The Role of $BF_3 \cdot Et_2O$ in Reactions of Lower Order (Gilman) Organocuprates

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Abstract: The effects of $BF_3 \cdot Et_2O$ on lower order organocuprate reactions in THF have been investigated so as to determine what factors are responsible for the oftentimes dramatic reaction-rate enhancements observed. From spectroscopic experiments on the reagents alone, supported further by chemical studies, it was found that an originally formed cuprate (R_2CuLi or $RR'CuLi$) is altered significantly upon exposure to this Lewis acid. The copper-containing species thereby generated, together with BF_3, form a more reactive combination and appear to be at least in part responsible for the accelerated chemistry.

Michael additions of lower order organocuprates, R_2CuLi, to α,β-unsaturated carbonyl systems enjoy a rich history of extremely valuable service to organic synthesis.[2] Nonetheless, these reactions are sensitive to several parameters and may not proceed in a synthetically useful manner should the substrate be too hindered or the cuprate be of limited reactivity or stability at the temperatures required to effect coupling. Potential difficulties such as these may oftentimes be overcome by simply admixing (1 equiv or more) $BF_3 \cdot Et_2O$ with the cuprate prior to introduction of the substrate.[3] The presumed impact of the Lewis acid is one of substrate activation via complexation with a lone pair of electrons on oxygen, thereby generating a more reactive cationic species which goes on to react with (unaffected) R_2CuLi at low temperatures and at usually remarkably accelerated rates. Such an assumption is quite reasonable, especially in light of Ganem's work attesting to the compatibility of far harder organometallics (RLi) with $BF_3 \cdot Et_2O$.[4] Contrary to this latter notion, we now report that, in fact, the $BF_3 \cdot Et_2O$ plays not one but two important roles: that is, in addition to substrate activation,[3] *the $BF_3 \cdot Et_2O$ serves to modify the original cuprate itself, the result of which affords a more reactive, different cuprate/Lewis acid combination.*

Results and Discussion

Spectroscopic Experiments. Examination of the ^1H NMR spectrum of Gilman's reagent, Me_2CuLi (**1**) (from 2MeLi + CuI in THF), containing 2 equiv of $BF_3 \cdot Et_2O$ at -80 °C revealed the immediate and reproducible presence of three new signals in addition to the singlet normally characteristic for **1** at ca. δ -1.5 (Figure 1).[5] These peaks could be readily assigned (via control experiments) and derive from the sequestering of MeLi by BF_3 from (presumably) dimeric **1**,[6] i.e., $Me_4Cu_2Li_2$ (**2**). Thus, in addition to $MeLi \cdot BF_3$ at δ 0.16 ppm,[7] the well-characterized[5a,b] aggregate Me_3Cu_2Li (**3**) is produced in equal amounts, both comprising ca. 70% of the total mixture. The ratio of the singlet at δ -0.35 ppm to that at δ -1.31 ppm is 1:2, precisely as expected for Me_3Cu_2Li, which contains magnetically dissimilar methyl groups, as shown in the pioneering work of Ashby on these aggregates over a decade ago.[5a]

Mixed Gilman cuprates, $RR'CuLi$, composed of two different organolithium precursors (RLi, R'Li) now present opportunities for added complexity, since the $BF_3 \cdot Et_2O$ may sequester either RLi or R'Li, leaving behind aggregates which themselves can have differing constitutions. The lower order (LO) cuprate R_T(2-Th)CuLi (**4**, R_T = Me, for example), prepared from CuI, an R_TLi, and 2-lithiothiophene as described by Ullenius and Nilsson,[8] shows two methyl signals in its ^1H NMR spectrum (Figure 2a), presumably due to geometrical isomerism within the dimeric cluster. In the presence of 2 equiv of $BF_3 \cdot Et_2O$ at -80 °C, however, there is nearly complete loss of this cuprate while two major signals appear which correspond to the mixed aggregates $Me(2\text{-}Th)_2Cu_2Li$[9a] and $Me_2(2\text{-}Th)Cu_2Li$,[9a] along with $MeLi \cdot BF_3$ (Figure 2b). Undoubtedly 2-ThLi·BF_3 is also produced although it is not observable in this region of the ^1H spectrum.[9b]

Another mixed cuprate, $Me(MeOCMe_2C{\equiv}C)CuLi$ (**5**), prepared from CuI, MeLi, and $MeOCMe_2C{\equiv}CLi$ (1:1:1) by following Corey's recipe,[10] also shows two methyl singlets as expected in the ^1H NMR spectrum (Figure 3a) at δ -1.53 and -1.57 ppm. Upon introduction of $BF_3 \cdot Et_2O$ (2 equiv) at -80 °C, these essentially disappear and are replaced by two significant signals at δ 0.16 and -1.26 ppm (Figure 3b). While the former is, again, $MeLi \cdot BF_3$, the upfield peak may be due to either aggregate $Me(MeOCMe_2C{\equiv}C)_2Cu_2Li$ or $Me_2(MeOCMe_2C{\equiv}C)Cu_2Li$ or both. Hence, each of these species was prepared independently, and their ^1H NMR spectra were recorded. In line with the growth of a single major upfield signal (Figure 3b), each aggregate affords a spectrum containing one signal at δ -1.27 ppm.

The data above establish that addition of 2 equiv of $BF_3 \cdot Et_2O$ to solutions of homocuprate Me_2CuLi at -78 °C generates, within ca. 10-15 min, a four-component system whose major copper-containing species is no longer the originally prepared cuprate. Over the course of 1.5 h, further buildup of Me_3Cu_2Li (**3**) and $MeLi \cdot BF_3$ occurs (to ca. 80%) at the expense of Me_2CuLi. If the Gilman cuprate is warmed to ca. -60 °C over 10 min following preparation and introduction of $2BF_3 \cdot Et_2O$, it is completely

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[1] A. P. Sloan Fellow, 1984-1988; Dreyfus Teacher-Scholar, 1984-1989.

[2] Posner, G. H. *An Introduction to Synthesis Using Organocopper Reagents*; Wiley: New York, 1980. Posner, G. H., *Org. React.* **1972**, *19*, 1.

[3] For a review, see: Yamamoto, Y., *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 947.

[4] Eis, M. J.; Wrobel, J. E.; Ganem, B. *J. Am. Chem. Soc.* **1984**, *106*, 3693.

[5] (a) Ashby, E. C.; Watkins, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 5312. (b) Lipshutz, B. H.; Kozlowski, J. A.; Breneman, C. M. *Ibid.* **1985**, *107*, 3197. (c) House, H. O.; Chu, C. Y. *J. Org. Chem.* **1976**, *41*, 3083. (d) House, H. O.; Respess, W. L.; Whitesides, G. M. *Ibid.* **1966**, *31*, 3128. (e) San Filippo, J. *Inorg. Chem.* **1978**, *17*, 275.

[6] Pearson, R. G.; Gregory, C. D. *J. Am. Chem. Soc.* **1976**, *98*, 4098. Hope, H.; Oram, D.; Power, P. P. *Ibid.* **1984**, *106*, 1149. Van Koten, G.; Jastrezebski, J. T. B. H.; Muller, F.; Stam, C. H. *Ibid.* **1985**, *107*, 697.

[7] We assume that MeLi + BF_3 gives the Lewis acid-Lewis base combination "$MeLi \cdot BF_3$", which is stable at -78 °C.[4] The ^1H NMR spectrum of this species in THF at -78 °C shows, in addition to a singlet at δ 0.16 ppm, a multiplet at δ -0.77 ppm, perhaps due to a different aggregation state for this species. No "free" MeLi (ca. δ -2.05 ppm)[5b] is observed in the presence of $BF_3 \cdot Et_2O$.

[8] Malmberg, H.; Nilsson, M.; Ullenius, C. *Tetrahedron Lett.* **1982**, *23*, 3823. Bergdahl, M.; Lindtstedt, E.-L., Nilsson, M.; Olsson, T. Tetrahedron **1988**, *44*, 2055. Lindstedt, E.-L.; Nilsson, M.; Olsson, T. *J. Organomet. Chem.* **1987**, *334*, 255.

[9] (a) The presence of $Me_2(2\text{-}Th)Cu_2Li$ and $Me(2\text{-}Th)_2Cu_2Li$ was confirmed by recording their ^1H NMR spectra, prepared from 2MeLi + 1ThLi + 2CuI, and 1MeLi + 2ThLi + 2 CuI, respectively. (b) The presence of 2-ThLi·BF_3 is clear from the ^1H NMR spectrum of Me(2-Th)CuLi + $1BF_3 \cdot Et_2O$, in which Me_3Cu_2Li is present. Hence, the BF_3 is sequestering (in part) 2-thienyllithium from the originally mixed ligand cluster.

[10] Corey, E. J.; Floyd, D. M.; Lipshutz, B. H. *J. Org. Chem.* **1978**, *43*, 3148.

