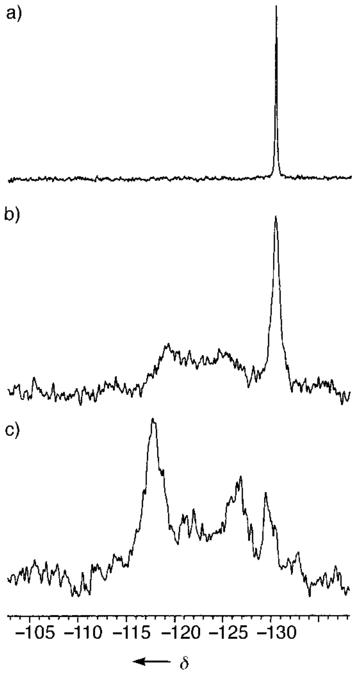

Figure 2. ^{15}N NMR spectra (50.65 MHz) in [D$_{10}$]diethyl ether at $-80\,^\circ$C of the cuprates prepared from various ratios of Bu^{6}Li:CuC^{15}N: a) 1:1, b) 1.4:1, and c) 2:1.

half-height, $\Delta\nu_{1/2}$), measured on a scale that assigns a value of $\delta = 0$ to neat nitromethane and $\delta = -77.7$ to trimethylsilylcyanide (TMSCN).[13] The spectrum of the 2:1 reagent Bu$_2$Cu^{6}Li$\cdot$^{6}LiC^{15}N is a singlet at $\delta = -117.5$ ($\Delta\nu_{1/2} = 10$ Hz) under these conditions. The spectrum of a mixture with intermediate stoichiometry (Figure 1b) has both peaks at their characteristic chemical shifts in the expected ratio. No "free" ^{6}LiC^{15}N is observed in any of these spectra.

Figure 2a shows that the ^{15}N NMR spectrum of the 1:1 reagent in [D$_{10}$]ether at $-80\,^\circ$C is also a singlet ($\delta = -130.5$, $\Delta\nu_{1/2} = 6$ Hz). It is critical that the BuLi be added slowly with sonication if the BuCu(CN)Li is to be obtained as pure as in Figure 2a. In contrast, the spectrum of the 2:1 reagent (Figure 2c) is dramatically different in [D$_{10}$]diethyl ether: there is a relatively broad peak at $\delta = -118.0$ ($\Delta\nu_{1/2} = 120$ Hz), but there is also a plethora of peaks at chemical shifts between the values for the 2:1 and 1:1 species. The intermediate peaks are due to aggregates (see below). Upon warming the sample to $-50\,^\circ$C, all the ^{15}N peaks in this spectrum coalesce into a single broad peak ($\delta = -121.5$, $\Delta\nu_{1/2} = 55$ Hz).

With 1.4:1 stoichiometry in [D$_{10}$]diethyl ether (Figure 2b), there was little of the 2:1 reagent ($\delta = -118$, 5%) relative to the 1:1 reagent ($\delta = -130.5$, $\Delta\nu_{1/2} = 50$ Hz, 35%) or "intermediate" species. When the reactant ratio was reduced to 1.3:1, the $\delta = -118$ peak increased to 15% of the total area as the intermediate peaks decreased to 25%, and when this solution was cooled from $-80\,^\circ$C to $-100\,^\circ$C, it further increased to 25% as the intermediate area diminished to 10%. The addition of THF to the [D$_{10}$]diethyl ether solution also converts the intermediate peaks cleanly to the $\delta = -118$ and -130 peaks. The effects of solvent, concentration, and temperature are similar to those observed for RLi,[14] and it can be concluded that the intermediate peaks in this case correspond to aggregates derived from both cuprates.[15]

