Electronic Supplementary Information

Catalytic Dehydrogenative Borylation of Terminal Alkynes by POCOP-Supported Palladium Complexes

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**General Considerations.** Unless otherwise specified, all manipulations were performed under an argon atmosphere using standard Schlenk line or glove box techniques. Toluene, THF, pentane, and isooctane were dried and deoxygenated (by purging) using a solvent purification system and stored over molecular sieves in an Ar-filled glove box. C₆D₆ was dried over and distilled from NaK/Ph₂CO/18-crown-6 and stored over molecular sieves in an Ar-filled glove box. 1,4-Dioxane, CH₂Cl₂, and CDCl₃ were dried with CaH₂ and vacuum transferred to be stored over molecular sieves in an Ar-filled glove box. NMR spectra were recorded on a Varian NMRS 500 (¹H NMR, 499.686 MHz; ¹³C NMR, 125.659 MHz; ³¹P NMR, 202.298 MHz) and Varian Inova 400 (¹¹B NMR, 128.185 MHz) spectrometer. Chemical shifts are reported in δ (ppm). For ¹H and ¹³C NMR spectra, the residual solvent peak was used as an internal reference. ³¹P NMR spectra were referenced externally using 85% H₃PO₄ to δ = 0 ppm. For ¹¹B NMR, spectra were referenced externally to δ = 0 ppm by using BF₃·Et₂O. Elemental analyses were performed by CALI Labs, Inc. (Parsippany, NJ). ²,¹ ²b,² ³,³ ⁴a,⁴ (4,6-ditetbutylPOCOP)PdCl,⁵ and ⁶b² were synthesized according to literature procedures.
Synthesis and Characterization

Synthesis of \((POCOP^{iPr})PdH\) (2a)

![Chemical Structure](image)

In a Schlenk flask, \(2^1\) (362 mg, 0.750 mmol) was dissolved in pyridine and treated with NaBEt₃H (750 μL, 1.0 M solution in toluene). The reaction was stirred for 1 h at room temperature. The volatiles were removed and the resulting solid was dissolved in toluene and passed through a pad of Celite. The volatiles were removed, and the resulting yellow solid was dissolved in minimum of Et₂O and placed in a -35 °C freezer. The resulting light yellow crystals were dissolved in Et₂O and placed back into a -35 °C freezer to be recrystallized again. The resulting yellow crystals were washed with cold pentane and dried under vacuum (77 mg, 23%). The spectral data matched that reported in the literature.⁴
Synthesis of (POCOP\textsuperscript{Pr})Pd(-C≡p-C\textsubscript{6}H\textsubscript{4}Me) (2c)

In a Schlenk flask, \textsuperscript{21} (227 mg, 0.47 mmol) was dissolved in toluene and treated with NaO\textsuperscript{t}Bu (68 mg, 0.705 mmol) and 4-ethynyltoluene (60 μL, 0.47 mmol). The reaction was stirred overnight and the volatiles removed under vacuum in the morning. The product was extracted with pentane and filtered through a plug of silica and Celite to be recrystallized from pentane at -35 °C to yield beige crystals (180 mg, 68%). \textsuperscript{31}P\{\textsuperscript{1}H\} NMR (C\textsubscript{6}D\textsubscript{6}): δ 193.0 (s); \textsuperscript{1}H NMR (C\textsubscript{6}D\textsubscript{6}): δ 7.59 (d, 2H, J = 8.0 Hz, Ar-H), 6.97 (d, 2H, J = 8.0 Hz, Ar-H), 6.93 (t, 1H, J = 8.0 Hz, POCOP-H), 6.77 (d, 2H, J = 8.0 Hz, Ar-H), 2.18 (m, 4H, PCHMe\textsubscript{2}), 2.07 (s, 3H, Ar-Me), 1.30 (m, 12H, PCHMe\textsubscript{2}), 1.11 (apparent q (dvt), 12H, J = 7 Hz, PCHMe\textsubscript{2}). \textsuperscript{13}C\{\textsuperscript{1}H\}(C\textsubscript{6}D\textsubscript{6}): δ 167.0 (t, J = 6.7 Hz, Ar-OP), 138.4 (t, J = 4.7 Hz, Ar-Pd), 134.4 (s), 131.3 (s), 129.1 (s), 128.8 (s), 127.2 (s), 119.2 (s, C≡C-tolyl), 108.6 (t, J\textsubscript{C-P} = 17.9 Hz, Pd-C≡C-tolyl), 105.7 (t, J\textsubscript{C-P} = 7.2 Hz, (POCOP)Ar-H), 29.5 (t, J\textsubscript{C-P} = 12.1 Hz, PCHMe\textsubscript{2}), 21.3 (s, Ar-Me), 17.8 (t, J\textsubscript{C-P} = 3.8 Hz, PCHMe\textsubscript{2}), 17.0 (s, PCHMe\textsubscript{2}). Elem. Anal. Found (Calculated) for C\textsubscript{27}H\textsubscript{38}O\textsubscript{2}P\textsubscript{2}Pd: C, 57.71 (57.61); H, 6.83 (6.80).
Figure 1: $^1$H NMR spectrum of 2c in C$_6$D$_6$. Pentane resonances visible at 0.86 and 1.22 ppm.
Synthesis of (POCOP$_{2}$Pr)PtH (3a)