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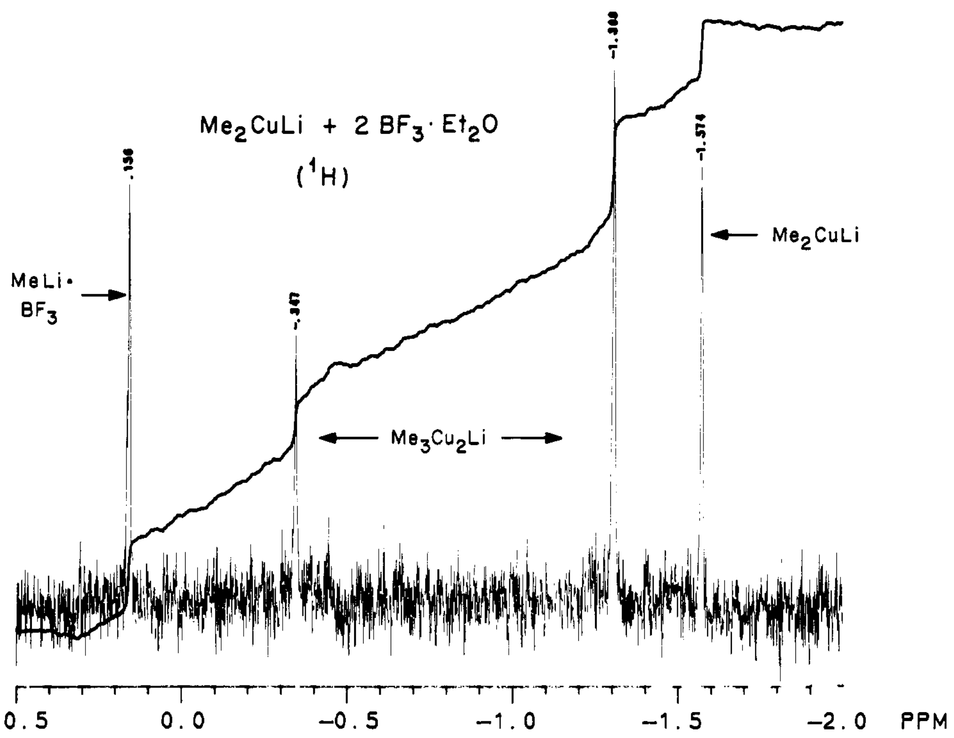
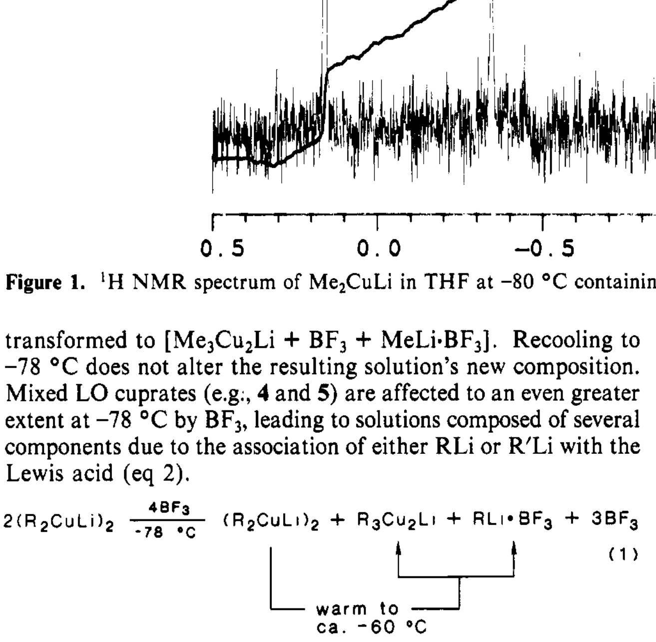


Figure 1. ^1H NMR spectrum of Me_2CuLi in THF at −80 °C containing 2 equiv of $BF_3 \cdot Et_2O$.

transformed to [$Me_3Cu_2Li + BF_3 + MeLi \cdot BF_3$]. Recooling to −78 °C does not alter the resulting solution's new composition. Mixed LO cuprates (e.g., **4** and **5**) are affected to an even greater extent at −78 °C by BF_3, leading to solutions composed of several components due to the association of either RLi or R′Li with the Lewis acid (eq 2).



$$2(R_2CuLi)_2 \xrightarrow[-78\ °C]{4BF_3} (R_2CuLi)_2 + R_3Cu_2Li + RLi \cdot BF_3 + 3BF_3 \quad (1)$$

warm to ca. −60 °C

$$2(RR'CuLi)_2 + 2BF_3 \xrightarrow{-78\ °C} R_2R'Cu_2Li + RR_2'Cu_2Li + RLi \cdot BF_3 + R_3Cu_2Li + R_3'Cu_2Li + R'Li \cdot BF_3 \quad (2)$$

With these spectroscopic results in hand, which attest to the presence of multiple species formed quickly in −78 °C solutions of originally discrete lower order cuprates, we set out to determine which copper reagent is actually responsible for the synthetic chemistry derived from "$R_2CuLi + 2BF_3$".

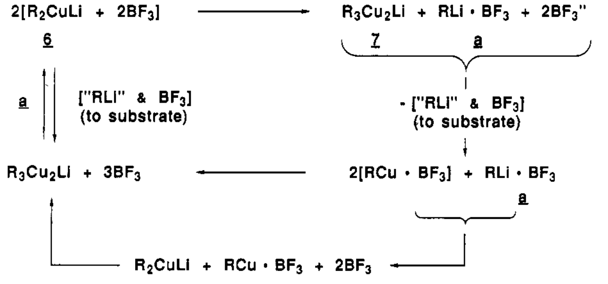
Chemical Probes. The salient feature in the NMR spectra of **1**, **4**, and **5** (vide supra) is the presence of other species which are generated *immediately* upon introduction of $BF_3 \cdot Et_2O$ to an initially prepared LO cuprate. With homocuprates (i.e., R_2CuLi, **6**) typified by Me_2CuLi, although Me_3Cu_2Li is by far the predominant species present and is likely to be the major contributor to product buildup, relative reactivites could be assessed from comparison experiments. At −78 °C, isophorone was added to solutions of "$Me_2CuLi + 2BF_3$", preformed $Me_3Cu_2Li + 2BF_3$, and "$Me_2CuLi + 2BF_3$" which had been warmed to −60 °C (thereby generating $Me_3Cu_2Li + BF_3 + MeLi \cdot BF_3$) and then recooled to −78 °C. Constant conditions of solvent (THF), temperature (−78 °C), time (3 min), and concentration (0.16 M) were used and all were quenched with excess acetic acid in THF. Table I shows that in the early stages of these 1,4-additions, $Me_3Cu_2Li + 2BF_3$ (entries 2 and 3) qualitatively consumes more educt than does "$Me_2CuLi + 2BF_3$" (entry 1). The numbers take on added significance in that while $Me_3Cu_2Li + BF_3$ can release only one methyl ligand (to form 2[$MeCu \cdot BF_3$], vide infra), the Gilman cuprate (plus BF_3) can transfer up to two methyl groups as "RLi",[11] the first of which would actually lead to Me_3Cu_2Li + BF_3. Scheme I provides an indication of the events initiated by this Lewis acid.

Table I. Comparison Reactions of "$Me_2CuLi + 2BF_3$" and $Me_3Cu_2Li + 2BF_3$ Using Isophorone in THF for 3 min, both at 0.16 M

entry	reagent	temp, °C	% yield[a]
1	"$(Me_2CuLi)_2 + 2BF_3$"	−78	1.4–1.6
2	"$(Me_2CuLi)_2 + 2BF_3$"	−78 to −60 10 min, recool to −78	2.1–2.2[b]
3	$Me_3Cu_2Li + 2BF_3$	−78	2.7

[a] Based on quantitative capillary GC analyses of crude reaction mixtures. [b] Range based on duplicate runs.

Scheme I. Reactivity Pathways for THF Solutions of "R_2CuLi + $2BF_3$"



Far more extensive comparison experiments were conducted with *n*-BuLi, MeLi, PhLi, and vinyllithium-derived reagents for longer time periods, as summarized in Table II. Michael reactions with enones and enoates, epoxide openings, and 1,2-additions to an aldehyde were all studied along with appropriate control reactions for some of the examples in the absence of Lewis acid. Many cases suggest that there is oftentimes little distinction between "$R_2CuLi + 2BF_3$" and $Me_3Cu_2Li + 2BF_3$ (entries 1 vs 2, 7 vs 8, 10 vs 11, 14 vs 15, 19 vs 20), implying that over time

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[11] House, H. O. *Acc. Chem. Res.* **1976**, *9*, 59. Smith, R. A. J.; Hannah, D. J. *Tetrahedron* **1979**, *35*, 1183. Berlan, J., Battioni, J.-P.; Koosha, K. *Bull. Soc. Chim. Fr.* **1979**, 183. Krauss, S. R.; Smith, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 141. Ullenius, C.; Christenson, B., submitted for publication.

