Supporting Information: Palladium Catalyzed Carboxylation of Allylstannanes and Allylboranes Using CO_2

Jianguo Wu and Nilay Hazari*

The Department of Chemistry, Yale University, P. O. Box 208107, New Haven, Connecticut, 06520, USA; E-mail: nilay.hazari@yale.edu

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. C_6D_6 and toluene-d_8 were dried over sodium metal, while CD_2Cl_2 and $CDCl_3$ were dried using P_2O_5. 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 $^{13}C\{^1H\}$ NMR spectra and to external an standard for ^{11}B spectra ($BF_3{\cdot}Et_2O$ at 0.0 ppm). All assignments are based on two dimensional ^1H,^{13}C-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($OC(O)C_4H_7$)(PMe_3),[2] (2-methylallyl)Pd($OC(O)C_4H_7$)(PEt_3),[2] (2-methylallyl)Pd($OC(O)C_4H_7$)(PPh_3),[2] (2-methylallyl)Pd($OC(O)C_4H_7$)(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 (($OCH_2CH_2CH_2O$)B(allyl)),[5] allylboronic acid catechol ester ((catechol)B(allyl)),[5] allylboronic acid ethane ester ((OCH_2CH_2O)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_6D_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_6D_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_6D_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.

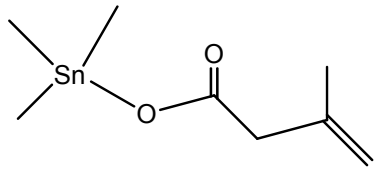
Product Characterization

$(\eta^{1}\text{-}CO_2C_3H_5)Sn(n\text{-}Bu)_3$ (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.

$(\eta^{1}\text{-}CO_2C_4H_7)SnMe_3$ (Table 2, Entry 1)

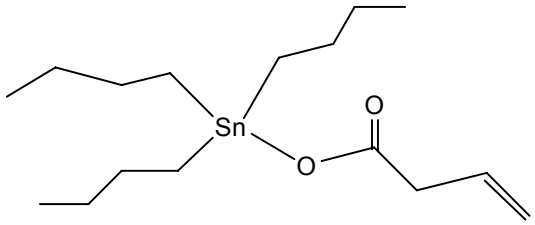
IR(cm^{-1}) 1566 ($\nu_{asymCO2}$), 1403 (ν_{symCO2}). ^{1}H NMR (400 MHz, C_6D_6): 4.91 (s, 1H, $=CH_2$), 4.86 (s, 1H, $=CH_2$), 3.09 (s, 2H, $-CH_2$ from Allyl), 1.86 (s, 3H, $-CH_3$ from Allyl), 0.47 (s with satellite, 9H, $J_{Sn\text{-}H}$ = 64 Hz , $-CH_3$). $^{13}C\{^{1}H\}$ NMR (125.8 MHz, C_6D_6): 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, $J_{C\text{-}Sn}$ = 425Hz, $-CH_3$). HRMS (EI) (*m*/*z*): calcd for ($C_8H_{16}O_2Sn$ - Me) 248.9932; found 248.9935.



$(\eta^{1}\text{-}CO_2C_4H_7)Sn(n\text{-}Bu)_3$ (Table 2, Entry 2)

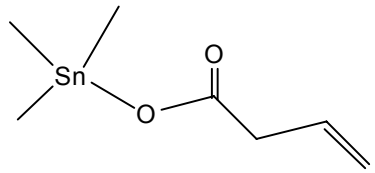
IR(cm^{-1}) 1571 ($\nu_{asymCO2}$), 1396 (ν_{symCO2}). ^{1}H NMR (500 MHz, CD_2Cl_2): 4.83 (s, 1H, $=CH_2$), 4.78 (s, 1H, $=CH_2$), 3.00 (s, 2H, $-CH_2$ from Allyl), 1.79 (s, 3H, $-CH_3$ from Allyl), 1.60 (m, 6H, $-CH_2$

from Bu), 1.32 (m, 6H, -CH_2 from Bu), 1.23 (m, 6H, -CH_2 from Bu), 0.90 (t, 9H, J_{H-H} = 10Hz , -CH_3 from Bu). $^{13}C\{^1H\}$ NMR (125.8 MHz, CD_2Cl_2): 177.0 (s, CO_2), 141.2 (s, -C(Me)=CH_2), 113.6 (s, =CH_2), 44.7 (s, -CH_2 from Allyl), 34.7(s) & 28.4 (s with satellite, J_{C-Sn} = 20Hz) & 27.6 (s with satellite, J_{C-Sn} = 64Hz) & 22.8 (s) & 16.9 (s with satellite, J_{C-Sn} = 345Hz) & 14.9 (s) (-CH_2 from Bu), 14.0(s, -CH_3 from Bu). HRMS (EI) (*m*/*z*): calcd for ($C_{17}H_{34}O_2Sn$+Na) 413.1476; found 413.1477.



