Supplementary Data for:

Phosphine Catalyzed Reduction of CO₂ with Boranes

Tongen Wang and Douglas W. Stephan

Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 3H6

General Remarks All manipulations were carried out under an atmosphere of dry, O₂-free N₂ employing an mBraun glove box and a Schlenk vacuum-line. Solvents were purified with a Grubbs-type column system manufactured by Innovative Technology and dispensed into thick-walled Schlenk glass flasks equipped with Teflon-valve stopcocks (pentane, hexanes, toluene, CH₂Cl₂). Deuterated solvents were dried over the appropriate agents, vacuum-transferred into storage flasks with Teflon stopcocks and degassed accordingly (C₆D₉Br, C₆D₆, CD₂Cl₂, and CDC₃). Toluene and pentane were stored over potassium mirrors, while bromobenzene and dichloromethane were stored over 4Å molecular sieves. ¹H, ¹³C and ³¹P NMR spectra were recorded at 25 °C on Varian 400 MHz, Agilent 500 MHz and Bruker 400 MHz spectrometers. Chemical shifts are given relative to SiMe₄ and referenced to the residue solvent signal (¹H, ¹³C) or relative to an external standard (³¹P: 85% H₃PO₄). In some instances, signal and/or coupling assignment was derived from two-dimensional NMR experiments. Chemical shifts are reported in ppm and coupling constants as scalar values in Hz. Combustion analyses were performed in house employing a Perkin-Elmer CHN Analyzer. GC measurements were performed using a Chirasil-DEX CB column at 130 °C. All other reagents were purchased from Aldrich, liquids were stored over 4Å molecular sieves, gases and solutions were used as received.
Stoichiometric reactions of (HBC₈H₁₄)₂, phosphine under an atmosphere of ¹³CO₂

These reactions were done in a similar fashion and only one is detailed. Tris(t-butyl)phosphine (35 mg, 0.1730 mmol) and (HBC₈H₁₄)₂ (23 mg, 0.0943 mmol) were dissolved in 0.80 mL of bromobenzene-d₅ in a 20 mL vial. The mixture was stirred and transferred into a J-Young tube. The sample was treated by frozen with liquid nitrogen and atmosphere replaced with ¹³CO₂. The sample was then warmed to room temperature affording a CO₂ pressure of 4 atm.[1] The sample was left at room temperature for 6 hours and monitored by NMR spectroscopy.

\[
\begin{align*}
\text{tBu₃P} & \quad + \quad 2.0 \quad \text{H-B} \quad \xrightarrow{\quad ¹³\text{CO₂} \quad} \quad \text{H}^{¹³}\text{COOBC₈H₁₄} & \quad + \quad ¹³\text{CH}_₂(\text{OBC₈H₁₄})₂ \\
& \quad + \quad \text{tBu₃P-}¹³\text{CH}_₂-\text{OB(}\text{OBC₈H₁₄)C₈H₁₄}
\end{align*}
\]

H\(^{¹³}\text{COOBC₈H₁₄}\): ¹H NMR (C₆D₅Br, 400 MHz): 8.74 (d, \(^{1}J_{C-H} = 208.0\) Hz, H-\(^¹³\text{COOBC₈H₁₄}\)); ¹³C \{¹H\} NMR (C₆D₅Br, 100 MHz): 169.08 (s, H-\(^¹³\text{COOBC₈H₁₄}\)); ¹³C NMR with proton coupling (C₆D₅Br, 100 MHz): 169.08 (d, \(^{1}J_{C-H} = 208.0\) Hz, H-\(^¹³\text{COOBC₈H₁₄}\)).

¹³CH₂(ΟΒC₈H₁₄)₂: ¹H NMR (C₆D₅Br, 400 MHz): 5.46 (d, \(^{1}J_{C-H} = 165.0\) Hz, ¹³CH₂(ΟΒC₈H₁₄)₂); ¹³C \{¹H\} NMR (C₆D₅Br, 100 MHz): 85.44 (s, ¹³CH₂(ΟΒC₈H₁₄)₂); ¹³C NMR with proton coupling (C₆D₅Br, 100 MHz): 85.44 (d, \(^{1}J_{C-H} = 165.0\) Hz, ¹³CH₂(ΟΒC₈H₁₄)₂).

tBu₃P-CH₂-OB(ΟΒC₈H₁₄)C₈H₁₄: ¹H NMR (C₆D₅Br, 400 MHz): 4.32 (dd, \(^{1}J_{C-H} = 144.9\) Hz, ²J_{H-P} = 1.2 Hz, tBu₃P-CH₂-OB(ΟΒC₈H₁₄)C₈H₁₄); ³¹P \{¹H\} NMR (C₆D₅Br, 162 MHz): 43.27 (d, \(^{1}J_{C-P} = 55.7\) Hz, tBu₃P-CH₂-OB(ΟΒC₈H₁₄)C₈H₁₄); ¹³C \{¹H\} NMR (C₆D₅Br, 100 MHz): 52.45 (d, \(^{1}J_{C-P} = 55.7\) Hz, tBu₃P-CH₂-OB(ΟΒC₈H₁₄)C₈H₁₄); ¹³C NMR with proton coupling (C₆D₅Br, 100 MHz): 52.45 (td, \(^{1}J_{C-H} = 144.9\) Hz, ¹³C \{¹H\} NMR (C₆D₅Br, 100 MHz): 52.45 (d, \(^{1}J_{C-P} = 55.7\) Hz, tBu₃P-CH₂-OB(ΟΒC₈H₁₄)C₈H₁₄).
The stoichiometric reaction between 9-BBN dimer and PtBu₃ in the atmosphere of 4 atm $^{13}$CO₂ at room temperature for 6 hours in C₆D₅Br