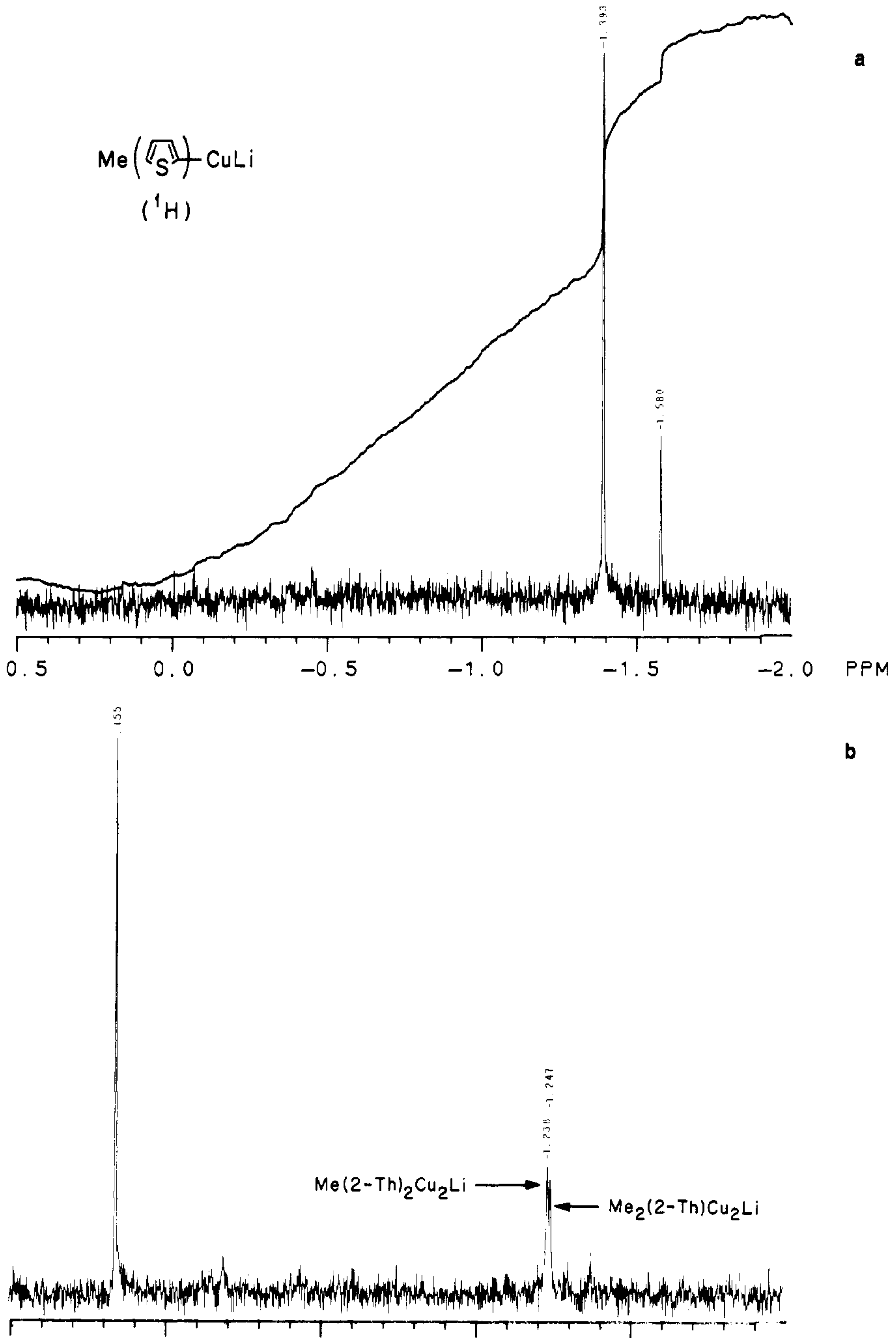

Figure 2. (a) ^1H NMR spectrum of Me(2-Th)CuLi in THF at -80 °C. (b) ^1H NMR spectrum of Me(2-Th)CuLi + $2BF_3$·Et_2O in THF at -80 °C.

Me_2CuLi dimer itself has a chance to "catch up" as a reagent delivering a methyl group or as a continuous source of Me_3Cu_2Li. There are, however, some cases where fluctuations outside of experimental error can be noted (entries 5 vs 6, 16 vs 17, 19 vs 20 in terms of ratio of products, and 24 vs 25). The yields, although determined by quantitative VPC, are somewhat misleading here in that the remaining mass is accounted for in starting material. Hence, even after prolonged treatment of a number of these substrates with equimolar amounts of "R_2CuLi + $2BF_3$" and R_3Cu_2Li + $2BF_3$, the latter aggregate consumes more starting material, consistent with the data in Table I.

It is interesting to note that R_3Cu_2Li (**7**) *alone*, however, is essentially inert when compared with Gilman cuprate **6**. Although conjugate and 1,2-additions of **6** and **7** (plus BF_3) are straightforward and for the most part high yielding, their reactions with an unhindered, unactivated epoxide were surprisingly nonproductive (Table I, entries 19, 20). Both unexpectedly afforded an iodohydrin as the primary adduct, clearly attributable to the LiI byproduct formed from an initial CuI + RLi metathesis. This competing mode of educt consumption is normally not observed with **6** or **7** themselves (entries 21, 22) and is completely obviated with CuCN-derived higher order reagents, which not only tolerate[12] but thrive on BF_3·Et_2O activation.[13]

Another interesting feature worthy of note in Scheme I is the necessary buildup of Yamamoto's reagent, RCu·BF_3,[3,14a,b] itself

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[12] Lipshutz, B. H.; Parker, D. A.; Kozlowski, J. A.; Nguyen, S. L. *Tetrahedron Lett.* **1984**, *25*, 5959.

[13] Lipshutz, B. H.; Ellsworth, E. L.; Siahaan, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 4834.

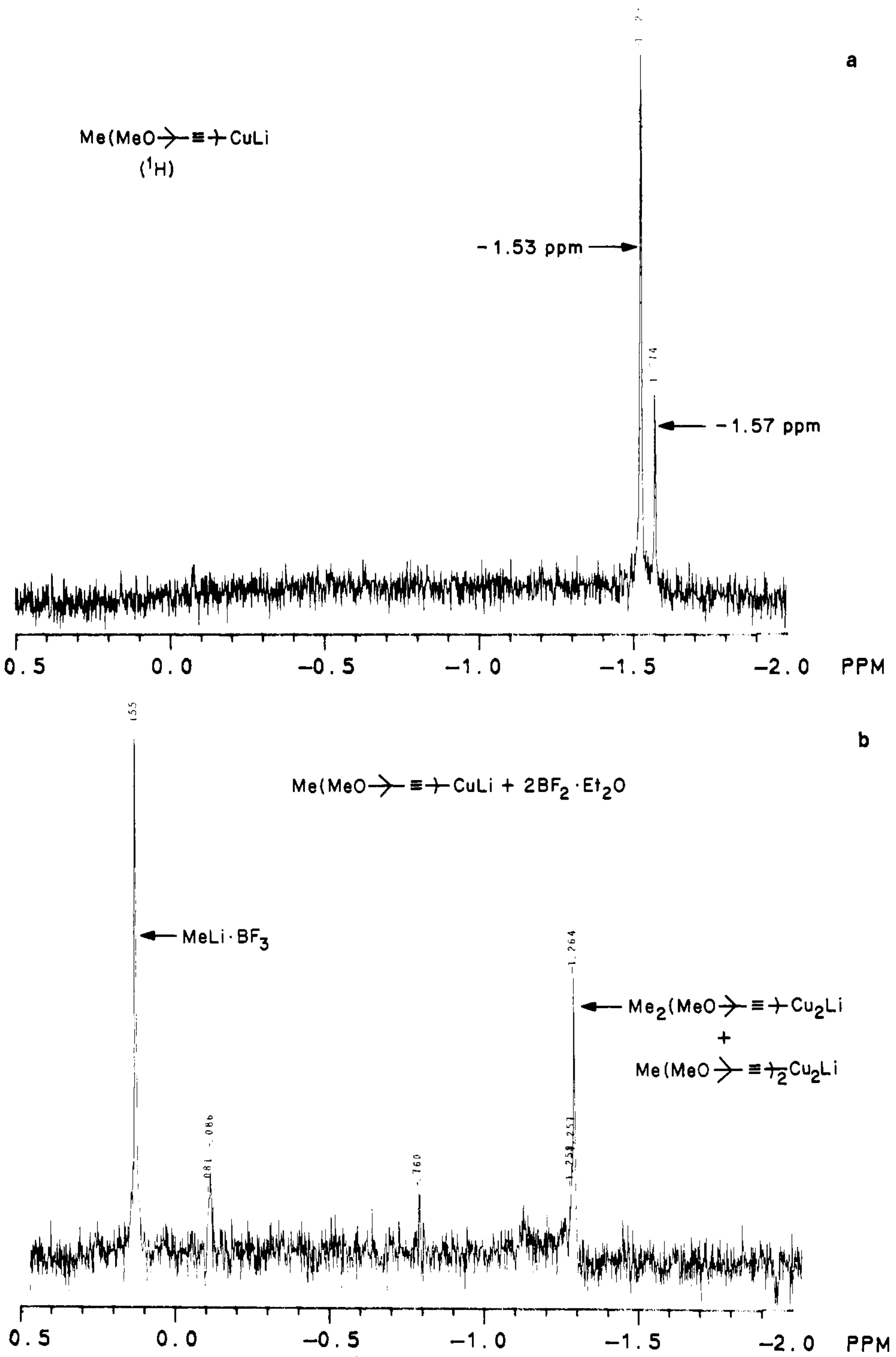

Figure 3. (a) ^{1}H NMR spectrum of Me(MeOCMe$_2$C≡C)CuLi in THF at -80 °C. (b) ^{1}H NMR spectrum of Me(MeOCMe$_2$C≡C)CuLi + 2BF$_3$·Et$_2$O in THF at -80 °C.

