Hydroamination Hot Paper

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Frustrated Lewis Pair Catalyzed Hydroamination of Terminal Alkynes**

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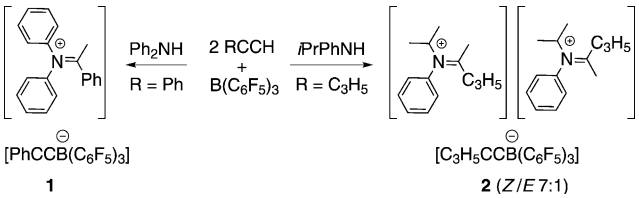
Much of the recent research in the area of frustrated Lewis pairs (FLPs) has focused on hydrogenation catalysis.[1] While initial reports described a limited substrate scope, recent advances have included the demonstration of metal-free hydrogenation of olefins,[2] anilines,[3] N-heterocyclic compounds,[4] and alkynes,[5] as well as enantioselective hydrogenation of imines.[6] Moreover, FLPs have also found applications in polymerization catalysis.[7] To date, the majority of the reported reactions of FLPs with small-molecule substrates is stoichiometric. For example, we have reported reactions of alkynes with FLPs comprised of $B(C_6F_5)_3$ or $Al(C_6F_5)_3$·(PhMe) with phosphines, resulting in either addition or deprotonation products.[8] The addition pathway affords zwitterionic vinyl phosphonium borate or alumininate salts. In contrast, the deprotonation pathway affords phosphonium alkynylborates or aluminates. The course of the reaction is dependent on the basicity of the phosphine. In related work, the groups of Berke[9] and Erker[10] have studied the reactivity of terminal and internal alkynes with the Lewis acid $B(C_6F_5)_3$, uncovering the fascinating 1,1-carboboration reactions, which afford alkenylboranes. Despite this reactivity, Erker and co-workers showed that $B(C_6F_5)_3$ can mediate the intramolecular cyclization of an *ortho*-ethynylaniline to access a cyclic anilinium borate.[11] Berke and co-workers investigated related intermolecular reactions of alkynes and $B(C_6F_5)_3$ with 2,6-lutidine and 2,2,5,5-tetramethylpiperidine,[9] demonstrating that these systems effect deprotonation of the terminal alkyne to afford ammonium alkynylborates.

In order to expand the scope of applying FLPs in catalysis, we turned our attention to hydroaminations. A wide variety of catalysts based on rare-earth metals,[12] early-[13,14] and late-transition metals,[15] as well as lanthanides[16] and actinides[17] have been previously reported. Nonetheless, metal-free routes remain less explored. In a recent report, the exploitation of hydroxylamines to effect metal-free hydroamination of alkynes was illustrated, although forcing conditions were required.[18] In the present study, we show that $B(C_6F_5)_3$ promotes the addition of aryl amines to alkynes, comprising a metal-free approach to catalytic hydroamination to afford the products of a Markovnikov addition. Moreover, subsequent to hydroamination catalysis, the borane catalyst can also be exploited for metal-free catalytic hydrogenation, providing a one-pot stepwise catalytic route to the corresponding amine derivatives.

Initially, we performed the three-component stoichiometric reaction of Ph_2NH, $B(C_6F_5)_3$, and phenylacetylene in CD_2Cl_2. The ^1H, ^{11}B, and ^{19}F NMR spectra showed the consumption of two equivalents of phenylacetylene to afford the salt $[Ph_2N{=}C(CH_3)Ph][PhC{\equiv}CB(C_6F_5)_3]$ (**1**; Scheme 1), leaving a portion of the starting materials Ph_2NH and $B(C_6F_5)_3$ unreacted. Adjustment of the alkyne



Scheme 1. Stoichiometric hydroaminations giving **1** and **2**.