$^1$H NMR spectrum (400M, C₆D₅Br)

$J_{C-H} = 208.0$ Hz

$J_{C-H} = 165.0$ Hz

$J_{C-H} = 144.9$ Hz
The stoichiometric reaction between 9-BBN dimer and PtBu$_3$ in the atmosphere of 4 atm $^{13}$CO$_2$ at room temperature for 6 hours in C$_6$D$_5$Br

$^{31}$P($^1$H) NMR spectrum (162 M, C$_6$D$_5$Br)

Free PtBu$_3$

43.27 ppm ($^1$J$_{CP}$ = 55.7 Hz)
The stoichiometric reaction between 9-BBN dimer and PtBu₃ in the atmosphere of 4 atm $^{13}$CO₂ at room temperature for 6 hours in C₆D₅Br

$^{11}$B{¹H} NMR spectrum (128 M, C₆D₅Br)
The stoichiometric reaction between 9-BBN dimer and PtBu₃ in the atmosphere of 4 atm ¹³CO₂ at room temperature for 6 hours in C₆D₅Br

¹³C{¹H} NMR spectrum (100 M, C₆D₅Br)

¹¹Jₐₓ = 55.7 Hz
The stoichiometric reaction between 9-BBN dimer and PtBu₃ in the atmosphere of 4 atm \(^{13}\)CO\(_2\) at room temperature for 6 hours in C\(_6\)D\(_5\)Br

\(^{13}\)C NMR spectrum (100 M, C\(_6\)D\(_5\)Br)

\(^{13}\)C \(^{1}\)H

\(^{1}\)J\(_{C-H}\) = 208.0 Hz

\(^{1}\)J\(_{C-P}\) = 55.7 Hz

\(^{1}\)J\(_{C-H}\) = 165.0 Hz

\(^{1}\)J\(_{C-H}\) = 144.9 Hz
Stoichiometric reaction between (HBC$_8$H$_{14}$)$_2$, PPh$_3$ in the atmosphere of $^{13}$CO$_2$

This reaction was performed in a similar fashion to that described above, using triphenylphosphine (22 mg, 0.0839 mmol) and (HBC$_8$H$_{14}$)$_2$ (14 mg, 0.0574 mmol).

\[
\begin{align*}
\text{Ph}_3\text{P} & \quad + \quad 2.0 \quad \text{H-B} \quad \xrightarrow{\text{C}_6\text{D}_5\text{Br}, \text{r.t., 12 h}} \quad \text{H}^{13}\text{COOBC}_8\text{H}_{14} & + & \text{H}^{13}\text{C}_2\text{(OBC}_8\text{H}_{14})_2 \\
\end{align*}
\]

\[\text{Ph}_3\text{P}\text{-}^{13}\text{CH}_2\text{-OBC}_8\text{H}_{14}\text{(OBC}_8\text{H}_{14}) \quad \text{H}_2\text{COBC}_8\text{H}_{14} & + & \text{C}_8\text{H}_{14}\text{B-O-BC}_8\text{H}_{14} \]

$^{13}$COOBC$_8$H$_{14}$: $^1$H NMR (C$_6$D$_5$Br, 400 MHz): 8.64 (d, $^1$J$_{13}$C-H = 206.5 Hz, $H^{13}$COOBC$_8$H$_{14}$); $^{13}$C {$^1$H} NMR (C$_6$D$_5$Br, 100 MHz): 169.06 (s, H-$^{13}$COOBC$_8$H$_{14}$); $^{13}$C NMR with proton coupling (C$_6$D$_5$Br, 100 MHz): 169.08 (d, $^1$J$_{13}$C-H = 206.5 Hz, H-$^{13}$COOBC$_8$H$_{14}$).

$^{13}$CH$_2$(OBC$_8$H$_{14}$): $^1$H NMR (C$_6$D$_5$Br, 400 MHz): 5.47 (d, $^1$J$_{13}$C-H = 164.7 Hz, $^{13}$CH$_2$(OBC$_8$H$_{14}$)$_2$); $^{13}$C {$^1$H} NMR (C$_6$D$_5$Br, 100 MHz): 85.47 (s, $^{13}$CH$_2$(OBC$_8$H$_{14}$)$_2$); $^{13}$C NMR with proton coupling (C$_6$D$_5$Br, 100 MHz): 85.47 (d, $^1$J$_{13}$C-H = 164.7 Hz, $^{13}$CH$_2$(OBC$_8$H$_{14}$)$_2$).

Ph$_3$P-CH$_2$-OBC$_8$H$_{14}$(OBC$_8$H$_{14}$): $^1$H NMR (C$_6$D$_5$Br, 400 MHz): 5.06 (d, $^1$J$_{13}$C-H = 146.3 Hz, Ph$_3$P-CH$_2$-OBC$_8$H$_{14}$(OBC$_8$H$_{14}$)); $^{31}$P {$^1$H} NMR (C$_6$D$_5$Br, 162 MHz): 17.74 (d, $^1$J$_{31}$P = 70.8 Hz, Ph$_3$P-CH$_2$-OBC$_8$H$_{14}$(OBC$_8$H$_{14}$)); $^{13}$C {$^1$H} NMR (C$_6$D$_5$Br, 100 MHz): 57.42 (d, $^1$J$_{13}$C-H = 146.3 Hz, $^1$J$_{31}$P = 70.8 Hz, Ph$_3$P-CH$_2$-OBC$_8$H$_{14}$(OBC$_8$H$_{14}$)).