3$^3$ (250 mg, 0.437 mmol) was dissolved in THF and treated with NaHB$\text{Et}_3$ (480 $\mu$L, 1.0 M toluene) and left to stir for 10 minutes. The volatiles were removed and the product was extracted with pentane and filtered through Celite. The volatiles were removed and the resulting solid was dissolved in a minimum amount of pentane and placed in a -35 °C freezer to recrystallize. 3a was isolated as a white solid (102 mg, 43% yield). $^{31}$P$\{^1$H$\}$ NMR (C$_6$D$_6$): $\delta$ 190.5 (s, $J_{P-Pt} = 3002$ Hz); $^1$H NMR (C$_6$D$_6$): $\delta$ 7.04 (m, 1H, Ar-$\text{H}$), 6.49 (m, 2H, Ar-$\text{H}$), 2.13 (m, 4H, PC$_2$HMe$_2$), 1.12 (dvt, $J = 9$ Hz, $J = 7$ Hz, 12H, PCHMe$_2$), 1.07 (apparent q (dvt), $J = 7$ Hz, 12H, PCHMe$_2$), 1.01 (t, $J_{H-P} = 17$ Hz, $J_{H-Pt} = 444$ Hz, 1H, Pt-$\text{H}$); $^{13}$C$\{^1$H$\}$ NMR (C$_6$D$_6$): $\delta$ 165.3 (t, $J_{C-P} = 6.4$ Hz, $J_{C-Pt} = 33$ Hz, Ar-OP), 144.3 (t, $J_{C-P} = 6.0$ Hz, $J_{C-Pt} = 467$ Hz, Ar-Pt), 127.6 (s, Ar-$\text{H}$), 105.0 (t, $J_{C-P} = 6.0$ Hz, Ar-$\text{H}$), 30.3 (t, $J_{C-P} = 17$ Hz, $J_{C-Pt} = 58.5$ Hz, P-CHMe$_2$), 18.7 (vt, $J_{C-P} = 3.9$ Hz, $J_{C-Pt} = 19.0$ Hz, PCHMe), 17.2 (s, $J_{C-Pt} = 24.7$ Hz, PCHMe$_2$).
Figure 2: $^1$H NMR spectrum of 3a in C$_6$D$_6$. Pentane resonances visible at 0.86 and 1.22 ppm.
**Synthesis of (POCOP<sup>Et</sup>)**

In a Schlenk flask, resorcinol (443 mg, 4.015 mmol) was dissolved in THF and treated with triethylamine (1.22 grams, 12.1 mmol). Diethylchlorophosphine (1.00 gram, 8.03 mmol) was added dropwise and the solution was left to stir overnight at room temperature. The volatiles were removed under vacuum, and the product was extracted with pentane and filtered through Celite. The volatiles were removed under vacuum to leave a clear oil that was determined to be >95% pure by $^1$H NMR spectroscopy and could be used in further reactions (1.04 g, 90% yield).

