Intramolecular 1,1-carboboration vs. intermolecular FLP addition in reactions of boranes and \textit{bis}(phenylethynyl)telluroether

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Supporting Information
General experimental procedure

All experimental manipulations were conducted in an O\textsubscript{2}-free, N\textsubscript{2}-filled MBraun LABmaster SP dry box equipped with a -35 °C freezer. All proteo solvents (purchased from Caledon Laboratories) were purified using a Grubbs-type column system (Innovative Technologies) and stored over 4 Å sieves in Straus flasks. CD\textsubscript{2}Cl\textsubscript{2} (purchased from Cambridge Isotopes) was dried over CaH\textsubscript{2} and distilled under reduced pressure. All solvents were degassed by repeated freeze-pump-thaw cycles prior to use.

All chemicals were used as received unless otherwise noted. \textsuperscript{n}BuLi (1.6 M in hexanes), phenylacetylene and N-bromosuccinimide (NBS) were purchased from Sigma-Aldrich, B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} was purchased from Boulder Scientific, Elemental tellurium was purchased from Alfa Aesar and AgNO\textsubscript{3} was purchased from Apollo Chemicals. BPh\textsubscript{3} was purchased from Strem Chemicals and recrystallized from diethyl ether prior to use. PhB(C\textsubscript{6}F\textsubscript{5})\textsubscript{2} and CH\textsubscript{3}B(C\textsubscript{6}F\textsubscript{5})\textsubscript{2} were prepared using standard literature procedure.

NMR spectroscopy was performed on either a Bruker Advance III 400 MHz, an Agilent DD2 500 MHz, or an Agilent DD2 600 MHz. Unless otherwise stated, all spectra were obtained at room temperature. All NMR spectra were referenced to residual proteo solvent peaks of CD\textsubscript{2}Cl\textsubscript{2} (\textsuperscript{1}H = 5.32 ppm; \textsuperscript{13}C = 53.84 ppm) or an external standard (\textsuperscript{19}F: CFCl\textsubscript{3}(δ 0.00), \textsuperscript{11}B: (Et\textsubscript{2}O)BF\textsubscript{3}(δ 0.00), \textsuperscript{125}Te: Ph\textsubscript{2}Te\textsubscript{2}(δ 420.8 ppm)).

Single-crystal X-ray crystallographic analyses were performed on crystals coated in Paratone oil and mounted on a Bruker Kappa Apex II diffractometer. UV-Vis absorption spectra of compounds 2, 4 and 6 were recorded on a Varian Cary 5000 UV-vis-NIR spectrophotometer using CH\textsubscript{2}Cl\textsubscript{2} as solvent at 298 K. Combustion elemental analyses were performed on a on a PerkinElmer CHN Analyzer. HR-MS was performed on a JEOL AccuTOF equipped with a Direct Analysis in Real Time (DART) ion source. Repeated attempts to obtain elemental analysis for compounds 3, 5 and 7 were all unsuccessful and gave extremely low carbon content. In addition, no molecular ion of these compounds could be detected using the same ionization method as those used for compounds 2, 4 and 6. This is likely a result of the unstable and zwitterionic nature of compounds 3, 5 and 7.

Synthesis of PhCCBr

\[
\begin{align*}
\text{Ph} & \xrightarrow{\text{NBS (1.2 eq)}} \text{AgNO}_3 (0.1 \text{ eq}) \xrightarrow{} \text{Ph} & \xrightarrow{\text{Br}} \\
\text{H (400.0 MHz, CD}_2\text{Cl}_2): \delta & 7.47-7.44 (m, 2H, o-Ph), 7.37-7.30 (m, 3H, m-, p-Ph) \\
\text{C}^{\text{1}} (\text{CD}_2\text{Cl}_2): \delta & 129.4 (s, m-Ph), 129.0 (s, o-Ph), 123.1 (s, i-Ph), 80.5 (s, ≡CPh), 50.1 (s, BrC≡)
\end{align*}
\]