H$_3^{13}$COBC$_8$H$_{14}$: $^1$H NMR (C$_6$D$_5$Br, 400 MHz): 3.57 (d, $^1$J$_{13}$C-H = 142.4 Hz, H$_3^{13}$COBC$_8$H$_{14}$); $^{13}$C {$^1$H} NMR (C$_6$D$_5$Br, 100 MHz): 52.68 (s, H$_3^{13}$COBC$_8$H$_{14}$); $^{13}$C NMR with proton coupling (C$_6$D$_5$Br, 100 MHz): 52.68 (q, $^1$J$_{13}$C-H = 142.4 Hz, H$_3^{13}$COBC$_8$H$_{14}$).
The stoichiometric reaction between 9-BBN dimer and PPh$_3$ in the atmosphere of 4 atm $^{13}$CO$_2$ at room temperature for 12 hours in C$_6$D$_5$Br

$^1$H NMR spectrum (400M, C$_6$D$_5$Br)

- 8.64 ppm ($^1$J$_{C-H}$ = 206.5 Hz)
- 5.06 ppm ($^1$J$_{C-H}$ = 146.3 Hz)
- 5.47 ppm ($^1$J$_{C-H}$ = 164.7 Hz)
The stoichiometric reaction between 9-BBN dimer and PPh$_3$ in the atmosphere of 4 atm $^{13}$CO$_2$ at room temperature for 12 hours in C$_6$D$_5$Br.

$^{31}$P($^1$H) NMR spectrum (162 M, C$_6$D$_5$Br)

Free PPh$_3$

17.74 ppm ($^1$J$_{CP}$ = 70.8 Hz)
The stoichiometric reaction between 9-BBN dimer and PPh$_3$ in the atmosphere of 4 atm $^{13}$CO$_2$ at room temperature for 12 hours in C$_6$D$_5$Br

$^{11}$B(¹H) NMR spectrum (128 M, C$_6$D$_5$Br)
The stoichiometric reaction between 9-BBN dimer and PPh$_3$ in the atmosphere of 4 atm $^{13}$CO$_2$ at room temperature for 12 hours in C$_6$D$_5$Br

$^{13}$C($^1$H) NMR spectrum (100 M, C$_6$D$_5$Br)

57.42 ppm ($^1$J$_{CP}$ = 70.8 Hz)
The stoichiometric reaction between 9-BBN dimer and PPh₃ in the atmosphere of 4 atm $^{13}\text{CO}_2$ at room temperature for 12 hours in C₆D₅Br

$^{13}\text{C}$ NMR spectrum (100 M, C₆D₅Br)
Stoichiometric reaction between (HBC₈H₁₄)₂, P(4-methylphenyl)₃ in the atmosphere of $^{13}$CO₂

In a similar fashion, Tri(4-methylphenyl)phosphine (31 mg, 0.1018 mmol) and (HBC₈H₁₄)₂ (24 mg, 0.0983 mmol) were combined and reacted with CO₂.

\[
\begin{array}{c}
(4-\text{MePh})_3\text{P} + 2.0 \text{H-B} \\
\xrightarrow{\text{C₆D₅Br, r.t., 24 h}} \quad \text{H}^{13}\text{COOBC₈H₁₄} + 13\text{CH₂(OC₈H₁₄)₂} \\
\end{array}
\]

$\text{H}^{13}\text{COOBC₈H₁₄}$: $^1$H NMR (C₆D₅Br, 400 MHz): 8.62 (d, $^1J^{13}_{\text{C-H}} = 208.3$ Hz, $H^{13}\text{COOBC₈H₁₄}$); $^{13}$C {$^1$H} NMR (C₆D₅Br, 100 MHz): 169.80 (s, $H^{13}\text{COOBC₈H₁₄}$); $^1$H NMR (C₆D₅Br, 400 MHz): 5.47 (d, $^1J^{13}_{\text{C-H}} = 164.6$ Hz, $^{13}\text{CH₂(OC₈H₁₄)₂}$); $^{13}$C {$^1$H} NMR (C₆D₅Br, 100 MHz): 85.43 (s, $^{13}\text{CH₂(OC₈H₁₄)₂}$); $^1$H NMR (C₆D₅Br, 400 MHz): 5.09 (d, $^1J^{13}_{\text{C-H}} = 146.5$ Hz, $\text{H}_3^{13}\text{CO-BC₈H₁₄}$); $^1$H NMR (C₆D₅Br, 400 MHz): 3.57 (d, $^1J^{13}_{\text{C-H}} = 142.5$ Hz, $H_3^{13}\text{COBC₈H₁₄}$); $^{13}$C {$^1$H} NMR (C₆D₅Br, 100 MHz): 52.68 (s, $H_3^{13}\text{COBC₈H₁₄}$); $^{13}$C NMR with proton coupling (C₆D₅Br, 100 MHz): 52.68 (q, $^1J^{13}_{\text{C-H}} = 142.5$ Hz, $H_3^{13}\text{COBC₈H₁₄}$).
The stoichiometric reaction between (4-methylphenyl)$_3$P and 9-BBN dimer at atmosphere of 4 atm $^{13}$CO$_2$ at room temperature for 1.5 hours in $C_6D_5Br$
The stoichiometric reaction between \((4\text{-methylpheny})_3P\) and 9-BBN dimer at atmosphere of 4 atm \(^{13}\text{CO}_2\) at room temperature for 1.5 hours in \(C_6D_5Br\)
The stoichiometric reaction between (4-methylphenyl)$_3$P and 9-BBN dimer at atmosphere of 4 atm $^{13}$CO$_2$ at room temperature for 1.5 hours in C$_6$D$_5$Br.
The stoichiometric reaction between (4-methylphenyl)$_3$P and 9-BBN dimer at atmosphere of 4 atm $^{13}$CO$_2$ at room temperature for 1.5 hours in C$_6$D$_5$Br
The stoichiometric reaction between (4-methylphenyl)_3P and 9-BBN dimer at atmosphere of 4 atm $^{13}$CO$_2$ at room temperature for 24 hours in C$_6$D$_5$Br
The stoichiometric reaction between (4-methylphenyl)$_3$P and 9-BBN dimer at atmosphere of 4 atm $^{13}$CO$_2$ at room temperature for 24 hours in C$_6$D$_5$Br
The stoichiometric reaction between (4-methylphenyl)$_3$P and 9-BBN dimer at atmosphere of 4 atm $^{13}$CO$_2$ at room temperature for 24 hours in C$_6$D$_5$Br.

