BF$_3$-Mediated Addition of Lithium Phenylacetylide to an Imine: Correlations of Structures and Reactivities. BF$_3$·R$_3$N Derivatives as Substitutes for BF$_3$·Et$_2$O

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Abstract: BF$_3$-mediated additions of lithium phenylacetylide (PhCCLi) to the *N*-(*n*-butyl)imine of cyclohexane carboxaldehyde were investigated. IR spectroscopic investigations reveal dramatic aging effects on the addition rates. ^{6}Li, ^{11}B, and ^{13}C NMR spectroscopic studies correlate the loss in reactivity with the condensation of PhCCLi and BF$_3$ and the consequent formation of a complex mixture of PhCCLi–BF$_3$ adducts. Employing BF$_3$·R$_3$N complexes eliminates the aging effects by retarding the formation of borates. Kinetic studies implicate a mechanism in which rate-limiting associative substitution of *n*-Bu$_3$N on the BF$_3$ by the imine is followed by a rapid 1,2-addition of PhCCLi. BF$_3$·R$_3$N complexes are potentially useful substitutes for BF$_3$·Et$_2$O.

Introduction

Many organolithium reactions are dramatically accelerated by adding BF$_3$·Et$_2$O. These include 1,2-additions to imines,[1–5] oximes,[6–8] carboxamides,[9,10] anhydrides,[11,12] aldehydes,[13,14] and ketones,[15] as well as cleavages of acetals,[16] epoxides,[17–22] and unstrained cyclic ethers.[23,24] BF$_3$ has been used in conjunction with alkyllithiums,[1,3,7,8,24] lithium acetylides,[5,6,9,11,12,14,15,17,22] aryllithiums,[4,6–8,21] vinyllithiums,[6,20] allyllithiums,[13] and lithium enolates.[24] The critical role of BF$_3$·Et$_2$O is often underscored

by dramatic rate increases and improved chemo-, regio-, and stereoselectivities.[13–15,24]

It is unclear how (or whether) such strong Lewis acids and bases avoid condensation long enough to function cooperatively. Indeed, many studies implicate substantial mechanistic complexity. Yields are often much higher if BF$_3$·Et$_2$O is added to the substrate/organolithium solution[16,23] or if the organolithium is added to a substrate/BF$_3$·Et$_2$O solution.[2,8] Premixing BF$_3$·Et$_2$O and the organolithium is often, but not always, detrimental.[1,9,15] For example, Yamaguchi and co-workers found that the sequence of reagent addition did not influence BF$_3$-mediated epoxide openings at −78 °C, but at −40 °C reasonable yields were obtained only if BF$_3$·Et$_2$O was added last.[23]

Several studies have afforded structural insights into BF$_3$-mediated organolithium reactions. Ganem and co-workers used ^{11}B NMR spectroscopy to study BF$_3$-promoted openings of

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cyclic ethers with alkyllithiums.[24a] Spectra of *n*-BuLi and BF_3·Et_2O in THF (i.e., BF_3·THF)[25] at -78 °C revealed lithium *n*-octyloxyboron trifluoride (the product of THF cleavage) and lithium tetrabutylborate. Brown and co-workers investigated BF_3-mediated additions of lithium acetylides to anhydrides by ^{11}B NMR spectroscopy.[11] A mixture of PhCCLi and BF_3·Et_2O provided a species assigned as $(PhCC)BF_3Li(THF)_n$ (**1**), which was converted to $(PhCC)_4BLi(THF)_n$ (**2**) on warming. Wheatley and co-workers crystallized $(PhCC)_3B$·THF (**3**) from a 1:1 mixture of PhCCLi and BF_3·Et_2O and suggested that it is a plausible intermediate in the 1,2-additions of lithium acetylides to imines, though they did not test this hypothesis.[26] Barr and co-workers monitored BF_3·Et_2O and *n*-BuLi in Et_2O/HMPA/ toluene using ^{7}Li and ^{11}B NMR spectroscopies,[27] observing $LiBF_4$ and several species tentatively assigned as mixed borates $(Bu_2BF_2)Li$ and $(BuBF_3)Li$.