N-bromosuccinimide (NBS) (2.061 g, 0.012 mol), and AgNO\textsubscript{3} (0.178 g, 0.0010 mol) were added to a solution of phenylacetylene (1.071 g, 0.010 mol) dissolved in ca. 30 ml acetone. The clear solution gradually turns opaque with grey precipitate over the course of 2 hours. This mixture was then filtered by gravity filtration to give a clear, colourless solution. All volatiles were removed in vacuo, leaving a light yellow thick oil. The product was extracted from the residue using 2x20 ml hexanes. The organic solution was filtered through a short plug of silica, then all
volatiles were removed \textit{in vacuo} to yield the target compound as a pale yellow oil (1.540 g, 0.0085 mol, 81\% yield).

\begin{center}
\includegraphics[width=\textwidth]{nmr_spectra.png}
\end{center}

\textbf{Preparation of compound 1, Te(CCPh)\textsubscript{2}}

\begin{center}
\begin{align*}
\text{Ph} & \quad \xrightarrow{1. \, \text{nBuLi}} \quad \text{Ph} \quad \xrightarrow{2. \, \text{Te, 55^\circ C}} \quad \text{Ph} \quad \xrightarrow{3. \, \text{PhCCBr}} \quad \text{Ph} \\
\end{align*}
\end{center}

\begin{itemize}
  \item \textbf{\textsuperscript{1}H (400.0 MHz, CD\textsubscript{2}Cl\textsubscript{2})}: \delta 7.49-7.47 (m, 4H, \textit{Ar}-H) 7.36-35 (m, 6H, \textit{Ar}-H)
  \item \textbf{\textsuperscript{13}C\{\textsuperscript{1}H\} (100.6 MHz, CD\textsubscript{2}Cl\textsubscript{2})}: \delta 132.6 (s, \textit{m}-Ph), 129.7 (s, \textit{p}-Ph), 128.9 (s, \textit{o}-Ph), 123.3 (s, \textit{i}-Ph), 113.0 (s, =CPh), 43.8(s, TeC=)
  \item \textbf{\textsuperscript{125}Te (189.3 MHz, CD\textsubscript{2}Cl\textsubscript{2})}: \delta 360.0 (s)
\end{itemize}
\( \text{BuLi (5.3 ml, 8.5 mmol, 1.6 M solution in hexanes) was added drop-wise to a solution of phenylacetylene (0.8704 g, 8.5 mmol) dissolved in ca. 15 ml THF cooled to -35 }^\circ\text{C. The solution was stirred and kept at this temperature of 30 min., upon which point elemental tellurium (1.0870 g, 8.5 mmol) was added and the resulting slurry transferred to a 100-ml Schlenk bomb and heated to 60 }^\circ\text{C for 2 hr in the dark, giving a clear yellow solution. The solution was then cooled to room temperature and quenched with freshly prepared 1-bromo-2-phenylacetylene (1.5400 g, 8.5 mmol) dissolved in ca. 10 ml THF. The solution was allowed to warm to room temperature in the dark over 16 h. All volatiles were then removed \textit{in vacuo}, giving a dark red oil. The product was extracted with 15 ml Et}_2\text{O and passed through a short plug of silica to give a clear red solution. All volatiles were removed again, giving a thick red oil that solidifies, which was then washed with DCM (5 ml x 2) and hexanes (5ml x 2) to precipitate out the desired product as a bright yellow solid (1.683 g, 5.1 mmol, 60\% yield).}

\textbf{Anal.} \text{Calc. for C}_{16}\text{H}_{10}\text{Te : C 58.26 }\%\text{, H 3.06 }\%\text{. Found: C 57.51 }\%\text{ H 3.01 }\%\text{.}
**Preparation of compound 2**

\[
\begin{array}{c}
1^H (500.0 \text{ MHz, } \text{CD}_2\text{Cl}_2): \; \delta 7.20-7.12 (m, 10H, Ar-H) \; 6.88-6.78 (m, 7H, Ar-H), \; 6.77-6.70 (m, 8H, Ar-H) \\
1^B\{1^H\} (128.3 \text{ MHz, } \text{CD}_2\text{Cl}_2): \; \delta 53.3 (\text{br s, } \nu_{1/2} \approx 820 \text{ Hz})
\end{array}
\]

