Angewandte Chemie
International Edition

DOI: 10.1002/anie.201107060

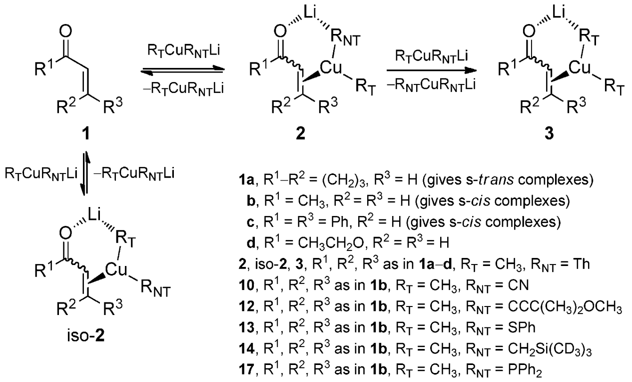
Organocuprates

Minimization of Organocuprate Complexity through Self-Organization: Remarkable Orientation Effect in Mixed Cuprate π Complexes**

Steven H. Bertz, Richard A. Hardin, Michael D. Murphy, Craig A. Ogle,* Joshua D. Richter, and Andy A. Thomas*

A great deal of effort has gone into the research, development and application of mixed organocuprate(I) reagents [R_TR_{NT}CuLi].[1–7] These "mixed cuprates" contain one group R_T that is transferred to a substrate and a second, non-transferred group R_{NT} (sometimes called a "dummy ligand") that is assumed to be inert under the reaction conditions. They were introduced in order to solve the efficiency problem of homocuprates R_2CuLi (Gilman reagents), which only transfer one equivalent of the R-group in most applications. Outstanding examples include thienyl (Th),[2] cyano,[3] alkynyl,[4] thiolato,[5] trimethylsilylmethyl,[6] and phosphido[7] groups.

We have found that upon addition of typical α,β-unsaturated ketones, esters, nitriles, or sulfones, these mixed cuprates give π complexes that exhibit a remarkable orientation effect in which R_T is *cis* to the site of the usual addition reaction, for example, the β-carbon in α,β-unsaturated carbonyl compounds **1** (Scheme 1). Complexes with C=N and C=S double bonds also display this effect. The self-organization we report here substantially reduces the complexity of mixed organocuprate reagents, and it is essential for a complete understanding of their reaction mechanisms.



1a, R^1–R^2 = $(CH_2)_3$, R^3 = H (gives s-*trans* complexes)
b, R^1 = CH_3, R^2 = R^3 = H (gives s-*cis* complexes)
c, R^1 = R^3 = Ph, R^2 = H (gives s-*cis* complexes)
d, R^1 = CH_3CH_2O, R^2 = R^3 = H
2, iso-**2**, **3**, R^1, R^2, R^3 as in **1a**–**d**, R_T = CH_3, R_{NT} = Th
10, R^1, R^2, R^3 as in **1b**, R_T = CH_3, R_{NT} = CN
12, R^1, R^2, R^3 as in **1b**, R_T = CH_3, R_{NT} = $CCC(CH_3)_2OCH_3$
13, R^1, R^2, R^3 as in **1b**, R_T = CH_3, R_{NT} = SPh
14, R^1, R^2, R^3 as in **1b**, R_T = CH_3, R_{NT} = $CH_2Si(CD_3)_3$
17, R^1, R^2, R^3 as in **1b**, R_T = CH_3, R_{NT} = PPh_2

Scheme 1. Stable η^2 π complexes from diverse mixed cuprates and α,β-unsaturated carbonyl compounds.