We describe structural and mechanistic investigations of the 1,2-addition of PhCCLi to unactivated imines (eq 1) first

$$\text{(1)}$$

with BF_3·Et_2O 70% yield
without BF_3·Et_2O no reaction
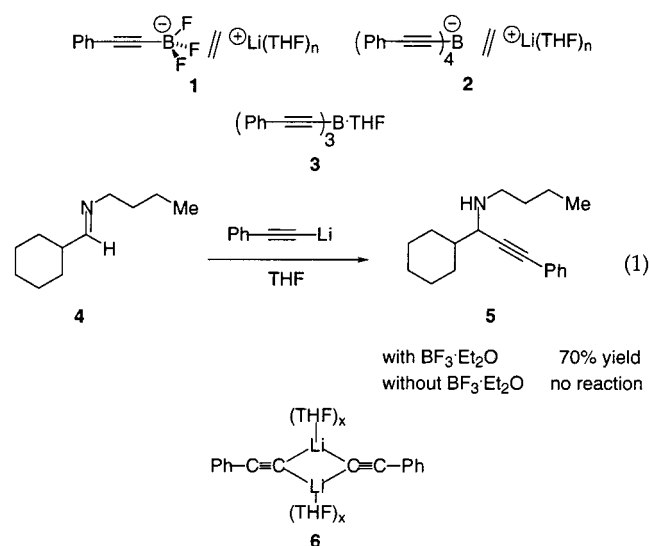
effected by Akiba and co-workers.[1] A striking loss in reactivity is correlated with the condensation of PhCCLi with BF_3·Et_2O. Detailed rate studies using BF_3·*n*-Bu_3N provide insights into the role of the Lewis acid. The air-stable, crystalline BF_3·R_3N complexes may offer significant advantages over BF_3·Et_2O by retarding the problematic aging effects.[28−30]

Results

Solutions containing BF_3·THF[25] were prepared by dissolving BF_3·Et_2O in THF. $[^6Li,^{13}C]$PhCCLi was prepared as a white

solid.[31] The BF_3·*n*-Bu_3N[32] was isolated as an air-stable, crystalline solid in 80% yield.

BF_3/THF. IR Spectroscopic Studies. IR spectroscopic studies using a ReactIR spectrometer fitted with a SiComp probe led to qualitative insights into the BF_3-mediated 1,2-addition shown in eq 1. Without BF_3, a THF solution containing PhCCLi (0.10 M) and imine **4** (0.024 M) at 25 °C for 10 h shows no loss of the imine absorbance at 1669 cm^{-1}. In contrast, if a THF solution of PhCCLi (0.10 M) and BF_3 (0.10 M) was prepared at -85 °C and promptly charged with imine **4**, the 1,2-addition is essentially instantaneous ($t_{1/2} < 10$ s) with no detectable BF_3·imine precomplex.[33] If the PhCCLi/BF_3 mixture stands at -85 °C for 5 min prior to addition of imine **4**, no 1,2-addition is observed even on warming to ambient temperature. A very low level of reactivity remains in aged samples containing a $\geq$2-fold excess of PhCCLi ($t_{1/2} > 8$ h at 0 °C). Under these conditions BF_3 is converted to a complex mixture of borates, eventually affording $(PhCC)_4BLi(THF)_n$ (**2**).[29,38,39] Independently prepared samples of borate **2**[38,39] and borane **3**[26] show no reactivity even with added BF_3.

BF_3/THF. NMR Spectroscopic Studies. [6]Li, ^{11}B, and ^{13}C NMR spectroscopic investigations reveal that the marked loss in reactivity of PhCCLi/BF_3 on standing at -85 °C coincides with the initial condensation to form a complex mixture of borates. The ^{11}B NMR spectrum recorded on a THF solution of $[^6Li,^{13}C]$PhCCLi (0.10 M) and BF_3 (0.10 M), which was prepared in liquid nitrogen and carefully warmed to -110 °C, displays a resonance (δ 1.36 ppm, br s)[37] consistent with BF_3·THF (Figure 1a). On standing at -85 °C, the resonance of BF_3·THF is replaced by a slightly upfield-shifted [11]B resonance at δ 0.25 ppm (Figure 1b). The ^{11}B NMR spectra do not change markedly on further warming the sample to near ambient temperature. Analogous ^{11}B NMR spectroscopic data observed by Brown were attributed to the formation of borate **1**.[11] The [6]Li NMR spectra appear to be equally straightforward. On standing at -85 °C, the characteristic triplet of dimer **6** (δ 0.37 ppm, $J_{Li-C} = 8.1$ Hz, -110 °C) is replaced by a singlet at δ -0.88 ppm (Figure 1c,d).

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(33) Spectra recorded on a 0.03 M THF solution of **4**[34] with 0.10 M BF_3 display an absorbance at 1671 cm^{-1} compared to 1669 cm^{-1} for the uncomplexed imine.[35] BF_3−imine complexes in Nujol typically display IR C=N stretches at 20−60 cm^{-1} higher frequencies than the parent imine.[36] Indeed, a heterogeneous mixture of imine **4** and 3.0 equiv of BF_3 in pentane containing poorly coordinating Et_2O (50 equiv) displays a major IR absorbance attributed to the putative BF_3·**4** complex at 1713 cm^{-1} and a smaller absorbance at the frequency of free imine **4**.

