Supporting Information: Palladium Catalyzed Carboxylation of Allylstannanes and Allylboranes Using CO₂

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General Methods
Experiments were performed under a dinitrogen atmosphere in an M-Braun dry box or using standard Schlenk techniques. (Under standard glovebox conditions purging was not performed between uses of petroleum ether, diethyl ether, benzene, toluene and tetrahydrofuran; thus when any of these solvents were used, traces of all these solvents were in the atmosphere and could be found intermixed in the solvent bottles.) Moisture- and air-sensitive liquids were transferred by stainless steel cannula on a Schlenk line or in a dry box. The solvents for air- and moisture-sensitive reactions were dried by passage through a column of activated alumina followed by storage under dinitrogen. All commercial chemicals were used as received except where noted. Tri-n-butyl(2-methylallyl)stannane and tri-n-butyl(allyl)stannane were purchased from Alfa Aesar. Allyltriphenyltin was purchased from Aldrich. Allylboronic acid pinacol ester and diisopropyl allylboronate were obtained from TCI America. Diallyldibutyltin, tetraallyltin were purchased from Strem. Tri-n-butyl(3,3-dimethylallyl)stannane (90%) was obtained from Acros. Deuterated solvents were obtained from Cambridge Isotope Laboratories. C₆D₆ and toluene-d₈ were dried over sodium metal, while CD₂Cl₂ and CDCl₃ were dried using P₂O₅. NMR spectra were recorded on Bruker AMX-400, -500 spectrometers at ambient probe temperatures unless noted. Chemical shifts are reported with respect to residual internal protio solvent for ¹H and ¹³C{¹H} NMR spectra and to external an standard for ¹¹B spectra (BF₃·Et₂O at 0.0 ppm). All assignments are based on two dimensional ¹H, ¹³C-HMQC and HMBC experiments. HRMS were recorded at The Mass Spectrometry (MS) and Proteomics Resource of the W.M. Keck Foundation Biotechnology Resource Laboratory at Yale University.
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Literature procedures were followed to prepare the following compounds: bis(2-methylallyl)Pd,\(^1\) bis(2-methylallyl)Pd(PMe\(_3\)),\(^2\) bis(2-methylallyl)Pd(PEt\(_3\)),\(^2\) bis(2-methylallyl)Pd(PPh\(_3\)),\(^2\) bis(2-methylallyl)Pd(NHC),\(^2\) (2-methylallyl)Pd(OC(O)C\(_6\)H\(_5\))(PMe\(_3\)),\(^2\) (2-methylallyl)Pd(OC(O)C\(_6\)H\(_5\))(PEt\(_3\)),\(^2\) (2-methylallyl)Pd(OC(O)C\(_6\)H\(_5\))(PPh\(_3\)),\(^2\) (2-methylallyl)Pd(OC(O)C\(_6\)H\(_5\))(NHC),\(^2\) tri-n-butyl(2-phenylallyl)stannane,\(^3\) trimethyl(2-methylallyl)stannane,\(^4\) trimethyl(allyl)stannane,\(^4\) 2-methylallylboronic acid pinacol ester ((pincaol)B(2-methylallyl)),\(^5\) allylboronic acid propane ester ((OCH\(_2\)CH\(_2\)CH\(_2\)O)B(allyl)),\(^5\) allylboronic acid catechol ester ((catechol)B(allyl)),\(^5\) allylboronic acid ethane ester ((OCH\(_2\)CH\(_2\)O)B(allyl)),\(^5\) and allylboronic acid 1,2-dimethylethane ester ((OCH(Me)CH(Me)O)B(allyl)).\(^5\)

The following general procedure was used for stoichiometric reactions between complexes 5-8 and tri-n-butyl(2-methylallyl)stannane

Compounds 5-8 (0.04mmol) were added to a solution of tri-n-butyl(2-methylallyl)stannane (14.7mg, 0.04mmol) in 0.5 mL C\(_6\)D\(_6\) in a J. Young NMR tube. The reaction progress was monitored by \(^1\)H NMR spectroscopy. The yield was based on integration of the olefinic peaks.