The observation of this heretofore "hidden" phenomenon was made possible by our rapid injection NMR method, in which a solution is injected from a glass capillary into an NMR tube that is spinning in the probe of an NMR spectrometer at a controlled temperature under a nitrogen atmosphere. For example, when 2-cyclohexenone (**1a**) was injected into a solution of [Me(Th)CuLi] in [D_8]THF at −100 °C, π complex **2a** was observed in equilibrium with the starting materials ($K_{eq} = 11$). The structure was tentatively assigned as **2a**, and not iso-**2a**, on the basis of the ^{1}H NMR shift (−0.09 ppm) for the methyl group on copper, Me_{Cu}, which was close to the downfield peak for the corresponding homocuprate complex **3a** (−0.10 ppm, Table 1).[8] This structure was confirmed by NOESY.

There were no new peaks in the ^{1}H NMR region at ca. −1 ppm, where Me_{Cu} for iso-**2a** would be expected to appear. However, in the vicinity of the Me_{Cu} peak for **2a**, we observed small (< 10%) side-product peaks, which may be due to aggregates, as in the case of **3a**, which was in equilibrium with a minor amount of **3a**·LiI.[8]

A number of diverse substrates with C=C, C=N and C=S double bonds were investigated by treating them with

Table 1: ^{1}H and ^{13}C NMR chemical shifts for the Me_{Cu} groups in complexes of [Me(Th)CuLi] (and [Me_2CuLi]) with selected substrates.

Substrate	Product	^{1}H NMR, ppm ([Me_2CuLi])[a]	^{13}C NMR, ppm ([Me_2CuLi])[a]
1a	**2a**	−0.09 (−0.10, −1.12)[b] (−0.24, −1.16)[c]	−1.30 (−0.57, −5.02)[b] (−1.85, −5.56)[c]
1b	**2b**	−0.13 (−0.36, −1.09)[b,d] (−0.14, −1.00)[c,d]	−4.74 (−4.74, −7.93)[b,d] (−3.05, −6.44)[c,d]
1c	**2c**	−0.11 (−0.43, −1.06)	8.33 (4.07, −3.44)
1d	**2d**	−0.28 (−0.54, −1.12)[b] (−0.48, −1.16)[c]	−7.23 (−8.22, −8.55)[b] (−6.71, −7.90)[c]
4a	**4b**	−0.29 (−0.48, −0.88)	−7.98 (−7.86, −8.37)
5a	**5b**	−0.10 (−0.42, −0.69)	−5.79 (−6.26, −8.18)
6a	**6b**	0.09 (−0.26, −1.07)	11.26 (5.02, −1.05)
7a	**7b**[e]	0.79 (0.43, −0.79)	14.29 (10.81, −9.09)
8a	**8b**	0.16 (−0.27, −0.52)	13.03 (9.18, −9.18)
	8c	0.01	−5.82
CS_2	**9**	0.76 (0.37, −0.76)	24.06 (20.10, −10.54)

[a] Me_2CuLi complexes were prepared from the substrates and their spectra were measured under the same conditions as the mixed cuprate complexes. [b] Major complex. [c] Minor complex (20–30%). [d] 2D NMR connects the downfield ^{1}H and upfield ^{13}C peak in this case. [e] C=S double-bond complex.

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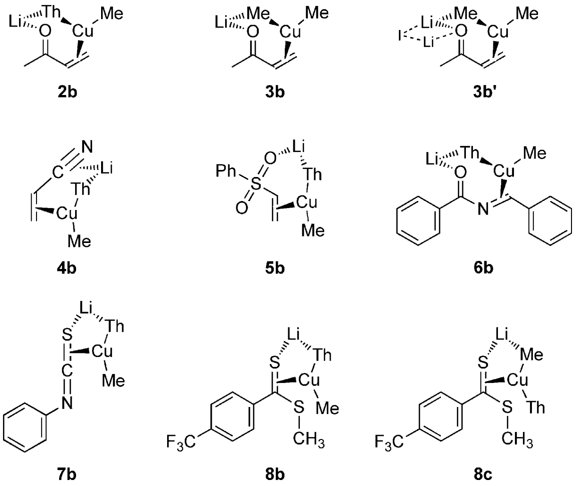
[*] Prof. Dr. S. H. Bertz, R. A. Hardin, Dr. M. D. Murphy,
Prof. Dr. C. A. Ogle, J. D. Richter, A. A. Thomas
Department of Chemistry, University of North Carolina-Charlotte
Charlotte, NC 28223 (USA)
E-mail: sbertz1@uncc.edu
cogle@uncc.edu