(34) The reaction was studied at a relatively dilute concentration because of the low solubilities of PhCCLi. The reaction shows limited conversion (28%) over 14 h at 25 °C. Neither borate **2** nor borane **3** undergo 1,2-additions to imine **4** with excess BF_3·Et_2O.

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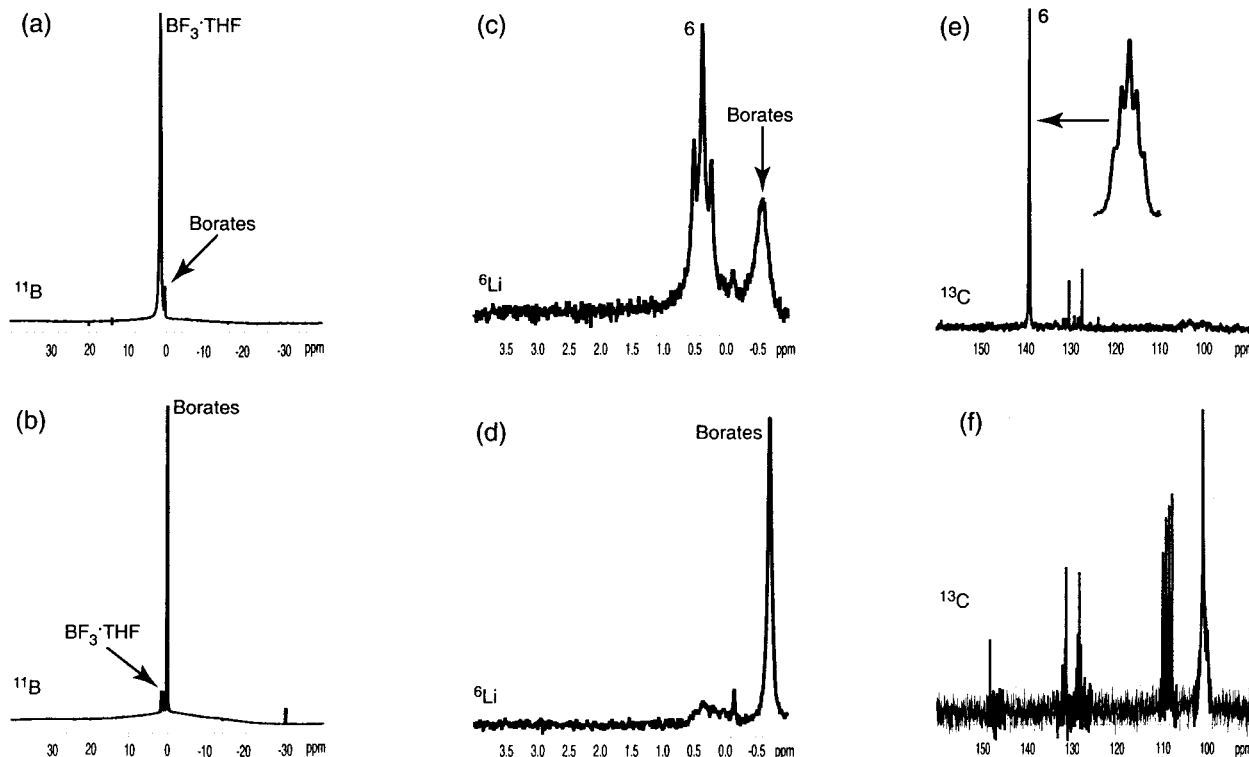
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Figure 1. NMR spectra of [^{6}Li,^{13}C]PhCCLi (0.10 M) in THF/pentane (10.6 M) with 1.0 equiv of BF$_3$·Et$_2$O at −110 °C: (a) ^{11}B NMR spectrum with no aging; (b) ^{11}B NMR after 5 min at −85 °C; (c) ^{6}Li NMR spectrum with no aging; (d) ^{6}Li NMR spectrum after 5 min at −85 °C; (e) ^{13}C NMR spectrum with no aging; (f) ^{13}C NMR spectrum after 5 min at −85 °C.

The simplicity of the ^{11}B and ^{6}Li NMR spectra conceals considerable structural complexity. The ^{13}C NMR spectrum recorded at −110 °C prior to aging displays the quintet (δ 139.3 ppm, $J_{\text{Li}-\text{C}} = 8.1$ Hz) corresponding to dimer **6** (Figure 1e). Standing at −85 °C, however, affords *at least five new* ^{13}C *resonances* (Figure 1f). Therefore, ^{6}Li and ^{11}B NMR spectroscopies are inadequate for monitoring the complex mixtures. We have described additional spectroscopic studies following the conversion of putative R$_x$F$_y$BLi borates[30] to borate **2**[39] in detail elsewhere.[29]

BF$_3$/*n*-Bu$_3$N. IR Spectroscopic Studies. We reasoned that reducing the steady-state concentration of the putative BF$_3$·imine complex by using a strongly coordinating amine (eq 2) would

$$\text{BF}_3\cdot\text{R}_3\text{N} + \text{imine} \rightleftharpoons \text{BF}_3\cdot\text{imine} + \text{R}_3\text{N} \qquad (2)$$
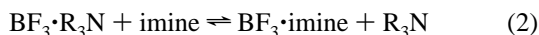
render the rate of the 1,2-addition tractable and attenuate aging effects.