The ^{6}Li NMR spectra contain vital new information.[12b] In [D$_8$]THF at $-80\,^\circ$C, the 1:1 and 2:1 reagents give rise to peaks at $\delta = -1.40$ ($\Delta\nu_{1/2} = 1$ Hz) and -1.18 ($\Delta\nu_{1/2} = 5$ Hz), respectively.[16] In the sample with 1.3:1 stoichiometry in [D$_8$]THF, there is a single peak at an intermediate chemical shift ($\delta = -1.25$, $\Delta\nu_{1/2} = 1$ Hz) instead of two peaks, as in the corresponding ^{15}N spectrum (Figure 1b). Apparently, an exchange process renders the Li ions equivalent, but not the N atoms. The ^{6}Li spectrum of BuCu(C^{15}N)^{6}Li in [D$_{10}$]diethyl ether is a single peak at $\delta = -0.87$ ($\Delta\nu_{1/2} = 2$ Hz). The major ^{6}Li peak in the spectrum of the 2:1 reagent in [D$_{10}$]diethyl ether is $\delta = -0.66$ ($\Delta\nu_{1/2} = 20$ Hz). The usual samples of the 2:1 reagent in this solvent had minor peaks at $\delta = 1.03$ and 1.90 (10.8% and 10.6% of the total area). These peaks have not been definitively assigned;[17] nevertheless, it is clear from the ^{15}N and ^{6}Li spectra that the situation in diethyl ether is much more complex than had previously been appreciated.

No ^{6}Li-^{15}N couplings could be observed for either the 1:1 or 2:1 reagent in [D$_{10}$]diethyl ether at temperatures down to $-110\,^\circ$C.[18] This is not unexpected: ^{6}Li-^{13}C couplings have not been observed for organocuprates R$_2$CuLi$\cdot$LiI, R$_2$CuLi$\cdot$LiCN or RCu(CN)Li (R = Me, Et, Bu, Ph),[3, 6] in spite of the fact that the corresponding organolithium compounds RLi do exhibit such couplings.[14] In light of the ^{6}Li NMR results presented above, rapid exchange of Li is responsible for the lack of coupling with this nucleus.

The only discernible ^{13}C-^{15}N coupling is the cyano-doublet ($J = 11.7$ Hz) at $\delta = 149.35$ ($\Delta\nu_{1/2} = 7$ and 9 Hz) in the ^{13}C spectrum of BuCu(C^{15}N)^{6}Li in [D$_8$]THF. Broadening precluded measurement of coupling in the CN peak ($\delta = 158.82$,

$\Delta\nu_{1/2} = 35$ Hz) for $Bu_2Cu^6Li \cdot {}^6LiC^{15}N$ in this solvent. In [D_{10}]diethyl ether $BuCu(C^{15}N)^6Li$ has a broad peak at $\delta = 150.96$ ($\Delta\nu_{1/2} = 80$ Hz), and the best spectrum of $Bu_2Cu^6Li \cdot {}^6LiC^{15}N$ has one at $\delta = 159.55$ ($\Delta\nu_{1/2} = 80$ Hz). Previously, ^{13}C NMR peaks at $\delta = 152$ and 163 were assigned without theoretical justification to "higher order" species.[5b]

The ^{15}N NMR chemical shifts measured for the 2:1 organocuprate in this study can be interpreted with the aid of calculations. Relative ^{15}N shifts were calculated by using Chesnut's locally dense basis set concept.[19] The calculations (Becke3LYP/6-311G*/GIAO)[20] were performed on the methyl analogues of **1**–**6** (R = Me) which also have one coordinated H_2O per Li to approximate ethereal solvation. We denote these hydrated methyl derivatives, which are the usual model compounds,[9, 11] as **1a**–**6a**. They were also performed on CN^- and TMSCN. We have scaled all the calculated ^{15}N NMR shifts so that TMSCN is set at the literature value $\delta = -77.7$.[13, 21] The ^{15}N NMR shift for "naked" CN^- is then $\delta = -125.8$, which is in reasonable agreement with the observed values for aqueous KCN ($\delta = -104$ to -106),[21] especially when the effect of solvation is considered. The calculated shifts for **1a**–**3a** are $\delta = -113.9$, -161.9, and -81.1, respectively, and for **5a** the calculated value is $\delta = -185.5$. Higher order structure **6a** has a calculated shift of $\delta = -81.2$. Only structure **1a** gives good agreement with the measured values (ca. $\delta = -118$) for the 2:1 species in this study.

