Frustrated Lewis pair catalyzed S-H bond borylation

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Frustrated Lewis pair catalyzed S-H bond borylation

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Supporting Information Placeholder

The frustrated Lewis pair (FLP) $[NMe_2\text{-}C_6H_4\text{-}BH_2]_2$ is shown to catalyze the dehydrogenative borylation of thiols. The scope of the reaction, the experimental and computational investigation of the mechanism and the application of the system to a one-pot Michael addition on α-β unsaturated carbonyl leading to the β sulfido ketone are reported.

INTRODUCTION

Boron-containing molecules are playing a predominant role in the construction of molecular architectures and are ubiquitous reagents in synthetic chemistry. The most notorious examples are alkyl- or aryl-boronates used as transmetallation agents in the Suzuki-Miyaura palladium cross-coupling reaction.[1] Although compounds containing boron-heteroelement (B-E) bonds are less common, they have been drawing attention as reagents in metal-free transformations.[2] For example, diboranes (B-B) have been used in diboration and borylation reactions[3] and the B-N compounds have been used in the Strecker-type aminative cyanation and in Mannich-type transformations.[4] The Michael addition on α,-β unsaturated carbonyl compounds can also be performed using B-N,[5] B-S,[6] B-P[7] and B-Se[8] reagents. Similarly, the insertion of the diazo Me_3SiCHN_2 in a B-S bond can lead to $H{-}C(SR)(Bpin)(SiMe_3)$.[9]

While many transition-metal catalyzed transformations have been reported to generate B-E (E = O, N, S, P) containing species,[10] it was recently demonstrated by Bertrand *et al*. that many of these reagents can be prepared directly from hydroboranes (B-H) and protic reagents (E-H) in the absence of a catalyst.[11] However, the preparation of B-S containing compounds in good yields is challenging since the uncatalyzed borylation of thiols require heating up at 120 °C for up to 96 h. Therefore, catalysis is a requirement in the preparation of thioboranes[12] which are useful precursors for the synthesis of a large array of sulfur containing bioactive molecules.[13]

Although transition metal catalysts remain ubiquitous in the construction of chemical bonds, a new paradigm in catalysis has emerged with the discovery of frustrated Lewis pairs (FLPs). FLPs have been shown to mediate the metal-free hydrogen activation[14] and acting as surrogates for transition metals in many catalytic transformations.[15] Several architectures have been used as FLPs with amine-boranes being one of the most active frameworks for bond activation and catalytic transformations.[16] It was notably shown that these species act as efficient catalysts for the metal-free dehydrogenative borylation of heteroarenes through C-H bond activation.[16c,17] The catalytic cycle that was proposed relies on three separate transformations. First, the FLP can activate the C-H bonds of heteroarenes similarly to previous reports of H_2 activation[14,18] (**Figure 1A**). Then the zwitterionic intermediate expels H_2, the thermodynamic driving force of the process (**Figure 1B**).[16c-e] As a last step, the latter intermediate undergoes sigma-bond metathesis to generate the desired product (**Figure 1C**). To extend our knowledge on this catalytic process, notably in regard to the metathesis step and the deactivation of the C-H borylation by protic sources, we investigated the activation of E-H bonds (E = O, N, S, Se) by simple amine-borane $[NMe_2\text{-}C_6H_4\text{-}BH_2]_2$ (**1**). We wish to report our conclusions and our observation that this FLP framework acts as a highly active catalyst for the borylation of thiols.

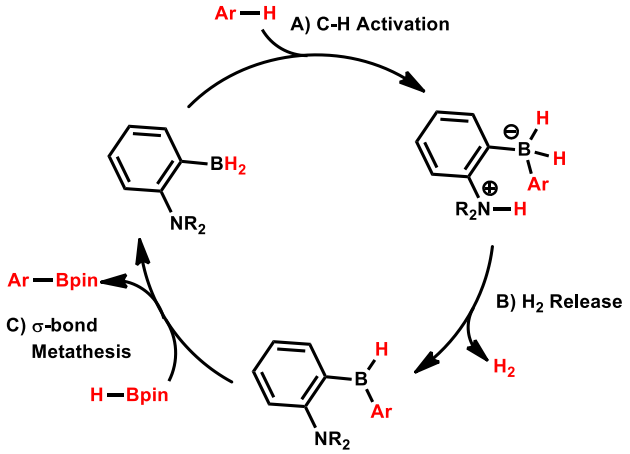


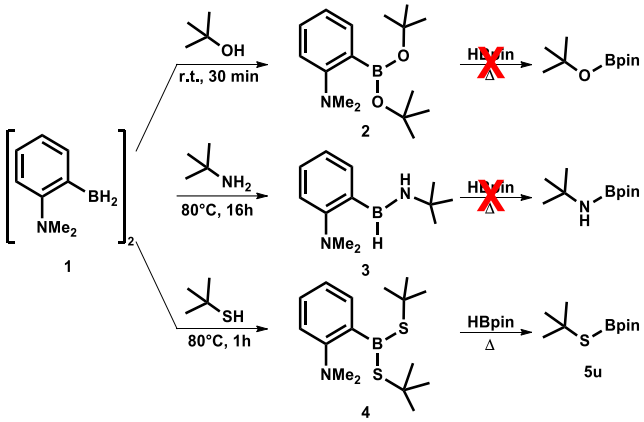
Figure 1: Catalytic cycle of the FLP mediated C-H bond borylation.

DISCUSSION

We first tested the reactivity of **1** with excess alcohol, amine or thiol (**Scheme 1**). The volatile *tert*-butyl derivatives were chosen to facilitate NMR monitoring and to ease purification. Unsurprisingly, **1** reacts rapidly with two equivalents of *tert*-butanol to give species **2** as evidenced by the ^{1}H NMR spectrum featuring a sharp singlet at 1.3 ppm integrating for 18 protons for the *t*Bu groups and by the ^{11}B NMR shift at 27.3 ppm. However, only one equivalent of *tert*-butylamine reacted with **1** resulting in the formation of species **3**. A resonance at 1.3 ppm integrating for 9 protons was observed by ^{1}H NMR spectroscopy for the *t*Bu moiety and the broad signal at 5.0 ppm sharpened upon ^{11}B decoupling, which is consistent with a boron hydride. The ^{11}B NMR spectrum is featuring a doublet (J = 96 Hz) at 36.5 ppm becoming a singlet upon ^{1}H decoupling, confirming the presence of a B-H moiety (See **Figure S9**). After one hour at 80 °C, the reaction between **1** and *tert*-butylthiol leads to product **4** where two thiolate moieties are on the boron atom. The *t*Bu signal (1.4 ppm) integrates for 18 protons in the

^{1}H NMR spectrum and the ^{11}B NMR shift of 62.5 ppm is characteristic of such compound.[19] It is possible to observe in all reactions a ^{1}H NMR resonance at 4.6 ppm characteristic of H_2.