The following general procedure was used for in situ catalytic reactions with tri-n-butyl(2-methylallyl)stannane:

The appropriate ligand (PMe\(_3\), PEt\(_3\), PPh\(_3\) or NHC) (0.059mmol) was added to a solution of bis(2-methylallyl)Pd (1.3mg, 0.059mmol) in 0.25 mL C\(_6\)D\(_6\) in a J. Young NMR tube at -78°C. The mixture was degassed under vacuum and then warmed to -40°C. Excess 1 atm CO\(_2\) was then added via a dual manifold Schlenk line at -40°C. The mixture was warmed to room temperature. The reaction progress was monitored by \(^1\)H NMR spectroscopy. The yield was based on integration of the olefinic peaks.

The following general procedure was used for the catalytic reactions described in Tables 1, 2 and 3 with isolated catalysts:

Catalyst 8 (3.8mg, 0.0059mmol) was added to a solution of the substrate (0.118mmol) in 0.25mL C\(_6\)D\(_6\) in a J. Young NMR tube. The mixture was degassed using three freeze-pump-thaw cycles. Excess 1 atm CO\(_2\) was then added via a dual manifold Schlenk line at room temperature. The
reaction progress was monitored by $^1$H NMR spectroscopy. The products could be separated either by column chromatography or vacuum transfer. In some cases the products were unstable and were treated with HCl in dioxane to generate the free carboxylic acid which was isolated using standard acid/base separation.

**Product Characterization**

($\eta^1$-CO$_2$C$_3$H$_5$)Sn(n-Bu)$_3$ (Table 2, Entry 4) was characterized by comparison of the $^1$H NMR data with those previously reported in the literature.$^6$

The characterizing data for all new compounds prepared in this work are given below. All compounds were characterized by $^1$H and $^{13}$C NMR spectroscopy, and in some cases by IR spectroscopy and HRMS. Hydrolysis of all compounds with HCl in dioxane gave the free corresponding carboxylic acid. If a tin or boron carboxylate was unstable or did not give a clear signal by HRMS, the corresponding known free carboxylic acids were isolated and the details are included in the product characterization.

($\eta^1$-CO$_2$C$_4$H$_7$)SnMe$_3$ (Table 2, Entry 1)

IR (cm$^{-1}$) 1566 ($\nu_{asymCO_2}$), 1403 ($\nu_{symCO_2}$). $^1$H NMR (400 MHz, C$_6$D$_6$): 4.91 (s, 1H, =CH$_2$), 4.86 (s, 1H, =CH$_2$), 3.09 (s, 2H, -CH$_2$ from Allyl), 1.86 (s, 3H, -CH$_3$ from Allyl), 0.47 (s with satellite, 9H, $J_{Sn-H} = 64$ Hz, -CH$_3$). $^{13}$C ($^1$H) NMR (125.8 MHz, C$_6$D$_6$): 178.3 (s, CO$_2$), 140.7 (s, -C(Me)=CH$_2$), 114.0 (s, -CH$_2$), 44.9 (s, -CH$_2$ from Allyl), 23.3 (s, -CH$_3$ from Allyl), -1.61 (s with satellite, $J_{C-Sn} = 425$Hz, -CH$_3$). HRMS (El) (m/z): calcd for (C$_8$H$_{16}$O$_2$Sn - Me) 248.9932; found 248.9935.

($\eta^1$-CO$_2$C$_4$H$_7$)Sn(n-Bu)$_3$ (Table 2, Entry 2)

IR (cm$^{-1}$) 1571 ($\nu_{asymCO_2}$), 1396 ($\nu_{symCO_2}$). $^1$H NMR (500 MHz, CD$_2$Cl$_2$): 4.83 (s, 1H, =CH$_2$), 4.78 (s, 1H, =CH$_2$), 3.00 (s, 2H, -CH$_2$ from Allyl), 1.79 (s, 3H, -CH$_3$ from Allyl), 1.60 (m, 6H, -CH$_2$).
from Bu), 1.32 (m, 6H, -CH₂ from Bu), 1.23 (m, 6H, -CH₂ from Bu), 0.90 (t, 9H, Jₖ₋ₖ = 10Hz , -CH₃ from Bu). ¹³C{¹H} NMR (125.8 MHz, CD₂Cl₂): 177.0 (s, CO₂), 141.2 (s, -C(Me)=CH₂), 113.6 (s, =CH₂), 44.7 (s, -CH₂ from Allyl), 34.7(s) & 28.4 (s with satellite, Jₖ₋ₖ = 20Hz) & 27.6 (s with satellite, Jₖ₋ₖ = 64Hz) & 22.8 (s) & 16.9 (s with satellite, Jₖ₋ₖ = 345Hz) & 14.9 (s) (-CH₂ from Bu), 14.0(s, -CH₃ from Bu). HRMS (EI) (m/z): calcd for (C₁₇H₃₄O₂Sn+Na) 413.1476; found 413.1477.