[**] Rapid Injection NMR in Mechanistic Organocopper Chemistry, part 10. For previous papers in this series, see references [8–15]. We are grateful to the National Science Foundation (USA) for their support of our work through grants 0353061 and 0321056.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201107060.

[Me(Th)CuLi] at −100 °C. A single mixed cuprate complex was formed in every case except for **8a**, which gave two complexes, **8b** and **8c** (Scheme 2). Initially, they were present in a 1:1 ratio; however, the latter slowly isomerized to the former at −100 °C, or rapidly upon warming the probe to −80 °C. Upon cooling it back to −100 °C, the sole product remained **8b**.



Scheme 2. Complexes from the treatment of [Me(Th)CuLi] with diverse substrates containing C–C, C–N and C–S double bonds.

With ^{13}C-labeled thienyl cuprate, [$^{13}CH_3(C_4H_3S)CuLi$], the more stable complex **8b** had a small *cis* two-bond coupling ($^2J_{C\text{-}C} = 1.4$ Hz) between Me$_{Cu}$ (13.03 ppm) and the thiocarbonyl carbon (92.80 ppm). Less stable isomer **8c** had a larger *trans* coupling ($^2J_{C\text{-}C} = 17.7$ Hz) between them (−5.82, 85.77 ppm, Figure 1). The use of scalar coupling across Cu to establish stereochemistry has been well-established.[9–15] Thus, the two products from **8a** result from different orientations and not different aggregation states.

The results for C–N double bonds deserve special comment. Complex **6b** from [Me(Th)CuLi] and 2-azachalcone **6a**, as well as the corresponding [Me_2CuLi] complex (Table 1), are rare examples of stable cuprate π complexes with C–N double bonds. An unstable C–N complex, which rearranged to a stable C–S complex, was observed with **7a** and [Me_2CuLi].[15] In the case of the less electron-rich cuprate, [Me(Th)CuLi], no intermediate C–N complex was observed, and only C–S complex **7b** appeared upon injection of **7a**.

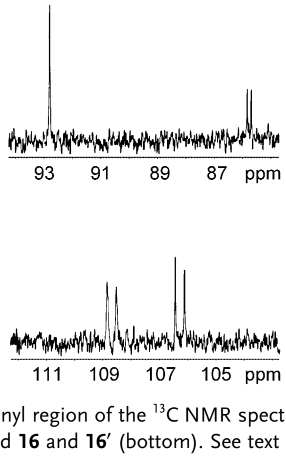
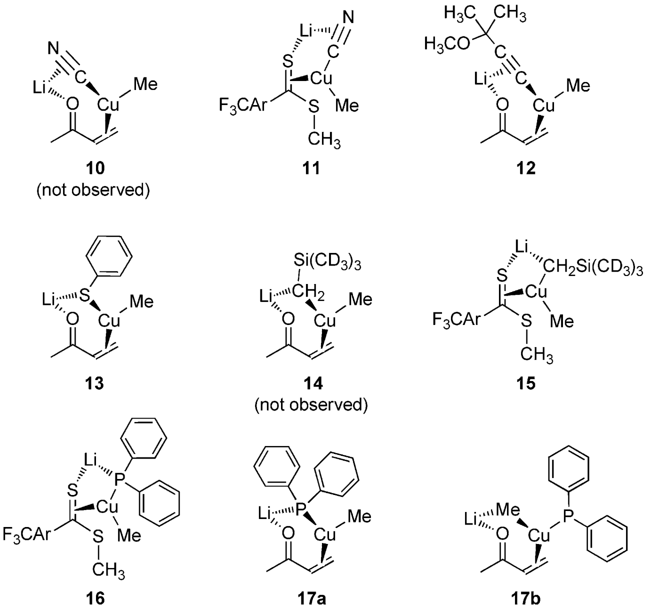


Figure 1. Thiocarbonyl region of the ^{13}C NMR spectra for complexes **8b** and **8c** (top) and **16** and **16′** (bottom). See text for δ and ^2J values.