Treating a 0.20 M solution of PhCCLi in THF at −25 °C sequentially with (a) a premixed solution of BF$_3$ (1.0 equiv), (b) *n*-Bu$_3$N (1.5 equiv), and (c) 0.02 equiv of imine **4** affords a clean pseudo-first-order decay. The 0.5 h half-life represents a marked decrease in the reaction rate relative to the BF$_3$/THF-mediated reaction. Importantly, the same pseudo-first-order rate constant (±5%) results if imine **4** is added immediately to the solution of PhCCLi/BF$_3$/THF/*n*-Bu$_3$N or to an analogous solution aged at −25 °C for 75 min. If the PhCCLi and BF$_3$·*n*-Bu$_3$N are allowed to stand at 25 °C for 60 min prior to adding imine **4**, the 1,2-addition is not observed. The reaction rates correlate inversely with the Lewis basicity of the amine:[25] PhNMe$_2$ >> *n*-Bu$_3$N = *n*-Pr$_3$N > Et$_3$N.[28] (1,2-Additions using BF$_3$/PhNMe$_2$/THF were too fast to monitor at −78 °C.)

BF$_3$/*n*-Bu$_3$N. NMR Spectroscopic Studies. The rate-retarding effects of trialkylamines and the accompanying attenuation of aging effects were investigated using NMR spectroscopy.

On adding [^{6}Li,^{13}C]PhCCLi to a solution of BF$_3$·*n*-Bu$_3$N in THF, the spectra recorded at −110 °C show a ^{6}Li triplet and ^{13}C quintet of dimer **6**[40] along with several minor resonances. After aging the sample at −15 °C for 2 h, the spectra showed no significant changes (Figure 2a,b). Aging at 25 °C for an hour provided a complex mixture. Once the complex mixture of putative borates appeared, subsequent addition of *n*-Bu$_3$N did not reverse their formation. Brown and co-workers suggested that addition of Me$_3$N reversed the condensation of PhCCLi with BF$_3$;[11] we suspect that they precluded, rather than reversed, the condensation.

BF$_3$/*n*-Bu$_3$N. Quantitative Rate Studies. Detailed rate studies were carried out using ReactIR spectroscopy to monitor the loss of imine **4** (1669 cm^{-1}). Pseudo-first-order conditions were established by maintaining the imine at low concentrations (0.01 M) and by using PhCCLi, BF$_3$·*n*-Bu$_3$N, free *n*-Bu$_3$N, and THF at high, yet adjustable, concentrations with pentane as the cosolvent.

The loss of imine **4** followed clean first-order behavior; yielding pseudo-first-order rate constants (k_{obsd}) that were independent of the initial imine concentration. A plot of k_{obsd} vs [BF$_3$·*n*-Bu$_3$N] shows a first-order dependence (Figure 3). Curiously, the 1,2-addition followed a zeroth-order dependence on the PhCCLi concentration (Figure 4), indicating that the ligand substitution at boron *preceding* the 1,2-addition is rate limiting.[41] We explored the influence of the solvents and ligands