(η¹-CO₂C₃H₅)SnMe₃ (Table 2, Entry 3)

IR(cm⁻¹) 1561 (νₐsCO₂), 1399 (νₕsCO₂). ¹H NMR (500 MHz, C₆D₆): 6.11 (m, 1H, =CHCH₂), 5.00 (m, 2H, =CH₂), 3.06 (d, 2H, Jₖ₋ₖ = 5 Hz, -CH₂), 0.36 (s with satellite, 9H, Jₖ₋ₖ = 60 Hz , -CH₃). ¹³C{¹H} NMR (125.8 MHz, C₆D₆): 178.0 (s, CO₂), 124.7 (s, -CH=CH₂), 117.1 (s, =CH₂), 40.9 (s, CH₂), -1.90 (s with satellite, Jₖ₋ₖ = 477Hz, -CH₃). HRMS (EI) (m/z): calcd for (C₇H₁₄O₂Sn - Me) 234.9776; found 234.9778.

(η¹-CO₂C₅H₉)Sn(n-Bu)₃ (Table 2, Entry 6)

IR(cm⁻¹) 1575 (νₐsCO₂), 1392 (νₕsCO₂). ¹H NMR (500 MHz, C₆D₆): 4.98 (s, 1H, =CH₂), 4.90 (s, 1H, =CH₂), 3.13 (s, 2H, -CH₂ from Allyl), 1.86(q, Jₖ₋ₖ = 20Hz, 2H, CH₂ from Et), 1.60 (m, 6H, -CH₂ from Bu), 1.32 (m, 6H, -CH₂ from Bu), 1.23 (m, 6H, -CH₂ from Bu), 1.79 (t, Jₖ₋ₖ = 20Hz, 3H, -CH₃ from Et), 0.93 (m, 9H, -CH₃ from Bu). ¹³C{¹H} NMR (125.8 MHz, C₆D₆): 177.1 (s, CO₂), 141.2 (s, -C(Et)=CH₂), 111.8 (s, =CH₂), 43.4 (s, -CH₂ from Allyl), 30.1(s), 30.0 & 29.6 &
28.2 & 14.3 & 14.2 (-CH₂ from Bu), 10.4(s, -CH₃ from Bu), 9.5(s, -CH₃ from Et). HRMS (EI) 
\(m/z\): calcd for (C₈H₃O₂Sn - Me) 389.1503; found 389.2946.

\[\eta^1\text{-CO}_2\text{PhC}_3\text{H}_4\text{Sn(n-Bu)}_3 \text{(Table 2, Entry 7)}\]

IR\(\text{(cm}^{-1}\text{)}\) 1574 (\(\nu_{\text{asymCO}_2}\)), 1375 (\(\nu_{\text{symCO}_2}\)). \(^1\)H NMR (500 MHz, C₆D₆): 7.48, 7.14, 7.07(Ph), 5.42 
(s, 1H, =CH₂), 5.17 (s, 1H, =CH₂), 3.52 (s, 2H, -CH₂ from Allyl), 1.64 (m, 6H, -CH₂ from Bu), 
1.37 (m, 6H, -CH₂ from Bu), 1.24 (m, 6H, -CH₂ from Bu), 0.93 (m, 9H, , -CH₃ from Bu).

\(^{13}\)C\{\(^1\)H\} NMR (125.8 MHz, C₆D₆): 176.7 (s, CO₂), 141.4 (s, -C(Ph)=CH₂), 114.0 (s, =CH₂), 42.9 
(s, -CH₂ from Allyl), 31.5(s), 30.0 & 29.6 & 28.2 & 14.3 &14.2 (-CH₂ from Bu), 11.0(s, -CH₃ 
from Bu). No HRMS could be obtained for this compound, however, addition of HCl (in 
dioxane) produced 3-phenyl-3-butenonic acid.\(^7\)

\[\eta^1\text{-CO}_2\text{C}_4\text{H}_7\text{B(OCMe}_2\text{CMe}_2\text{O)} \text{(Table 3, Entry 1)}\]