Free 9-BBN

(4-Methylphenyl)$_3$P-$^{13}$CH$_2$-OBC$_8$H$_{14}$OBC$_8$H$_{14}$)
The stoichiometric reaction between (4-methylphenyl)$_3$P and 9-BBN dimer at atmosphere of 4 atm $^{13}$CO$_2$ at room temperature for 24 hours in C$_6$D$_5$Br

$^{13}$C NMR spectrum (100 MHz, C$_6$D$_5$Br)
The stoichiometric reaction between (4-methylphenyl)$_3$P and 9-BBN dimer at atmosphere of 4 atm $^{13}\text{CO}_2$ at room temperature for 24 hours in C$_6$D$_5$Br
The stoichiometric reaction between (4-methylphenyl)$_3$P and 9-BBN dimer at atmosphere of 4 atm $^{13}$CO$_2$ at room temperature for 24 hours in C$_6$D$_5$Br
Isolation of \((R_3PCH_2O)(HC(O)O)B(C_8H_{14})\) \((R = tBu 1, 4-MeC_6H_4 2)\)

After testing NMR spectra of the stoichiometric reaction between \((HBC_8H_{14})_2\), tris(t-butyl)phosphine in the atmosphere of \(^{13}\)CO\(_2\), the sample above was taken into glove-box and transferred into a 20 mL vial. The solution was layered with 8.0 mL of hexanes. The mixture was left at room temperature for overnight to obtain color less crystals (15 mg) for X-ray analysis.

1: \(^1\)H NMR \((C_6D_5Br): 0.91 – 1.30 \text{ (m, 2H, C-H for } HBC_8H_{14}, \text{ overlapping with the resonance of } tBu), 1.09 \text{ (d, } ^3J_{C-P} = 13.2 \text{ Hz, 27 H, } \text{3 x C(CH}_3)_3\text{), } 1.74-1.79 \text{ (m, 2H), } 1.94-1.99 \text{ (m, 4H), 2.07-2.23 \text{ (m, 6 H), 4.36 \text{ (d, } ^1J_{C-H} = 143.8 \text{ Hz, 2 H), 8.91 \text{ (d, } ^1J_{C-H} = 198.6 \text{ Hz, 1 H).}^{13}\)C\{\(^1\)H\} NMR \((C_6D_5Br): 25.33, 28.64, 32.02, 36.98 \text{ (d, } ^2J_{C-P} = 28.1 \text{ Hz), 52.41 \text{ (d, } ^1J_{C-P} = 54.4 \text{ Hz), 165.54.}^{31}\)P\{\(^1\)H\} NMR \((C_6D_5Br): 42.55 \text{ (d, } ^1J_{C-P} = 54.4 \text{ Hz).}^{11}\)B\{\(^1\)H\} NMR \((C_6D_5Br): 8.83 \text{ (s). Anal. Calcd. for } C_{22}H_{44}BO_3P \text{ (398.37): C, 66.33; H, 11.13; N, 0. Found: C, 65.41; H, 11.14; N, 0. (Repeated analyses resulted in consistently low carbon analysis. This is attributed to the formation of boron-carbide during combustion.)

\[ \text{tBu}_3\text{P}^{13}\text{CH}_2\text{O-BO} \quad + \quad H^{13}\text{COOB}_{C_8H_{14}} \quad \rightarrow \quad \text{tBu}_3\text{P}^{13}\text{CH}_2\text{O-BO} \quad + \quad C_{8H_{14}}\text{B-O-BC}_{8H_{14}} \]
$^1$H NMR spectrum (400M, C$_6$D$_5$Br) (species 1)

$^1$J$_{CH}$ = 198.6 Hz

$^1$J$_{CH}$ = 143.8 Hz
$^{31}$P$^{1}$H NMR spectrum (162 M, C$_6$D$_5$Br) (species 1)

42.55 ppm ($^{1}$J$_{PC}$ = 54.4 Hz)
$^{11}$B$^1$H NMR spectrum (128 M, C$_6$D$_5$Br) (species 1)
$^{13}$C($^1$H) NMR spectrum (100 M, C$_6$D$_5$Br) (species 1)