$^{31}$P$\{^1$H$\}$ NMR (C$_6$D$_6$): $\delta$ 138.7 (s); $^1$H NMR (C$_6$D$_6$): $\delta$ 7.26 (m, 1H, Ar-H), 7.01 (t, 1H, $J = 8.0$ Hz, Ar-H), 6.88 (m, 2H, Ar-H), 1.58 (m, 4H, PC$_2$H$_2$Me), 1.36 (m, 4H, PC$_2$H$_2$Me), 0.99 (dt, 12H, $J_{H-P} = 14.5$ Hz, $J_{H-H} = 7.5$ Hz, PCH$_2$Me); $^{13}$C$\{^1$H$\}$ (C$_6$D$_6$): $\delta$ 160.1 (d, $J_{C-P} = 8.2$ Hz, Ar-OP), 130.2 (s, Ar-H), 112.5 (d, $J_{C-P} = 11.2$ Hz, Ar-H), 109.7 (t, $J_{C-P} = 11.2$ Hz, Ar-H), 25.4 (d, $J_{C-P} = 18.6$ Hz, PCH$_2$), 8.0 (d, $J_{C-P} = 13.2$, PCH$_2$Me).
Figure 3: $^1$H NMR spectrum of (POCOP$^{Et}$) in C$_6$D$_6$. 
(POCOP\textsuperscript{Et})PdCl (5)

In a Schlenk flask, (POCOP\textsuperscript{Et}) (380 mg, 1.33 mmol) was refluxed in toluene with Pd(COD)Cl\textsubscript{2} (379 mg, 1.33 mmol) overnight. The volatiles were removed from the reaction mixture, which was then dissolved in dichloromethane and passed through a pad of silica and Celite. The volatiles were removed under vacuum and the resulting solid was washed with diethyl ether and pentane to yield a white solid (438 mg, 77\% Yield). $^{31}$P{$^{1}$H} NMR (C\textsubscript{6}D\textsubscript{6}): 177.8 (s); $^{1}$H NMR (C\textsubscript{6}D\textsubscript{6}): $\delta$ 6.86 (t, 1H, $J = 8.5$ Hz, Ar-H), 6.67 (d, 2H, $J = 8.0$ Hz, Ar-H), 1.76 (m, 4H, PCH\textsubscript{2}Me), 1.67 (m, 4H, PCH\textsubscript{2}Me), 1.08 (m, 12H, PCH\textsubscript{2}Me); $^{13}$C{$^{1}$H} NMR (CDCl\textsubscript{3}): $\delta$ 165.5 (t, $J_{C-P} = 7.0$ Hz, Ar-OP), 129.8 (t, $J_{C-P} = 3.0$ Hz, Ar-Pd), 128.4 (s, Ar-H), 106.3 (t, $J_{C-P} = 8$ Hz, Ar-H), 24.0 (t, $J_{C-P} = 13$ Hz, PCH\textsubscript{2}Me), 7.6 (s, PCH\textsubscript{2}Me).
Figure 4: $^1$H NMR spectrum of 5 in C$_6$D$_6$. Pentane resonances visible at 1.22 and 0.86 ppm. Silicone grease is visible at 0.28 ppm.
\((POCOP^E_t)Pd(OAc)\) (5b)

5 (185 mg, 0.433 mmol) was dissolved in toluene in a culture tube and treated with AgOAc (80 mg, 0.476 mmol) and stirred overnight in the dark. The solution was filtered through a plug of silica and Celite and the volatiles were removed under vacuum. The product was recrystallized from pentane to yield a white crystalline solid (137 mg, 70%). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 172.6 (s); $^1H$ NMR ($C_6D_6$): $\delta$ 6.90 (m, 1H, Ar-$H$), 6.68 (d, 2H, $J = 8.0$ Hz, Ar-$H$), 2.26 (s, OAc), 2.14 (m, 4H, PCH$_2$Me), 1.84 (m, 4H, PCH$_2$Me), 1.12 (m, 12H, PCH$_2$Me); $^{13}C\{^1H\}$ NMR ($C_6D_6$): $\delta$ 175.0 (t, $J_{C-P} = 2.3$ Hz, OAc), 166.7 (t, $J_{C-P} = 7.1$ Hz, Ar-OP), 129.0 (s), Ar-Pd signal not present (obscured by $C_6D_6$), 106.1 (s), 25.4 (t, $J_{C-P} = 14.5$ Hz, PCH$_2$Me), 22.3 (s, OAc), 8.4 (s, PCH$_2$Me). Elem. Anal. Found (Calculated) for $C_{16}H_{26}O_4P_2Pd$: C, 42.59 (42.63); H, 5.89 (5.81).
**Figure 5:** $^1$H NMR spectrum of 5b in C$_6$D$_6$. Resonances of pentane visible at 1.22 and 0.87 ppm. Silicone grease resonance visible at 0.28 ppm.
Synthesis of (POCOPEt)Pd(C≡C-p-C₆H₄Me) (5c)