(40) (a) PhCCLi is insoluble in *n*-Bu$_3$N/toluene. Further evidence that PhCCLi is not competitively solvated by trialkylamines in the presence of THF is as follows: A 0.10 M solution of [^{6}Li,^{13}C]PhCCLi in toluene containing 5.0 equiv of Et$_3$N reveals a ^{6}Li quartet (δ 0.58, $J_{\text{Li}-\text{C}} = 5.4$ Hz) and a broad (highly split) ^{13}C resonance (δ 130.7) consistent with a prismatic oligomer.[40b] In contrast, an analogous 0.10 M solution of [^{6}Li,^{13}C]PhCCLi in THF containing 5 equiv of Et$_3$N reveals the characteristic resonances of THF-solvated dimer **6** rather than the amine-solvated oligomer. (b) Brown, T. L.; Gerteis, R. L.; Bafus, D. A.; Ladd, J. A. *J. Am. Chem. Soc.* **1964**, *86*, 2135.
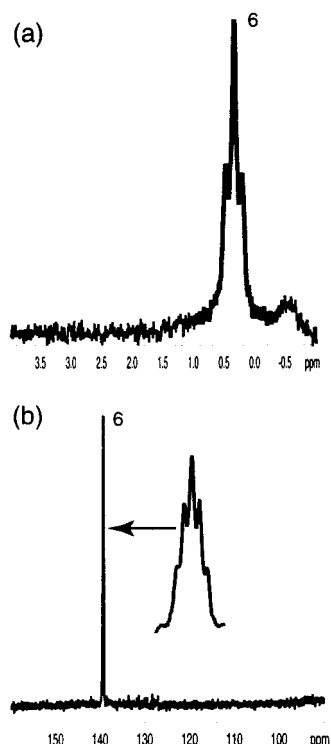
Figure 2. NMR spectra of [^{6}Li,^{13}C]PhCCLi (0.10 M) in THF/pentane (10.6 M) with 1.0 equiv of BF$_3$·n-Bu$_3$N and 0.5 equiv of n-Bu$_3$N at −110 °C (aged 2 h at −15 °C): (a) ^{6}Li NMR spectrum; (b) ^{13}C NMR spectrum.
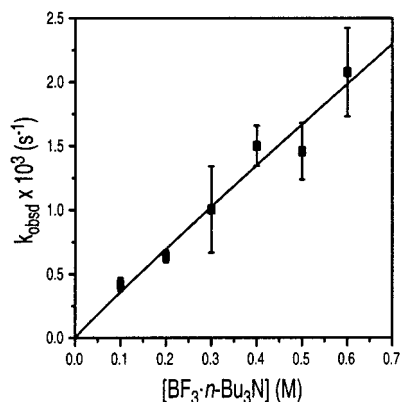
Figure 3. Plot of k_{obsd} vs [BF$_3$·n-Bu$_3$N] for the addition of PhCCLi (0.2 M) to imine **4** (0.01 M) with BF$_3$·n-Bu$_3$N and n-Bu$_3$N (0.5 M) in 8.8 M THF/pentane at −15 °C. The data are fit to $f(x) = ax^b$ ($a = (3.2 \pm 0.3) \times 10^{-3}$; $b = 1.0 \pm 0.1$).

on reaction rates in the context of dissociative and associative substitutions (eqs 3−5).[42] An associative ligand substitution at

$$\text{BF}_3\text{·}n\text{-Bu}_3\text{N} + \mathbf{4} \rightarrow [\mathbf{4}-\text{BF}_3-n\text{-Bu}_3\text{N}]^{\ddagger} \xrightarrow{\text{fast}} \text{product} \quad (3)$$

$$\text{BF}_3\text{·}n\text{-Bu}_3\text{N} \rightleftharpoons \text{BF}_3 + n\text{-Bu}_3\text{N} \quad (4)$$

$$\text{BF}_3 + \mathbf{4} \xrightarrow{\text{fast}} \text{BF}_3\text{·}\mathbf{4} \rightarrow \text{product} \quad (5)$$

boron (eq 3) would manifest a zeroth-order dependence on the n-Bu$_3$N concentration. In contrast, a mechanism involving a reversible ligand dissociation followed by rate-limiting trapping

Figure 4. Plot of k_{obsd} vs [PhCCLi] for the addition of PhCCLi to imine **4** (0.01 M) with BF$_3$·n-Bu$_3$N (0.2 M) and n-Bu$_3$N (0.2 M) in 11.8 M THF/pentane at −15 °C.

Figure 5. Plot of k_{obsd} vs [n-Bu$_3$N] for the addition of PhCCLi (0.2 M) to imine **4** (0.01 M) with BF$_3$·n-Bu$_3$N (0.1 M) in 10.6 M THF/pentane at −15 °C. The data are fit to $f(x) = ax^b$ ($a = (2.3 \pm 0.4) \times 10^{-4}$; $b = -0.69 \pm 0.07$).

of the three-coordinate BF$_3$ by the imine **4** (eqs 4 and 5) would manifest an inverse-first-order dependence on the n-Bu$_3$N concentration. (A rate-limiting n-Bu$_3$N dissociation can be excluded by the first-order imine dependence.)