$^{13}$C with $^1$H coupling

52.41 ppm ($^{1}J_{P,C} = 54.4$ Hz)
After testing NMR spectra of the stoichiometric reaction between (HBC₈H₁₄)₂, P(4-methylphenyl)₃ in the atmosphere of ¹³CO₂, the sample was taken into glove-box and transferred into a 20 mL vial. The solution was layered with 8.0 mL of hexanes. The mixture was left at room temperature for two days to obtain colorless crystals (12 mg) for X-ray analysis. (note: this crystal has low solubility in C₆D₅Br, therefore, CD₂Cl₂ was used for NMR spectroscopy). ¹H NMR (CD₂Cl₂): 0.62 – 0.72 (m, 2H, C-H for (BC₈H₁₄)), 1.33 -1.93 (m, 12H, BC₈H₁₄)), 2.33 (s, CH₃ for (4-MePh)₃P), 2.47 (s, 9 H, 3 x CH₃ on (4-MePh)₃P for 2), 4.99 (d, ¹J₃C-H = 145.8 Hz, 2 H, P-CH₂O on 2), 7.15-7.20 (m, phenyl for (4-MePh)₃P), 7.43 (dd, ³J_H-H = 8.0 Hz, ⁴J_H-P = 2.7 Hz, 6 H, phenyl for 2), 7.57 (dd, ³J_H-P = 11.9 Hz, ³J_H-H = 8.0 Hz, 6 H, phenyl for 2), 8.33 (d, ¹J₁₃C-H = 200.6 Hz, 1 H). ³¹P{¹H} NMR (CD₂Cl₂): 16.87 (d, ¹J₁₃C-P = 71.5 Hz), -8.20 (s, free (4-MePh)₃P). ¹¹B{¹H} NMR (CD₂Cl₂): 10.28 (bs). ¹³C{¹H} NMR (CD₂Cl₂): 21.37 (CH₃ for (4-MePh)₃P), 21.97, 21.98(CH₃ for (4-MePh)₃PCH₂-O-B(OC(O)H)C₈H₁₄), 25.58, 32.31, 58.86 (d, ¹J_C-P = 71.5 Hz, P-¹³CH₂-O), 115.53 (dd, ¹J_C-P = 86.6 Hz, ²J₁₃C-C = 1.8 Hz, C-P-¹³CH₂), 131.00 (d, ²J_C-P = 12.7 Hz, phenyl carbon on phosphine), 134.14 (d, ³J_C-P = 9.4 Hz, phenyl carbon on phosphine), 146.46 (d, ⁴J_C-P = 3.0 Hz, phenyl carbon on phosphine), 167.74 (H¹³COO). Anal. Calcd. for C₃₁H₃₈BO₃P (500.41): C, 74.40; H, 7.65; N, 0. Found: C, 73.48; H, 7.61; N, 0. (Repeated analyses resulted in consistently low carbon analysis. This is attributed to the formation of boron-carbide during combustion.)
$^1$H NMR spectrum (400M, CD$_2$Cl$_2$) (species 2)

Free (4-MePh)$_3$P

$^3$J$_{13C-H} = 200.6$ Hz

$^3$J$_{13C-H} = 145.8$ Hz
$^{31}\text{P}^{1\text{H}}$ NMR spectrum (162 M, CD$_2$Cl$_2$) (species 2)

SpinWorks 3: bbo_p31_dec CD$_2$Cl$_2$

16.87 ppm ($^{1}J_{P,C}$ = 71.5 Hz)

Free (4-MePh)$_3$P
$^{11}$B$^1$H NMR spectrum (128 M, CD$_2$Cl$_2$) (species 2)
$^{13}$C\textsuperscript{1H} NMR spectrum (125 M, CD$_2$Cl$_2$) (species 2)
Catalytic Reactions

These reactions were done in a similar fashion and only one is detailed.

**Catalyst: tBu₃P**

Tri(t-butyl)phosphine (1.5 mg, 0.00741 mmol)² and (HBC₈H₁₄)₂ (23 mg, 0.0943 mmol) were dissolved in 0.70 mL of bromobenzene-d₅ in a 20 mL vial. The mixture was stirred and transferred into J-Young tube. The sample was frozen with liquid nitrogen and the atmosphere was replaced with ¹³CO₂. The sample was warmed to room temperature to give a pressure of CO₂ of 4 atm. The sample was left at room temperature and monitored by NMR spectroscopy.

\[
\begin{align*}
\text{H}^{13}\text{COBC}_8\text{H}_{14} + 13\text{CH}_2(\text{OBC}_8\text{H}_{14})_2 \\
\text{tBu}_3\text{P}-^{13}\text{CH}_2\text{OBC}_8\text{H}_{14}(\text{OBC}_8\text{H}_{14}) \\
\text{H}_3\text{COBC}_8\text{H}_{14} + \text{C}_8\text{H}_{14}\text{B-O-BC}_8\text{H}_{14}
\end{align*}
\]
The reaction between 9-BBN dimer and $^{13}\text{CO}_2$ catalyzed by PtBu$_3$ at room temperature for 15.5 hours in C$_6$D$_5$Br

$^1$H NMR spectrum (400M, C$_6$D$_5$Br)
The reaction between 9-BBN dimer and $^{13}\text{CO}_2$ catalyzed by $\text{PtBu}_3$ at room temperature for 15.5 hours in $\text{C}_6\text{D}_5\text{Br}$

$^1\text{H}$ NMR spectrum (400M, $\text{C}_6\text{D}_5\text{Br}$)
The reaction between 9-BBN dimer and $^{13}$CO$_2$ catalyzed by PtBu$_3$ at room temperature for 15.5 hours in C$_6$D$_5$Br

$^{31}$P{${}^1$H} NMR spectrum (162 M, C$_6$D$_5$Br)

tBu$_3$P-$^{13}$CH$_2$-OB (OBC$_3$H$_{14}$)C$_8$H$_{14}$
The reaction between 9-BBN dimer and $^{13}\text{CO}_2$ catalyzed by $\text{PtBu}_3$ at room temperature for 15.5 hours in $\text{C}_6\text{D}_5\text{Br}$

$^{11}\text{B}^{[\text{H}]}$ NMR spectrum (128 M, $\text{C}_6\text{D}_5\text{Br}$)
The reaction between 9-BBN dimer and $^{13}$CO$_2$ catalyzed by PtBu$_3$ at room temperature for 15.5 hours in C$_6$D$_5$Br

$^{13}$C($^1$H) NMR spectrum (100 M, C$_6$D$_5$Br)
The reaction between 9-BBN dimer and $^{13}$CO$_2$ catalyzed by PtBu$_3$ at room temperature for 15.5 hours in C$_6$D$_5$Br