(η^1-$CO_2C_3H_5$)$SnMe_3$ (Table 2, Entry 3)

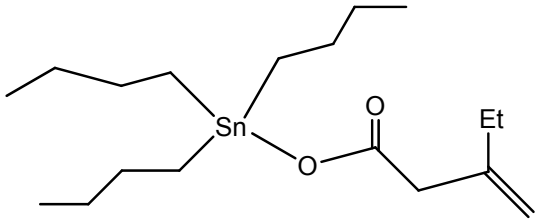
IR(cm^{-1}) 1561 ($\nu_{asymCO2}$), 1399 (ν_{symCO2}). ^1H NMR (500 MHz, C_6D_6): 6.11 (m, 1H, =$CHCH_2$), 5.00 (m, 2H, =CH_2), 3.06 (d, 2H, J_{H-H} = 5 Hz, -CH_2), 0.36 (s with satellite, 9H, J_{Sn-H} = 60 Hz , -CH_3). $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6): 178.0 (s, CO_2), 124.7 (s, -CH=CH_2), 117.1 (s, =CH_2), 40.9 (s, CH_2), -1.90 (s with satellite, J_{C-Sn} = 477Hz, -CH_3). HRMS (EI) (*m*/*z*): calcd for ($C_7H_{14}O_2Sn$ - Me) 234.9776; found 234.9778.



(η^1-$CO_2C_5H_9$)$Sn(n\text{-}Bu)_3$ (Table 2, Entry 6)

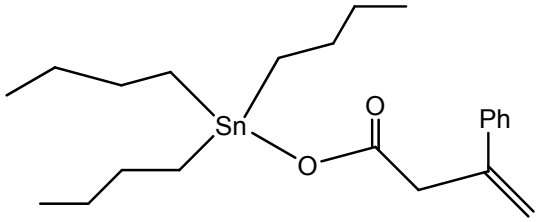
IR(cm^{-1}) 1575 ($\nu_{asymCO2}$), 1392 (ν_{symCO2}). ^1H NMR (500 MHz, C_6D_6): 4.98 (s, 1H, =CH_2), 4.90 (s, 1H, =CH_2), 3.13 (s, 2H, -CH_2 from Allyl), 1.86(q, J_{H-H} = 20Hz, 2H, CH_2 from Et), 1.60 (m, 6H, -CH_2 from Bu), 1.32 (m, 6H, -CH_2 from Bu), 1.23 (m, 6H, -CH_2 from Bu), 1.79 (t, J_{H-H} = 20Hz, 3H, -CH_3 from Et), 0.93 (m, 9H, , -CH_3 from Bu). $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6): 177.1 (s, CO_2), 141.2 (s, -C(Et)=CH_2), 111.8 (s, =CH_2), 43.4 (s, -CH_2 from Allyl), 30.1(s), 30.0 & 29.6 &

28.2 & 14.3 &14.2 (-CH_2 from Bu), 10.4(s, -CH_3 from Bu), 9.5(s, -CH_3 from Et). HRMS (EI) (*m*/*z*): calcd for ($C_8H_{36}O_2Sn$ - Me) 389.1503; found 389.2946.