\[
\begin{array}{c}
13^C\{1^H\} (125.7 \text{ MHz, } \text{CD}_2\text{Cl}_2): \; \delta 162.2 (s, \text{TeC=}), \; 155.6 (\text{br s, } \equiv \text{CB}), \; 148.8 (\text{br s, } i-\text{Ph}^B), \; 145.6 (s, i-\text{Ph}), \; 143.9 (s, i-\text{Ph}^\text{Te}), \; 131.9 (s, \text{Ar-C}), \; 131.1 (s, \text{Ar-C}), \; 128.7(s, \text{Ph}^\text{Te}), \; 128.3 (s, \text{Ph}^\text{Te}), \; 127.8 (s, \text{Ph}^\text{Te}), \; 127.2 (s, \text{Ph}), \; 126.1 (s, \text{Ar-C}), \; 125.8 (s, \text{Ar-C}), \; 125.0 (s, \text{Ar-C})
\end{array}
\]

\[
125^\text{Te} (189.3 \text{ MHz, } \text{CD}_2\text{Cl}_2): \; \delta 772.8 (s)
\]

[Note: Ph\text{Te} denotes the Ph(\text{Te})C=C phenyl ring, Ph denotes the Ph(\text{B})C=C phenyl ring and Ph\text{B} denotes the BPh phenyl ring]

A solution of BPh\text{3} (23.6 mg, 0.1 mmol) dissolved in 2 ml 1:4 solution of DCM: pentane was cooled to -35 °C, and to it was added dropwise a solution of compound 1 (31.1 mg, 0.1 mmol) also cooled to -35 °C in 3 ml of the same solvent. No immediate colour change was observed, and the reaction mixture was allowed to warm to room temperature over 20 h, giving an opaque light orange solution. The clear orange supernatant was decanted and the light orange powder leftover was collected and dried under vacuum, giving compound 2 as an orange powder (51.0 mg, 0.09 mmol, 93% yield). Single crystal suitable for x-ray diffraction studies was grown from letting a saturated pentane solution of 2 stand at room temperature over 12 h. Repeated attempts of obtaining accurate elemental analysis always gave exceptionally low carbon contents.

**MS (DART+):** cal’d for C\text{34}H\text{29}BN\text{Te} [M+\text{NH}_4]: 592.14553 amu. Found: 592.14850 amu
Preparation of compound 3

\[
\text{Ph} \equiv \text{Te} \equiv \text{Ph} \xrightarrow{\text{B(C}_6\text{F}_5)_3} \text{Ph} \equiv \text{Te} \equiv \text{Ph}
\]

\(^1\text{H} (400.0 \text{ MHz, CD}_2\text{Cl}_2, 193 \text{ K})\): \(\delta 6.89 \text{ (m, 16H } Ar\text{-H}), 6.63 \text{ (t, 2H, } J_{H-H} = 7.2 \text{ Hz, } o\text{-Ph}), 6.57 \text{ (m, 2H, } o\text{-Ph) \})

\(^{11}\text{B}\{^1\text{H}\} (128.3 \text{ MHz, CD}_2\text{Cl}_2): \delta -4.1 \text{ (s, } J_{\text{B-H}} \approx 60 \text{ Hz) \})\}

\(^{13}\text{C}\{^1\text{H}\} (100.6 \text{ MHz, CD}_2\text{Cl}_2, 193 \text{ K}): \text{(partial, } C_6\text{F}_5 \text{ signals not listed) } \delta 169.8 \text{ (br s, (Te)PhC=C(B)(C}_6\text{F}_5)), 149.3 \text{ (1:1:1:1 q, } J_{C-B} = 128 \text{ Hz, (Te)(B)C=C(Te)(Ph)), 142.6 \text{ (s, (Te)PhC=C(B)(C}_6\text{F}_5)), 139.4 \text{ (s, (Te)(B)C=C(Te)(Ph)), 135.1 \text{ (s, } i\text{-Ph}^{\text{Te}}, 133.4 \text{ (s, } i\text{-Ph), 128.6 \text{ (s, } Ar\text{-C), 128.5 \text{ (s, } Ar\text{-C), 128.4 \text{ (s, } Ar\text{-C), 128.2 \text{ (s, } Ar\text{-C), 126.7 \text{ (s, } Ar\text{-C), 124.4 \text{ (s, } Ar\text{-C) \}})\}