$^{13}$C$[\text{H}]$ NMR spectrum (100 M, C$_6$D$_5$Br)

tBu$_3$P-$^{13}$CH$_2$-OB(OBC$_8$H$_{14}$)C$_3$H$_{14}$
The reaction between 9-BBN dimer and $^{13}\text{CO}_2$ catalyzed by PtBu$_3$ at room temperature for 15.5 hours in C$_6$D$_5$Br

$^{13}$C NMR spectrum (100 M, C$_6$D$_5$Br)
The reaction between 9-BBN dimer and $^{13}$CO$_2$ catalyzed by PtBu$_3$ at room temperature for 15.5 hours in C$_6$D$_5$Br

$^{13}$C NMR spectrum (100 M, C$_6$D$_5$Br)

The reaction involves the formation of a compound with the formula tBu$_3$P-$^{13}$CH$_2$-OBC$_3$H$_{14}$ (OBC$_3$H$_{14}$)

Additional labels:
- H$_3^{13}$COB C$_6$H$_{14}$
- tBu$_3$P-$^{13}$CH$_2$-OBC$_3$H$_{14}$ (OBC$_3$H$_{14}$)
Catalyst: Ph₃P

In a similar fashion triphenylphosphine (2.0 mg, 0.00763 mmol), (HBC₈H₁₄)₂ (23 mg, 0.0943 mmol) were dissolved in 0.80 mL of bromobenzene-d₅ under a $^{13}$CO₂ atmosphere.

\[
\begin{align*}
\text{Ph₃P} & \quad \text{4.0 mol\% Ph₃P} \\
\text{H-B} & \quad \text{r.t., 19 h} \quad \text{C₆D₅Br,} \\
& \quad \text{H}^{13}\text{COOB}C₈H₁₄ + ^{13}\text{CH}_{2}(OBC₈H₁₄)₂ \\
& \quad \text{Ph₃P-}^{13}\text{CH}_{2}-\text{OB(OBC₈H₁₄)}C₈H₁₄ \\
& \quad \text{H₃}^{13}\text{COOB}C₈H₁₄ + C₈H₁₄-\text{B-O-BC₈H₁₄}
\end{align*}
\]
The reaction between 9-BBN dimer and $^{13}\text{CO}_2$ catalyzed by PPh$_3$ at room temperature for 19 hours in C$_6$D$_5$Br

$^1$H NMR spectrum (400M, C$_6$D$_5$Br)
The reaction between 9-BBN dimer and $^{13}$CO$_2$ catalyzed by PPh$_3$ at room temperature for 19 hours in C$_6$D$_5$Br

$^1$H NMR spectrum (400M, C$_6$D$_5$Br)
The reaction between 9-BBN dimer and $^{13}$CO$_2$ catalyzed by PPh$_3$ at room temperature for 19 hours in C$_6$D$_5$Br

$^{31}$P{$^1$H} NMR spectrum (162 M, C$_6$D$_5$Br)

Ph$_3$P-$^{13}$CH$_2$-OB(OBC$_8$H$_{14}$)C$_8$H$_{14}$

Free PPh$_3$
The reaction between 9-BBN dimer and $^{13}$CO$_2$ catalyzed by PPh$_3$ at room temperature for 19 hours in C$_6$D$_5$Br

$^{11}$B$^{1}$H NMR spectrum (128 M, C$_6$D$_5$Br)
The reaction between 9-BBN dimer and $^{13}$CO$_2$ catalyzed by PPh$_3$ at room temperature for 19 hours in C$_6$D$_5$Br.

$^{13}$C($^1$H) NMR spectrum (100 M, C$_6$D$_5$Br)
The reaction between 9-BBN dimer and $^{13}\text{CO}_2$ catalyzed by PPh$_3$ at room temperature for 19 hours in C$_6$D$_5$Br

$^{13}$C NMR spectrum with $^1$H coupling (100 M, C$_6$D$_5$Br)
Catalyst: (4-MeC₆H₄)₃P

Similarly a solution of (HBC₈H₁₄)₂ (23 mg, 0.0943 mmol) in 0.70 mL C₆D₅Br was added 0.1 mL of tri(4-methylphenyl)phosphine stock solution (0.082 M in C₆D₅Br) in a 20 mL vial was pressured with ¹³CO₂. The sample was then warmed up to room temperature and the pressure of CO₂ was 4 atm.¹ The sample was left at room temperature and then monitored by NMR spectroscopy. The reaction was completed in 19 h.

\[
\begin{align*}
\text{H}^{13}\text{COOBC₈H₁₄} & \quad + \quad ¹³\text{CH₂(OBC₈H₁₄)₂} & \quad + \quad (4-\text{MePh})₃\text{P-}¹³\text{CH₂-OBC₈H₁₄(OBC₈H₁₄)} \\
\text{H₃COBC₈H₁₄} & \quad + \quad \text{C₈H₁₄B-O-BC₈H₁₄}
\end{align*}
\]
The reaction between 9-BBN dimer and $^{13}$CO$_2$ catalyzed by P(4-methylphenyl)$_3$ at room temperature for 18.5 hours in C$_6$D$_5$Br

$^1$H NMR spectrum (400M, C$_6$D$_5$Br)
The reaction between 9-BBN dimer and $^{13}$CO$_2$ catalyzed by P(4-methylphenyl)$_3$ at room temperature for 18.5 hours in C$_6$D$_5$Br

$^{31}$P{^1H} NMR spectrum (162 M, C$_6$D$_5$Br)

$\text{Ph}_3\text{P}^{^{13}}\text{CH}_2\text{-OBC}_8\text{H}_{14}$ ($\text{OBC}_8\text{H}_{14}$)

$J_{\text{CP}} = 72.7 \text{ Hz}$
The reaction between 9-BBN dimer and $^{13}$CO$_2$ catalyzed by P(4-methylphenyl)$_3$ at room temperature for 18.5 hours in C$_6$D$_5$Br.