HBpin (pin = pinacol) was then added to products **2-4** to monitor the metathesis step and possible formation of *t*Bu-E-Bpin (E = O, NH, S) which would enable catalysis. Species **2** and **3** were shown to be inert under such conditions but **4** reacted within 1 h at 80 °C with HBpin to generate compound **5u**. Although some precedents do exist,[20] it is not surprising for metathesis to be more challenging with alkoxy and amido derivatives because the π overlap between the lone pair of the heteroelements and the boron atom reduces the Lewis acidity of boron and slows down metathesis. This observation also rationalizes the lack of catalytic activity in the borylation of heteroarenes in the presence of alcohols and protic amines.[16c] Interestingly, the weak B-S π bond allows sulfido compounds to undergo metathesis.



Scheme 1: Stoichiometric reactions between **1** and *tert*-butanol, *tert*-butylamine and *tert*-butylthiol.

DFT calculations (ωB97XD/6-31+G**, SMD solvent=chloroform level of theory) were performed in order to rationalize this reactivity (**Figure 2**). According to DFT data, a similar reaction pathway to the catalytic borylation of heteroarenes is observed. First, the activation of the E-H bond is shown to be endergonic for the *tert*-butylthiol with an intermediate at 1.8 kcal.mol^{-1}, but exergonic for *tert*-butylamine (ΔG = -9.6 kcal.mol^{-1}). The release of H_2, which has been shown to be an important driving force in FLP-type transformations,[16c-e] requires a ΔG‡ of 26.7 kcal.mol^{-1} for *tert*-butylamine but is more favorable for *tert*-butylthiol with a barrier of 18.7 kcal.mol^{-1}. Whereas a second S-H bond activation is possible with the thiol (ΔG‡ of 27.3 kcal.mol^{-1}), the second activation of an amine is more difficult with a ΔG‡ of 32.3 kcal.mol^{-1}, supporting the experimental observations. The high stability of **3**, which is more stable by 12.8 kcal.mol^{-1} compared to the starting material, explains this lack of reactivity. The summation of the angles around N of 360° for the minimized structure of **3** confirms the planarity of the nitrogen atom and the presence of a π bond with boron, which leads to reduced Lewis acidity and to a detrimental effect in the metathesis step.

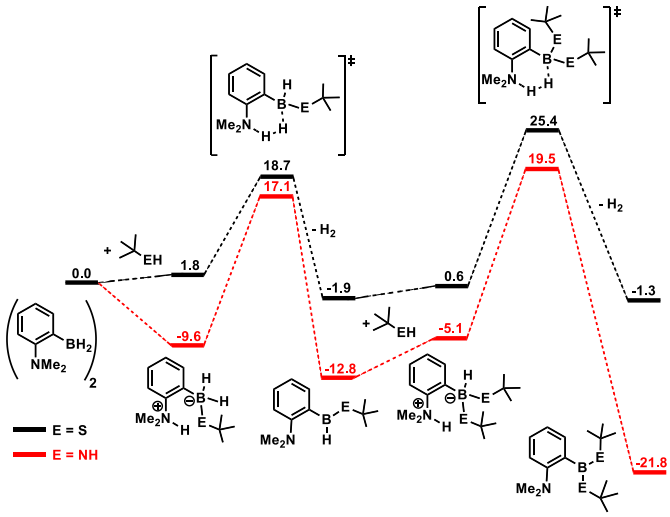
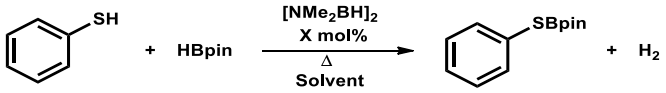


Figure 2: DFT investigation of the borylation of *tert*-butylamine and *tert*-butylthiol. ΔG in kcal.mol^{-1}, ωB97XD/6-31+G**, SMD solvent=chloroform.

With this information in hand, we examined the possibility of using **1** as a catalyst for the borylation of thiols using thiophenol as a model substrate for optimization (**Table 1**). As highlighted recently by Bertrand, the borylation of thiols operates sluggishly at 80 °C and only low yields of the desired products was observed after 48 h (run 1). In the presence of 0.5 mol% of **1**, near complete conversion was observed after 2 h under identical conditions (run 2) confirming that the FLP is acting as a catalyst for the borylation of thiols. It is possible to reduce the reaction time to one hour by increasing the catalyst loading to 2.5 mol% (run 3). It is also possible to operate the reaction at room temperature but the rate of the reaction is greatly reduced, taking about 24 h to reach completion (run 6). As expected, it is possible to observe the rate of the reaction increasing with higher temperature (runs 4-5). The nature of the solvent ($CDCl_3$, C_6D_6 and THF-d_8) seems to have little impact on the reaction rate (runs 3,7-8).

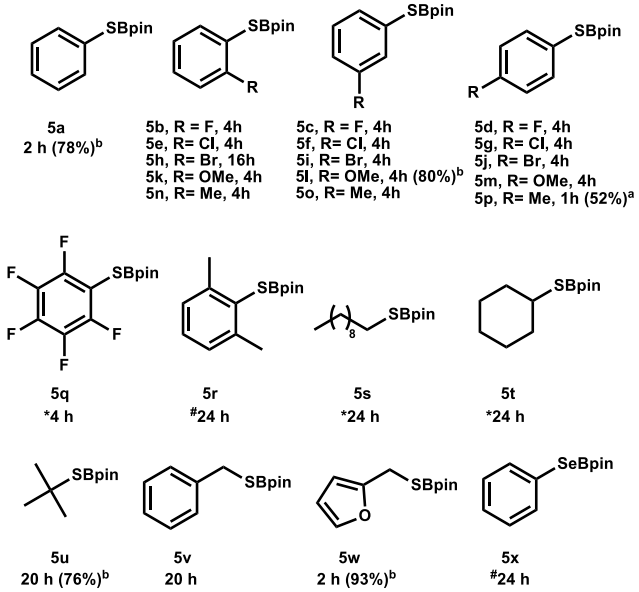
Table 1: Optimization of the borylation of thiophenol catalyzed by **1**.