The solvent dependencies proved more complex than anticipated. A plot of k_{obsd} vs [n-Bu$_3$N] (Figure 5) shows an inverse dependence consistent with a reversible amine dissociation (eqs 4 and 5); however, the nonlinear least-squares fit affords a noninteger order ($k_{obsd} \propto 1/[n\text{-Bu}_3\text{N}]^{0.69\pm0.07}$). A plot of k_{obsd} vs [THF] (Figure 6) also reveals a considerable non-integer inverse correlation ($k_{obsd} \propto 1/[\text{THF}]^{1.7\pm0.2}$). The combination of non-integer reaction orders and limited precedent for a five-coordinate BF$_3$·THF·n-Bu$_3$N complex[43] suggests that the rate inhibitions may stem from more generalized medium effects caused by the replacement of pentane with the more polar solvents. Indeed, holding the THF and n-Bu$_3$N concentrations constant and replacing pentane with the sterically demanding (poorly coordinating) 2,2,5,5-tetramethyltetrahydrofuran (Me$_4$-THF) or i-Pr$_2$NEt caused analogous inhibitions. Even replacing pentane with toluene caused up to 65% inhibition. Therefore, the pronounced solvent effects appear to be secondary shell rather than primary shell effects. Consequently, the "idealized" rate equation (eq 7)—the rate equation with so-called "medium effects" omitted—consistent with the associative substitution (eq

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(41) For rate studies of the displacement of phosphines from Lewis acidic boron centers by a lithium acetylide, see: Qiao, S.; Hoic, D. A.; Fu, G. C. *J. Am. Chem. Soc.* **1996**, *118*, 6329.
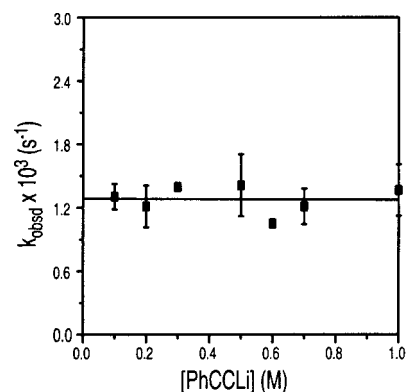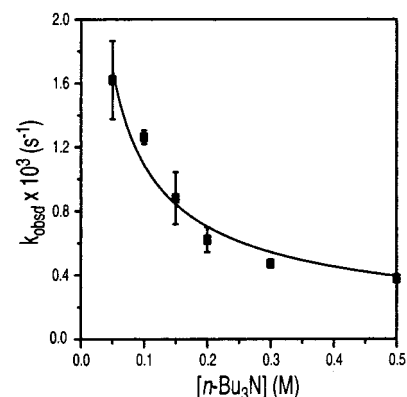
(42) For a discussion and leading references to ligand substitutions of BR$_3$ derivatives, see: Toyota, S.; Futawaka, T.; Asakura, M.; Ikeda, H.; Oki, M. *Organometallics* **1998**, *17*, 4155.

(43) Ooi, T.; Uraguchi, D.; Kagoshima, N.; Maruoka, K. *J. Am. Chem. Soc.* **1998**, *120*, 5327. Maruoka, K.; Ooi, T. *Chem. Eur. J.* **1999**, *5*, 829.
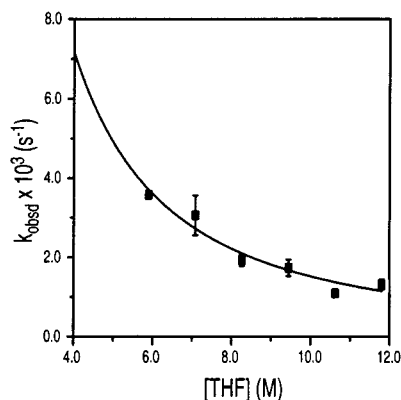
Figure 6. Plot of k_{obsd} vs [THF] for the addition of PhCCLi (0.2 M) to imine **4** (0.01 M) with $BF_3 \cdot n\text{-}Bu_3N$ (0.1 M) and $n\text{-}Bu_3N$ (0.05 M) in pentane at -15 °C. The data are fit to $f(x) = ax^b$ ($a = (7.5 \pm 3) \times 10^{-2}$; $b = -1.7 \pm 0.2$).

3) is very different than the empirically determined rate equation (eq 6).

$$-d[\mathbf{4}]/dt = k'[\text{PhCCLi}]^0[BF_3 \cdot n\text{-}Bu_3N]^{1.0 \pm 0.1} \times$$
$$[n\text{-}Bu_3N]^{-0.69 \pm 0.07}[\text{THF}]^{-1.7 \pm 0.2}[\mathbf{4}] \quad (6)$$

$$-d[\mathbf{4}]/dt = k''[BF_3 \cdot n\text{-}Bu_3N][\mathbf{4}] \quad (7)$$

Discussion

We investigated the role BF_3 plays in the addition of PhCCLi to imine **4** (eq 1). ReactIR spectroscopy offered an excellent probe of the reaction rates. A combination of ^6Li, ^{11}B, and ^{13}C NMR spectroscopies provided several key structural insights. The combined results enable us to outline the mechanism in Scheme 1.