To further elucidate the scope of the orientation effect, we investigated the reactions of a number of mixed cuprates with the prototypical α-enone, methyl vinyl ketone (MVK; **1b**). In addition to Nilsson's thienylcuprate [$CH_3(C_4H_3S)CuLi$],[2] we examined Levisalles' cyanocuprate [$CH_3(CN)CuLi$],[3] Corey's alkynylcuprate [$CH_3\{CH_3O(CH_3)_2CC{\equiv}C\}CuLi$],[4] Posner's phenylthiocuprate [$CH_3(C_6H_5S)CuLi$],[5] Bertz's (partially deuterated) trimethylsilylmethylcuprate [$CH_3\{(CD_3)_3SiCH_2\}CuLi$],[6] and his diphenylphosphidocuprate [$CH_3\{(C_6H_5)_2P\}CuLi$],[7] all under the usual conditions ([D$_8$]THF, −100 °C). Complexes from MVK and dithioester **8a** are summarized in Scheme 3 (see Scheme 2 for **2b**).



Scheme 3. Complexes from mixed cuprates and methyl vinyl ketone (**1b**) or methyl dithio-4-(trifluoromethyl)benzoate (**8a**).

Upon injection of MVK, [$CH_3(C_4H_3S)CuLi$] gave π complex **2b**. The orientations of Me$_{Cu}$ and Th were confirmed by NOESY, which also proved that the α-enone moiety adopted the s-*cis* conformation in the π complex. Likewise, both major and minor complexes **3b** and **3b′** from MVK and [Me_2CuLi] had the s-*cis* conformation. Therefore, we tentatively assign **3b′** to an aggregate of **3b** with LiI. Complex **2b** was stable over the period of ca. 6 h, during which NMR spectra were collected.

Injection of $(CD_3)_2(C_6H_5)SiCl$ into the solution at −100 °C gave a quantitative conversion of **2b** to a 9:1 *Z*/*E* mixture of silyl enol ethers from the 1,4-addition of methyl. The *Z* isomer corresponds to trapping the observed s-*cis* conformation of the π complex in what appears to be a "least motion" process. The minor amount of lithium enolate (20 %, ca. 1:1 *Z*/*E*) that appeared immediately upon injection of the substrate was not silylated under the reaction conditions. We believe its formation was the result of local heating during the injection, since the amount did not increase significantly thereafter.

When MVK was injected into a solution of $[CH_3(CN)CuLi]$, a π complex was not observed; nevertheless, the presence of a small equilibrium concentration of one such complex (e.g., **10**) was inferred from the relative broadening of the cuprate methyl peak and enone vinyl peaks in the ^1H NMR spectrum. Reversible π-complex formation between [*t*Bu(CN)CuLi] and methyl phenylpropiolate was reported by Nilsson et al.[16]

In contrast, $[CH_3(CN)CuLi]$ formed a stable complex **11** with dithioester **8a**, a more powerful electron acceptor than MVK.

Upon injection of MVK, $[CH_3\{CH_3O(CH_3)_2CC{\equiv}C\}CuLi]$ and $[CH_3(C_6H_5S)CuLi]$ each gave the expected π complex, **12** and **13**, respectively, with the usual orientation of Me_{Cu}. Unexpectedly, they underwent metathesis to homocuprate complex **3b** during the course of several hours.

