

Communication

Catalytic Hydroarylation of Alkenes with Phenols using B(C₆F₅)₃

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Supporting Information

ABSTRACT: We demonstrate that tris(pentafluorophenyl)borane, B- $(C_6F_5)_{31}$ is shown to be an effective catalyst for the hydroarylation of olefins to yield substituted phenols. This system features fast reaction times, mild conditions, and good yields for a select scope of olefinic substrates and various phenols, resulting in C-C bond formation. Experimental data support two possible mechanisms, where the Lewis



acid can activate either the olefin or the phenol as the first step in the catalytic mechanism.

he significant growth in main-group-catalyzed reactions has brought focus on pushing the boundaries into new reactivity. The formation of alkyl-substituted arenes can be traditionally achieved through Friedel-Crafts substitution reactions (electrophilic aromatic substitution).¹ These reactions generally exploit stoichiometric or catalytic amounts of a Lewis acid to proceed. Another atom-economical route toward the desired C-C bond formation is through the reductive coupling of olefins with arenes via hydroarylation. This reaction results in the addition of an aromatic C-H bond across an unsaturated substrate, but Lewis acid catalysts limit application to weakly Lewis basic substrates. Transition-metal catalysts have been used to promote this reaction.² For example, Beller and co-workers described the use of FeCl₃ as a catalyst for the hydroarylation of styrenes at elevated temperatures.³ Tunge et al. reported that catalytic TiCl₄ can promote the formation of dihydrocoumarins via a hydroarylation-lactonization reaction from phenols and benzylidene malonic esters (Scheme 1).^{2c} One recent example by Bertrand

Scheme 1. Examples of Lewis acid Catalyzed Hydroarylation



et al. has shown that an anti-Bredt bis(amino)carbene cationic Au(I) complex can tolerate Lewis bases, catalyzing the hydroarylation of alkenes with diarylamines at >135 °C (Scheme 1).⁴ However, the recent renaissance in main-group chemistry and the discovery of frustrated Lewis pairs have provided effective alternatives to transition-metal catalysts.⁵ Strong Lewis acids have been used independently, or in frustrated Lewis pair (FLP) combinations, to promote C-C bond formation.⁶

Nevertheless, the transition-metal-free hydroarylation of olefins has been less studied. Niggemann and colleagues have reported the calcium-catalyzed hydroarylations of alkenes using $Ca(NTf_2)_2$.⁷ Heterogeneous aluminum chlorofluoride (ACF) has also been shown to promote the hydroarylation of olefins with arenes. The substrates described in this work did not contain Lewis basic functionalities.⁸ Stephan and co-workers have shown that highly reactive electrophilic phosphonium cations can catalyze the hydroarylation of olefins or alkynes with diarylamines under mild conditions (Scheme 1).⁹ In these cases the steric bulk of the diarylamine prevents adduct formation of the amine Lewis base with the Lewis acid catalyst, allowing for activation of the olefin. In 2017, Werner and coworkers illustrated the use of $B(C_6F_5)_3$ as a catalyst for the Michael reaction between arene C-H bonds and electron deficient α,β -unsaturated carbonyl compounds at 80 °C.¹⁰ In these reactions, the arenes were limited to N,N'-disubstituted anilines, indoles, and furans. Very recently, Yuan, Yao, and coworkers have utilized $[Ph_3C][B(C_6F_5)_4]$ as a catalyst for the hydroarylation of sterically encumbered anilines with a series of olefins at elevated temperatures.¹¹

Alcohols, while less Lewis basic than amines, may still interact with Lewis acids, and main-group-catalyzed hydroarylation reactions with phenol have been sparsely reported. Catalytic reactions developed for these combinations have predominately focused on the hydroalkoxylation reaction, the addition of the O-H bond across the olefin.¹² One report from scientists at Bayer in 1957 reported the use of aluminum

Received: August 28, 2018

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with phenol at >150 °C and high pressures, resulting in the hydroarylation of alkenes, presumably through an Al(OPh)₃ catalyst.¹³ The aforementioned examples of main-group Lewis acid catalyzed hydroarylation reactions generally are done at higher temperatures, where lower yields are reported at room temperature, presumably attributed to adduct formation with the Lewis basic arene. Still, it has been shown through frustrated Lewis pair chemistry that an equilibrium exists between Lewis acid/base adduct and free components, such as ethers and B(C₆F₅)₃, which can be exploited to activate small molecules.¹⁴ This led us to believe that similar reactivity may be possible with phenols. Herein, we describe the use of B(C₆F₅)₃ as a hydroarylation catalyst to achieve C–C bond formation between olefins and phenols at room temperature.