highly reactive toward a variety of substrates. Judging from entries 4 and 9 in Table II, however, it would appear that this RCu·BF$_3$ combination, while potentially capable of contributing to product buildup, is not the primary reagent effecting the chemistry of either **6** or **7** under the standard conditions used. Moreover, the ^{1}H NMR of Me$_2$CuLi + BF$_3$ shows no detectable amount of MeCu·BF$_3$ (**8**). Only traces of **8** are observed in the proton spectrum of Me$_3$Cu$_2$Li + BF$_3$ in THF at -80 °C, which shows that the Lewis acid has little effect on Me$_3$Cu$_2$Li.

We have verified that RCu·BF$_3$ is in fact the end product of reactions of **6** by treatment of Me$_3$Cu$_2$Li + BF$_3$ with 3-methyl-2-cyclohexenone in THF at -78 °C, in an NMR tube. The two signals in the ^{1}H NMR (see assignment in Figure 1) for **7**, R = Me, completely disappear and are replaced by one major peak at δ -1.25 ppm characteristic of **8** (Figure 4).[15]

From the synthetic viewpoint, a recommendation for the use of R$_3$Cu$_2$Li + 2BF$_3$ over "R$_2$CuLi + 2BF$_3$" would seem justified.

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(14) (a) Yamamoto, Y.; Yamamoto, S.; Yatagai, H.; Ishihara, Y.; Maruyama, K.; *J. Org. Chem.* **1982**, *47*, 119. (b) The RLi·BF$_3$ present, however, reconverts the RCu·BF$_3$ back to R$_3$Cu$_2$Li + 2BF$_3$ until consumption of RLi by substrate is complete (see Scheme I).

(15) The proton spectrum of MeCu·BF$_3$ in THF at -80 °C shows a peak at δ -1.25 ppm. The fact that the chemical shift for the methyl group is close to those observed for other copper species, such as Me$_3$Cu$_2$Li and (Me$_2$CuLi)$_2$, suggests that it is located on copper, rather than on boron (i.e., RCu·BF$_3$, as opposed to RBF$_3^-$Cu$^+$; cf. ref 3).

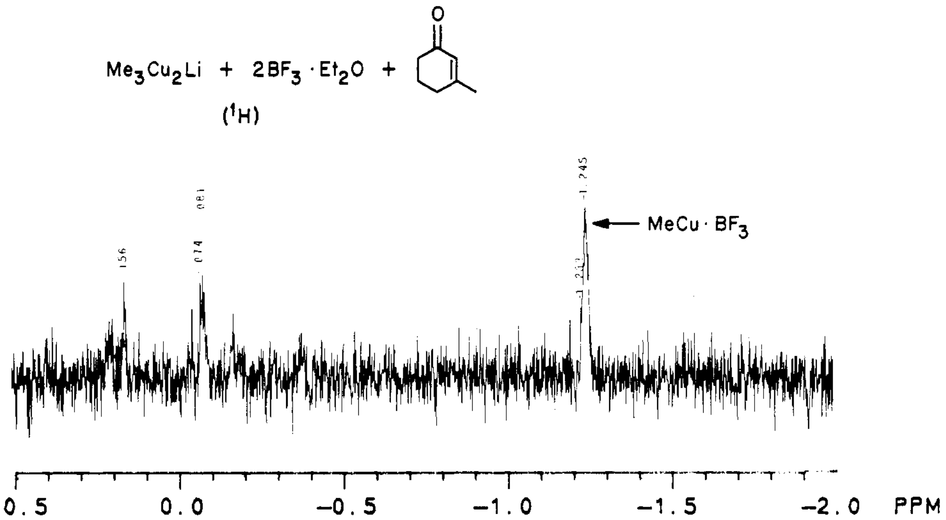
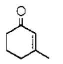
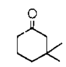
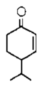
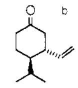
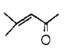
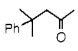
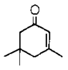
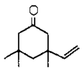
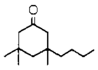
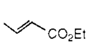
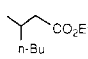
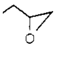
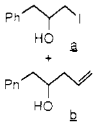
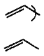
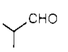
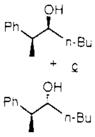


Figure 4. ^{1}H NMR spectrum of $Me_3Cu_2Li + 2BF_3 \cdot Et_2O$ in the presence of 3-methylcyclohexenone in THF at -80 °C.

Table II. Comparison Reactions of $R_2CuLi + BF_3 \cdot Et_2O$ vs $R_3Cu_2Li + BF_3 \cdot Et_2O$ with Various Substrates in THF at -78 °C

Entry	Substrate	Reagent	Time	Product(s)	Yield(%)[a]
1		$Me_2CuLi + 2 BF_3$	1.25h		quant
2		$Me_3Cu_2Li + 2 BF_3$			quant
3		Me_2CuLi			25
4		$MeCu \cdot BF_3$			45
5		 $_2CuLi + 2 BF_3$	2h		63
6		 $_3Cu_2Li + 2 BF_3$			77
7		$Ph_2CuLi + 2 BF_3$	2h		90
8		$Ph_3Cu_2Li + 2 BF_3$			89
9		$3 PhCu + BF_3$			74
10		 $_2CuLi + 2 BF_3$	1.5h		50
11		 $_3Cu_2Li + 2 BF_3$			46
12		 $_2CuLi$			trace
13		 $_3Cu_2Li$			no reaction
14		$n\text{-}Bu_2CuLi + 2 BF_3$	2h		84
15		$n\text{-}Bu_3Cu_2Li + 2 BF_3$			91
16		$n\text{-}Bu_2CuLi + 2 BF_3$	1.5h		83
17		$n\text{-}Bu_3Cu_2Li + 2 BF_3$			98
18		$0.5 [n\text{-}Bu_3Cu_2Li + 2 BF_3]$			47
19		 $_2CuLi + 2 BF_3$	2h		93 (75a:18b)
20		 $_3Cu_2Li + 2 BF_3$			97+ (>95a: 2b)
21		 $_2CuLi$			28 (b only)
22		 $_3Cu_2Li$			28 (b only)
23		 $Cu \cdot BF_3$			quant (72a: 28b)
24		$n\text{-}Bu_2CuLi + 4 BF_3$	3h		63-80 (2c:1d)
25		$n\text{-}Bu_3Cu_2Li + 4 BF_3$			quant (5c:1d)
26		$n\text{-}Bu_2CuLi$			87 (7c:1d)

[a] Determined by quantitative capillary GC analysis. [b] A single diastereomer was formed.

The former could be preformed (3RLi + 2CuI, then $2BF_3$), or generated to the exclusion of the latter species by following the usual protocols for R_2CuLi formation. Simply adding $2BF_3 \cdot Et_2O$ to **6** at -78 °C and warming ca. 10 °C over ca. 10 min prior to adding the substrate should suffice to maximize the concentration of R_3Cu_2Li in THF.

Summary and Conclusions

Low-temperature NMR experiments unequivocally establish that $BF_3 \cdot Et_2O$ has a profound impact on lower order homo- and mixed cuprates *well before a substrate enters the reaction medium.* Homocuprates (i.e., R_2CuLi) form mixtures with their R_3Cu_2Li congeners, as RLi is sequestered by the BF_3 from the cuprate complex $R_4Cu_2Li_2$. Cuprates prepared from two different organolithiums (i.e., RR′CuLi) are likewise effected to an even greater extent at -78 °C, although more complicated mixtures may result from Lewis acid complexation of either RLi or R′Li, thereby leaving multiple aggregates behind. The species responsible for effecting the chemistry in the case of "$R_2CuLi + BF_3$", on the basis of comparison reactions after both short and long reaction periods, appears to be predominantly the homoaggregate R_3Cu_2Li, where $BF_3 \cdot Et_2O$ is essential for (maximum) activity especially with hindered enones.[16] Thus, it now seems that $BF_3 \cdot Et_2O$ is doing double duty in couplings of lower order cuprates; it not only engenders a hotter electrophilic partner via Lewis acid–Lewis base associations, but it also generates a distinctively different, kinetically more reactive reagent in THF,[17,18] contrary to that which one normally *assumes* is present.[19] Obviously both phenomena work in concert, and this may explain the rate enhancements by $BF_3 \cdot Et_2O$ which can oftentimes make the difference between success and failure in cuprate reactions. This study also suggests that by simply warming "$R_2CuLi + nBF_3$" by ca. 10 °C prior to addition of the substrate, one may maximize both rate and yield for a particular cuprate-mediated transformation.