Entry	Catalyst loading mol%	Temperature °C	Solvent	Time h	Conversion %
1	0	80	$CDCl_3$	48	31
2	0.5	80	$CDCl_3$	2	>95
3	2.5	80	$CDCl_3$	1	>95
4	2.5	60	$CDCl_3$	2	>95
5	2.5	40	$CDCl_3$	8	>95
6	2.5	20	$CDCl_3$	24	>95
7	2.5	80	C_6D_6	1	>95
8	2.5	80	THF-d_8	1	>95

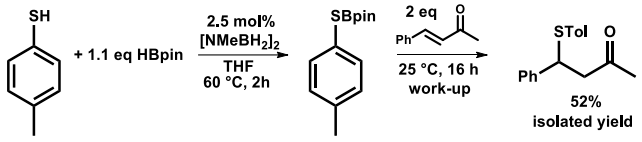
The scope of the reaction is illustrated in **Table 2**. Catalysis proceeds smoothly to completion with several thiophenols, using 2.5 mol% of **1** in $CDCl_3$ at 60 °C for 4 hours. Interestingly, the reaction proceeds with reagents that were not purified beforehand containing residual moisture. The presence of pinBOBpin suggests that HBpin is hydrolyzed before catalyst deactivation. Similarly to the unsubstituted thiophenol (**5a**), 2-, 3-, and 4-substituted fluoro (**5b-d**), chloro (**5e-g**), bromo (**5h-j**), methoxy (**5k-m**) and methyl (**5n-p**) substituted thiophenols were all completely borylated under 4h at 60 °C, with the exception of 2-bromo-thiophenol (**5h**) that proved to be more challenging and required 16 h to get to complete conversion. Pentafluorophenylthiol (**5q**) was fully converted under 4h, but required a larger catalyst loading and a higher temperature. Since 2,6-dimethylphenylthiol (**5r**) also took longer time (24 h) and required 2 equiv of HBpin, it can be assumed that steric hindrance around the sulfur atom reduces the rate of the reaction. Less acidic alkanethiols such as decane- (**5s**), cyclohexyl- (**5t**), *tert*-butyl- (**5u**), and benzylthiols (**5v**) are also less reactive than thiophenols, requiring between 20 and 24 hours to get full conversion to the borylated analogues. Surprisingly, the borylation of bulky *tert*-butylthiol is relatively easy compared to other alkylthiols and does not require higher catalyst loading and higher temperature. The borylation of benzylfuranethiol (**5w**) in presence of **1** equiv of HBpin was also possible under 2 h, suggesting that the activation of the S-H bond occurs more rapidly than the activation of the C-H bond since species **1** has been shown to activate the C-H bonds of furans. Finally, we were able to expend this transformation to the borylation of selenophenol (**5x**) albeit the reaction took about 24 h to proceed to completion with 10 mol% of catalyst at 80 °C.

Table 2: Scope of the catalytic borylation of thiols and time required for full ^{1}H NMR conversion.



Standard conditions: 2.5 mol% of **1**, 60 °C, $CDCl_3$, 1.1 equiv HBpin; *10 mol% of **1**, 80 °C, $CDCl_3$, 1.1 equi HBPin; #10 mol% of **1**, 80 °C, $CDCl_3$, 2 eq HBpin. Isolated yields are in parenthesis; [a]after recrystallization in hexane; [b]after vacuum distillation.

In order to demonstrate the usefulness of the procedure in metal-free synthesis, the one-pot borylation/Michael addition was carried out under similar conditions than those previously reported by Fernandez and Westcott.[6] After mixing HBpin and 4-tolylthiol for 2 h to generate **5u**, 4-phenyl-3-buten-2-one was added to afford the β sulfido ketone. After an aqueous work up and chromatography on silica gel, the final product was isolated in 52 % yield.



Scheme 2: One-pot Michael addition of thiophenol on 4-phenyl-3-buten-2-one through catalytic borylation.

The mechanism of the borylation reaction was studied both experimentally and using DFT (**Figure 3**). Since two B-H bonds are present on the catalyst, one or two S-H activations can occur before the transfer of the thiolate to HBpin by metathesis. Monitoring of the reaction by ^{11}B NMR confirmed the resting state proposed by DFT for the substrates studied. In the case of thiophenol and decane thiol (simplified by ethyl thiol for the DFT calculations) the resting state of the catalyst was shown to be the double activation product, as supported by the presence of singlets at 62.3 and 59.8 ppm, respectively, by ^{11}B NMR. DFT data support this observation, with the double activation products of ethane thiol and thiophenol being more stable than the mono addition products by 8.0 and 7.2 kcal.mol^{-1}, respectively. Since the TS of the S-H activation are alike in cycles A and B, it is likely that both substrates undergo the latter catalytic cycle. However, in the case of *tert*-butylthiol, although we know from our early experiments that a double activation can occur, the resting state of the catalyst was identified as the mono activation product, characterized as a doublet (J = 146 Hz) at 60.0 ppm by ^{11}B NMR, becoming a singlet upon ^{1}H decoupling. In the latter system, cycle A is more likely responsible for the catalytic activity, which is also consistent with DFT where the mono addition adduct is more stable by 0.6 kcal.mol^{-1}. Since the transition barriers are overall lower in cycle A than B, this result explains the unexpected difference in activity between *tert*-butylthiol and decanethiol, where the former reagent undergoes borylation faster, even if it possesses more steric bulk that the latter compound. Although we were not able to locate the transition state for the metathesis step with thiophenol, this transformation was shown to be rate-determining with EtSH and tBuSH with $\Delta G^{\ddagger}$ of 30.5 and 25.9 kcal.mol^{-1}, which is consistent with the observed reaction rates. It should be noted that the FLP-catalyzed transformations are favored over the uncatalyzed systems by 15 to 20 kcal.mol^{-1}.

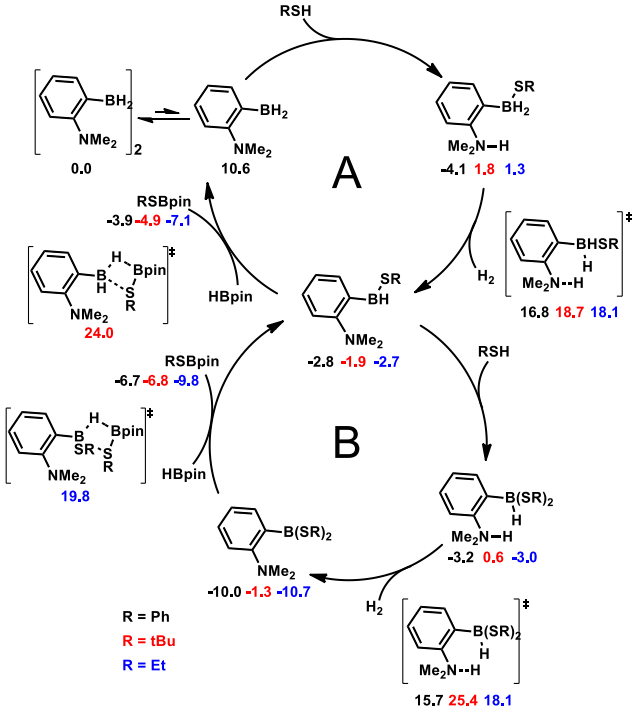


Figure 3: Proposed mechanism for the FLP catalyzed borylation of thiol. ΔG in kcal/mol, ωB97XD/6-31+G**, SMD solvent=chloroform.