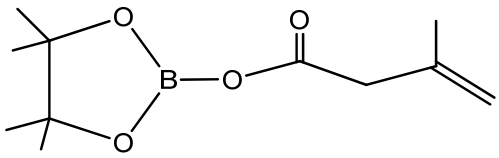
(η^1-$CO_2PhC_3H_4$)Sn(n-Bu)$_3$ (Table 2, Entry 7)

IR(cm^{-1}) 1574 ($\nu_{asymCO2}$), 1375 (ν_{symCO2}).^{1}H NMR (500 MHz, C_6D_6): 7.48, 7.14, 7.07(Ph), 5.42 (s, 1H, =CH_2), 5.17 (s, 1H, =CH_2), 3.52 (s, 2H, -CH_2 from Allyl), 1.64 (m, 6H, -CH_2 from Bu), 1.37 (m, 6H, -CH_2 from Bu), 1.24 (m, 6H, -CH_2 from Bu), 0.93 (m, 9H, , -CH_3 from Bu). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): 176.7 (s, CO_2), 141.4 (s, -C(Ph)=CH_2), 114.0 (s, =CH_2), 42.9 (s, -CH_2 from Allyl), 31.5(s), 30.0 & 29.6 & 28.2 & 14.3 &14.2 (-CH_2 from Bu), 11.0(s, -CH_3 from Bu). No HRMS could be obtained for this compound, however, addition of HCl (in dioxane) produced 3-phenyl-3-butenonic acid.[7]



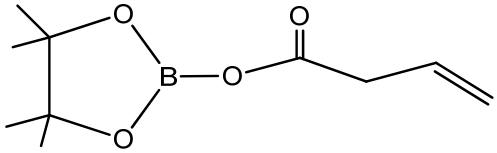
(η^1-$CO_2C_4H_7$)B($OCMe_2CMe_2O$) (Table 3, Entry 1)

^{1}H NMR (500 MHz, C_6D_6): 4.76 (s, 1H, =CH_2), 4.72 (s, 1H, =CH_2), 2.82 (s, 2H, -CH_2), 1.64 (s, 3H, -CH_3 from Allyl), 1.03 (s, 12H, $(CH_3)_2C$). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): 168.6 (s, CO_2), 138.8 (s, -C(Me)=CH_2), 115.4 (s, =CH_2), 84.4 (s, -CMe_2), 44.6 (s, -CH_2), 24.9 (s, $(CH_3)_2C$), 22.6 (s, -CH_3 from Allyl). ^{11}B{^{1}H} NMR (160.4 MHz, C_6D_6): 22.7 (s). Addition of HCl (in dioxane) produced 3-methyl-3-butenonic acid.[8]



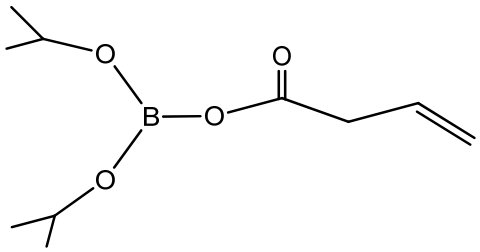
(η^1-$CO_2C_3H_5$)B($OCMe_2CMe_2O$) (Table 3, Entry 2)

^{1}H NMR (500 MHz, C_6D_6): 5.76 (s, 1H, -CH=CH_2), 4.89 (dd, 2H, J_{H-H} = 8, 16Hz, =CH_2), 2.73 (m, 2H, -CH_2), 1.01 (s) & 0.98(s) & 0.97 (s) (12H, $(CH_3)_2$C). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): 177.9 (s, CO_2), 130.4 (s, -CH=CH_2), 118.9 (s, =CH_2), 83.3 (s, CMe_2), 39.0 (s, -CH_2), 24.8 (s, $(CH_3)_2$C). ^{11}B{^{1}H} NMR (160.4 MHz, C_6D_6): 22.8 (s). Addition of HCl (in dioxane) produced 3-butenonic acid.[8]



(η^1-$CO_2C_3H_5$)B(O^iPr)$_2$ (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}H NMR (500 MHz, C_6D_6): 5.88 (m, 1H, -CH=CH_2), 5.08 (br m, 2H, =CH_2), 4.52 (m, 2H, CHO^iPr), 2.54 (m, 2H, -CH_2), 1.17 (m,12H, $(CH_3)_2$C). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): 172.2 (s, CO_2), 135.1 (s, -CH=CH_2), 118.4 (s, =CH_2), 65.8 (s, CH^{i}Pr), 43.0 (s, -CH_2), 24.8 (s, $(CH_3)_2$CH). ^{11}B{^{1}H} NMR (160.4 MHz, C_6D_6): 17.9 (s). Addition of HCl (in dioxane) produced 3-butenonic acid, which could be isolated.[8]



(η^1-$CO_2C_3H_5$)B($OCH_2CH_2CH_2O$) (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-butenonic acid,[7] which could be isolated.

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