stoichiometry afforded **1** in 90% yield. The ^1H NMR spectrum of **1** exhibits a diagnostic methyl singlet at 2.89 ppm with the corresponding carbon resonance at 28.3 ppm. In addition, a downfield carbon resonance at 190.1 ppm is attributable to the iminium carbon atom (N=C). The alkynylborate anion $[PhC{\equiv}CB(C_6F_5)_3]$ gave rise to the ^{11}B NMR signal at −20.8 ppm and the ^{19}F NMR resonances at −132.7, −163.8, and −167.3 ppm.[8] In a similar fashion, the reaction of two equivalents of ethynylcyclopropane with $B(C_6F_5)_3$ and *i*PrPhNH at room temperature afforded yellow crystals formulated $[i\text{PrPhN}{=}C(CH_3)C_3H_5]$-$[C_3H_5C{\equiv}CB(C_6F_5)_3]$ (**2**; Scheme 1), evidenced by ^1H, ^{11}B, ^{13}C, and ^{19}F NMR data. In this case, the ^1H NMR spectrum showed the formation of the iminium cation as a mixture of the *Z* and *E* isomers in a ratio of 7:1. The nature of compounds **1** and **2** was confirmed unambiguously by X-ray crystallographic studies (Figure 1). According to these data, the N=C bond lengths in the cations were 1.308(2) Å and 1.305(3) Å in **1** and **2**, respectively, while the sum of the angles about the N atoms were 359.9° in both cases.

These hydroamination reactions were also performed under catalytic conditions. Slow addition of the terminal alkyne 2-ethynylanisole to a solution of Ph_2NH and 10 mol% of $B(C_6F_5)_3$ in toluene at room temperature over a period of 10 hours afforded the catalytic formation of the 2-methoxylphenyl-substituted enamine product $Ph_2N(2\text{-}MeOC_6H_4)C{=}CH_2$ (**3**) in 84% yield of isolated product. The ^1H NMR

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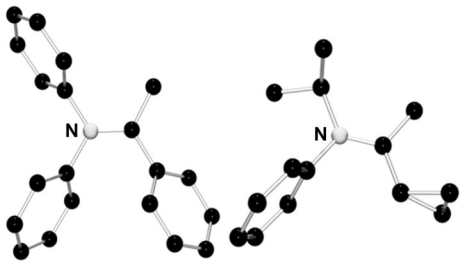


Figure 1. POV-ray depiction of the cations of **1** (left) and **2** (right). Anions and hydrogen atoms have been omitted for clarity.

spectrum of **3** displayed two singlets at 5.01 and 4.90 ppm, which are characteristic of the inequivalent geminal hydrogen atoms. The corresponding carbon center gives rise to a $^{13}C\{^1H\}$ NMR signal at 107.7 ppm. Furthermore, the adjacent quaternary carbon atom resulted in a resonance at 149.8 ppm. These NMR data as well as the results of the MS analysis support the formulation of **3**. The NMR data were consistent with the formation of the Markovnikov product in which the nitrogen is added to the substituted carbon of the terminal alkyne.

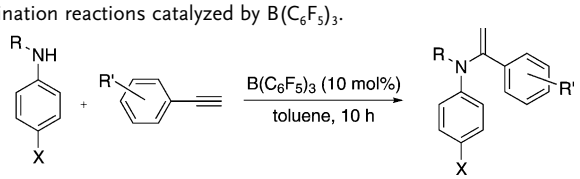
The analogous treatment of Ph_2NH with 2-ethynyltoluene in the presence of the $B(C_6F_5)_3$ catalyst afforded $Ph_2N(2\text{-}MeC_6H_4)C{=}CH_2$ (**4**) in 69% yield of isolated product, while the reaction with 1-ethynylnaphthalene gave $Ph_2N(C_{10}H_7)C{=}CH_2$ (**5**) in 62% yield (Table 1). The corresponding reactions of Ph_2NH with phenylacetylene and 2-bromo-phenylacetylene afforded $Ph_2N(C_6H_5)C{=}CH_2$ (**6**) and $Ph_2N(2\text{-}BrC_6H_4)C{=}CH_2$ (**7**) in 74 and 52% yield, respectively (Table 1). Similar to **3**, the ^1H and $^{13}C\{^1H\}$ NMR data for these products were consistent with these formulations.