Injection of MVK into a solution of $[CH_3\{(CD_3)_3SiCH_2\}CuLi]$, which had deuterated methyl groups on silicon in order to simplify the ^1H NMR spectral window from 1 to −1 ppm, did not result in the expected π complex **14**. Instead, a quantitative conversion of starting cuprate to enolate (ca. 1:1 *Z*/*E*) from 1,4-addition of Me was observed in the first ^1H NMR spectrum of the rapid-injection experiment, which was obtained within 5 s at −100 °C. (We note that 30 % of a π complex was formed between MVK and $[\{(CD_3)_3SiCH_2\}_2CuLi]$.)

$[Me_2CuLi(MVK)]$ complex **3b** was stable under the same conditions, which confirmed the dramatic activating effect of β-silicon on copper reagents, predicted by Bertz and Snyder.[17] Yamanaka and Nakamura further elucidated the retention of the trimethylsilylmethyl group on copper.[18]

Treatment of $[CH_3\{(CD_3)_3SiCH_2\}CuLi]$ with **8a** gave complex **15** with the usual Me_{Cu} orientation. Complexes **11** and **15** highlight the remarkable stability of cuprate–thiocarbonyl complexes.

Treatment of $[CH_3\{(C_6H_5)_2P\}CuLi]$ with **8a** afforded two stable products (ca. 1:1), designated **16** and **16′**. Their ^1H NMR (−0.34 ppm, $^3J_{H\text{-}P} = 6.2$ Hz; −0.40 ppm, $^3J_{H\text{-}P} = 5.9$ Hz) and ^{13}C NMR shifts (14.91, 13.88 ppm, $^2J_{C\text{-}P} = 8.5$ Hz each) for Me_{Cu} were very similar. The thiocarbonyl ^{13}C shifts (108.71, 106.29 ppm, $^2J_{C\text{-}P} = 40.5$ Hz each, Figure 1) and ^{31}P shifts (9.47, 7.26 ppm, Figure 2) were also similar. Since they both had the same large *trans* two-bond ^{13}C-^{31}P coupling across Cu, we concluded that they both had the usual orientation, Me_{Cu} *cis* to thiocarbonyl carbon (cf. **16**).

This conclusion was further supported by using $[^{13}CH_3\{(C_6H_5)_2P\}CuLi]$ to prepare the complexes, which both had small *cis* splittings ($^2J_{C\text{-}C} = 2$ Hz) in the thiocarbonyl carbon peaks in addition to the large *trans* splittings ($^2J_{C\text{-}P} = 40$ Hz). We tentatively view **16′** as an aggregate of **16**.

When MVK was injected into a solution of $[CH_3\{(C_6H_5)_2P\}CuLi]$, approximately equal amounts of four π complexes were observed in addition to a substantial amount of enolate from 1,4-addition of Me (50 %, ca. 1:1 *Z*/*E*). The ^1H NMR data indicated that one pair of complexes (−0.39 ppm, $^3J_{H\text{-}P} = 5.2$ Hz; −0.51 ppm, $^3J_{H\text{-}P} = 5.3$ Hz) had Me_{Cu} groups oriented toward the β-carbon (**17a** and **17a′**), and the other pair (−0.91 ppm, $^3J_{H\text{-}P} = 2.0$ Hz; −0.94 ppm, $^3J_{H\text{-}P} = 4.9$ Hz) had them oriented toward the α-carbon (**17b** and **17b′**). NOE data was not conclusive, as ROESY indicated rapid exchange of Me_{Cu} groups.