Experimental Section

CuI was purchased from Fischer Scientific Co. and was purified according to the method of Whitesides.[20] Thiophene was purchased from Aldrich Chemical Co. and was distilled from CaH_2. 3-Methyl-3-methoxy-1-butyne was prepared according to Corey's procedure.[10] *n*-Butyllithium, methyllithium, and phenyllithium were obtained from Aldrich and titrated according to the method of Watson and Eastham.[21] Vi-

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(16) Ashby, E. C.; Lin, J. J.; Watkins, J. J. *J. Org. Chem.* **1977**, *42*, 1099.

(17) As pointed out by an astute referee, these studies were conducted predominantly in THF solutions, where the fundamental reagent is R_3Cu_2Li.[5a,b] Such is not the case in reactions lacking THF, where e.g., in Et_2O, $R_5Cu_3Li_2$ is the basic cuprate formed initially from 0.66 RLi + CuX (X = I, Br).[5b,18] Hence, it may well be that a similar study in non-THF-containing media would show that $R_5Cu_3Li_2$ is formed from $(R_2CuLi)_2$ in the presence of $BF_3 \cdot Et_2O$.

(18) Clive, D. L. J.; Farina, V.; Beaulieu, P. L. *J. Org. Chem.* **1982**, *47*, 2572.

(19) The sequestering of MeLi by BF_3 at very low temperatures from the Gilman reagent to form Me_3Cu_2Li would seem to provide additional evidence in solution that Me_2CuLi may well be dimeric; cf. ref 6.

(20) Linstrumelle, G.; Krieger, J. K.; Whitesides; G. M. *Org. Synth.* **1976**, *55*, 103.

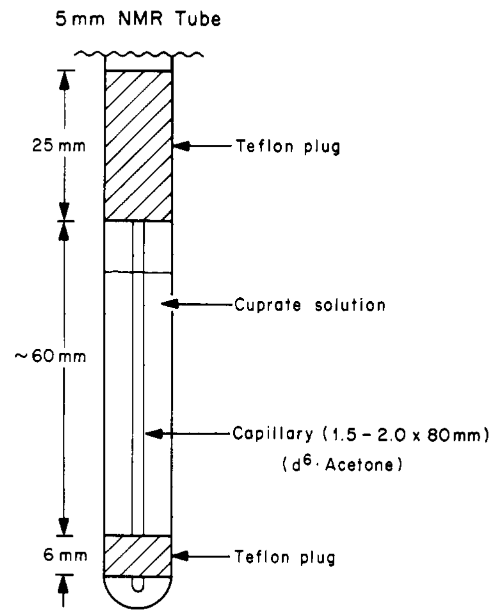

Figure 5. Configuration of the 5-mm NMR tubes containing a capillary insert used for these experiments.

nyllithium was obtained from Organometallics and titrated as above. 4-Isopropyl-2-cyclohexenone, isophorone, 2-phenylpropanal, and ethyl crotonate were purchased from Aldrich and distilled from CaH_2. 3-Methyl-2-cyclohexanone and mesityl oxide are also available from Aldrich. 1,2-Epoxy-3-phenylpropane was prepared by the reaction of allylbenzene with MCPBA in CH_2Cl_2.

NMR spectra were recorded on a General Electric GN500 or a Nicolet NT300 spectrometer at 500 and 300 MHz, respectively. Samples were situated in 5-mm NMR tubes as illustrated in Figure 5. Mass spectra were run on a VG 70-250 instrument. IR spectra were recorded on a Perkin-Elmer 283 spectrometer. VPC analyses were run on either a Hewlett-Packard Model 5890A or a United Technologies Packard Model 439, using decane as internal standard unless otherwise noted.

Reactions of R_2CuLi, R_3Cu_2Li, RCu: Table II, Entry 1. Reaction of $Me_2CuLi{\cdot}2BF_3$ with 3-Methyl-2-cyclohexenone. CuI (143 mg, 0.75 mmol) was added to a dry 10-mL round-bottom flask equipped with a stir bar and sealed under argon with a septum. The flask was evacuated with a vacuum pump and purged with argon. This process was repeated three times. THF (1.5 mL) was injected and the slurry was cooled to −78 °C, where MeLi (0.98 mL, 1.5 mmol) was added dropwise. The mixture was allowed to warm until homogeneous (colorless solution) and was recooled to −78 °C, where $BF_3{\cdot}Et_2O$ (0.18 mL, 1.5 mmol) was added via a syringe. 3-Methyl-2-cyclohexenone (0.085 mL, 0.75 mmol) was added neat and the reaction mixture was stirred for 1.25 h. The reaction was quenched with 5 mL of a 10% NH_4OH/90% saturated NH_4Cl solution. VPC analysis indicated the quantitative formation of 3,3-dimethylcyclohexanone.

Entry 2. Reaction of $Me_3Cu_2Li{\cdot}2BF_3$ with 3-Methyl-2-cyclohexenone. $Me_3Cu_2Li{\cdot}2BF_3$ was prepared as a clear solution in the same manner as described above. The following amounts of reagents were used: CuI, 0.286 g, 1.5 mmol; THF, 1 mL; methyllithium, 1.47 mL, 2.25 mmol; $BF_3{\cdot}Et_2O$, 0.18 mL, 1.5 mmol; and 3-methyl-2-cyclohexenone, 0.085 mL, 0.75 mmol. The reaction was allowed to proceed for 1.25 h (−78 °C) before being quenched in the same manner as described above. VPC analysis revealed the formation of 3,3-dimethylcyclohexanone in a quantitative yield.

Entry 3. Reaction of Me_2CuLi with 3-Methyl-2-cyclohexenone. Me_2CuLi was prepared as a colorless solution as described above. The following amounts of reagents were used: CuI, 143 mg, 0.75 mmol; THF, 2 mL; methyllithium, 0.97 mL, 1.50 mmol; and 3-methyl-2-cyclohexenone, 0.085 mL, 0.75 mmol. The reaction was allowed to proceed for 1.25 h (−78 °C) before being quenched with 5 mL of a 10% NH_4OH/90% saturated NH_4Cl solution. VPC analysis indicated the formation of 3,3-dimethylcyclohexanone to the extent of 25%.

Entry 4. Reaction of $MeCu{\cdot}BF_3$ with 3-Methyl-2-cyclohexenone. CuI (143 mg, 0.75 mmol) was added to a dry 10-mL round-bottom flask equipped with a stir bar and rubber septum. The flask was evacuated with a vacuum pump and purged with argon. This process was repeated three times. THF (2 mL) was injected and the slurry cooled to −78 °C, where MeLi (0.49 mL, 0.75 mmol) was added dropwise. The mixture was warmed to −20 °C for 8 min. The resulting heterogeneous, orange solution was recooled to −78 °C, where $BF_3{\cdot}Et_2O$ (0.09 mL, 0.75 mmol) was added *via* a syringe. 3-Methyl-2-cyclohexenone (0.085 mL, 0.75 mmol) was added neat and the reaction mixture was stirred for 1.25 h. The reaction was quenched with 5 mL of a 10% NH_4OH/90% saturated NH_4Cl solution. VPC analysis indicated the formation of 3,3-dimethylcyclohexanone to the extent of 45%.

Entry 5. Reaction of $(Vinyl)_2CuLi{\cdot}2BF_3$ with 4-Isopropyl-2-cyclohexenone. The cuprate $(vinyl)_2CuLi{\cdot}2BF_3$ was prepared as a dark solution according to the procedure above. The following amounts of reagents were used: CuI, 0.0524 g, 0.275 mmol; THF, 1 mL; vinyllithium, 0.33 mL, 0.55 mmol; $BF_3{\cdot}Et_2O$, 0.066 mL, 0.55 mmol; and 4-isopropyl-2-cyclohexenone, 0.037 mL, 0.25 mmol. The reaction was allowed to proceed for 2 h (−78 °C) before being quenched with a 10% NH_4OH/90% saturated NH_4Cl solution. VPC indicated the formation of 3-vinyl-4-isopropylcyclohexanone to the extent of 63%: TLC [10% EtOAc in Skellysolve] R_f 0.35; ^1H NMR, δ 5.67–5.60 (ddd, 1 H, J_{gem} = 3 Hz, J_{cis} = 8 Hz, J_{trans} = 19 Hz), 5.04–5.00 (m, 2 H), 2.45–22.0 (m, 6 H), 2.00–1.90 (m, 1 H), 1.55–1.40 (m, 2 H), 0.97 (d, 3 H), 0.76 (d, 3 H); IR (neat) cm^{-1} 3080, 2960, 2900, 2880, 1730, 1640, 1420, 1220, 920; mass spectrum (EI), *m/z* (relative intensity) 166 (9), 138 (11), 111 (33), 96 (16), 95 (20), 83 (25), 81 (24), 69 (54), 55 (77), 43 (100); exact mass calcd for $C_{11}H_{18}O$ (M^+) 166.1358, found 166.1355.