This hydroamination strategy also proved effective for substituted diphenylamines. For example, $(p\text{-}FC_6H_4)_2NH$ in combination with 10 mol% of $B(C_6F_5)_3$ reacted with halogenated phenylacetylenes to afford $(p\text{-}FC_6H_4)_2N(2\text{-}BrC_6H_4)C{=}CH_2$ (**8**) and $(p\text{-}FC_6H_4)_2N(2\text{-}FC_6H_4)C{=}CH_2$ (**9**), while the corresponding 2-thiophenylacetylene gave $(p\text{-}FC_6H_4)_2N(2\text{-}SC_4H_4)C{=}CH_2$ (**10**) and *i*PrPhN(2-SC_4H_4)C=CH_2 (**11**) when reacted with *i*PrPhNH (Table 1). The reaction of Ph_2NH with 9-ethynylphenanthrene gave $Ph_2N(C_{14}H_9)C{=}CH_2$ (**12**) and $(p\text{-}FC_6H_4)_2NH$ was used to prepare $(p\text{-}FC_6H_4)_2N(C_{14}H_9)C{=}CH_2$ (**13**). Similarly, reactions of the appropriate combinations of amine and alkyne using the borane catalyst afforded $(p\text{-}FC_6H_4)_2N(3\text{-}FC_6H_4)C{=}CH_2$ (**14**), $Ph_2N(3,5\text{-}F_2C_6H_4)C{=}CH_2$ (**15**), and $Ph_2N(3\text{-}CF_3C_6H_4)C{=}CH_2$ (**16**), although in these cases cooling to −30 °C was necessary to maximize yields to between 68–77% (Table 1). This impact of the temperature was most dramatically demonstrated with the formation of **14**, where performing the reaction at 25 °C gave **14** in a poor yield (19%), while at −30 °C the yield of **14** was enhanced to 74%.

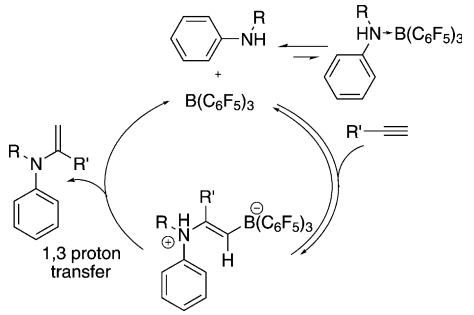
The interpretation of the results of these hydroamination reactions requires the FLP nature of the amine/borane combination. The interaction of the borane with the alkyne prompts the addition of the amine to generate a zwitterionic intermediate. Analogous additions to alkynes have been previously described for phosphine/borane,[8] thioether/borane,[19] and pyrrole/borane[8b] FLPs. In the present arylammonium intermediate, the ammonium proton is acidic and migrates to the carbon atom adjacent to boron center, prompting the formation of the enamine product with concurrent release of $B(C_6F_5)_3$. The borane is then available to participate in further hydroamination catalysis. It is noteworthy that the postulate of an FLP-type addition intermediate in the proposed mechanism (Scheme 2) accounts for the observed Markovnikov addition of the amines to the alkynes and thus the nature of the enamine products. It is noted above that this catalytic formation of the enamine requires the slow addition of the alkyne. This is a result of the subsequent deprotonation of the alkyne by the FLP derived from the enamine/borane combination, affording iminium alkynylborate salts analogous to **1** and **2**. The observation of catalytic hydroamination infers that the amine addition is faster than the alkyne deprotonation by the enamine.

The catalytic generation of these enamines together with the previously established ability of FLPs to mediate hydrogenations of enamines[20] prompted us to investigate one-pot stepwise hydroamination/hydrogenation processes. Following the catalytic hydroaminations described above, the reaction mixtures containing the two enamines **9** and **15** were exposed to H_2 (4 atm) and heated to 80 °C for 14 hours. Pleasingly, the $B(C_6F_5)_3$ catalyst successfully promoted the second catalytic process,

Table 1: Hydroamination reactions catalyzed by $B(C_6F_5)_3$.