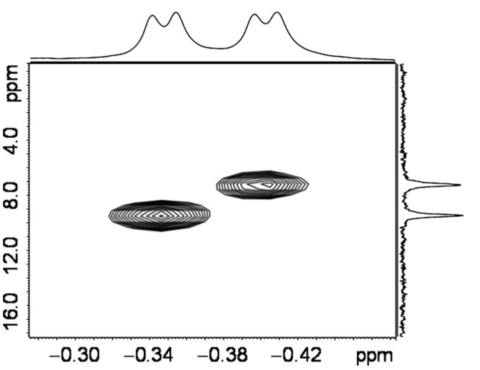
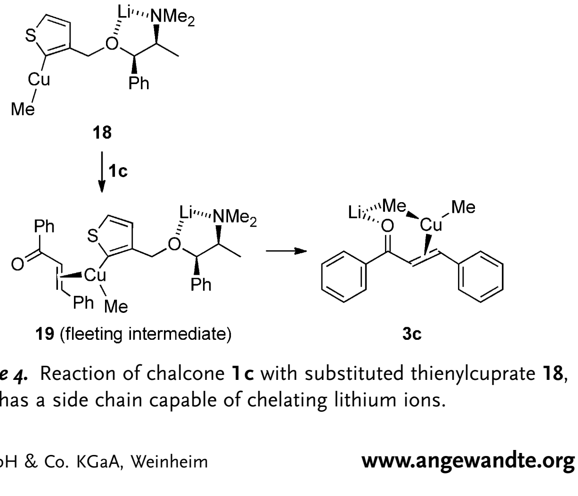


Figure 2. ^1H-^{31}P HMQC for **16** and **16′** from $[Me(Ph_2P)CuLi]$ and **8a**.

The downfield peak in each pair (−0.39, −0.91 ppm) was correlated with a ^{31}P NMR peak at −0.47 ppm, and the upfield peak in each pair (−0.51, −0.94 ppm) with a ^{31}P peak at −1.36 ppm. Thus, it appears that there were two orientations of the methyl group, as shown in **17a** and **17b** (in analogy to **8b** and **8c**), and we propose an aggregated version of each, **17a′** and **17b′** (in analogy to **16** and **16′**), for a total of four complexes.

Injection of $(CD_3)_2(C_6H_5)SiCl$ into the mixture of π complexes at −100 °C converted them to the silyl enol ethers from 1,4-addition of both Me (40 %, 9:1 *Z*/*E*) and Ph_2P (10 %, 3:2 *Z*/*E*). The initial lithium enolate (50 %, 1:1 *Z*/*E*) did not react under these conditions. The product distribution appears to be determined by the relative rates of reductive elimination of Me versus PPh_2.

We chose thienylcuprates for additional study because our group had previously prepared scalemic thienyl ligands for use as chiral auxiliaries in asymmetric induction reactions with α-enones.[19] Upon rapid injection of chalcone **1c** into a solution of scalemic cuprate **18** (Scheme 4, prepared from the corresponding lithium reagent), $[Me_2CuLi(chalcone)]$ complex **3c** grew monotonically as cuprate **18** disappeared at −100 °C.



Scheme 4. Reaction of chalcone **1c** with substituted thienylcuprate **18**, which has a side chain capable of chelating lithium ions.

The simple thienylcuprate–chalcone complex **2c** (Table 1) was stable under the reaction conditions. Apparently, the presence of a moiety capable of chelating Li ions destabilized the mixed cuprate π complex and promoted the metathesis reaction. This experiment highlights the importance of Li ions in the structures of mixed cuprate π complexes, as predicted by Yamanaka and Nakamura.[18]

The second major factor that influences the structures of mixed cuprates with dummy ligands such as cyano, alkynyl, and thiolato was identified as a structural *trans* effect ("*trans* influence").[18] Erdik and Özkan have presented experimental evidence that the strength of the $Cu-R_{NT}$ bond plays an important role in mixed cuprate chemistry.[20]

The observation of small *cis* and large *trans* two-bond coupling across Cu in the NMR spectra of cuprate–thiocarbonyl complexes suggests a pseudo square planar arrangement of ligands,[15,21] which in turn implies a significant degree of Cu^{III} character. We believe there is a small but significant amount of Cu^{III} character in the α-enone complexes, as well. An intermolecular S_N2-like mechanism for ligand exchange reactions in square-planar Cu^{III} complexes has been proposed by Nakamura, Gschwind et al.[22]