In a Schlenk flask, 5 (111 mg, 0.26 mmol) was dissolved in toluene and was treated with NaO'Bu (37 mg, 0.39 mmol), and 4-ethynyltoluene (33 ml, 0.26 mmol). The reaction was stirred overnight and the volatiles were removed under vacuum. The product was extracted in benzene and filtered through Celite. The volatiles were removed and the product was recrystallized from pentane in a -35 °C freezer (94 mg, 71%). ³¹P{¹H} NMR (C₆D₆): δ 179.5 (s); ¹H (C₆D₆): δ 7.63 (d, J = 8.0 Hz, 2H, Ar-H), 6.96 (d, J = 8.0 Hz, 2H, Ar-H), 6.95 (t, J = 8.0 Hz, 1H, Ar-H), 6.78 (d, J = 8.0 Hz, 2H, Ar-H), 2.06 (s, 3H, Ar-Me), 1.81 (m, 8H, P(CH₂C₃H₃)₂), 1.12 (app. pent. (overlapping tvt), J = 7.5 Hz, 12H, P(CH₂CH₃)₂); ¹³C{¹H} NMR (C₆D₆): δ 166.2 (t, J_C-P = 7.3 Hz, Ar-OP), 139.1 (t, J_C-P = 5.2, Ar), 134.5 (s), 131.4 (s), 129.1 (s), 128.4 (s), 127.0 (s), 117.0 (s, C≡C-tolyl), 109.2 (t, J_C-P = 18.1 Hz, C≡C-tol), 106.1 (t, J_C-P = 18.1 Hz, Ar), 24.7 (t, J_C-P = 13.5 Hz, PCH₂Me), 21.3 (s, Ar-Me), 8.0 (s, PCH₂Me). Elem. Anal. Found (Calculated) for C₂₃H₂₀O₂P₂Pd: C, 54.29 (54.50); H, 5.79 (5.97).
Figure 6: $^1$H NMR spectrum of 5c in C$_6$D$_6$. Resonances of pentane visible at 1.22 and 0.87 ppm. Silicone grease is also visible at 0.28 ppm.
Synthesis of (4,6-ditertbutylPOCOP)Pd(OAc) (7b)

![Synthesis of (4,6-ditertbutylPOCOP)Pd(OAc) (7b)](image)

In a culture tube, (4,6-ditertbutylPOCOP)PdCl₅ (155 mg, 0.26 mmol) was dissolved in toluene and treated with Ag(OAc) (48 mg, 0.29 mmol) and stirred overnight. The reaction mixture was passed through a pad of silica and Celite and stripped down. The product was recrystallized from isooctane as white crystals (72 mg, 44% yield). $^{31}$P{$^1$H} NMR (C₆D₆): δ 185.1 (s); $^1$H NMR (C₆D₆): δ 7.26 (s, 1H, Ar-H), 2.40 (m, 4H, P(CHMe₂)₂), 2.28 (s, 3H, OAc), 1.46 (s, 18H, ArCMe₃), 1.30 (apparent q (dvt), 12H, J = 9.0 Hz, PCHMe₂), 1.16 (apparent q (dvt), 12H, J = 7.0 Hz, PCHMe₂); $^{13}$C{$^1$H} NMR (C₆D₆): δ 174.8 (s, OAc), 162.7 (t, J$_{C-P}$ = 6.2 Hz, Ar-OP), 130.9 (t, J$_{C-P}$ = 4.2 Hz, Ar-Pd), 127.4 (t, J$_{C-P}$ = 5.9 Hz, Ar-tBu), 123.3 (s, Ar-H), 34.8 (s, Ar-CMe₃), 30.4 (s, OAc), 29.8 (t, J$_{C-P}$ = 12.0 Hz, PCHMe₂), 17.9 (t, J$_{C-P}$ = 3.8 Hz, PCHMe₂), 17.3 (s, ArCMe₃). Elem. Anal. Found (Calculated) for C₃₈H₅₀O₄P₂Pd: C, 54.24 (54.32); H, 8.06 (8.14).
Figure 7: $^1$H NMR spectrum of 7b in C$_6$D$_6$. Residual isooctane resonances are visible at 1.60, 1.10, 0.91, and 0.88 ppm.
Synthesis of PhOBpin