The reaction between phenol and $B(C_6F_5)_3$ in CDCl₃ strongly implied that a weak, reversible adduct was being formed. Using 10 mol % of $B(C_6F_5)_3$, the ¹⁹F NMR spectrum of the reaction mixture exhibited three resonances at -129.7, -147.2, and -160.9 ppm with a para-meta gap of $\Delta p \cdot m =$ 13.7 ppm, indicating adduct formation with phenol (free $B(C_6F_5)_3 \Delta p - m = 17.4 \text{ ppm}).^{6c}$ Nevertheless, only one species was observed in the ¹H NMR spectrum, implying that a rapid and reversible exchange is occurring. A 1D ¹H-¹⁹F HOESY experiment was undertaken on the reaction mixture and showed through-space correlation between the O-H and ortho C-H protons on the phenol with the borane, supporting that a reversible adduct was forming. No C₆F₅H was observed, even after 48 h, implying that protodeboronation, a common degradation pathway for $B(C_6F_5)_3$, was not occurring. We also observed analogous spectral features for mixtures of olefins and $B(C_6F_5)_{3}$, where no difference was evident in the ¹H NMR spectrum but signals in the ¹⁹F NMR spectrum broadened and shifted from those of the free Lewis acid (see the Supporting Information). These data are corroborated by previous reports that olefins can weakly interact with Lewis acidic boranes.¹

The respective equilibria observed for both phenol and olefins with $B(C_6F_5)_3$ prompted us to investigate the feasibility of the borane to activate the olefin for hydroarylation with phenols. We initially probed the reaction of phenol with 1,1diphenylethylene in the presence of 10 mol % of $B(C_6F_5)_3$. This reaction rapidly produced the para-substituted hydroarylated product 4-(1,1-diphenylethyl)phenol (1) in 98% yield after 3 h at 25 °C (Scheme 2), as evidenced by the disappearance of the olefin resonance in the ¹H NMR spectrum and the appearance of two apparent doublets at 7.04 and 6.77 ppm, respectively, indicating a para-substituted aromatic ring. Strong Lewis acids have previously been shown to catalyze the Friedel-Crafts dimerization of 1,1-diphenylethylene.¹⁶ Nonetheless, in the presence of phenol this product is not observed, suggesting that the weak phenol adduct with the borane prevents dimerization.

We endeavored to explore the olefin substrate scope, and in a similar fashion, phenol reacts with α -methylstyrene, affording the para-substituted phenols and a minor amount of polymerized products. The hydroarylated product could be isolated in good yield (90%; 2). Chlorinated styrenes also undergo reactivity, with the hydroarylated product 4-(2-(4chlorophenyl)propan-2-yl)phenol (5) isolated in 88% yield. Strained aromatic substrates also undergo hydroarylation reactivity. Acenaphthylene will rapidly react with phenol under these conditions to yield the hydroarylated product **6** in 76% isolated yield. This is very evident in the ¹H NMR spectrum through depletion of the olefinic resonance at 7.07



^{*a*}Conversions were calculated by ¹H NMR integration. Isolated yields are reported in parentheses. A catalyst loading of 10 mol % was found to be optimal; a lower catalyst loading resulted in a decrease in conversion.

ppm and the formation of three new resonances corresponding to the reduced acenaphthene C₂H₃Ar fragment at 5.16, 3.98, and 3.39 ppm. All three peaks have complex multiplicities, indicating significant coupling to protons on the aromatic rings and the diastereotopic nature of the CH₂ protons (see the Supporting Information). A control experiment with 10 mol % of $B(C_6F_5)_3$ and acenaphthylene resulted in immediate broadening of all peaks in the ¹H NMR, yet free $B(C_6F_5)_3$ was observed in the ¹⁹F NMR spectrum. The sample was analyzed by variable- temperature NMR to determine whether or not this was a rapid equilibrium; however, even at -40 °C, no evidence of coalescence was observed. Finally, norbornene also underwent hydroarylation with phenol, resulting in a mixture of para- and ortho-substituted products 11a,b in 58% and 39% yields, respectively, after 3 h. Interestingly, transstilbene does not show any reactivity, nor do more highly substituted aryl olefins, as observed with triphenylethylene. Simple aliphatic alkenes such as cyclohexene and 1-hexene also do not react under these conditions or at elevated temperatures.