$^{11}$B($^1$H) NMR spectrum (128 M, C$_6$D$_5$Br)
The reaction between 9-BBN dimer and $^{13}$CO$_2$ catalyzed by P(4-methylphenyl)$_3$ at room temperature for 18.5 hours in C$_6$D$_5$Br

$^{13}$C($^1$H) NMR spectrum (100M, C$_6$D$_5$Br)
The reaction between 9-BBN dimer and $^{13}$CO$_2$ catalyzed by P(4-methylphenyl)$_3$ at room temperature for 18.5 hours in C$_6$D$_5$Br

$^{13}$C NMR spectrum (100M, C$_6$D$_5$Br)
The reaction between 9-BBN dimer and $^{13}$CO$_2$ catalyzed by P(4-methylphenyl)$_3$ at room temperature for 18.5 hours in C$_6$D$_5$Br.

$^{13}$C NMR spectrum (100M, C$_6$D$_5$Br)
Catalyst: (3,5 Me₂C₆H₃)₃P

Performed as above using (HBC₈H₁₄)₂ (23 mg, 0.0943 mmol) and 0.10 mL tri(3,5-dimethylphenyl)phosphine stock solution (0.082 M in C₆D₅Br) under ¹³CO₂. The sample was then warmed up to room temperature and the pressure of CO₂ was 4 atm.¹ The sample was left at room temperature and monitored by NMR spectroscopy. The reaction was completed in 14.5 h.

\[
\begin{align*}
\text{H}^{13}\text{COOB} & \text{C}_8\text{H}_{14} & \text{+} & \text{CH}_2\text{(OBC}_8\text{H}_{14})_2 \\
\text{(3,5-dimethylphenyl)}_3\text{P-}^{13}\text{CH}_2\text{-OBC}_8\text{H}_{14} & \text{(OBC}_8\text{H}_{14}) \\
\text{H}_3\text{COB} & \text{C}_8\text{H}_{14} & \text{+} & \text{C}_8\text{H}_{14}\text{B-O-BC}_8\text{H}_{14}
\end{align*}
\]
The catalytic reaction between and 9-BBN dimer and $^{13}\text{CO}_2$ catalyzed by P(3,5-dimethylphenyl)$_3$ at room temperature for 14.5 hours in $\text{C}_6\text{D}_5\text{Br}$

$^1\text{H}$ NMR spectrum (400 M, $\text{C}_6\text{D}_5\text{Br}$)
The catalytic reaction between and 9-BBN dimer and $^{13}$CO$_2$ catalyzed by P(3,5-dimethylphenyl)$_3$ at room temperature for 14.5 hours in C$_6$D$_5$Br

$^{31}$P NMR spectrum (162 M, C$_6$D$_5$Br)

(3,5-dimethylphenyl)$_3$P-$^{13}$CH$_2$OBCC$_8$H$_{14}$(OBC$_8$H$_{14}$)
The catalytic reaction between and 9-BBN dimer and $^{13}\text{CO}_2$ catalyzed by $\text{P}(3,5\text{-dimethylphenyl})_3$ at room temperature for 14.5 hours in $\text{C}_6\text{D}_5\text{Br}$

$^{11}\text{B} \text{NMR spectrum (128 M, C}_6\text{D}_5\text{Br)}$
The catalytic reaction between and 9-BBN dimer and $^{13}$CO$_2$ catalyzed by P(3,5-dimethylphenyl)$_3$ at room temperature for 14.5 hours in C$_6$D$_5$Br

$^{13}$C($^1$H) NMR spectrum (100 M, C$_6$D$_5$Br)
The catalytic reaction between 9-BBN dimer and $^{13}$CO$_2$ catalyzed by P(3,5-dimethylphenyl)$_3$ at room temperature for 14.5 hours in C$_6$D$_5$Br

$^{13}$C[$^1$H] NMR spectrum (100 M, C$_6$D$_5$Br)
The catalytic reaction between and 9-BBN dimer and $^{13}$CO$_2$ catalyzed by P(3,5-dimethylphenyl)$_3$ at room temperature for 14.5 hours in C$_6$D$_5$Br

$^{13}$C{'H} NMR spectrum (100 M, C$_6$D$_5$Br)

$^{13}$CH$_3$OBC$_8$H$_{14}$

(3,5-dimethylphenyl)$_3$P$^{13}$CH$_3$OBC$_8$H$_{14}$(OBC$_8$H$_{14}$)
Larger scale and Lower Catalyst loadings:

The vial with (HBC₈H₁₄)₂ (100 mg, 0.410 mmol) and PR₃ (1.0 mol% PrBu₃; 1.0 mol% PPh₃; 1.0 mol% P(4-MethylPhenyl)₃, based on the amount of H-BC₈H₁₄) was added with 1.1 mL of C₆D₅Br. The mixture was stirred till all (HBC₈H₁₄)₂ was dissolved before it was transferred into J-Young tube which was then tightened with Teflon cap. The sample was treated by frozen and atmosphere replaced with ¹³CO₂. The sample was then warmed to room temperature affording a CO₂ pressure of 5.3 atm.¹ The reactions were monitored by ¹H, ³¹P, ¹¹B and ¹³C NMR spectroscopy. When all (HBC₈H₁₄)₂ was consumed after 35-36 h at room temperature, ¹³CO₂ was released and another 100 mg (HBC₈H₁₄) was added to the sample. The samples were left at room temperature for another one day, finding that MeO-BC₈H₁₄ was the major product (96-98%) and the minor product is CH₂(OC₈H₁₄)₂.