In a J. Young tube, phenol (32 mg, 0.34 mmol) was dissolved in C₆D₆ and treated with pinacolborane (49 μL, 0.34 mmol). Hydrogen gas was produced immediately upon mixing. Analysis by ¹H NMR spectroscopy showed that the reaction was completed within minutes. The reaction mixture was transferred to a flask, and the volatiles were removed under vacuum to yield a fine white powder (54 mg, 72%). ¹H NMR (C₆D₆): 7.22 (d, J = 8 Hz, 2H), 7.06 (m, 2H), 6.83 (t, J = 7.5 Hz, 1H), 1.01 (s, 12H); ¹³C ¹H NMR (C₆D₆): 154.4, 129.6, 123.3, 120.1, 83.3, 24.6; ¹¹B ¹H NMR (C₆D₆): 21.9 (s).
Figure 8: $^1$H NMR spectrum of PhOBpin in C$_6$D$_6$. 
Stoichiometric Reactions

Treatment of 2a with 4-ethynyltoluene

2a (15 mg, 0.033 mmol) was dissolved and treated with 4-ethynyltoluene (4 μL, 0.033 mmol). Analysis by $^1$H and $^{31}$P{H} NMR spectroscopy <15 minutes after the addition of 4-ethynyltoluene showed complete conversion to 2c by $^{31}$P{1H} NMR spectroscopy and $^1$H NMR spectroscopy showed the evolution of H$_2$.

Figure 9: $^1$H NMR spectrum of the treatment of 2a with 1 eq. of 4-ethynyltoluene. Inset is the $^{31}$P{1H} NMR spectrum of the same reaction.
Treatment of 2b with pinacolborane

2b (35 mg, 0.069 mmol) was dissolved in C₆D₆ and treated with pinacolborane (10 μL, 0.069 mmol), which immediately made the solution turn from clear to a light yellow. Analysis by ¹H and ³¹P{¹H} NMR spectroscopy <15 minutes after the addition of pinacolborane showed 100% conversion to 2a and the appearance of two new singlets at 1.597 ppm (3H) and 1.025 ppm (12H) showing the formation of pinBOAc.

![Figure 10: ¹H NMR spectrum resulting from the treatment of 2b with pinacolborane in C₆D₆.](image)
Treatment of 2b with 4-ethynyltoluene

2b (40 mg, 0.079 mmol) was treated with 4-ethynyltoluene (10 μL, 0.079 mmol). Within 23 h at room temperature, a 3:2 2b:2c equilibrium was established as seen by $^{31}$P{${}^1$H} NMR spectroscopy. $^1$H NMR spectroscopy shows the formation of acetic acid from the characteristic broad singlet at 13.25 ppm. Addition of 1 equivalent of pinacolborane (11.5 μL, 0.079 mmol) consumed the acetic acid and gave immediate production of PinBOAc and 2a, which subsequently reacted with free alkyne resulting in >98% conversion to 2c by $^{31}$P{${}^1$H} NMR spectroscopy.
Figure 11: $^1$H NMR spectrum resulting from the treatment of 2b with 4-ethynyltoluene after 23 h at room temperature in C$_6$D$_6$. Inset is the $^{31}$P{$^1$H} NMR spectrum of the same mixture.
Figure 12: $^1$H NMR spectrum resulting from the treatment of the equilibrium mixture of 2b and 2c with 1 eq. of pinacolborane.
Treatment of 2c with pinacolborane

2c (15 mg, 0.027 mmol) was dissolved in C_{6}D_{6} and treated with pinacolborane (20 μL, 0.14 mmol) and heated at 80 °C. After 5 h, the reaction showed ~50% conversion to 2a by $^{31}$P{¹H} NMR spectroscopy, and $^{1}$H NMR spectroscopy showed formation of A. However, further heating of the reaction mixture led to the formation of other products visible by $^{31}$P{¹H} NMR spectroscopy at 198.5 (s), 185.1 (s), 183.6 (s) ppm.

Figure 13: $^{1}$H NMR spectrum resulting from 5 h of heating 2c and 5 eq. of HBpin in C_{6}D_{6} for 5 h. Inset is the $^{31}$P{¹H} NMR of the same mixture.
Treatment of 2a with 4-Me-C₆H₄-C≡C-Bpin (A)