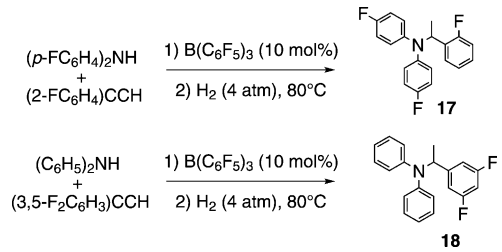


Amine	Alkyne	*T* [°C]	Product	Yield [%]
Ph_2NH	2-$MeOC_6H_4CCH$	25	$Ph_2NC(2\text{-}MeOC_6H_4){=}CH_2$ (**3**)	84
Ph_2NH	2-MeC_6H_4CCH	25	$Ph_2NC(2\text{-}MeC_6H_4){=}CH_2$ (**4**)	69
Ph_2NH	$C_{10}H_7CCH$	25	$Ph_2NC(C_{10}H_7){=}CH_2$ (**5**)	62
Ph_2NH	PhCCH	25	$Ph_2NC(Ph){=}CH_2$ (**6**)	74
Ph_2NH	2-BrC_6H_4CCH	25	$Ph_2NC(2\text{-}BrC_6H_4){=}CH_2$ (**7**)	52
$(p\text{-}FC_6H_4)_2NH$	2-BrC_6H_4CCH	25	$(p\text{-}FC_6H_4)_2NC(2\text{-}BrC_6H_4){=}CH_2$ (**8**)	67
$(p\text{-}FC_6H_4)_2NH$	2-FC_6H_4CCH	25	$(p\text{-}FC_6H_4)_2NC(2\text{-}FC_6H_4){=}CH_2$ (**9**)	78
$(p\text{-}FC_6H_4)_2NH$	2-SC_4H_4CCH	25	$(p\text{-}FC_6H_4)_2NC(2\text{-}SC_4H_4){=}CH_2$ (**10**)	54
*i*PrPhNH	2-SC_4H_4CCH	25	*i*PrPhNC(2-SC_4H_4)=CH_2 (**11**)	58
Ph_2NH	$C_{14}H_9CCH$	25	$Ph_2NC(C_{14}H_9){=}CH_2$ (**12**)	75
$(p\text{-}FC_6H_4)_2NH$	$C_{14}H_9CCH$	25	$(p\text{-}FC_6H_4)_2NC(C_{14}H_9){=}CH_2$ (**13**)	75
$(p\text{-}FC_6H_4)_2NH$	3-FC_6H_4CCH	−30	$(p\text{-}FC_6H_4)_2NC(3\text{-}FC_6H_4){=}CH_2$ (**14**)	74
Ph_2NH	3,5-$F_2C_6H_3CCH$	−30	$Ph_2NC(3,5\text{-}F_2C_6H_3){=}CH_2$ (**15**)	68
Ph_2NH	3-$CF_3C_6H_4CCH$	−30	$Ph_2NC(3\text{-}CF_3C_6H_4){=}CH_2$ (**16**)	77



Scheme 2. Proposed mechanism of catalytic hydroamination.

which gave the amines $(p\text{-}FC_6H_4)_2N(2\text{-}FC_6H_4)C(H)CH_3$ (**17**) and $Ph_2N(3,5\text{-}F_2C_6H_3)C(H)CH_3$ (**18**) in 77 and 64% overall yield of isolated product, respectively (Scheme 3). Monitoring the hydrogenation part of these reactions by ^1H NMR spectroscopy showed in both cases the appearance of a quartet



Scheme 3. One-pot stepwise catalytic hydroamination/hydrogenation.

(attributable to the methine proton) and a doublet (assignable to the methyl moiety of the respective amine products) with the corresponding demise of the signals attributable to the geminal protons of the enamines. In an alternative approach to the hydrogenation catalysis, 5 mol% of the hydrogenation catalyst $Mes_2PH(C_6F_4)BH(C_6F_5)_2$[21] was added to the reaction mixture subsequent to the hydroamination reaction, and the resulting mixture was pressurized with H_2 and heated to 80 °C. In this case, the reaction time was reduced to 3 hours.

In summary, $B(C_6F_5)_3$ catalyzes the Markovnikov hydroamination of alkynes by a variety of secondary aryl amines, resulting in a metal-free route to enamines. The regiochemistry is consistent with transient ammonium–borate addition intermediates, which undergo subsequent proton migration to release the borane and the enamine product. This view is also supported by stoichiometric reactions of amine, borane, and two equivalents of alkyne, which afford iminium alkynylborate salts. This metal-free hydroamination is also amenable to the subsequent use of the catalyst in hydrogenation catalysis, allowing the conversion of the enamines to the corresponding amines in a one-pot stepwise manner. Efforts to expand the application of FLPs in catalysis and to exploit these findings in the development of metal-free syntheses are areas of active pursuit in our laboratories.