CONCLUSION

In this contribution we demonstrate that ambiphilic amine-boranes can act as efficient metal-free catalysts for the borylation of thiols. In presence of amines and alcohols, the E-H activation leads to stable products that prevent catalysis because of a strong π bond between boron and the lone pair of nitrogen and the oxygen, respectively. The proposed borylation mechanism relies on a FLP type transformation, with the release of H is an important driving force. This process can be applied to one-pot metal-free Michael additions directly from thiols and boranes. This chemistry is another step toward the development of useful metal-free catalysts and we hope it will help in the design of C-C, C-N, C-O or C-S bond forming processes which would be major contributions to FLP chemistry.

EXPERIMENTAL SECTION

General Procedures. Unless specified otherwise, manipulations were carried out under a nitrogen atmosphere using standard glovebox and Schlenk techniques. NMR spectra were recorded on an Agilent Technologies NMR spectrometer at 500.0 MHz (^{1}H), 470.59 (^{19}F), 125.758 MHz (^{13}C), 160.46 MHz (^{11}B) and on a Varian Inova NMR AS400 spectrometer, at 400.0 MHz (^{1}H), 376.50 (^{19}F), 100.580 MHz (^{13}C). ^{1}H NMR and ^{13}C{^{1}H} NMR chemical shifts are referenced to residual protons or carbons in deuterated solvent. ^{11}B{^{1}H} was calibrated using an external reference of $BF_3.Et_2O$. ^{19}F NMR was calibrated using $CFCl_3$ as external standard. Multiplicities are reported as singlet (s), doublet (d), triplet (t), quadruplet (q), multiplet (m). Chemical shifts are reported in ppm. Coupling constants are reported in Hz. Mass Spectroscopy analyses were carried out on an Agilent Technologies 6210 LC Time of Flight Mass Spectrometer.

Materials. Solvents were purified by distillation over Na/benzophenone. C_6D_6 was dried over Na/K alloy and distilled, THF-*d*$_8$ was dried on molecular sieves and $CDCl_3$ was dried over P_2O_5 and distilled. N,N-dimethylaniline, *n*-BuLi, TMEDA, $B(OMe)_3$, $LiAlH_4$, and TMSBr were purchased from Sigma-Aldrich and used as received. [NMe_2-C_6H_4-BH_2]$_2$ was synthesized according to previously reported procedures.[16d] HBpin was either: purchased from Sigma-Aldrich and used as received, synthesized according to reported procedure,[21] or graciously given by BASF for the larger scale reactions (containing NEt_3 as stabilizer). The source of HBpin did not influence the reaction rate, but when the synthesized HBpin was used, residual dichloromethane was observed by NMR spectroscopy. Thiophenol (precursor for **5a**) was bought from Alfa Aesar. Precursors for **5b-g**, **5i**, **5k**, **5m**, **5p**, **5q**, **5t** and **5v** were bought from Oakwood and precursors for **5h**, **5j**, **5o**, **5r**, **5s, 5u**, **5w** and **5x** were bought from Sigma-Aldrich. All thiols were used without further purification.

Stoichiometric Experiments.

NMe_2-C_6H_4-B(OtBu)$_2$ (2). 10.0 mg (1.0 equiv) of [NMe_2-C_6H_4-BH_2]$_2$ was dissolved in $CDCl_3$ and placed in a J-Young NMR tube after which 5.0 equiv (36.0 µL) of *t*BuOH was added. The reaction was left at room temperature for 30 min and the volatiles were removed under vacuum. $CDCl_3$ was then added and the product NMe_2-C_6H_4-B(O*t*Bu)$_2$ was characterized using multi-nuclear NMR spectroscopy. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 – 7.17 (m, 2H), 6.86 – 6.80 (m, 2H), 2.86 (s, 6H), 1.31 (s, 18H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 154.5 (s), 132.6 (s), 128.4 (s), 119.5 (s), 115.5 (s), 73.8 (s), 43.7 (s), 30.5 (s). The carbon linked directly to boron was not observed. ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$) δ 27.3 (s).

NMe_2-C_6H_4-BHNHtBu (3). 10.0 mg (1.0 equiv) of [NMe_2-C_6H_4-BH_2]$_2$ was dissolved in $CDCl_3$ and placed in a J-Young NMR tube after which 5.0 equiv (39.5 µL) of *t*BuNH_2 was added. The reaction was heated at 80 °C for 16 h and the volatiles were removed under vacuum. $CDCl_3$ was then added and the product NMe_2-C_6H_4-B(H)(NH*t*Bu) was characterized using multi-nuclear NMR spectroscopy. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.32 – 7.27 (m, 1H), 7.03 – 6.98 (m, 2H), 4.97 (very broad, 1H), 2.78 (s, 6H), 1.32 (s, 9H). ^{1}H{^{11}B} NMR (500 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.32 – 7.27 (m, 1H), 7.03 – 6.98 (m, 2H), 4.97 (s, 1H), 2.78 (s, 6H), 1.32 (s, 9H). The N-H signal was not observed. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.3 (s), 137.8 (s), 129.9 (s), 121.7 (s), 116.4 (s), 45.5 (s), 32.3 (s), 28.4 (s). The carbon linked directly to boron was not observed. ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$) δ 36.5 (s). ^{11}B NMR (160 MHz, $CDCl_3$) δ 36.5 (d, *J* = 96 Hz).

NMe_2-C_6H_4-B(S*t*Bu)$_2$ (4). 10.0 mg (1.0 equiv) of [NMe_2-C_6H_4-BH_2]$_2$ was dissolved in $CDCl_3$ and placed in a J-Young NMR tube after which 5.0 equiv (42.0 µL) of *t*BuSH was added. The reaction was heated at 80 °C for 1 h and the volatiles were removed under vacuum. $CDCl_3$ was added and the product NMe_2-C_6H_4-B(StBu)$_2$ was characterized using multi-nuclear NMR spectroscopy. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (ddd, J = 8.2, 7.3, 1.8 Hz, 1H), 7.15 (dd, J = 7.3, 1.7 Hz, 1H), 6.81 – 6.76 (m, 2H), 2.94 (s, 6H), 1.40 (s, 18H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.5 (s), 133.0 (s), 129.3 (s), 118.1 (s), 115.1 (s), 48.0 (s), 43.7 (s), 32.8 (s). The carbon linked directly to boron was not observed. ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$) δ 62.5 (s).

Catalytic Experiments. All catalytic experiments were carried out in in $CDCl_3$ in standard NMR tubes for experiments at 60 °C, and in J-Young tubes for experiments at 80°C. Compounds **5a**, **5l**, **5p**, **5u** and **5w** were also prepared starting with 500 mg of the respective thiols and isolated either by distillation or recrystallization. As previously reported,[12] thioboranes exhibit significant air and moisture sensitivity and no satisfactory EA and HRMS could be obtained.