\(^{13}\text{C}\{^1\text{H}\} (125.7 \text{ MHz, CD}_2\text{Cl}_2) \text{ NMR spectrum of } 2

\(^{11}\text{B}\{^1\text{H}\} (128.3 \text{ MHz, CD}_2\text{Cl}_2) \text{ NMR spectrum of } 2
$^{19}$F{$^1$H} (376.4 MHz, CD$_2$Cl$_2$, 193 K): δ -126.6 (s, 1F, o-C$_6$F$_5^{B'}$), -128.7 (s, 1F, o-C$_6$F$_5^{B'}$), -129.5 (s, 1F, o-C$_6$F$_5^{B'}$), -129.9 (s, 1F, o-C$_6$F$_5^{B'}$), -139.4 (s, 1F, o-C$_6$F$_5$), -143.3 (s, 1F, o-C$_6$F$_5$), -154.4 (s, 1F, p-C$_6$F$_5$), -157.1 (s, 1F, p-C$_6$F$_5^{B'}$), -158.8 (s, 1F, p-C$_6$F$_5^{B'}$), -161.6 (s, 1F, m-C$_6$F$_5$), -162.0 (s, 1F, m-C$_6$F$_5$), -162.6 (s, 1F, m-C$_6$F$_5^{B'}$), -163.7 (s, 1F, m-C$_6$F$_5^{B'}$), -164.3 (s, 1F, m-C$_6$F$_5^{B'}$), -167.3 (s, 1F, m-C$_6$F$_5^{B'}$)

$^{125}$Te (157.8 MHz, CD$_2$Cl$_2$, 193 K): δ 947.2 (s), 945.9 (s) [Note: no $^{125}$Te resonance could be observed at room temperature]

[C$_6$F$_5^{B'}$ and C$_6$F$_5^{B''}$ denotes different =CB(C$_6$F$_5$)$_2$ aryl rings and C$_6$F$_5$ denotes =C(C$_6$F$_5$)]

[Note: Ph denotes the Ph( Te)C=C phenyl ring, Ph$^\text{Te}$ denotes the Ph( Te)C=C( Te)( B) phenyl ring in the central 6-membered ring]

A solution of B(C$_6$F$_5$)$_3$ (51.6 mg, 0.10 mmol) dissolved in 2 ml 1:4 solution of DCM: pentane was cooled to -35 °C, and to it was added drop-wise a solution of compound 1 (33.8 mg, 0.10 mmol) also cooled to -35 °C in 3 ml of the same solvent. The solution immediately turned orange and gets darker over time. After stirring at this temperature for 10 min. the cold well was removed and this solution was stirred at room temperature for an additional 7 hours. Lots of light yellow powder precipitated out of solution over this time. The dark orange supernatant was decanted, and the yellow powder was then washed 3 times with a 1:10 solution of DCM: pentane and dried under vacuum to yield compound 3 (40.5 mg, 0.02 mmol 47% yield).

$^1$H (400.0 MHz, CD$_2$Cl$_2$, 298 K) NMR spectrum of 3
$^1$H (400.0 MHz, CD$_2$Cl$_2$, 193 K) NMR spectrum of 3

$^{13}$C$\{^1$H$\}$ (100.6 MHz, CD$_2$Cl$_2$, 298 K) NMR spectrum of 3

$^{13}$C$\{^1$H$\}$ (100.6 MHz, CD$_2$Cl$_2$, 193 K) NMR spectrum of 3
$^{19}\text{F}^{1}\text{H}$ (376.4 MHz, CD$_2$Cl$_2$, 298 K) NMR spectrum of 3

$^9\text{F}^{1}\text{H}$ (376.4 MHz, CD$_2$Cl$_2$, 193 K) NMR spectrum of 3
Preparation of compound 4