Scheme 1
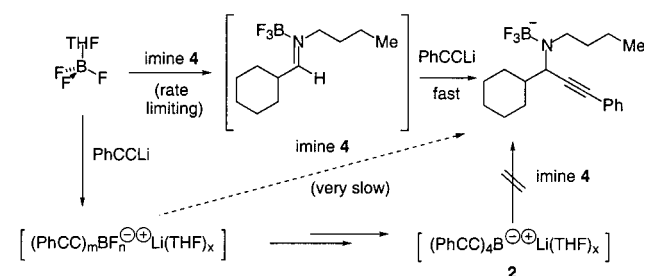
BF_3/THF. The condition-dependent reaction rates and structural changes using BF_3/THF mixtures fit into four groups:

(1) PhCCLi in THF does not undergo 1,2-addition to imine **4**; BF_3 is an essential component.

(2) If a THF solution of PhCCLi and $BF_3 \cdot$THF (derived from $BF_3 \cdot Et_2O$) is prepared at -85 °C and *immediately* treated with imine **4**, the 1,2-addition is too fast to monitor. IR and NMR spectroscopic studies confirm that PhCCLi adds to imine **4** substantially faster than it condenses with BF_3 to give a complex mixture of borates. Alternatively, if *premixed* solutions of $BF_3 \cdot$THF and imine **4** are added to the PhCCLi, the 1,2-addition is too fast to monitor regardless of temperature.

(3) If 1:1 mixtures of PhCCLi and $BF_3 \cdot$THF stand at -85 °C for several minutes, subsequent addition of imine **4** affords no 1,2-addition. ^{11}B NMR spectroscopic studies reveal a single new ^{11}B resonance that Brown tentatively assigned as borate **1**. ^{13}C NMR spectroscopic studies, however, reveal many more borates than the ^{11}B NMR spectroscopy suggests. The highly

condition-dependent structural changes coincide with the precipitous decrease in the rates of 1,2-addition, consistent with the marked aging effects observed by Yamaguchi on BF_3-mediated oxetane openings.[23]

(4) Once the PhCCLi$-BF_3$ adducts are formed, the 1,2-addition is slow even at ambient temperature. Under these relatively harsh conditions, however, further deep-seated and irreversible structural changes occur. Although these changes are poorly defined,[29] they appear to involve a cascade of reactions proceeding via mixed fluoro-alkynyl borane and borate complexes, ultimately affording $(\text{PhCC})_4BLi(\text{THF})_n$ (**2**). Notably, neither borate **2**[38,39] nor borane **3**[26] displays any reactivity.

$BF_3/n\text{-}Bu_3N$. The nearly instantaneous 1,2-additions observed before PhCCLi and BF_3 have condensed to form borates are certainly striking, yet they also pose severe technical challenges. From a synthetic perspective, the rapid self-destruction of the PhCCLi and BF_3 may limit the application of this technology, especially in large-scale reactions where mixing times can be prohibitively long. From a mechanistic perspective, the BF_3-mediated 1,2-addition is too fast to monitor by standard kinetic methods.

Since $BF_3 \cdot$THF mediates the 1,2-addition substantially faster than it reacts with PhCCLi, we suspected that complexing BF_3 with more strongly Lewis basic trialkylamines would retard the formation of borates *and* decrease the rate of 1,2-addition. Indeed, the rates of the 1,2-addition are substantially slower with added amines and correlate inversely with the Lewis basicity of the amine. NMR spectroscopic studies reveal that mixtures of $BF_3 \cdot n\text{-}Bu_3N$ and PhCCLi at -15 °C for 2 h do not condense to give borates. Of considerable importance, the 1,2-addition mediated by $BF_3 \cdot n\text{-}Bu_3N$ is highly reproducible and insensitive to aging effects.

Detailed rate studies of the $BF_3 \cdot n\text{-}Bu_3N$-mediated 1,2-addition evolved into a study of the basic coordination chemistry of BF_3 by revealing a rate-limiting associative ligand substitution at boron (eq 3).[42] The first-order dependencies on the concentrations of BF_3 and imine **4** and the zeroth-order dependence on the organolithium concentration reveal a rapid (post-rate-limiting) 1,2-addition. Rate inhibitions at elevated THF and $n\text{-}Bu_3N$ concentrations—initially suggesting an unprecedented double ligand dissociation from a putative five-coordinate $BF_3 \cdot$THF$\cdot n\text{-}Bu_3N$ complex—were eventually ascribed to surprisingly large medium effects. We surmise that these medium effects stem from disproportionate stabilization of the dipolar amine borane **7**[44] relative to transition structure **8**.[45]
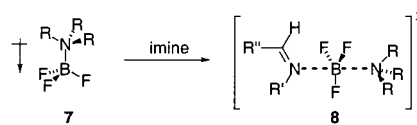
Conclusion

This investigation offers insights into the role of BF_3 in 1,2-additions of lithium acetylides. PhCCLi and BF_3 were shown to function efficiently and cooperatively before the onset of a mutual destruction. Although the details underlying the condensation of PhCCLi and BF_3 were precluded by an inordinate structural complexity and nonoptimal spectroscopic properties, we were able to exclude several borane and borates as viable intermediates. By employing $BF_3 \cdot n\text{-}Bu_3N$, detailed rate studies

(44) Jonas, V.; Frenking, G.; Reetz, M. T. *J. Am. Chem. Soc.* **1994**, *116*, 8741.