Entry 6. Reaction of $(Vinyl)_3Cu_2Li{\cdot}2BF_3$ with 4-Isopropyl-2-cyclohexenone. The aggregate $(vinyl)_3Cu_2Li{\cdot}2BF_3$ was prepared as a dark solution according to the procedure above. The following amounts of reagents were used: CuI, 0.105 g, 0.55 mmol; THF, 1 mL; vinyllithium, 0.49 mL, 0.825 mmol; $BF_3{\cdot}Et_2O$, 0.066 mL, 0.55 mmol; and 4-isopropyl-2-cyclohexenone, 0.037 mL, 0.25 mmol. The reaction was allowed to proceed for 2 h (−78 °C) before being quenched as described above. VPC analysis indicated the formation of 3-vinyl-4-isopropylcyclohexanone to the extent of 77%.

Entry 7. Reaction of $Ph_2CuLi{\cdot}2BF_3$ with Mesityl Oxide. $Ph_2CuLi{\cdot}BF_3$ was prepared as a dark solution according to the procedure above. The following amounts of reagents were used: CuI, 0.143 g, 0.75 mmol; THF, 2 mL; phenyllithium, 0.67 mL, 1.5 mmol; $BF_3{\cdot}Et_2O$, 0.18 mL, 1.50 mmol; and mesityl oxide, 0.086 mL, 0.75 mmol. The reaction was allowed to proceed for 2 h (−78 °C) before being quenched as described above. VPC analysis indicated the formation of 4-methyl-4-phenyl-2-pentanone in 90% yield.

Entry 8. Reaction of $Ph_3Cu_2Li{\cdot}2BF_3$ with Mesityl Oxide. $Ph_3Cu_2Li{\cdot}2BF_3$ was prepared as a dark solution according to the above procedure. The following amounts of reagents were used: CuI, 0.286 g, 1.5 mmol; THF 2 mL; phenyllithium, 0.98 mL, 2.25 mmol; $BF_3{\cdot}Et_2O$, 0.18 mL, 1.5 mmol; and mesityl oxide, 0.086 mL, 0.75 mmol. The reaction was allowed to proceed for 2 h (−78 °C) before being quenched as described above. VPC analysis indicated the formation of 4-methyl-4-phenyl-2-pentanone in 89% yield.

Entry 9. Reaction of $PhCu{\cdot}BF_3$ with Mesityl Oxide. $PhCu{\cdot}BF_3$ was prepared as a dark solution according to the above procedure. The following amounts of reagents were used: CuI, 0.143 g, 0.75 mmol; THF, 2.5 mL; phenyllithium, 0.33 mL, 0.75 mmol; $BF_3{\cdot}Et_2O$, 0.09 mL, 0.75 mmol; and mesityl oxide, 0.086 mL, 0.75 mmol. The reaction was allowed to proceed for 2 h (−78 °C) before being quenched as described above. VPC analysis indicated the formation of 4-methyl-4-phenyl-2-pentanone in 74% yield.

Entry 10. Reaction of $(Vinyl)_2CuLi{\cdot}2BF_3$ with Isophorone. The cuprate $(vinyl)_2CuLi{\cdot}2BF_3$ was prepared as a dark solution according to the above procedure. The following amounts of reagents were used: CuI, 0.0952 g, 0.5 mmol; THF, 1.5 mL; vinyllithium, 0.49 mL, 1.0 mmol; $BF_3{\cdot}Et_2O$, 0.12 mL, 1.0 mmol; and isophorone, 0.067 mL, 0.45 mmol. The reaction was allowed to proceed for 1.5 h (−78 °C) before being quenched as described above. VPC analysis indicated the formation of 3,5,5-trimethyl-3-vinylcyclohexanone in 50% yield.

Entry 11. Reaction of $(Vinyl)_3Cu_2Li{\cdot}2BF_3$ with Isophorone. The aggregate $(vinyl)_3Cu_2Li{\cdot}2BF_3$ was prepared as a dark solution according to the above procedure. The following amounts of reagents were used: CuI, 0.3142 g, 1.65 mmol; THF, 3 mL; vinyllithium, 1.08 mL, 2.475 mmol; $BF_3{\cdot}Et_2O$, 0.20 mL, 1.65 mmol; and isophorone, 0.112 mL, 0.75 mmol. The reaction was allowed to proceed for 1.5 h (−78 °C) before being quenched as described above. VPC indicated the formation of 3,5,5-trimethyl-3-vinylcyclohexanone in 46% yield.

Entry 12. Reaction of $(Vinyl)_2CuLi$ with Isophorone. The cuprate $(vinyl)_2CuLi$ was prepared as described above. The following amounts of reagents were used: CuI, 0.0952 g, 0.5 mmol; THF, 1.5 mL; vinyllithium, 0.49 mL, 1.0 mmol; and isophorone, 0.067 mL, 0.45 mmol. The reaction was allowed to proceed for 1.5 h (−78 °C) before being quenched as described above. VPC analysis indicated the formation of 3,5,5-tri-

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(21) Watson, S. C.; Eastham, J. F.; *J. Organomet. Chem.* **1967**, *9*, 165.

methyl-3-vinylcyclohexanone in only a trace amount.

Entry 13. Reaction of $(Vinyl)_3Cu_2Li$ with Isophorone. The aggregate $(vinyl)_3Cu_2Li$ was prepared as described above. The following amounts of reagents were used: CuI, 0.0952 g, 0.5 mmol; THF, 1.5 mL; vinyllithium, 0.37 mL, 0.75 mmol; and isophorone, 0.067 mL, 0.45 mmol. The reaction was allowed to proceed for 1.5 h (−78 °C) before being quenched as described above. VPC analysis indicated only starting material to be present.

Entry 14. Reaction of *n*-$Bu_2CuLi{\cdot}2BF_3$ with Isophorone. The cuprate *n*-$Bu_2Cu{\cdot}2BF_3$ was prepared as described above. The following amounts of reagents were used: CuI, 0.143 g, 0.75 mmol; THF, 2.5 mL; *n* BuLi, 0.57 mL, 1.5 mmol; $BF_3{\cdot}Et_2O$, 0.18 mL, 1.5 mmol; and isophorone, 0.112 mL, 0.75 mmol. The reaction was allowed to proceed for 2 h (−78 °C) before being quenched as described above. VPC analysis indicated the formation of 3-*n*-butyl-3,5,5-trimethylcyclohexanone in a yield of 84%: TLC [10% EtOAc in Skellysolve] R_f 0.45; ^1H NMR ($CDCl_3$) δ 2.19–2.08 (m, 4 H), 1.59 (t, 2 H, J = 15 Hz), 1.49 (d, 2 H, J = 14 Hz), 12.6–1.21 (m, 4 H), 1.03 (s, 3 H), 1.02 (s, 3 H), 0.98 (s, 3 H), 0.88 (t, 3 H, J = 7 Hz); IR (neat) cm^{-1} 2960, 2940, 2880, 1730, 1460, 1280; mass spectrum (CI), m/z (relative intensity) 197 (M^+ + H, 100), 181 (11), 139 (46); exact mass calcd for $C_{13}H_{25}O$ (M^+ + H) 197.1905, found 197.1907.

Entry 15. Reaction of *n*-$Bu_3Cu_2Li{\cdot}2BF_3$ with Isophorone. The aggregate *n*-$Bu_3Cu_2Li{\cdot}2BF_3$ was prepared as described above. The following amounts of reagents were used: CuI, 0.286 g, 1.5 mmol; THF, 2 mL; *n*-BuLi, 0.86 mL, 2.25 mmol; $BF_3{\cdot}Et_2O$, 0.18 mL, 1.5 mmol; and isophorone, 0.112 mL, 0.75 mmol. The reaction was allowed to proceed for 2.0 h (−78 °C) before being quenched as described above. VPC analysis indicated the formation of 3-*n*-butyl-3,5,5-trimethylcyclohexanone in a yield of 91%.

Entry 16. Reaction of *n*-$Bu_2CuLi{\cdot}BF_3$ with Ethyl Crotonate. The cuprate *n*-$Bu_2CuLi{\cdot}BF_3$ was prepared as described above. The following amounts of reagents were used: CuI, 0.143 g, 0.75 mmol; THF, 2 mL, *n*-BuLi, 0.57 mL, 1.5 mmol; $BF_3{\cdot}Et_2O$, 0.18 mL, 1.50 mmol; and ethyl crotonate, 0.093 mL, 0.75 mmol. The reaction was allowed to proceed for 1.5 h (−78 °C) before being quenched as described above. VPC analysis indicated the formation of ethyl 4-methylheptanoate in 83% yield.