2a (14 mg, 0.031 mmol) was dissolved in C₆D₆ and treated with A (8 mg, 0.03 mmol) and heated at 80 °C. After 3 h, the sample was analyzed by ³¹P{¹H} NMR spectroscopy, which showed 16% conversion to 5c, pinacolborane was also visible by ¹H NMR spectroscopy. After 6 h at 80 °C, ³¹P{¹H} NMR analysis showed 23% conversion to 2c and 8% formation of a product at 185.1 ppm. Heating the sample for 4 days at 80 °C showed a distribution of 8% 2a, 21% 2c, and 71% accounting for compounds 2d and 2e (62% 185.1 ppm, and 9% 183.6 ppm) by ³¹P{¹H} NMR integration. Analysis of the mixtures by ¹H NMR spectroscopy showed two new singlets presumed to be olefinic protons at 7.39 ppm and 6.42 ppm. After HCl (50 μL, 37%) was added to the J. Young tube, analysis by ³¹P{¹H} NMR spectroscopy showed complete conversion of phosphorus-containing compounds to 2. The volatiles were removed under vacuum and the products extracted with diethyl ether. The ether solution was dried over magnesium sulfate, decanted, and the volatiles were removed under vacuum. The resulting solid was dissolved in CDCl₃, and ¹H NMR spectroscopy showed the presence of (Z)-(4-methylstyryl)Bpin.⁷
Figure 14: $^1$H NMR spectrum of the treatment of 2a with A after 4 days at 80 °C. Inset is the $^{31}$P{$^1$H} NMR spectrum of the same mixture. Resonances at 185.1 and 183.6 ppm in the $^{31}$P{$^1$H} NMR spectrum are expected to be products 2d and 2e, but which signal corresponds to which compound has not been determined.

**Treatment of 5b with 4-ethyltoluene**

5b (36 mg, 0.079 mmol) was dissolved in C$_6$D$_6$ and treated with 4-ethyltoluene (10 μL, 0.079 mmol). Within 30 minutes at room temperature, the reaction mixture reached an equilibrium mixture of 15:85 5c:5b, observed by $^{31}$P{$^1$H} NMR spectroscopy. $^1$H NMR spectroscopy showed that free acetic acid was present in the reaction mixture. 5b has been
shifted in the $^{31}$P{$^1$H} NMR spectrum to 173.3 ppm due to an interaction with free acetic acid in solution. Further treatment with pinacolborane forms a black solution and decomposition of the palladium complex.

Figure 15: $^1$H NMR spectrum resulting from the treatment of 5b with 4-ethynyltoluene after 30 min at room temperature in C$_6$D$_6$. Inset is the $^{31}$P{$^1$H} NMR spectrum of the same mixture.

Treatment of 5b with acetic acid

5b (9 mg, 0.02 mmol) was dissolved in C$_6$D$_6$ and treated with acetic acid (1 μL, 0.02 mmol). Analysis of mixture by $^{31}$P{$^1$H} NMR spectroscopy showed a downfield shift of the signal for 5b to 174.2 ppm.
Treatment of 5b with pinacolborane

5b (25 mg, 0.055 mmol) was dissolved in C₆D₆ and treated with pinacolborane (8 µL, 0.552 mmol). Upon mixing, the solution formed bubbles and quickly turned from clear to orange, red, and finally a dark brown. ¹H NMR spectroscopy showed the formation of dihydrogen, and 5b was observed to the major identifiable complex by ³¹P{¹H} NMR spectroscopy. The reaction mixture was filtered through silica and Celite and the volatiles were removed under vacuum to produce a brown solid, which contained 5b and other unidentifiable decomposition products.

Treatment of 5 with NaHBET₃

5 (30 mg, 0.070 mmol) was dissolved in C₆D₆ and treated with NaBHEt₃ (77 µL, 1.0 M solution in toluene). The reaction mixture turned bright orange and quickly turned to red and finally brown with black precipitate. Analysis by ³¹P{¹H} NMR spectroscopy showed several products.

Treatment of 5c with pinacolborane

5c (27 mg, 0.053 mmol) was dissolved in C₆D₆ and treated with pinacolborane (8 µL, 0.055 mmol). After 1 day at room temperature, there was a 20% conversion of the pinacolborane to A, and the solution turned from a clear yellow to brown. Dihydrogen was also detected by ¹H NMR spectroscopy. ³¹P{¹H} NMR spectroscopy showed only the presence of 5c.
**General Procedure for Catalytic Reactions**

A stock solution of the desired catalyst was used to deliver 0.017 mmol of catalyst in C₆D₆. 1,4-dioxane (100 μL of 0.035 mmol stock solution in C₆D₆), pinacolborane (49 μL, 0.34 mmol), and 4-ethynyltoluene (43 μL, 0.34 mmol) were added to the J. Young tube. The reaction was then heated at 80 °C until completion. In addition to the hydrogenation of 4-ethynyltoluene to 4-methylstyrene, there was trace production of 4-ethyltoluene in reactions where hydrogenation was significant.