(45) Brown and co-workers noted similar medium effects on the hydroboration of alkenes using amine−borane complexes. Brown, H. C.; Kanth, J. V. B.; Zaidlewicz, M. *Organometallics* **1999**, *18*, 1310.

revealed an associative imine complexation to be the rate-limiting step. Importantly, $BF_3 \cdot n\text{-}Bu_3N$ and related $BF_3 \cdot R_3N$ complexes are air-stable, crystalline solids that may offer considerable advantages over $BF_3 \cdot Et_2O$ by precluding the aging effects associated with many BF_3-mediated organolithium reactions. Further studies of the synthetic utility of $BF_3 \cdot R_3N$ complexes are under way.

Experimental Section

Reagents and Solvents. All solvents were distilled by vacuum transfer from blue or purple solutions containing sodium benzophenone ketyl. The hydrocarbon stills contained 1% tetraglyme to dissolve the ketyl. ^6Li metal (95.5% enriched) was obtained from Oak Ridge National Laboratory. The [^6Li]n-BuLi, used to prepare [^6Li,^{13}C]PhCCLi, was prepared and purified by the standard literature procedure.[46] [^6Li,^{13}C]PhCCLi was isolated as a solid as described previously.[31] The n-BuLi used to prepare the PhCCLi in the rate studies also was recrystallized from pentane solutions.[46] $BF_3 \cdot Et_2O$ was distilled with 10 mol % Et_2O from CaH_2. The diphenylacetic acid used to check solution titers[47] was recrystallized from MeOH and sublimed at 120 °C under full vacuum. Air- and moisture-sensitive materials were manipulated under argon or nitrogen using standard glovebox, vacuum line, and syringe techniques.

$BF_3 \cdot n\text{-}Bu_3N$. Neat n-Bu$_3$N (94 mL, 0.40 mol) was added to neat $BF_3 \cdot Et_2O$ (56 g, 0.40 mol) stirred at 0 °C under a flow of nitrogen in a 300 mL round-bottom flask over 1 h. The resulting white suspension was stirred an additional 20 min, filtered under aspirator pressure, and washed with 50 mL of cold Et_2O. Et_2O was removed and the rinse was repeated. The resulting white solid was dried in vacuo to a constant weight of 80 g (0.32 mol, 80% yield). The spectroscopic properties were identical to those described previously.[32]

NMR Spectroscopic Analyses. Samples for spectroscopic analyses were prepared by using a protocol described elsewhere.[48] Routine ^6Li, ^{11}B, and ^{13}C NMR spectra were recorded on a Varian XL-400 spectrometer operating at 58.84, 128.23, and 100.58 MHz, respectively. The ^6Li, ^{11}B, and ^{13}C resonances are referenced to 0.30 M [^6Li]LiCl/MeOH (0.0 ppm, −100 °C), neat $BF_3 \cdot Et_2O$ (0.0 ppm, 25 °C), and the THF β-methylene resonance (25.37 ppm, −100 °C), respectively.

IR Spectroscopic Analyses. IR spectra were recorded using a ReactIR 1000 from ASI Applied Systems[49] fitted with a 30-bounce silicon-tipped (SiComp) probe optimized for sensitivity. A representative reaction was carried out as follows: The IR probe was inserted through a nylon adapter and FETFE O-ring seal into an oven-dried cylindrical flask fitted with a magnetic stir bar and T-joint. The T-joint was fitted with an argon line and septum for injections. After evacuation under full vacuum and flushing with argon, the flask was charged with the solution of interest and cooled to the indicated temperature in a Neslab model ULT80 cooling bath. The flask was charged with reagents as described above, a background spectrum was recorded, and imine **4** was added neat with stirring. Spectra were acquired at 1 min intervals. Data manipulation and statistical analyses were carried out by using the system 2.1a ReactIR software in conjunction with the nonlinear least-squares fitting protocols in the Scientist package provided by Micromath.

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(47) Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879.

(48) Romesberg, F. E.; Bernstein, M. P.; Fuller, D. J.; Harrison, A. T.; Collum, D. B. *J. Am. Chem. Soc.* **1993**, *115*, 3475.

(49) ASI Applied Systems, Millersville, MD 21108.