There is no evidence that any of the minor species observed in solutions of the 2:1 reagent are higher order cuprates, which in any event would be unfavorable energetically.[11] Moreover, our results do not indicate how tightly the R_2Cu^- core in **1** is bonded to the $LiCNLi^+$ moiety, nor do they rule out minor equilibrium amounts of other species such as **2** or **3** (see below).

The IR stretching frequencies calculated for cyanide in methyl analogues **1a** and **3a** (2101 and 2099 cm^{-1}, respectively) are consistent with the observed value for $Me_2CuLi \cdot LiCN$ in THF (2115 cm^{-1}).[10] A recent ^{13}C NMR study by Berger et al. concluded that the "dimethylcuprate core" in $Me_2CuLi \cdot LiCN$ is the same as in "halide-free" Me_2CuLi,[22a] which is consistent with **1**–**3**, but not **5**. Cryoscopy indicates that $Me_2CuLi \cdot LiCN$ is essentially monomeric in THF,[22b] which is consistent with **1**–**3** or **5**, although some dissociation was postulated. ^{15}N NMR spectroscopy is the first technique that allows all the structures that have been proposed for the major component of the 2:1 reagent to be ruled out except **1**, which is in good agreement with both ^{15}N NMR and IR measurements.

We believe that the location of the CN is now "triangulated" by two independent experimental techniques and by calculations. These results establish that the very useful[23, 24] organocopper compounds prepared from two equivalents of RLi and one equivalent of CuCN are cyanide-modified Gilman reagents and not "higher order cyanocuprates." Consequently, they should be called *cyano-Gilman reagents* and written $R_2CuLi \cdot LiCN$ in analogy with other Gilman reagents based on linearly bonded copper(I) structural units ($R_2CuLi \cdot LiI$, $R_2CuLi \cdot LiBr \cdot DMS$ (DMS = dimethyl sulfide), $R_2CuLi \cdot LiOTf$, etc.[23]). NMR spectroscopic measurements were responsible for the first doubt about the higher order formulation of the cyanocuprates,[3, 6, 25] and they have now come full circle to definitively settle the ensuing controversy.[24]

Experimental Section

All NMR spectra were obtained on a Varian Unity 500 spectrometer at the canonical frequencies (^{15}N: 50.65; ^{13}C: 125.7; ^6Li: 73.6 MHz). All NMR shifts were calculated by using the "low frequency positive" convention.[13b] ^6Li NMR spectra were referenced with external 0.3 M ^6LiCl in [D_4]methanol set at $\delta = 0$. ^{13}C NMR spectra were referenced to the solvent signals: $\delta = 14.60$ (ether) or $\delta = 25.37$ (THF). ^{15}N NMR spectra were referenced with 4 M TMSCN in [D_8]THF set at $\delta = -81.7$.[13c]

$CuC^{15}N$ (12.7 mg, 0.14 mmol, MSD Isotopes) was sealed under Ar in an NMR tube (∅ 5 mm) with a rubber septum and Teflon tape. A 0.5 mL aliquot of freshly-distilled [D_{10}]diethyl ether was added by syringe and the contents were sonicated before being cooled to −78 °C (dry ice/acetone). A 30 μL aliquot of 2 M Bu^6Li (0.06 mmol, precise titer determined by Gilman double-titration)[12a] in pentane was added, and the mixture was sonicated at 0 °C for 1.0 min. It was then cooled to −78 °C for 3 min, and the cycle was repeated two more times. The tube was inserted in a ceramic spinner, wiped with an ethanol-soaked tissue, and lowered into the NMR probe, precooled to −80 °C. The ^{13}C NMR spectrum was obtained to confirm the identity of the product,[3, 6] and then the ^{15}N and ^6Li spectra were measured.