Entry 17. Reaction of *n*-$Bu_3Cu_2Li{\cdot}BF_3$ with Ethyl Crotonate (1 equiv). The aggregate *n*-$Bu_3Cu_2Li{\cdot}2BF_3$ was prepared as described above. The following amounts of reagents were used: CuI, 0.286 g, 1.5 mmol; THF, 4 mL; *n*-BuLi, 0.859 mL, 2.25 mmol; $BF_3{\cdot}Et_2O$, 0.18 mL, 1.5 mmol; and ethyl crotonate, 0.093 mL, 0.75 mmol. The reaction was allowed to proceed for 1.5 h (−78 °C) before being quenched as described above. VPC analysis indicated the formation of ethyl 4-methylheptanoate in 98% yield.

Entry 18. Reaction of *n*-Bu_3Cu_2Li with Ethyl Crotonate (2 equiv). The aggregate *n*-$Bu_3Cu_2Li{\cdot}2BF_3$ was prepared as described above. The following amounts of reagents were used: CuI, 0.143 g, 0.75 mmol; THF, 2.0 mL; *n*-BuLi, 0.43 mL, 1.125 mmol; $BF_3{\cdot}Et_2O$, 0.09 mL, 0.75 mmol; and ethyl crotonate, 0.093 mL, 0.75 mmol. The reaction was allowed to proceed for 1.5 h (−78 °C) before being quenched as described above. VPC analysis indicated the formation of ethyl 4-methylheptanoate in 47% yield.

Entry 19. Reaction of $(Vinyl)_2CuLi{\cdot}2BF_3$ with Allylbenzene Oxide. The cuprate $(vinyl)_2CuLi{\cdot}BF_3$ was prepared as described above. The following amounts of reagents were used: CuI, 0.190 g, 1.0 mmol; THF, 2.5 mL; vinyllithium, 1.19 mL, 2.0 mmol; $BF_3{\cdot}Et_2O$, 0.24 mL, 2.0 mmol; and allylbenzene oxide, 0.13 mL, 0.95 mmol. The reaction was allowed to proceed for 2 h (−78 °C) before being quenched as described above. VPC analysis indicated the formation of 1-iodo-3-phenyl-2-propanol in 75% yield and an 18% yield of 4-hydroxy-5-phenyl-1-pentene. The iodohydrin gave the following data: TLC [10% EtOAc in Skellysolve] R_f 0.23; ^1H NMR ($CDCl_3$) δ 7.34–7.23 (m, br, 5 H, Ph), 3.79–3.73 (m, 1 H, CH), 3.39–3.36 (dd, 1 H, J_{ax} = 7 Hz, J_{gem} = 10 Hz), 3.25–3.21 (dd, 1 H, J_{bx} = 6 Hz, J_{gem} = 10 Hz); IR (neat) cm^{-1} 3500, 3090, 3010, 2910, 1950, 1880, 1800, 1600, 1280, 1005, 740, 700; mass spectrum (CI), m/z (relative intensity) 262 (M^+ + H,3), 135 (6.0), 119 (4), 117 (100); exact mass calcd for $C_9H_{11}IO$ (M^+) 261.9854, found 261.9839.

Entry 20. Reaction of $(Vinyl)_3Cu_2Li{\cdot}2BF_3$ with Allylbenzene Oxide. The aggregate $(vinyl)_3Cu_2Li{\cdot}2BF_3$ was prepared as described above. The following amounts of reagents were used: CuI, 0.190 g, 1.0 mmol; THF, 2.5 mL; vinyllithium, 0.898 g, 1.0 mmol; $BF_3{\cdot}Et_2O$, 0.12 mL, 1.0 mmol; and allylbenzene oxide, 0.067 mL, 0.5 mmol. The reaction was allowed to proceed for 2 h (−78 °C) before being quenched as described above. VPC analysis indicated the formation of 1-iodo-3-phenyl-2-propanol (>95% yield) and 4-hydroxy-5-phenyl-1-pentene (2.0% yield).

Entry 21. Reaction of $(Vinyl)_2CuLi$ with Allylbenzene Oxide. The cuprate $(vinyl)_2CuLi$ was prepared as described above. The following amounts of reagents were used: CuI, 0.143 g, 0.75 mmol; THF, 1.0 mL; vinyllithium, 0.898 mL, 1.5 mmol; and allylbenzene oxide, 0.067 mL, 0.5 mmol. The reaction was allowed to proceed for 2 h (−78 °C) before being quenched as described above. VPC analysis indicated the formation of 4-hydroxy-5-phenyl-1-pentene only in a yield of 28%.

Entry 22. Reaction of $(Vinyl)_3Cu_2Li$ with Allylbenzene Oxide. The aggregate $(vinyl)_3Cu_2Li$ was prepared as described above. The following amounts of reagents were used: CuI, 0.2857 g, 1.5 mmol; THF, 1.0 mL; vinyllithium, 1.35 mL, 2.25 mmol; and allylbenzene oxide, 0.067 mL, 0.5 mmol. The reaction was allowed to proceed for 2 h (−78 °C) before being quenched as described above. VPC analysis indicated the formation of 4-hydroxy-5-phenyl-1-pentene as the only product in a yield of 28%.

Entry 23. Reaction of $(Vinyl)Cu{\cdot}BF_3$ with Allylbenzene Oxide. Organocopper $(vinyl)Cu{\cdot}BF_3$ was prepared in the same manner as described above. The following amounts of reagents were used: CuI, 0.28 g, 1.5 mmol; THF, 2.0 mL, vinyllithium, 0.90 mL, 1.5 mmol; $BF_3{\cdot}Et_2O$, 0.18 mL, 1.5 mmol; and allylbenzene oxide, 0.067 mL, 0.50 mmol. The reaction was allowed to proceed for 2 h (−78 °C) before being quenched as described above. VPC analysis indicated the formation of 1-iodo-3-phenyl-2-propanol (72% yield) and 4-hydroxy-5-phenyl-1-pentene (29% yield).

Entry 24. Reaction of *n*-$Bu_2CuLi{\cdot}4BF_3$ with 2-Phenylpropanal. The cuprate *n*-$Bu_2CuLi{\cdot}2BF_3$ was prepared as above with the following amounts of reagents: CuI, 0.0952 g, 0.5 mmol; THF, 1.5 mL; *n*-BuLi, 0.35 mL, 1.0 mmol; $BF_3{\cdot}Et_2O$, 0.24 mL, 2.0 mmol; and 2-phenylpropanal, 0.032 mL, 0.25 mmol. The reaction was allowed to proceed for a period of 3 h (−78 °C) before being quenched as above. VPC analysis indicated the formation of 2-phenyl-3-hexanol in 80% yield (vs phenylcyclohexane as an internal standard).

Entry 25. Reaction of *n*-$Bu_3Cu_2Li{\cdot}4BF_3$ with 2-Phenylpropanal. The aggregate *n*-$Bu_3Cu_2Li{\cdot}4BF_3$ was prepared as above with the following amounts of reagents: CuI, 0.0952 g, 0.5 mmol; THF, 1.5 mL; n-BuLi, 0.28 mL, 0.75 mmol; $BF_3{\cdot}Et_2O$, 0.12 mL, 1.0 mmol; and 2-phenylpropanal, 0.032 mL, 0.25 mmol. The reaction was allowed to proceed for a period of 3 h (−78 °C) before being quenched as described above. VPC analysis indicated the formation of 2-phenyl-3-hexanol in quantitative yield (vs phenylcyclohexane as an internal standard).

Entry 26. Reaction of *n*-Bu_2CuLi with 2-Phenylpropanal. The cuprate *n*-Bu_2CuLi was prepared as above with the following amounts of reagents: CuI, 0.0952 g, 0.5 mmol; THF, 1.5 mL; *n*-BuLi, 0.35 mL, 1.0 mmol; and 2-phenylpropanal, 0.032 mL, 0.25 mmol. The reaction was allowed to proceed for a period of 3 h (−78 °C) before being quenched as above. VPC analysis indicated the formation of 2-phenyl-3-hexanol in 87% yield (vs phenylcyclohexane as an internal standard).

Figure 1. Preparation of $Me_2CuLi{\cdot}2BF_3$. CuI (0.143 g, 0.75 mmol) was placed in a dry 10-mL round-bottom flask, equipped with a magnetic stir bar, and sealed with a septum. The flask was then evacuated with a vacuum pump and purged with argon. This process was repeated three times. THF (4 mL) was injected and the slurry was cooled to −78 °C, where MeLi (0.99 mL, 1.5 mmol) was added dropwise. The mixture was warmed to yield a colorless, homogeneous solution, which was recooled to −78 °C. An aliquot (0.45 mL, 0.068 mmol) was then transferred via a syringe under argon to a dry NMR tube (−78 °C) with the NMR-tube spinner already in place. Prior to the addition of cuprate, the NMR tube was fitted with a Teflon plug and a capillary insert (acetone-d_6) and purged thoroughly with argon for a minimum of 10 min and then cooled to −78 °C (see Figure 5). Two equivalents (0.135 mL, 0.136 mmol) of a 1.01 M solution (−78 °C) of $BF_3{\cdot}Et_2O$/THF was also added via a syringe. The NMR tube was then fitted with a second Teflon plug to hold the capillary tube in place, and it was finally sealed with parafin prior to the NMR experiment at −80 °C.