A slurry of compound 1 (145.3 mg, 0.44 mmol) in ca. 5 ml pentane was added to a solution of B(C₆F₅)₃ (224.7 mg, 0.44 mmol) dissolved in ca. 10 ml pentane. The mixture immediately turned dark red and over time became opaque with lots of orange precipitate. All volatiles of this mixture were removed in vacuo after 1 h, leaving a dark red oil. The residue was then re-dissolved in ca. 10 ml toluene and heated at 60 °C for 16 h, then 80 °C for 1 h. All volatiles were removed again in vacuo, and the deep red residue was extracted with 5 ml pentane and 3 ml benzene, precipitating out a light orange powder with dark red supernatant. The mother liquor was then, leaving an orange powder. This powder washed with minimal amounts of cold
hexamethyldisiloxane (O(TMS)$_2$) to give the title compound. More product can be collected from the supernatant (210.5 mg, 0.25 mmol 57% yield). Single crystal suitable for x-ray diffraction studies was grown from a saturated solution of 4 in dichloromethane (DCM) at -35 °C.

**Anal.** Calc. for C$_{34}$H$_{10}$BF$_{15}$Te: C 48.51 %, H 1.20 %. Found: C 48.70 % H 1.10 %

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**$^1$H NMR (400 MHz, CD$_2$Cl$_2$) spectrum of 4**

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**$^{13}$C{$^1$H} (100.6 MHz, CD$_2$Cl$_2$) NMR spectrum of 4**

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**$^{19}$F{$^1$H} (376.4 MHz, CD$_2$Cl$_2$) NMR spectrum of 4**
Preparation of Compound 5

A solution of PhB(C₆F₅)₂ (38.9 mg, 0.09 mmol) dissolved in 2 ml 1:4 solution of DCM: pentane was cooled to -35 °C, and to it was added drop-wise a solution of compound 1 (30.3 mg, 0.09 mmol) also cooled to -35 °C in 3 ml of the same solvent. The solution immediately turned orange. After stirring at this temperature for 10 min. the cold well was removed and this solution was stirred at room temperature for an additional 7 hours. Lots of light yellow powder precipitated out of solution over this time. The clear orange supernatant was decanted, and the light yellow powder was then washed 3 times with a 1:10 solution of DCM: pentane and dried under vacuum to yield compound 5 (36.6 mg, 0.024 mmol, 53% yield).
$^1$H (400.0 MHz, CD$_2$Cl$_2$, 298 K) NMR spectrum of 5

$^1$H (400.0 MHz, CD$_2$Cl$_2$, 193 K) NMR spectrum of 5

$^{13}$C{$^1$H} (100.6 MHz, CD$_2$Cl$_2$, 298 K) NMR spectrum of 5
Preparation of compound 6

$^1$H (400.0 MHz, CD$_2$Cl$_2$): $\delta$ 7.32-7.31 (m, 3H, Ph$^{Te}$), 7.28-7.26 (m, 2H, Ph$^{Te}$), 7.24-7.20 (m, 5H, Ph$^{Te}$), 7.00-6.93 (m, 3H, m, p-Ph), 6.87-6.85 (d, $^3$J$_{H-H} = 7.2$ Hz, 2H, o-Ph)

$^{11}$B$^1$H (128.3 MHz, CD$_2$Cl$_2$): $\delta$ 50.6 (br s, $\nu_{1/2}$ $\approx$ 1070 Hz)

$^{13}$C$^1$H (100.6 MHz, CD$_2$Cl$_2$): $\delta$ n.o (BC=), 175.9 (s, TeC=), 169.5 (s, TeC=), 144.7 (dm, $^1$J$_{C-F}$ $\approx$ 239 Hz, o-C$_6$F$_5$), 144.0 (s, i-Ph), 143.5 (dm, $^1$J$_{C-F}$ $\approx$ 247 Hz, o-C$_6$F$_5$), 142.4 (s, i-Ph$^{Te}$), 142.0 (s,
$^1$H (500.0 MHz, CD$_2$Cl$_2$) NMR spectrum of 6
$^{13}\text{C} \{^1\text{H}\}$ (125.7 MHz, CD$_2$Cl$_2$) NMR spectrum of 6