**Catalysis with (POCOPiPr)NiH (1a)**

1a (0.017 mmol) was dissolved in C₆D₆ in a J. Young tube and 1,4-dioxane (100 μL of 0.035 mmol stock solution in C₆D₆), pinacolborane (49 μL, 0.34 mmol), and 4-ethynyltoluene (43 μL, 0.34 mmol) were added. The reaction was heated at 80 °C for 1 day. Analysis by ¹H NMR spectroscopy showed complete consumption of 4-ethynyltoluene and a complex mixture of compounds with olefinic signals. However, 83% of the pinacolborane was still present at the end of the reaction time.

**Catalysis with (POCOPiPr)PtH (3a)**

3a (0.017 mmol) was dissolved in C₆D₆ in a J. Young tube and 1,4-dioxane (100 μL of 0.035 mmol stock solution in C₆D₆), pinacolborane (49 μL, 0.34 mmol), and 4-ethynyltoluene (43 μL, 0.34 mmol) were added. The reaction was heated at 80 °C for 1 day. Analysis by ³¹P{¹H} NMR spectroscopy showed that 5% of 4-ethynyltoluene was converted to (E)-(4-methylstyryl)Bpin, which was identified by ¹H NMR spectroscopy and comparison to the reported ¹H NMR spectral data.⁸
NMR analysis of catalytic mixtures with 5b

Approximately 10 min. after mixing 5b (5%, 0.017 mmol) with 4-ethynyltoluene, pinacolborane, and a dioxane standard, the sample was monitored by $^1$H and $^{31}$P{$^1$H} NMR spectroscopy. PinBOAc and dihydrogen were visible by $^1$H NMR spectroscopy, and 5c was observed by $^{31}$P{$^1$H} NMR spectroscopy.

Figure 16: Initial $^1$H NMR spectrum of catalytic mixture showing the presence of pinBOAc. Inset is $^{31}$P{$^1$H} NMR spectrum showing 5c.
Elemental Mercury as an Additive

Mercury was capable of drastically inhibiting the hydrogenation reaction, and allowed for nearly complete conversion of the terminal alkyne to the alkynylboronate and hydrogen. Monitoring the reaction with mercury (Entry 6) showed that after 1 day at 80 °C the reaction with mercury as an additive had undergone 37% conversion to the alkynylboronate. The control reaction (Entry 3) showed complete consumption of the terminal alkyne at this time with a 40% conversion to the alkynylboronate.

Turnover tests for 5b

A stock solution of the desired catalyst was used to deliver 0.0017 mmol of 5b in C₆D₆. 1,4-dioxane (100 μL of 0.035 mmol stock solution in C₆D₆), pinacolborane (49 μL, 0.34 mmol), and 4-ethynyltoluene (43 μL, 0.34 mmol) were added to the J. Young tube along with the desired amount of mercury or triphenylphosphine. The reaction was then heated at 80 °C until completion.

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<th>Table SI-1: Turn over test with 5b</th>
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<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>5</td>
</tr>
</tbody>
</table>

When 0.0034 mmol of triphenylphosphine was used in entry 3, there was a significant inhibition of 4-methylstyrene production for the first 24 h, but hydrogenation did occur beyond the first day.
Figure 17: Stacked $^1$H NMR spectra from (table SI-1, entry 3). 4-methylstyrene is not produced until after day 1.

5b Turnover test with mercury (Table SI-1, Entry 5)

When mercury was used as an additive the reaction was heated for 1 day at 80 °C. Palladium black had precipitated out on the sides of the J. Young tube, the solution was a pale clear yellow color, and no reactivity was seen after this point. 38% of the starting alkyne had been converted to A and there were trace amounts of 4-methylstyrene and trace amounts of 4-ethyltoluene. The catalyst was seen to perform about 76 turn overs.
Higher HBpin : Alkyne ratios

A stock solution of the desired catalyst was used to deliver 0.017 mmol of 5b in C₆D₆. 1,4-dioxane (100 μL of 0.035 mmol stock solution in C₆D₆), pinacolborane (49 μL, 0.34 mmol), (54 μL, 0.37 mmol), (74 μL, 0.51 mmol), triphenylphosphine (0.034 mmol), and 4-ethynyltoluene (43 μL, 0.34 mmol) were added to the J. Young tube. The reaction was then heated at 80 °C until completion.