Method A: Used for 5a-p, 5u-w. In a glovebox, 400 µL of a solution containing 2.5 mg/mL (1.0 mg / 400 µL) of the catalyst [NMe_2-C_6H_4-BH_2]$_2$ in $CDCl_3$ (0,0038 mmol, 2.5 mol%) and 24 µL of HBpin (0.165 mmol, 1.1 equiv) were added to an NMR tube. The substrate (0.150 mmol, 1.0 equiv) was subsequently added. Liquid substrates were added with a micropipette outside the glovebox and solid substrates were weighted and added inside the glovebox. The reaction was left in an oil bath at 60 °C and ^{1}H NMR spectra were taken periodically until complete conversion was observed.

Method B: Used for 5q, 5s and 5t. The procedure is the same as in method A with the exception that a solution containing 10 mg/mL of the catalyst (increasing the catalyst loading at 10 mol%) and a temperature of 80 °C were used.

Method C: Used for 5r and 5x. The procedure is the same as in method B with the exception that the quantity of HBpin was doubled (48 µL 0.330 mmol, 2.2 equiv).

Phenylsulfur pinacolborane (5a). 30.0 mg (2.5 mol%) of [NMe_2-C_6H_4-BH_2]$_2$ was placed in a Schlenk tubed and dissolved in about 4 ml of toluene. 500 mg of thiophenol (1 equiv) was then added followed by the addition of 725 µL (1.1 eq) of HBpin. The reaction was then heated at 60 °C for about 2 h after which the solution was evaporated to dryness. The reaction was followed by the release of H_2 causing effervescence. The residual oil was distilled under reduced pressure (boiling point of 75 °C at 1 mbar). 832 mg (78% yield) of the title compound was obtained. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 2H), 7.31 – 7.19 (m, 3H), 1.31 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 135.5 (s, 1C), 131.6 (s, 1C), 129.9 (s, 1C), 129.9 (s, 1C), 85.2 (s, 2C), 24.5 (s, 4C). ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$) δ 32.9.

***ortho*-Fluorophenylsulfur pinacolborane (5b).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (m, 1H), 7.24 (m, 1H), 7.06 (m, 2H), 1.29 (s, 12H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 161.9 (d, J = 246.4 Hz, 1C), 135.8 (s, 1C), 129.2 (d, J = 7.66 Hz, 1C), 124.2 (d, J = 3.83 Hz, 1C), 116.8 (d, J = 18.6 Hz, 1C), 115.7 (d, J = 23.3 Hz, 1C), 85.5 (s, 2C), 24.4 (s, 4C). ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$) δ 32.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.5 (td, *J* = 7.7, 5.3 Hz, 1F).

***meta*-Fluorophenylsulfur pinacolborane (5c).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.13 (m, 3H), 6.97 – 6.86 (m, 1H), 1.31 (s, 12H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 162.3 (d, J = 247.2 Hz, 1C), 131.9 (d, J = 8.4 Hz, 1C), 129.7 (d, J = 8.5 Hz, 1C), 128.5 (d, J = 3.0 Hz, 1C), 119.8 (d, J = 23.2 Hz, 1C), 113.8 (d, J = 21.1 Hz, 1C), 85.5 (s, 2C), 24.5 (s, 4C). ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$) δ 32.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.7 – -112.8 (m, 1F).

***para*-Fluorophenylsulfur pinacolborane (5d).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.38 (m, 2H), 7.00 – 6.92 (m, 2H), 1.29 (s, 12H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) : δ 162.0 (d, J = 246.1 Hz, 1C), 134.8 (d, J = 8.08 Hz, 2C), 124.6 (d, J = 3.51 Hz, 1C), 115.7 (d, J = 21.9 Hz, 2C), 85.4 (s, 2C), 24.5 (s, 4C). ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$) δ 32.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.6 (ddd, J = 13.8, 8.58, 5.08 Hz, 1F).

***ortho*-Chlorophenylsulfur pinacolborane (5e).** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 – 7.65 (m, 1H), 7.43 – 7.39 (m, 1H), 7.23 – 7.16 (m, 2H), 1.31 (s, 12H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 137.3 (s, 1C), 135.8 (s, 1C), 129.8 (s, 1C), 129.2 (s, 1C), 128.5 (s, 1C), 126.8 (s, 1C), 85.5 (s, 2C), 24.5 (s, 4C). ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$) δ 32.4.

***meta*-Chlorophenylsulfur pinacolborane (5f).** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 1H), 7.39 (dt, *J* = 6.7, 1.9 Hz, 2H), 7.23 – 7.17 (m, 2H), 1.32 (s, 12H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 134.1 (s,1C), 132.7 (s, 1C), 131.7 (s, 1C), 131.1 (s, 1C), 129.6 (s, 1C), 127.0 (s, 1C), 85.5 (s, 2C), 24.5 (s, 4C). ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$) δ 32.7.

***para*-Chlorophenylsulfur pinacolborane (5g).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.38 (m, 2H), 7.27 – 7.19 (m, 2H), 1.30 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 134.3 (s, 2C), 132.9 (s, 1C), 128.8 (s, 2C), 128.2 (s, 1C), 85.4 (s, 2C), 24.5 (s, 4C). ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$) δ 32.7.

***ortho*-Bromophenylsulfur pinacolborane (5h).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, J = 7.8, 1.7 Hz, 1H), 7.59 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.27 – 7.22 (m, 1H), 7.11 (m, 1H), 1.30 (s, 12H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 135.6, 133.1, 131.4, 128.6, 127.5, 85.5, 24.5. ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$) δ 32.6.

***meta*-Bromophenylsulfur pinacolborane (5i).** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (t, *J* = 1.8 Hz, 1H), 7.43 (ddd, *J* = 7.9, 1.8, 1.0 Hz, 1H), 7.36 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H), 7.13 (t, *J* = 7.9 Hz, 1H), 1.32 (s, 12H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 135.5 (s, 1C), 131.6 (s, 1C), 129.9 (s, 1C), 129.9 (s, 1C), 122.2 (s, 1C), 85.2 (s, 2C), 24.5 (s, 4C). The quaternary carbon bonded to the sulfur atom could not be assigned. ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$) δ 32.6.

***para*-Bromophenylsulfur pinacolborane (5j).** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 4H), 1.31 (s, 12H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 136.3 (s, 1C), 134.6 (s, 2C), 132.4 (s, 2C), 131.7 (s, 2C), 85.5 (s, 2C), 24.5 (s, 4C). ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$) δ 32.6.

***ortho*-Methoxyphenylsulfur pinacolborane (5k).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 8.25, 1.67 Hz, 2H), 7.25 (ddd, J = 8.25, 7.47, 1.95 Hz, 2H), 3.85 (s, 3H), 1.28 (s, 12H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) 158.5 (s, 1C), 135.3 (s, 1C), 128.7 (s, 1C), 120.8 (s, 1C), 117.7 (s, 1C), 110.9 (s, 1C), 85.0 (s, 2C), 55.7 (s, 1C), 24.5 (s, 4C). ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$) : δ 32.7.