Another 30 μL of 2 M Bu^6Li was added to the tube, and the above procedure was repeated to get high-quality spectra of 0.2 M $BuCu(C^{15}N)^6Li$. A small amount of $CuC^{15}N$ remained at the bottom of the tube to make sure none of the 2:1 reagent was present. (None was detected by ^{13}C, ^{15}N, or ^6Li NMR.) When the Bu^6Li was added all at once to $CuC^{15}N$ in [D_{10}]diethyl ether, the spectrum resembled the one in Figure 2b.

Addition of a third 30 μL aliquot gave a mixture of 1:1 and 2:1 reagents, which was analyzed by ^{13}C NMR spectroscopy to determine the ratio of cyano-carbon atoms and from this the effective titer of the Bu^6Li. The ratio of these reagents was also determined by integration of the ^{15}N NMR spectra. For the final sample of 2:1 reagent, a total of 1.90 equiv of Bu^6Li was used, as calculated from the effective titer.

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[1] For earlier uses of CuCN in organocopper chemistry, see a) N. V. Kondyreva, D. A. Fomina, *Zh. Russ. Fiz.-Khim. O-va, Chast Khim.* **1915**, *47*, 190–198; b) H. Gilman, J. M. Straley, *Rec. Trav. Chim. Pays-Bas.* **1936**, *55*, 821–834.

[2] J.-P. Gorlier, L. Hamon, J. Levisalles, J. Wagnon, *J. Chem. Soc. Chem. Commun.* **1973**, 88.

[3] S. H. Bertz, *J. Am. Chem. Soc.* **1991**, *113*, 5470–5471.

[4] B. H. Lipshutz, R. S. Wilhelm, D. M. Floyd, *J. Am. Chem. Soc.* **1981**, *103*, 7672–7674.

[5] a) B. H. Lipshutz, J. A. Kozlowski, R. S. Wilhelm, *J. Org. Chem.* **1984**, *49*, 3943–3949; b) See also B. H. Lipshutz, S. Sharma, E. L. Ellsworth, *J. Am. Chem. Soc.* **1990**, *112*, 4032–4034.

[6] S. H. Bertz, *J. Am. Chem. Soc.* **1990**, *112*, 4031–4032.

[7] a) B. H. Lipshutz, R. S. Wilhelm, J. A. Kozlowski, *Tetrahedron* **1984**, *40*, 5005–5038: "These species are differentiated from 'lower order' or Gilman-like cuprates, R_2CuLi, in that the Cu-cluster contains an additional ligand (originally negatively charged). Hence, they are formally Cu^I dianionic salts." b) See also B. H. Lipshutz, B. James, *J. Org. Chem.* **1994**, *59*, 7585–7587.

[8] a) T. Stemmler, J. E. Penner-Hahn, P. Knochel, *J. Am. Chem. Soc.* **1993**, *115*, 348–350; b) T. M. Barnhart, H. Huang, J. E. Penner-Hahn, *J. Org. Chem.* **1995**, *60*, 4310–4311; c) T. M. Barnhart, J. E. Penner-Hahn, *Physica B* **1995**, *208&209*, 709–710.

[9] T. L. Stemmler, T. M. Barnhart, J. E. Penner-Hahn, C. E. Tucker, P. Knochel, M. Böhme, G. Frenking, *J. Am. Chem. Soc.* **1995**, *117*, 12489–12497.

[10] H. Huang, K. Alvarez, Q. Lui, T. M. Barnhart, J. P. Snyder, J. E. Penner-Hahn, *J. Am. Chem. Soc.* **1996**, *118*, 8808–8816.

[11] a) J. P. Snyder, S. H. Bertz, *J. Org. Chem.* **1995**, *60*, 4312–4313; b) J. P. Snyder, D. P. Spangler, J. R. Behling, B. E. Rossiter, *ibid.* **1994**, *59*, 2665–2667; c) J. P. Snyder, G. E. Tipsword, D. P. Spangler, *J. Am. Chem. Soc.* **1992**, *114*, 1507–1510.