To further investigate the scope of the reaction, we explored a series of para-substituted phenols. 4-Methylphenol, 4-*tert*butylphenol, and 4-methoxyphenol undergo catalytic hydroarylation under these conditions, resulting in products 3, 4, 7, **10**, **12**, and **15** (Scheme 2). Unexpectedly, phenols containing a deactivating fluorine or bromine substituent still underwent hydroarylation with acenaphthylene or norbornene with varying yields (19–69%), resulting in their respective *ortho*substituted products **8**, **9**, **13**, and **14** (Scheme 2). The selective hydroarylation of olefins with phenols was initially surprising because $B(C_6F_5)_3$ is an effective catalyst for hydroelementation reactions, including hydrosilylation, hydroamination, and hydrothiolation.¹⁷ Thus, we sought out further studies to explore the mechanism of the hydroarylation reaction. We hypothesized that the reaction could proceed via two possible mechanisms (Scheme 3). The Lewis acidic





borane could activate the phenol (A) and protonation of the olefin could occur (B) followed by a Friedel–Crafts C–C bond formation (C) and proton migration (D) to release the catalyst and product. Alternatively, the borane could activate the olefin (E), allowing for rapid Friedel–Crafts C–C bond formation (F), followed by proton migration to release the product and regenerate the catalysts.

We investigated the reactions between 1,1-diphenylethylene with both 2,4,6-trimethylphenol and anisole under standard catalytic conditions. Unsurprisingly, no reaction was observed with 2,4,6-trimethylphenol, as the ortho and para positions in the aromatic ring are blocked to substitution. Interestingly, no reaction occurred with anisole; only the Friedel–Crafts cyclodimerized olefin was observed. This unexpected result raised the possibility that the O–H functionality can act as a Brønsted acid in the catalytic cycle. Further, Parkin et al. had shown that the pK_a values of aqua and alcohols increase upon coordination to $B(C_6F_5)_3$.¹⁸ However, Hartwig and He reported that Brønsted acid catalysts mediate the hydroalkoxylation reaction between phenols and olefins.¹⁹

In order to further probe the role of the hydroxyl functionality, a series of alcohols were explored under the standard catalytic conditions with various olefins. Nevertheless, no conversion was observed when aliphatic alcohols, such as *tert*-butyl alcohol, benzyl alcohol, and 1,1-diphenylmethanol, were used. Furthermore, hexafluoroisopropyl alcohol, which has a pK_a similar to that of phenol (9.3 vs 9.98),²⁰ also does not undergo any reaction. In these reactions, it was clear by multinuclear NMR analysis that an adduct between the alcohol and the borane was being formed. 2-Allylphenol has been

shown to readily undergo intramolecular hydroalkoxylation, resulting in the cyclized dihydrobenzofuran.²¹ Nevertheless, under our reaction conditions no appreciable yield of the cyclized product was observed (Scheme 4, top). Additionally,

Scheme 4. Hydroalkoxylation Attempts Using 2-Allylphenol (Top) and 1-Naphthol Isomerization Mediated by $B(C_6F_5)_3$ (Bottom)



we screened the ability of triflic acid to act as a catalyst for the model reaction between norbornene and *p*-methoxyphenol, and these results confirmed that $B(C_6F_5)_3$ and Brønsted acid catalysts produce different products (see the Supporting Information).

Finally, we explored the use of phenol-*d* in the reaction. The preparation of phenol-d also results in the partial deuteration of the para and ortho positions, as observed in the ²H NMR spectrum.²² The deuterated analogue of 1 was prepared from phenol-d, showing substitution at only the para position of the phenol as evidenced by the ¹H, ²H, and ¹³C NMR spectra. Only two resonances were observed in the ²H NMR at 6.72 and 2.09 ppm, corresponding to the o-C-D and the CH₂D resonances, respectively (see the Supporting Information). These results imply that protonation of the olefin may be occurring; however, the disappearance of the O-D resonance at 5.64 ppm is not unprecedented. Erker et al. have reported that $B(C_6F_5)_3$ can promote the formation of the keto isomer of 1-naphthol (Scheme 4, bottom);²³ thus, the O-D may be scrambled into the phenol ring and this implies that the mechanism may be more complicated than was initially presumed.

In summary, we have shown that $B(C_6F_5)_3$ is an effective catalyst for the reductive hydroarylation of olefins with phenols. Preliminary experiments indicate that the reaction mechanism could proceed via activation of the olefin or phenol by the Lewis acid with a subsequent Friedel–Crafts C–C bond formation step. Ongoing efforts are underway in our laboratory to further investigate this reaction to fully elucidate the mechanism and expand the scope.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.8b00621.

Experimental details, characterization data of all compounds, and multinuclear NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors dedicate this paper to Professor Douglas W. Stephan in celebration of his 65th birthday. The authors gratefully acknowledge financial support from the NSERC of Canada and the Canadian Foundation for Innovation. C.B.C. is grateful for the award of a Canada Research Chair. The authors thank Professors Thomas Baumgartner and Barry Lever for the use of laboratory space and equipment while our laboratory was being constructed.

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