***meta*-Methoxyphenylsulfur pinacolborane (5l).** 23.7 mg (2.5 mol%) of [NMe_2-C_6H_4-BH_2]$_2$ was placed in a Schlenk tubed and dissolved in about 4 ml of toluene. 500 mg of *meta*-methoxythiophenol (1 equiv) was then added and followed by the addition of 570 µL (1.1 equiv) of HBpin. The reaction was then heated at 60 °C for about 4 h after which the solution was evaporated to dryness. The reaction can be followed by the release of H_2 causing effervescence. The residual oil was distilled under reduced pressure (boiling point of 85 °C at 1 mbar). 761 mg (80% yield) of the title compound was obtained. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 - 7.15 (m, 1H), 7.09 – 7.06 (m, 2H), 6.78 (ddd, *J* = 8.2, 2.3, 1.3 Hz, 1H), 3.79 (s, 3H), 1.31 (s, 12H). ^{13}C{^{1}H} (126 MHz, $CDCl_3$) δ 159.4 (s, 1C), 130.7 (s, 1C), 129.4 (s, 1C), 125.3 (s, 1C), 118.2 (s, 1C), 112.9 (s, 1C), 85.3 (s, 2C), 55.2 (s, 1C), 24.5 (s, 4C). ^{11}B{^{1}H} (160 MHz, $CDCl_3$) δ 32.8.

***para*-Methoxyphenylsulfur pinacolborane (5m).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.9 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 3H), 1.29 (s, 12H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.8 (s, 1C), 134.5 (s, 2C), 119.9 (s, 1C), 114.4 (s, 2C), 85.16 (s, 2C), 55.2 (s, 1C), 24.5 (s, 4C). ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$) δ 33.0.

***ortho*-Methylphenylsulfur pinacolborane (5n).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.50 (m, 1H), 7.23 – 7.08 (m, 3H), 2.43 (s, 3H), 1.29 (s, 12H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 140.5 (s,1C), 134.9 (s, 1C), 130.2 (s, 1C), 128.9 (s, 1C), 127.4 (s, 1C), 126.1 (s, 1C), 85.2 (s, 2C), 24.5 (s, 4C), 21.6 (s, 1C). ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$) δ 32.7.

***meta*-Methylphenylsulfur pinacolborane (5o).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 2H), 7.16 (dd, J = 8.5, 7.4 Hz, 1H), 7.08 – 7.02 (m, 1H), 2.33 (s, 3H), 1.31 (s, 12H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 138.3 (s,1C), 133.7 (s, 1C), 130.1 (s, 1C), 128.5 (s, 1C), 127.6 (s, 1C), 85.2 (s, 2C), 24.5 (s, 4C), 21.3 (s, 1C). The carbon bonded to the sulfur atom could not be assigned. ^{11}B {^{1}H} NMR (160 MHz, $CDCl_3$) δ 32.9.

***para*-Methylphenylsulfur pinacolborane (5p).** 26.8 mg (2.5 mol%) of [NMe_2-C_6H_4-BH_2]$_2$ was placed in a Schlenk tube and dissolved in about 4 ml of toluene. 500 mg of 4-methylthiophenol (1 equiv) was then added, followed by 645 µL of HBpin (1.1 equiv). The reaction was then heated at 60 °C for 2 h after which the solution was evaporated to dryness. The reaction was followed by the release of H_2 causing effervescence. The residual white solid was dissolved in hot hexane, the mixture was filtered and placed at -35 °C overnight. The next morning, an appreciable amount of white crystals had formed. The supernatant was removed and the crystals dried under vacuum. 525 mg (52% yield) of the title compound was obtained. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 2H), 7.13 – 7.05 (m, 2H), 2.33 (s, 3H), 1.31 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 136.6 (s,1C), 133.0 (s, 2C), 129.5 (s, 2C), 125.9 (s, 1C), 85.2 (s, 2C), 24.5 (s, 4C), 21.1 (s, 1C). ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$) δ 32.9.

Pentafluorophenylsulfur pinacolborane (5q). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (s, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.6 – 145.0 (m, 2C), 142.2 – 139.6 (m, 1C), 139.1 – 136.4 (m, 2C), 86.4 (s, 2C), 24.3 (s, 4C). The quaternary carbon bonded to the sulfur atom could not be assigned. ^{11}B {^{1}H} NMR (160 MHz, $CDCl_3$) δ 31.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -131.54 – -131.67 (m, 2F), -154.20 (tt, *J* = 21.1, 1.9 Hz, 1F), -161.70 – -161.97 (m, 2F).

2,6-dimethylphenylsulfur pinacolborane (5r). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (s, 3H), 2.47 (s, 6H), 1.27 (s, 12H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.1 (s, 1C), 128.5 (s, 1 or 2C), 127.8 (s, 2C), 127.4 (s, 1 or 2C), 85.0 (s, 2C), 24.5 (s, 4C), 22.8 (s, 2C). ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$) δ 32.4.

Decanesulfur pinacolborane (5s). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.64 (t, *J* = 7.3 Hz, 2H), 1.63 – 1.53 (m, 2H), 1.43 – 1.14 (m, 26H), 0.87 (t, *J* = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 84.6 (s, 2C), 32.4 (s, 1C), 31.9 (s, 1C), 29.6 (s, 1C), 29.5 (s, 1C), 29.3 (s, 1C), 29.1 (s, 1C), 28.5 (s, 1C), 26.6 (s, 1C), 24.5 (s, 4C), 22.7 (s, 1C), 14.1 (s, 1C). ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$) δ 33.5.

Cyclohexylsulfur pinacolborane (5t). ^{1}H NMR (400 MHz, $CDCl_3$) : δ 3.16 – 3.04 (m, 1H), 2.00 – 1.93 (m, 2H), 1.76 – 1.68 (m,

3H), 1.46 – 1.28 (m, 5H), 1.27 (s, 12H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 84.4 (s, 2C), 44.1 (s, 1C), 40.4 (s, 1C), 36.4 (s, 1C), 26.2 (s, 1C), 25.5 (s, 1C), 24.9 (s, 1C), 24.5 (s, 4C). $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$, borosilicate tube) : δ 33.4.

***tert*-Butylsulfur pinacolborane (5u).** 36.8 mg (2.5 mol%) of $[NMe_2\text{-}C_6H_4\text{-}BH_2]_2$ was placed in a Schlenk tube and dissolved in about 4 ml of toluene. 500 mg of *tert*-butythiol (1 equiv) was then added, followed by the addition of 885 µL (1.1 eq) of HBpin. The reaction was then heated at 60 °C for about 20 h after which the solution was evaporated to dryness under reduced pressure. The reaction was followed by the release of H_2 causing effervescence. The residual colorless oil was distilled under reduced pressure (boiling point of 35 °C at a pressure of 1 mbar). 1.164 g (76% yield) of the title compound was obtained. ^1H NMR (400 MHz, $CDCl_3$) δ 1.46 (s, 9H), 1.28 (s, 12H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 84.1 (s, 2C), 43.8 (s, 1C), 33.5 (s, 3C), 24.5 (s, 4C). $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ 33.1.