\(^1\)H NMR (500 MHz, C₆D₆): 4.76 (s, 1H, =CH₂), 4.72 (s, 1H, =CH₂), 2.82 (s, 2H, -CH₂), 1.64 (s, 
3H, -CH₃ from Allyl), 1.03 (s, 12H, (CH₃)₂C). \(^{13}\)C\{\(^1\)H\} NMR (125.8 MHz, C₆D₆): 168.6 (s, 
CO₂), 138.8 (s, -C(Me)=CH₂), 115.4 (s, =CH₂), 84.4 (s, -CMe₂), 44.6 (s, -CH₂), 24.9 (s, 
(CH₃)₂C), 22.6 (s, -CH₂ from Allyl). \(^{11}\)B\{\(^1\)H\} NMR (160.4 MHz, C₆D₆): 22.7 (s). Addition of 
HCl (in dioxane) produced 3-methyl-3-butenonic acid.\(^8\)
\((\eta^1\text{CO}_2\text{C}_3\text{H}_5)\text{B(OCMe}_2\text{CMe}_2\text{O})\) (Table 3, Entry 2)

\(^1\text{H NMR (}500\text{ MHz, C}_6\text{D}_6): 5.76\text{ (s, }1\text{H, -CH=CH}_2\text{), }4.89\text{ (dd, }2\text{H, }J_{\text{H-H}} = 8, 16\text{Hz, =CH}_2\text{), }2.73\text{ (m, }2\text{H, -CH}_2\text{), }1.01\text{ (s) & }0.98\text{(s) & }0.97\text{ (s) (}12\text{H, (CH}_3\text{)}_2\text{C}). \ ^{13}\text{C}\{^{1}\text{H}\} \text{NMR (}101\text{ MHz, C}_6\text{D}_6): }177.9\text{ (s, CO}_2\text{), }130.4\text{ (s, -CH=CH}_2\text{), }118.9\text{ (s, =CH}_2\text{), }83.3\text{ (s, CMe}_2\text{), }39.0\text{ (s, -CH}_2\text{), }24.8\text{ (s, (CH}_3\text{)}_2\text{C}). \ ^{11}\text{B}\{^{1}\text{H}\} \text{NMR (}160.4\text{ MHz, C}_6\text{D}_6): 22.8\text{ (s). Addition of HCl (in dioxane) produced 3-butenoic acid.}\text{8}

\((\eta^1\text{CO}_2\text{C}_3\text{H}_5)\text{B(OiPr)}_2\) (Table 3, Entry 3)

This reaction resulted in the formation of a number of products (hence the low yield) and the boron carboxylate was unstable. It was not cleanly isolated but 2D NMR spectroscopy allowed us to assign the spectrum from the product mixture. \(^1\text{H NMR (}500\text{ MHz, C}_6\text{D}_6): 5.88\text{ (m, }1\text{H, -CH=CH}_2\text{), }5.08\text{ (br m, }2\text{H, =CH}_2\text{), }4.52\text{ (m, }2\text{H, CHO}_\text{iPr}, 2.54\text{ (m, }2\text{H, -CH}_2\text{), }1.17\text{ (m,}\_12\text{H, (CH}_3\text{)}_2\text{C).} \ ^{13}\text{C}\{^{1}\text{H}\} \text{NMR (}101\text{ MHz, C}_6\text{D}_6): 172.2\text{ (s, CO}_2\text{), }135.1\text{ (s, -CH=CH}_2\text{), }118.4\text{ (s, =CH}_2\text{), }65.8\text{ (s, CH}_\text{iPr}, 43.0\text{ (s, -CH}_2\text{), }24.8\text{ (s, (CH}_3\text{)}_2\text{CH}). \ ^{11}\text{B}\{^{1}\text{H}\} \text{NMR (}160.4\text{ MHz, C}_6\text{D}_6): 17.9\text{ (s). Addition of HCl (in dioxane) produced 3-butenoic acid, which could be isolated.}\text{8}

\((\eta^1\text{CO}_2\text{C}_3\text{H}_5)\text{B(OCH}_2\text{CH}_2\text{CH}_2\text{O})\) (Table 3, Entry 4)

This reaction was particularly messy and it was not possible to assign all the peaks for the NMR spectrum of the product. The yield was estimated by integration of the olefinic peaks. Addition of HCl (in dioxane) produced 3-butenoic acid, which could be isolated.

References