Experimental Section

Synthesis of $[Ph(CH_3)C{=}NPh_2][PhC{\equiv}CB(C_6F_5)_3]$ (**1**) and $[Z\text{-}C_3H_5(Me)C{=}N(i\text{Pr})Ph][C_3H_5C{\equiv}CB(C_6F_5)_3]$ (**2**): These compounds were prepared in a similar fashion, thus the preparation of only one is detailed. In a glovebox, a 4-dram vial equipped with a stir bar was charged with a slurry of $B(C_6F_5)_3$ (0.379 g, 0.740 mmol) and diphenylamine (0.125 g, 0.740 mmol) in pentane (20 mL). The phenylacetylene was added to the vial in one portion (0.151 g, 1.48 mmol), resulting in the instant formation of a yellow precipitate. The reaction was stirred at RT for 2 h, after which the solvent was decanted. The solid was washed with *n*-pentane (3×10 mL) to give a yellow precipitate in 90% yield.

Synthesis of **3**–**15:** These compounds were prepared in a similar fashion, thus the preparation of only one is detailed. In a glovebox, a 4-dram vial equipped with a stir bar was charged with Ph_2NH (12.5 mg, 0.074 mmol), $(p\text{-}C_6H_4F)_2NH$ (15.2 mg, 0.074 mmol), or *i*PrPhNH (10.0 mg, 0.074 mmol) and $B(C_6F_5)_3$ (3.8 mg, 0.0074 mmol) in toluene (4 mL). The respective alkyne (0.074 mmol) was added by microsyringe at a rate of 10 mol%/h (oils) or by weighing the portions into a vial (solids). The total reaction time was 10 h, after which the work-up of the reaction was conducted under normal atmosphere (outside the glovebox). The solvent was removed in vacuo and the crude mixture dissolved in ethyl acetate (5 mL) and passed through a short (4 cm) column of silica gel previously treated with Et_2NH. The product was purified by column chromatography using *n*-hexane/ethyl acetate (6:1) as eluent.

Synthesis of **14**–**16**: These compounds were prepared with slight modifications to the procedure described above. Before the addition of the alkyne, the vial was cooled at −30 °C (freezer) for 5 min. The vial was then placed in a pre-cooled brass well and the alkyne was added by microsyringe or from another vial after weighing. The reaction vial was kept in the pre-cooled brass well. Before the addition of another aliquot of the alkyne, the brass well was placed in the freezer at −30 °C for 5 min. The work-up of the reactions was similar to the procedure described above.

Tandem hydroamination and hydrogenation of **9** and **15** to **17** and **18**, respectively: A general procedure is provided for the preparation of compounds **17** and **18**. Following the catalytic hydroamination reaction (10 h), in the glovebox, the reaction mixture was transferred to an oven-dried glass tube with Teflon screw cap. The reaction tube was degassed once through a freeze-pump-thaw cycle on a vacuum/H_2 line and filled with H_2 (4 atm) at −196 °C. The tube was placed in an oil bath at 80 °C for 14 h. The solvent was removed in vacuo and the mixture was dissolved in ethyl acetate (5 mL) and passed through a short (4 cm) column of silica gel previously treated with Et_2NH. The crude mixtures consisted of the starting materials (amine and alkyne) and the product. The product was purified by column chromatography using *n*-hexane/ethyl acetate (6:1) as eluent. Alternatively hydrogenation can be performed with the addition of (5 mol%) $Mes_2PH(C_6F_4)BH(C_6F_5)_2$ (2.8 mg, 0.0037 mmol) to the reaction mixture before the transfer to the glass tube. The tube was filled with H_2 (4 atm) and placed in an oil bath at 80 °C. The reaction was stopped after 3 h at 80 °C and the work-up was similar to the procedure described above.

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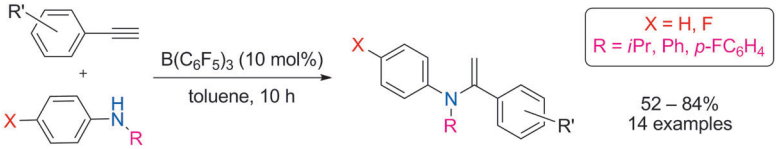
Communications

Hydroamination

T. Mahdi, D. W. Stephan* ▬ ▮▮▮▮–▮▮▮▮

Frustrated Lewis Pair Catalyzed Hydroamination of Terminal Alkynes



Catalytic amounts of the Lewis acid B-$(C_6F_5)_3$ enable the hydroamination of terminal alkynes by aryl amines to the corresponding enamines. In accord with the results of stoichiometric reactions, the mechanism of this reaction involves a frustrated Lewis pair (FLP). The hydroamination can be followed by an FLP-catalyzed hydrogenation, resulting in a one-pot stepwise synthesis of amine derivatives.