Benzylsulfur pinacolborane (5v). ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 2H), 7.33 – 7.28 (m, 2H), 7.26 – 7.22 (m, 1H), 3.92 (s, 2H), 1.32 (s, 12H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 140.5 (s, 1C), 128.6 (s, 2C), 128.4 (s, 2C), 126.8 (s, 1C), 85.1 (s, 2C), 30.7 (s, 1C), 24.6 (s, 4C). $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ 33.5.

Furfurylsulfur Pinacolborane (5w). 29.0 mg (2.5 mol%) of $[NMe_2\text{-}C_6H_4\text{-}BH_2]_2$ was placed in a Schlenk tubed and dissolved in about 4 ml of toluene. 500 mg of 2-furanmethanethiol (1 equiv) was then added and followed by the addition of 700 µL (1.1 eq) of HBpin. The reaction was then heated at 60 °C for about 2 h after which the solution was evaporated to dryness. The reaction was followed by the release of H_2 causing effervescence. The residual colorless oil was distilled under reduced pressure (boiling point 60 °C at about 1 mbar). 978 mg (93% yield) of the title compound was obtained. ^1H NMR (500 MHz, $CDCl_3$) δ 7.31 (s, 1H), 6.28 (s, 1H), 6.18 (s, 1H), 3.90 (s, 2H), 1.30 (s, 12H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 153.4 (s, 1C), 141.6 (s, 1C), 110.3 (s, 1C), 106.7 (s, 1C), 85.1 (s, 2C), 24.5 (s, 4C), 22.9 (s, 1C). $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ 33.4.

Phenylselenyl pinacolborane (5x). ^1H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.56 (m, 2H), 7.26 – 7.19 (m, 3H), 1.32 (s, 12H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 134.4 (s, 2C), 129.2 (s, 2C), 128.9 (s, 1C), 126.7 (s, 1C), 85.6 (s, 2C), 24.6 (s, 4C). $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$) δ 33.8.

One-pot Michael addition. In a glovebox, 6.5 mg (0.025 mmol, 2.5 mol%) of $[NMe_2\text{-}C_6H_4\text{-}BH_2]_2$ was weighted, dissolved in THF and added to a Schlenk flask. 0.177 mL (1.10 mmol, 1.1 eq.) of HBpin was added to the flask followed by the substrate (122 mg, 0.98 mmol, 1 equiv). The reaction was left in an oil bath at 60 °C for 2 h, then cooled at room temperature and 0.28 mL of 4-phenylbut-3-en-2-one (1.93 mmol, 2 equiv) was added. The reaction was left at room temperature for 16 h. The reaction was then quenched with methanol (2 mL) for 2 h, the product extracted with chloroform and purified by chromatography using 80/20 hexanes/ethyl acetate as eluent. After evaporation, 138 mg (52 % yield) of the product was obtained as a pale yellow solid. ^1H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.18 (m, 7H), 7.07 – 7.03 (m, 2H), 4.65 (dd, J = 8.1, 6.6 Hz, 1H), 3.13 – 2.98 (m, 2H), 2.31 (s, 3H), 2.07 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 205.7 (s, 1C), 141.1 (s, 1C), 137.9 (s, 1C), 133.6 (s, 2C), 130.2 (s, 1C), 129.6 (s, 2C), 128.4 (s, 2C), 127.7 (s, 2C), 127.4 (s, 1C), 49.4 (s, 1C), 48.4 (s, 1C), 30.7 (s, 1C), 21.2 (s, 1C). $[M+H]^+$ = 271.1150 (calc.: 271.1157), $[M - C_3H_5O]^+$ = 213.07356 (calc.: 213.0738).

Computational details. Unless specified otherwise, all the calculations were performed on the full structures of the reported compounds. Calculations were performed with the GAUSSIAN 09 suite of programs.[22] The ωB97XD functional[23] was qualified as promising by Grimme[24] and was used to accurately describe the mechanism of FLP mediated hydrogenation of alkynes[25] and was thus used in combination with the 6-31++G** basis set for all atoms.[26] The transition states were located and confirmed by frequency calculations (single imaginary frequency). The stationary points were characterized as minima by full vibration frequencies calculations (no imaginary frequency). All geometry optimizations were carried out without any symmetry constraints at the ωB97XD /6-31G** level of theory. The energies were then refined by single point calculations to include solvent effects using the SMD solvation model[27] and chloroform as solvent at the ωB97XD /6-31+G** level of theory.[28]

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

It contains NMR spectra of the compounds, details on the determination of the catalyst resting state (PDF) and the Cartesian coordinates of the optimized structures with their associated free enthalpy and Gibbs free energies (XYZ).

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Notes

The authors declare no competing financial interests.

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REFERENCES

(1) (a) Miyaura, N. and Suzuki, A. *Chem. Commun.* **1979**, 866–867. (b) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457–2483.

(2) Cuenca, A. B.; Shishido, R.; Ito, H.; Fernández, E. *Chem. Soc. Rev.* **2017**, *46*, 415–430.

(3) a) Neeve, E. C.; Geier, S. J.; Mkhalid, I. A. I.; Westcott, S. A.; Marder, T. B. *Chem. Rev.* **2016**, *116* (16), 9091–9161. (b) Mkhalid, I. a I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. *Chem. Rev.* **2009**, *110* (2), 890–931. (c) Marder, T. B.; Norman, N. C. *Top. Catal.* **1998**, *5*, 63–73.

(4) (a) Suginome, M. *Pure Appl. Chem.* **2006**, *78* (7), 1377–1387. (b) Suginome, M.; Uehlin, L.; Yamamoto, A.; Murakami, M. *Org. Lett.* **2004**, *6* (7), 1167–1169. (c) Suginome, M.; Uehlin, L.; Murakami, M. *J. Am. Chem. Soc.* **2004**, *126* (41), 13196–13197. (d) Suginome, M.; Yamamoto, A.; Ito, Y. *Chem. Commun.* **2002**, *1* (99), 1392.

(5) Solé, C.; Fernández, E. *Angew. Chem. Int. Ed.* **2013**, *52* (43), 11351–11355.

(6) Civit, M. G.; Sanz, X.; Vogels, C. M.; Webb, J. D.; Geier, S. J.; Decken, A.; Bo, C.; Westcott, S. A.; Fernández, E. *J. Org. Chem.* **2015**, *80* (4), 2148–2154.