The only case where both orientations of the ligands appear to have essentially the same stability comprises the π complexes from MVK and $[Me(Ph_2P)CuLi]$. The *trans* effects of $^-CH_3$ and $^-PPh_2$ are expected to be comparable, given that phosphines PR_3 are only slightly below methyl anion on the *trans*-effect scale.[23]

With the exception of complexes involving $[Me(Ph_2P)CuLi]$, we do not see evidence for substantial aggregation in complexes of mixed cuprates from CuI in THF. Aggregates of cuprates and lithium halides are the major species in ether, and THF has been used to break them down.[24] Thus, by working in $[D_8]$THF at −100 °C, we can study the simple π complexes that are the foundation upon which the aggregates in ether are built, as elucidated by Gschwind et al.[25]

Aggregation at the carbonyl oxygen of an α-enone π complex is favored by the large negative charge on this atom.[18,26] This high electron density also enables the 1,4-addition reaction to be triggered at low temperatures by treatment with chlorosilanes.[27]

In summary, mixed organocuprate(I) reagents are not as generic as might be assumed from the formula $[R_TR_{NT}CuLi]$. Each "dummy" ligand R_{NT} imparts peculiar properties to its π complexes; nevertheless, it is possible to generalize. Most of the ligands exhibit a powerful orientation effect, which positions R_T *cis* to the site of addition, as required for facile reductive elimination.[23] Some of the initial mixed cuprate π complexes undergo metathesis to the corresponding homocuprate π complexes, which complicates mechanistic schemes. Trimethylsilylmethylcuprates were engineered to be more reactive than the corresponding homocuprates, and our new results tend to confirm this expectation. The rapid injection NMR study reported herein has materially improved our understanding of the structures and dynamics of mixed organocuprates, and it may be hoped that this new knowledge will contribute to further advances in their synthetic applications.

Experimental Section

Mixed cuprates were prepared by adding MeLi·THF[28] in $[D_6]$benzene (1 M, 1 equiv) to a suspension of CuI (30 μmol, Aldrich "Ultrapure") in $[D_8]$THF (420 μL, freshly distilled from Na/K) to give a suspension of MeCu in a new NMR tube, dried in an oven (150 °C), sealed under argon with a septum, and cooled to −80 °C in a dry ice/acetone bath. Addition of the dummy ligand in its lithiated form (ca. 0.9 equiv, e.g., ThLi, $RC{\equiv}CLi$, $TMSCH_2Li$, Ph_2PLi) to the NMR tube at −80 °C gave the mixed cuprate. The sample was checked by ^1H NMR at −100 °C, and additional dummy ligand was added when needed, based on integration of the spectrum. In the case of [Me(PhS)CuLi], the precursor was [PhSCu] (Aldrich) and in the case of [Me(Th)CuLi], CuCN was also used.[2c] In all cases, the suspension of copper salt (CuI, CuCN, or PhSCu) was sonicated for 1 min at 0–20 °C before addition of the lithium reagents. When a satisfactory sample was obtained, the septum was removed in a stream of dry nitrogen, and the tube immediately lowered into the probe, which was filled with dry nitrogen (used to spin the sample). The substrate was then injected and single-pulse ^1H NMR spectra were obtained periodically (2–20 s, depending on the rate of reaction). ^1H NMR (^{13}C NMR) spectra were referenced to benzene at 7.340 (128.59) ppm, and ^{31}P NMR spectra were referenced to $MePPh_2$ at −27.00 ppm (external std method).

Received: October 5, 2011
Revised: November 23, 2011

Keywords: 1,4-addition · copper · isotopic labeling · NMR spectroscopy · rapid injection

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