Figure 2. Preparation of Me(2-thienyl)CuLi. 2-Thienyllithium (0.75 mmol) was prepared from thiophene (0.060 mL, 0.75 mmol) and *n*-BuLi (0.28 mL, 2.7 M) in THF (4 mL) at −30 to −40 °C (30 min) and then was added via a cannula to a precooled (−78 °C) slurry of CuI (0.143 g, 0.75 mmol) in THF (0.5 mL) followed by the addition of MeLi (0.42 mL, 0.75 mmol). The mixture was then warmed until an amber-colored, homogeneous solution resulted. The solution was then recooled to −78 °C and an aliquot (0.45 mL, 0.064 mmol) was transferred via a syringe under argon to a dry NMR tube (−78 °C) as described above. The NMR tube was then fitted with a second Teflon plug and sealed.

Preparation of Me(2-thienyl)CuLi·$2BF_3$. Me(2-Thienyl)CuLi was prepared and transferred to an NMR tube as described above (0.45 mL, 0.064 mmol). Two equivalents (0.102 mL, 0.138 mmol) of a 1.36 M solution of $BF_3{\cdot}Et_2O$/THF was also added via a syringe and the NMR tube was sealed as described above.

Figure 3. Preparation of $Me(MeOCMe_2C{\equiv}C)CuLi$. (3-Methyl-3-methoxy-1-butynyl)lithium was prepared from 3-methyl-3-methoxy-1-butyne (0.093 mL, 0.75 mmol) and MeLi (0.48 mL, 1.55 M) in THF (2 mL) at 0 °C (10 min). It was then added via a cannula to a precooled

(−78 °C) slurry of CuI (0.143 g, 0.75 mmol) in THF (2 mL), followed by the addition of MeLi (0.48 mL, 0.75 mmol). The mixture was then warmed until a colorless, homogeneous solution formed. The solution was recooled to −78 °C and transferred to an NMR tube in the manner described above.

Preparation of $Me(MeOCMe_2C{\equiv}C)CuLi{\cdot}2BF_3$. $Me(MeOCMe_2C{\equiv}C)CuLi$ was prepared in the same manner as described above. The following amounts of reagents were used: 3-methyl-3-methoxy-1-butyne, 0.093 mL, 0.75 mmol; THF, 4 mL; MeLi, 0.888 mL, 1.5 mmol; and CuI, 0.143 g, 0.75 mmol. An aliquot (0.45 mL, 0.068 mmol) was transferred to an NMR tube as described above. A 0.976 M solution (−78 °C) of $BF_3{\cdot}Et_2O$/THF (2 equiv, 0.136 mL, 0.132 mmol) was also added via a syringe and the NMR tube was sealed for use as described above.

Figure 4. Reaction of 3-Methyl-2-cyclohexenone and $Me_3Cu_2Li{\cdot}BF_3$. Me_3Cu_2Li was prepared in the same manner as described above. The following amounts of reagents were used: CuI, 0.143 g, 0.75 mmol; THF, 2 mL; MeLi, and 0.73 mL, 1.125 mmol. An aliquot (0.45 mL, 0.063 mmol) of the colorless, homogeneous solution was transferred to a dry NMR tube as described above. One equivalent (0.062 mL, 0.060 mmol) of a 0.976 M solution (−78 °C) of $BF_3{\cdot}Et_2O$/THF was also added via a syringe followed by the addition of 1 equiv of 3-methyl-2-cyclohexenone (0.007 mL, 0.06 mmol). The NMR tube was then sealed and used in the NMR experiment at −80 °C.

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Registry No. **1**, 15681-48-8; **3**, 61303-82-0; **4**, 110140-36-8; **5**, 79135-33-4; **6** (R = $H_2C{=}CH$), 22903-99-7; **6** (R = Ph), 23402-69-9; **6** (R = *n*-Bu), 24406-16-4; **7** (R = $H_2C{=}CH$), 118398-08-6; **7** (R = Ph), 118376-86-6; **7** (R = *n*-Bu), 118376-85-5; **8**, 65139-98-2; (*E*)-$H_3CCH{=}CHCO_2Et$, 623-70-1; $H_3CCH(Ph)CHO$, 93-53-8; $H_3CC(CH_3)(Ph)CH_2COCH_3$, 7403-42-1; $H_3C(CH_2)_3CH(CH_3)CH_2CO_2Et$, 37492-08-3; $PhCH_2CH(OH)CH_2I$, 86151-59-9; $PhCH_2CH(OH)CH_2CH{=}CH_2$, 61077-65-4; ($R$*,$R$*)-$H_3CCH(Ph)CH(OH)(CH_2)_3CH_3$, 96929-99-6; ($R$*,$S$*)-$H_3CCH(Ph)CH(OH)(CH_2)_3CH_3$, 96930-05-1; $BF_3{\cdot}Et_2O$, 109-63-7; MeCu, 1184-53-8; PhCu, 3220-49-3; $H_2C{=}CHCu$, 37616-22-1; $MeLi{\cdot}BF_3$, 82977-34-2; $Me(2\text{-}Th)_2Cu_2Li$, 118376-87-7; $Me_2(2\text{-}Th)Cu_2Li$, 118376-88-8; $Me(MeOC(CH_3)_2C{\equiv}C)_2Cu_2Li$, 118376-89-9; $Me_2(MeOC(CH_3)_2C{\equiv}C)Cu_2Li$, 118376-90-2; $H_2C{=}CHCu{\cdot}BF_3$, 104747-24-2; CuI, 7681-65-4; 3-methyl-2-cyclohexenone, 1193-18-6; 4-isopropyl-2-cyclohexenone, 500-02-7; mesityl oxide, 141-79-7; isophorone, 78-59-1; 1,2-epoxy-3-phenylpropane, 4436-24-2; 3,3-dimethylcyclohexanone, 2979-19-3; *trans*-3-vinyl-4-isopropylcyclohexanone, 118376-84-4; 3,5,5-trimethyl-3-vinylcyclohexanone, 27749-07-1; 3,5,5-trimethyl-3-butylcyclohexanone, 41601-84-7; allylbenzene, 300-57-2; thiophene, 110-02-1; 2-thienyllithium, 2786-07-4; 3-methyl-3-methoxy-1-butyne, 13994-57-5; 3-methyl-3-methoxy-1-butynyllithium, 76320-69-9.

Interaction of the (Dimethylglyoximato)(pyridine)cobalt Anion, $[Co(dmgH)_2py]^-$, with Vinyl Triflates. Stereochemistry and Mechanism of Formation of Vinyl–Cobaloxime Complexes[†]

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Abstract: Reaction of $[Co(dmgH)_2py]^-$ with simple alkylvinyl triflates occurs at 0 °C in CH_3OH/H_2O (9:1) in less than 10 min to give stable, crystalline σ-vinyl–cobaloxime complexes in 18–51% isolated yields. The reaction of isomeric (*E*)- and (*Z*)-vinyl triflates results in stereoconvergence. The data indicate that reaction most likely occurs by a stepwise addition–elimination process with an anionic intermediate of sufficient lifetime to undergo bond rotation before elimination.

A large variety of organic substrates, alkyl, benzyl, allyl, propargyl, acyl, aryl, and some vinyl systems (usually halides), react with low valent transition metal nucleophiles, resulting in diverse carbon–metal σ-bond complexes.[2,3] From a classical organic chemical prospective these reactions may be viewed as the alkylation, acylation, arylation, etc., via the appropriate electrophiles, of transition-metal complexes with the metal serving as a nucleophile. Hence, in parallel with organic chemistry, the reactions of alkyl, acyl, benzyl, allyl, propargyl, and aryl systems are extensively investigated and reasonably well understood. However, in classical organic as well as organometallic chemistry, nucleophilic vinyl substitutions (S_NV),[4-6] i.e. displacements at a C_{sp^2} center, are much less common and, until recently, less understood. The reason for this anomaly is generally attributed to the inertness of *simple alkylvinyl* substrates (usually halides) to S_NV processes, even under forcing conditions with powerful nucleophiles.[4] Therefore, in organic[4] as well as organometallic[7,8] chemistry, nucleophilic vinylic substitutions usually require "activated", i.e. halo, cyano, carbonyl, aryl, etc., substituted vinylic systems for reaction to occur. For example, with one exception,[9] even the supernucleophilic[10] $[Co(dmgH)_2py]^-$ anion only reacts with β-chloroacrylate[11] and β-bromostyrene[12] and not with simple alkylvinyl halides.

The ready availability[13] and high reactivity, $k_{CF_3SO_3^-}/k_{X^-} \cong 10^6–10^9$, of vinyl triflates offers a potential solution to this problem, as exemplified by the easy generation of both alkylidenecarbenes[14]

[†] Dedicated to Professor Donald J. Cram on the occasion of his 70th birthday.

(1) Abstracted in part from: Datta, A. K. Ph.D. Dissertation, University of Utah, 1988.

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