(7) Daley, E. N.; Vogels, C. M.; Geier, S. J.; Decken, A.; Doherty, S.; Westcott, S. A. *Angew. Chem. Int. Ed.* **2015**, *54* (7), 2121–2125.

(8) (a) Civit, M. G.; Sanz, X.; Vogels, C. M.; Bo, C.; Westcott, S. A.; Fernández, E. *Adv. Synth. Catal.* **2015**, *357* (14–15), 3098–3103. (b) Sanz, X.; Vogels, C. M.; Decken, A.; Bo, C.; Westcott, S. A; Fernández, E. *Chem. Commun.* **2014**, *50* (61), 8420–8423.

(9) Civit, M. G.; Royes, J.; Vogels, C. M.; Westcott, S. A.; Cuenca, A. B.; Fernández, E. *Org. Lett.* **2016**, *18* (15), 3830–3833.

(10) (a) Harinath, A.; Anga, S.; Panda, T. K. *RSC Adv.* **2016**, *6* (42), 35648–35653. (b) Yang, Z.; Zhong, M.; Ma, X.; Nijesh, K.; De, S.; Parameswaran, P.; Roesky, H. W. *J. Am. Chem. Soc.* **2016**, *138* (8), 2548–2551. (c) Liptrot, D. J.; Hill, M. S.; Mahon, M. F.; Wilson, A. S. S. *Angew. Chem. Int. Ed.* **2015**, *54* (45), 13362–13365. (d) Bolaño, T.; Esteruelas, M. A.; Gay, M.

P.; Oñate, E.; Pastor, I. M.; Yus, M. *Organometallics* **2015**, *34* (15), 3902–3908.
(11) Romero, E.; Peltier, J. L.; Jazzar, R.; Bertrand, G. *Chem. Commun.* **2016**, *52*, 10563–10565.
(12) (a) Fernández-Salas, J. A.; Manzini, S.; Nolan, S. P. *Chem. Commun*. **2013**, *49* (52), 5829. (b) Westcott, S. A., Webb, J. D. McIsaac, D. I. Vogels, C. M. WO Patent 2006/089402 A1, 2006.
(13) Feng, M.; Tang, B.; Liang S. H.; Jiang, X.; Curr. *Top. Med. Chem*. **2016**, *16*, 1200-1216.
(14) Welch, G. C.; San Juan, R. R.; Masuda, J. D.; Stephan, D. W. *Science* **2006**, *314*, 1124–1126.
(15) (a) Fontaine, F.-G.; Courtemanche, M.-A.; Légaré, M.-A.; Rochette, É. *Coord. Chem. Rev.* **2016**, *334*. (b) Stephan, D. W. *Science* **2016**, *354*, 1248. (c) Stephan, D. W. *J. Am. Chem. Soc.* **2015**, *137* (32), 10018–10032. (d) Stephan, D. W.; Erker, G. *Angew. Chem. Int. Ed.* **2015**, *54* (22), 6400–6441. (e) Erker, G.; Stephan, D. W. *Frustrated Lewis Pairs I*. (f) Erker, G.; Stephan, D. W. *Frustrated Lewis Pairs II Expanding the Scope*.
(16) (a) Chernichenko, K.; Kótai, B.; Pápai, I.; Zhivonitko, V.; Nieger, M.; Leskelä, M.; Repo, T. *Angew. Chem. Int. Ed.* **2015**, *54* (6), 1749–1753. (b) Courtemanche, M.-A.; Pulis, A. P.; Rochette, É.; Légaré, M.-A.; Stephan, D. W.; Fontaine, F.-G. *Chem. Commun.* **2015**, *51* (48), 9797–9800. (c) Légaré, M.-A.; Courtemanche, M.-A.; Rochette, E.; Fontaine, F.-G. *Science* **2015**, *349* (6247), 513–516. (d) Rochette, É.; Bouchard, N.; Légaré Lavergne, J.; Matta, C. F.; Fontaine, F. G. *Angew. Chem. Int. Ed.* **2016**, *55* (41), 12722–12726. (e) Rochette, É.; Courtemanche, M.-A.; Fontaine, F.-G. *Chem. A Eur. J.* **2017**, 3567–3571.
(17) (a) Légaré, M.-A.; Rochette, É.; Légaré Lavergne, J.; Bouchard, N.; Fontaine, F.-G. *Chem. Commun.* **2016**, *52*, 5387–5390. (b) Chernichenko, K.; Lindqvist, M.; Kótai, B.; Nieger, M.; Sorochkina, K.; Pápai, I.; Repo, T. *J. Am. Chem. Soc*. **2016**, *138* (14), 4860–4868. (c) Iashin, V.; Chernichenko, K.; Pápai, I.; Repo, T. *Angew. Chem. Int. Ed.* **2016**, *55* (45), 14146–14150.
(18) (a) Schwendemann, S.; Fröhlich, R.; Kehr, G.; Erker, G. *Chem. Sci.* **2011**, *2* (9), 1842–1849. (b) Chernichenko, K.; Nieger, M.; Repo, T.; Feldhaus, P.; Schirmer, B.; Wibbeling, B.; Daniliuc, C. G.; Grimme, S.; Kehr, G.; Erker, G.; Theuergarten, E.; Freytag, M.; Daniliuc, C. G.; Jones, P. G.; Tamm, M. **2012**. (c) Jiang, C.; Blacque, O.; Berke, H. *Organometallics* **2009**, *28* (17), 5233–5239.
(19) Odom, J. D.; Moore, T. F.; Goetze, R.; Nöth, H.; Wrackmeyer, B. *J. Organomet. Chem.* **1979**, *173*, 15–32.
(20) Chong, C. C.; Hirao, H.; Kinjo, R. *Angew. Chem. Int. Ed*. **2015**, *54* (1), 190–194.
(21) Macé, A.; Touchet, S.; Andres, P.; Cossío, F.; Dorcet, V.; Carreaux, F.; Carboni, B. *Angew. Chem. Int. Ed.* **2016**, *55* (3), 1025–1029.
(22) Gaussian 09, revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.; Gaussian, Inc.: Wallingford, CT, 2009.
(23) Chai, J. Da; Head-Gordon, M. *J. Chem. Theory Comput.* **2013**, *9* (1), 263–272.
(24) Goerigk, L.; Grimme, S. *Phys. Chem. Chem. Phys.* **2011**, *13*, 6670–6688.
(25) Chernichenko, K.; Madarász, A.; Pápai, I.; Nieger, M.; Leskelä, M.; Repo, T. *Nat. Chem.* **2013**, *5* (8), 718–723.
(26) (a) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. a. *J. Chem. Phys.* **1982**, *77* (7), 3654–3665. (b) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56* (5), 2257–2261.
(27) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B.* **2009**, *113*, 6378–6396.
(28) Grimme, S. *J. Comput. Chem.* **2006**, *27* (15), 1787–1799.