$^{19}\text{F} \{^1\text{H}\}$ (376.4 MHz, CD$_2$Cl$_2$) NMR spectrum of 6

$^{11}\text{B} \{^1\text{H}\}$ (128.3 MHz, CD$_2$Cl$_2$) NMR spectrum of 6
Preparation of compound 7

\[ \begin{align*}
\text{Ph} & \equiv \text{Te} \equiv \text{Ph} \\
\text{CH}_3 \cdot \text{B} (\text{C}_6\text{F}_5)_2 & \quad \text{CH}_3 \cdot \text{B} (\text{C}_6\text{F}_5)_2
\end{align*} \]

\[ \begin{align*}
\delta & \text{6.93-6.86 (m, 2H, Ar-H)} \\
& \text{6.86-6.77 (m, 10H, Ar-H), 6.6 (br s, 4H, Ar-H), 6.51-6.49 (m, 4H, Ar-H), 1.60 (br s, 6H, Me)}
\end{align*} \]

\[ \begin{align*}
\delta & \text{-3.8 (s)}
\end{align*} \]

\[ \begin{align*}
\delta & \text{144.3 (s, (Te)PhC=C(B)(CH}_3\text{)), 138.5 (s, (Te)(B)C=C(Ph)(Te)), 137.1 (s, i-PhTe), 135.3 (s, i-Ph), 130.6 (s, o-Ph), 129.8 (s, p-Ph), 129.4 (s, m-Ph), 129.2 (s, PhTe), 128.4 (s, PhTe), 20.6 (br s, Me)}
\end{align*} \]

\[ \begin{align*}
\delta & \text{-126.3 (br m, 1F, o-C}_6\text{F}_5\text{B}), -126.8 (br m, 1F, o-C}_6\text{F}_5\text{B}), -127.8 (br m, 1F, o-C}_6\text{F}_5\text{B}), -134.4 (br m, 1F, o-C}_6\text{F}_5\text{B}), -161.4 (br t, 1F, J_{F-F} = 20.3 Hz, p-C}_6\text{F}_5\text{B}), -161.8 (br t, 1F, J_{F-F} = 18.8 Hz, p-C}_6\text{F}_5\text{B}), -165.6 (br m, 2F, m-C}_6\text{F}_5\text{B}), -166.6 (br m, 2F, m-C}_6\text{F}_5\text{B}^\prime)
\end{align*} \]

\[ 125\text{Te} \text{–no resonance could be observed even at -80 °C – compound 7 is not very soluble in CD}_2\text{Cl}_2\text{ and precipitated out at low temperature.} \]

A solution of MeB(C}_6\text{F}_5\text{)_2} (32.6 mg, 0.09 mmol) dissolved in 2 ml 1:4 solution of DCM: pentane was cooled to -35 °C, and to it was added drop-wise a solution of compound 1 (29.8 mg, 0.09 mmol) also cooled to -35 °C in 3 ml of the same solvent. The solution immediately turned orange. After stirring at this temperature for 10 min. the cold well was removed and this solution was stirred at room temperature for an additional 7 hours. Lots of light yellow powder precipitated out of solution over this time. The clear orange supernatant was decanted, and the light yellow powder was then washed 3 times with a 1:10 solution of DCM: pentane and dried under vacuum to yield compound 7 (40.5 mg, 0.029 mmol, 65% yield).
$^{13}\text{C}^{3}\text{H}] (100.6 \text{ MHz, CD}_2\text{Cl}_2, 298 \text{ K}) \text{ NMR spectrum of 7}$

$^{19}\text{F}^{3}\text{H}] (376.4 \text{ MHz, CD}_2\text{Cl}_2, 298 \text{ K}) \text{ NMR spectrum of 7}$

$^{11}\text{B}^{3}\text{H}] (128.3 \text{ MHz, CD}_2\text{Cl}_2, 298 \text{ K}) \text{ NMR spectrum of 7}$
Thermal conversion of compound 3 to compound 4

(a)

(b)

$^{19}$F-$^1$H (376.4 MHz, tol-d8, 298 K) NMR spectra of (a) compound 3 after isolation (b) compound 3 after heating at 80°C for 8 h, showing quantitative conversion to compound 4
Thermal conversion of compound 5 to 6

\[ \text{\textsuperscript{19}F\{\textsuperscript{1}H\} NMR (376.4 MHz, tol-d8, 298 K) spectra of (a) compound 5 after isolation (b) compound 5 after heating at 80°C for 8 h, showing conversion to compound 6 (highlighted) and a number of side products} \]
UV-Vis absorption spectra of compounds 2, 4, and 6

References