Table SI-2: Higher HBpin:Alkyne Ratios

<table>
<thead>
<tr>
<th>HBpin: alkyne</th>
<th>4 Hours @ 80 °C</th>
<th>1 Day @ 80°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SM</td>
<td>A</td>
</tr>
<tr>
<td>1:1</td>
<td>7%</td>
<td>6%</td>
</tr>
<tr>
<td>1.1 : 1</td>
<td>13%</td>
<td>6%</td>
</tr>
<tr>
<td>1.5 : 1</td>
<td>14%</td>
<td>5%</td>
</tr>
</tbody>
</table>

Control reaction with Pd(COD)Cl₂

In a J. Young tube, Pd(COD)Cl₂ (5 mg, 0.0175 mmol) was dissolved in C₆D₆ with 4-ethynyltoluene (43 μL, 0.34 mmol) and pinacolborane (49 μL, 0.34 mmol). The reaction mixture was heated for 24 h at 80 °C. Analysis by ¹H NMR spectroscopy showed no visible production of A or 4-methylstyrene.

Control reactions with Pd₂(DBA)₃ and triphenylphosphine

In a J. Young tube, Pd₂(DBA)₃ (8 mg, 0.0087 mmol) was treated with PPh₃ (9 mg, 0.034 mmol), 4-ethynyltoluene (43 μL, 0.34 mmol) and pinacolborane (49 μL, 0.34 mmol) in C₆D₆. The reaction mixture was heated for 24 h at 80 °C. Analysis of the reaction mixture by ¹H NMR spectroscopy shows >90% of the starting alkyne remains, and there was no visible production of A.
Control reaction with Pd$_2$(DBA)$_3$

In a J. Young tube, Pd$_2$(DBA)$_3$ (8 mg, 0.0087 mmol) was dissolved in C$_6$D$_6$ and treated with 4-ethynyltoluene (43 μL, 0.34 mmol) and pinacolborane (49 μL, 0.34 mmol). The reaction mixture was heated for 24 h at 80 °C. Analysis of the reaction mixture by $^1$H NMR spectroscopy shows that >90% of the pinacolborane remains. Broad signals at around 7.00 ppm and 2.00 ppm suggest that the alkyne has been converted to polymeric and oligomeric products.
Characterization of Alkynylboronates

Alkynylboronates were characterized in situ by $^1$H NMR spectroscopy and compared to literature data.9

4-Me-C₆H₄-C≡C-Bpin (A): $^1$H NMR (500 MHz, C₆D₆): δ 7.34 (d, J = 7.5 Hz, 2H), 6.65 (d, J = 7.5 Hz, 2H), 1.87 (s, 3H, Ar-CH₃), 1.02 (s, 12H, -CH₃ on Bpin).

n-Bu-C≡C-Bpin: $^1$H NMR (500 MHz, C₆D₆): δ 1.95 (t, J = 7 Hz, 2H), 1.21 (m, 4H), 0.99 (s, 12H, -CH₃ on Bpin), 0.66 (t, J = 7 Hz, 3H).

Me₃Si-C≡C-Bpin: $^1$H NMR (500 MHz, C₆D₆): δ 0.94 (s, 12H, -CH₃ on Bpin), 0.06 (s, 9H, -CH₃ on Me₃Si).

Me₃SiO-CH₂-C≡C-Bpin: $^1$H NMR (500 MHz, C₆D₆): δ 4.07 (s, 2H, O-CH₂-C≡C), 0.97 (s, 12H, -CH₃), 0.07 (s, 9H, -CH₃ on Me₃Si). $^{11}$B NMR (128 MHz, C₆D₆): δ 24.0.

PhO-CH₂-C≡C-Bpin: Selected data for PhO-CH₂-C≡C-Bpin: $^1$H NMR (500 MHz, C₆D₆): δ 4.22 (s, 2H, O-CH₂-C≡C), 0.93 (s, 12H, -CH₃ on Bpin); $^{11}$B NMR (128 MHz, C₆D₆): δ 23.7. Selected NMR data for PhO-CH₂-C≡CH: $^1$H NMR (500 MHz, C₆D₆): δ 4.19 (d, J = 2Hz, 2H, O-CH₂-C≡C).

Me₃Si-O-Bpin: $^1$H NMR (500 MHz, C₆D₆): δ 1.04 (s, 12H, -CH₃ on Bpin), 0.19 (s, 9H, -CH₃ on Me₃Si); $^{11}$B NMR (128 MHz, C₆D₆): δ 20.8.10
References