Table S1. The reaction with additional (HBC₈H₁₄) to convert formate and CH₂(OC₈H₁₄)₂ to methoxyl product

<table>
<thead>
<tr>
<th>Catalysts/Time</th>
<th>Formate</th>
<th>CH₂(OC₈H₁₄)₂</th>
<th>MeO₈H₁₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>tBu₃P/35 h</td>
<td>0</td>
<td>2</td>
<td>98</td>
</tr>
<tr>
<td>Ph₃P/36 h</td>
<td>0</td>
<td>4</td>
<td>96</td>
</tr>
<tr>
<td>(4-MePh)₃P/36 h</td>
<td>0</td>
<td>2</td>
<td>98</td>
</tr>
</tbody>
</table>

0.24 mol% PrBu₃ catalyzed reduction of CO₂ with (HBC₈H₁₄) at room temperature

The vial with (HBC₈H₁₄)₂ (100 mg, 0.410 mmol) and 0.10 mL PrBu₃ stock solution (0.0198 M)⁴ was added with 1.00 mL of C₆D₅Br. The mixture was stirred till all (HBC₈H₁₄)₂ was dissolved before it was transferred into J-Young tube which was then tightened with Teflon cap. The sample was treated by frozen and atmosphere replaced with ¹³CO₂. The sample was then warmed to room temperature affording a CO₂ pressure of 5.3 atm.¹ The reactions were monitored by ¹H, ³¹P, ¹¹B and ¹³C NMR spectroscopy at 1.5 h, 4 h, 8 h, 12 h, 14 h and 16 h. The reaction was completed in 16 h.

0.0180 mol% PrBu₃ catalyzed reduction of CO₂ with (HBC₈H₁₄):

The vial with (HBC₈H₁₄)₂ (100 mg, 0.410 mmol) was added 0.10 mL of stock solution of PrBu₃ (0.00148 M)⁵ in C₆D₅Br and 1.00 mL of C₆D₅Br. The mixture was stirred till all (HBC₈H₁₄)₂ was dissolved before it was transferred into J-Young tube which was then tightened with Teflon cap. The sample was treated by frozen and atmosphere replaced with ¹³CO₂. The sample was then warmed to
room temperature affording a $\text{CO}_2$ pressure of 5.3 atm. The sample was then warmed up to room temperature and heated at 60 °C and monitored by NMR spectroscopy.

![Chemical Reaction Diagram]

1.0 mol% $\text{PPh}_3$ and 2.0 mol% $\text{PPh}_3$ catalyzed reduction of $\text{^{13}CO}_2$ with (HBC$_8$H$_{14}$):

**1.0 mol% PPh$_3$ reaction:** The vial with (HBC$_8$H$_{14}$)$_2$ (100 mg, 0.410 mmol) was added 0.10 mL of stock solution of PPh$_3$ (0.082 M) in C$_6$D$_5$Br and 1.00 mL of C$_6$D$_5$Br. The mixture was stirred till all (HBC$_8$H$_{14}$) was dissolved before it was transferred into J-Young tube which was then tightened with Teflon cap. The sample was treated by frozen and atmosphere replaced with $\text{^{13}CO}_2$. The sample was then warmed to room temperature affording a $\text{CO}_2$ pressure of 5.3 atm. The sample was then warmed up to room temperature and monitored by $^1\text{H}$, $^{31}\text{P}$, $^{11}\text{B}$ and $^{13}\text{C}$ NMR spectroscopy. **2.0 mol% PPh$_3$ catalyzed reaction sample was prepared in the same procedure:** The vial with (HBC$_8$H$_{14}$)$_2$ (100 mg, 0.410 mmol) was added 0.20 mL of stock solution of PPh$_3$ (0.082 M) in C$_6$D$_5$Br and 0.90 mL of C$_6$D$_5$Br.

![Conversion vs Time Graph]

Comparision of induction periods in reactions catalyzed 2.0 mol% and 1.0 mol% PPh$_3$
Footnotes

1. The amount of $^{13}\text{CO}_2$ filled was calculated to be 0.195 mmol. The volume of J-Young tube is 2.0 mL. Therefore, the pressure of $^{13}\text{CO}_2$ at the beginning was calculated as following: $P= \frac{nRT}{V} = 0.19466 \times 0.0821 \times 298/1.2 = 3.97 \text{ atm}$ when 0.8 mL of bromobenzene was used. When 1.1 mL of bromobenzene was used, the pressure of $^{13}\text{CO}_2$ at the beginning was calculated as following: $P=\frac{nRT}{V} = 0.19466 \times 0.0821 \times 298/(2.0-1.1) = 5.29 \text{ atm}$.

2. Tri($t$-butyl)phosphine (15.0 mg, 0.0741 mmol) was dissolved in 1.00 mL of bromobenzene-d5 and 0.10 mL of the mother solution was taken to prepare the sample.

3. Triphenylphosphine (20.0 mg, 0.0763 mmol) was dissolved in 1.00 mL of bromobenzene and 0.10 mL of the mother solution was taken to prepare the sample.

4. The stock solution was prepared in the following steps: a) 40.0 mg of tri(t-butyl)phosphine was dissolved in 1.00 mL of bromobenzene-d5 to obtain 0.198 M solution; b) 0.10 mL of the above 0.198 M solution was taken and diluted into 1.00 mL bromobenzene-d5 solution to obtain 0.0198 M solution.

5. The stock solution was prepared in the following steps: a) 30.0 mg of tri(t-butyl)phosphine was dissolved in 1.00 mL of bromobenzene-d5 to obtain 0.148 M solution; b) 0.10 mL of the above 0.148 M solution was taken and diluted into 1.00 mL bromobenzene-d5 solution to obtain 0.0148 M solution; c) 0.10 mL of the 0.0148 M solution was taken and diluted into 1.00 mL bromobenzene-d5 solution to obtain 0.00148 M solution.