[12] a) Bu^{6}Li was prepared in pentane by the method of G. Hilmersson, Ö. Davidsson, *Organometallics* **1995**, *14*, 912–918; b) NMR samples were prepared as described in S. H. Bertz, A. S. Vellekoop, R. A. J. Smith, J. P. Snyder, *ibid.* **1995**, *14*, 1213–1220, except that 5 mm tubes were used instead of 10 mm. See also Experimental Section.

[13] a) B. Wrackmeyer, *Z. Naturforsch. B* **1988**, *43*, 923–926; b) D. E. J. Arnold, S. Cradock, E. A. V. Ebsworth, J. D. Murdoch, D. W. H. Rankin, D. C. J. Skea, R. K. Harris, B. J. Kimber *J. Chem. Soc. Dalton Trans.* **1981**, 1349–1351; c) reference [13a] reports $\delta = -77.7$ vs. nitromethane for TMSCN and reference [13b] observes $\delta = 254.7$ vs. tetramethylammonium iodide (both with ca. 10% [D$_6$]benzene for lock). The latter is $\delta = -82.6$ vs. nitromethane. We measure $\delta = -79.7$ vs. nitromethane, which is close to the average ($\delta = -80.1$) of the previous measurements. Since nitromethane freezes at $-29\,^\circ$C, we believe more work needs to be done on a primary standard, and we provisionally take the TMSCN shift to be $\delta = -77.7$, as listed in a critical review.[21] For 4 M TMSCN in [D$_8$]THF, we measure $\delta = -81.7$ on this scale. Since the calculated shifts are referenced to the same value as the experimental ones, our conclusions are independent of the standard.

[14] a) G. Fraenkel, A. M. Fraenkel, M. J. Geckle, F. Schloss, *J. Am. Chem. Soc.* **1979**, *101*, 4745–4747; b) D. Seebach, R. Hässig, J. Gabriel, *Helv. Chim. Acta* **1983**, *66*, 308–337; c) for a recent review see *Lithium Chemistry-A Theoretical and Experimental Overview* (Eds.: A.-M. Saspe, P. von R. Schleyer), Wiley, Chichester, **1995**.

[15] Similar observations have been reported for PhCu and Ph$_2$CuLi: S. H. Bertz, G. Dabbagh, X. He, P. P. Power, *J. Am. Chem. Soc.* **1993**, *115*, 11640–11641.

[16] a) There are also small peaks at $\delta = 0.56$ and 1.26 (each about 5% of the total area) in the ^{6}Li spectrum of the 2:1 reagent which may be attributable to CN-free cuprates, presumably similar to "halide-free" cuprates: E. C. Ashby, J. J. Watkins, *J. Am. Chem. Soc.* **1977**, *99*, 5312–5317; b) see also reference [25a].

[17] These minor peaks may be assigned to ^{6}LiC^{15}N and Bu^{6}Li, respectively, possibly in the form of a 1:1 complex. The "LiCN" was not detectable in the ^{15}N spectra of these samples, due to its low concentration and the broadness of its peak. One preparation contained about 20% of the presumed ^{6}LiC^{15}N $\cdot$ Bu^{6}Li (^{6}Li peaks at $\delta = 0.95$ and 1.83) and had a ^{15}N peak at $\delta = -67.5$ ($\Delta\nu_{1/2} = 95$ Hz). The peak at $\delta = 1.83$ was assigned to Bu^{6}Li by a standard addition experiment.

[18] The samples froze out at $-120\,^\circ$C. This was also true with the mixed solvent system THF/[D$_{10}$]diethyl ether/pentane.

[19] a) D. B. Chesnut, *Rev. Comput. Chem.* **1996**, *8*, 245–297; b) D. B. Chesnut, *Ann. Rep. NMR Spectr.* **1994**, *29*, 71–122; c) D. B. Chesnut, B. E. Rusiloski, K. D. Moore, D. A. Egolf, *J. Comput. Chem.* **1993**, *14*, 1364–1375; d) D. B. Chesnut, K. D. Moore, *ibid.* **1989**, *10*, 648–659.

[20] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; b) P. J. Stevens, F. F. Devlin, C. F. Chablowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623–11627.

[21] M. Witanowski, L. Stefaniak, G. A. Webb, *Ann. Rep. NMR Spectr.* **1993**, *25*, 214–219. These authors use the opposite convention for ^{15}N NMR shifts as in reference [13], for example, TMSCN at $\delta = 77.7$.

[22] a) T. A. Mobley, F. Müller, S. Berger, *J. Am. Chem. Soc.* **1998**, *120*, in press; b) A. Gerold, J. T. B. H. Jastrzebski, C. M. P. Kronenburg, N. Krause, G. van Koten, *Angew. Chem.* **1997**, *109*, 778–780; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 755–757.

[23] a) S. H. Bertz, E. H. Fairchild in *Encyclopedia of Reagents for Organic Synthesis*, (Ed.: L. Paquette), Wiley, New York, **1995**, pp. 1312–1315 (CuBr), 1341–1343 (CuCN), 1346–1349 (CuI); b) S. H. Bertz, G. Dabbagh, L. M. Williams, *J. Org. Chem.* **1985**, *50*, 4414–4415 (CuOTf).

[24] B. H. Lipshutz in *Advances in Metal-Organic Chemistry, Vol. 4* (Ed.: L. S. Liebeskind), JAI Press, Greenwich CT, **1995**, pp. 1–64. The dispute was succinctly stated in the title of reference [5b]: "'Higher Order' Cyanocuprates R$_2$Cu(CN)Li$_2$: Discrete Reagents or 'Lower Order' LiCN-Modified Gilman Cuprates?"

[25] Two classes of bona fide higher order cuprates that do not contain CN are known: a) S. H. Bertz, G. Dabbagh, *J. Am. Chem. Soc.* **1988**, *110*, 3668–3670 (aryl); b) F. Olbrich, J. Kopf, E. Weiss, *Angew. Chem.* **1993**, *105*, 1136–1138; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1077–1079 (alkynyl).

Analysis of the Symmetry of Crystal Packing Forces by Methyl Proton Tunneling: A Strategy for the Unambiguous Assignment of the Magnetic Jahn–Teller Effect in Molecules**

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Recent work on polynuclear complexes of magnetic metal ions is tending to confirm a hypothesis that was put forward some time ago in which it was stated that in such complexes there is an inherent tendency towards structural distortion with lowering of symmetry, due to spin-frustration or the magnetic Jahn–Teller effect.[1] For example, according to X-ray diffraction studies the complex [Cu$_4$OCl$_6$(OPPh$_3$)$_4$] crystallizes in a cubic lattice in which the molecules are located on sites of tetrahedral symmetry; however, recent FTIR measurements have revealed a lower symmetry, as shown by splittings of the vibrational frequency of the central oxygen atom.[2] Other systems have triangular clusters, and inelastic neutron scattering (INS) measurements have shown that these deviate from equilateral symmetry at low temperatures.[3] But before attempting to assign structural anomalies to intrinsic forces within the metal atom cluster as such, it is important to consider to what extent they may be driven by extrinsic forces, such as crystal packing or steric hindrance between peripheral groups in the ligands, unrelated to electronic forces at the center.

One classic approach to such problems is to compare structures of two materials that are chemically as similar as possible, apart from the asymmetry of the electron configuration. This has worked well in studies of Jahn–Teller effects in mononuclear systems, for example by comparing structures of copper(II) and zinc(II) complexes with identical ligands and counterions.[4] A similar approach to the phenomenon of spin-frustration or magnetic Jahn–Teller effect would need isostructural pairs of magnetic and nonmagnetic polynuclear

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