Palladium-Catalyzed Carboxylative Coupling of Allylstannanes and Allyl Halides

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Summary: A three-component carboxylative coupling between allyl halides, allylstannanes, and CO_2 to produce allyl esters is catalyzed by Pd and Pt phosphine complexes. Tentative mechanistic pathways for the catalytic reaction are proposed.

The abundance of carbon dioxide, combined with its thermodynamic stability and low reactivity, presents a formidable challenge for chemists seeking to develop new catalytic reactions for its conversion into useful organic chemicals and renewable fuels.[1] Reactions of CO_2 which result in carbon−carbon bond formation are especially synthetically attractive. In considering the development of new catalytic carbon−carbon bond-forming reactions which incorporate CO_2, we took note of the diversity and utility of transition-metal-catalyzed cross-coupling reactions (eq 1)[2] as well as variants which incorporate carbon monoxide to form ketones (eq 2).[2b,c] Could the inclusion of CO_2 in metal-catalyzed cross-coupling reactions provide processes for the formation of esters (eq 3)?

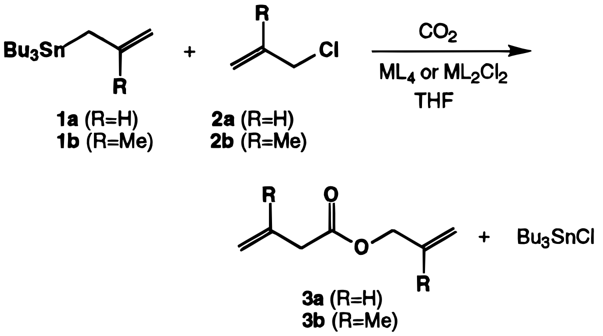
$$\mathrm{R{-}X + R'{-}M \rightarrow R{-}R' + M{-}X} \quad (1)$$

$$\mathrm{R{-}X + CO + R'{-}M \rightarrow R{-}CO{-}R' + M{-}X} \quad (2)$$

$$\mathrm{R{-}X + CO_2 + R'{-}M \rightarrow R'{-}CO_2{-}R + M{-}X} \quad (3)$$

Such *carboxylative coupling* reactions might likely proceed via CO_2 insertion into the M−R′ bond followed by substitution of R−X by the resulting metal carboxylate. Although insertions of CO_2 into metal−carbon bonds of electropositive main-group metals and many transition metals are common,[1] the resulting metal carboxylates ($R{-}CO_2{-}M$) rarely have been converted to organic products other than carboxylic acids.[3] In this report we describe the first examples of catalytic carboxylative coupling utilizing organostannanes and organic halides as reaction partners with carbon dioxide.

The efficiency of carbonylative cross coupling of organostannanes (eq 2),[2b,c] our recent demonstration of Pd-catalyzed *carboxylation* of allylstannanes,[4] and the high substitutional reactivity of allyl halides (both uncatalyzed[5] and Pd-catalyzed[6]) led us first to test the viability of homocarboxylation of allyl halides and allylstannanes. Heating a 1:1 THF solution of allyltributyltin (**1a**) and allyl chloride (**2a**) under 30−50 atm of CO_2 with 10 mol % $Pd(PPh_3)_4$ produced the allyl butenoate **3a** in 50% isolated yield (eq 4).[7] It is noteworthy that under these conditions direct allyl−allyl (Stille-type) coupling[2b,c] is completely suppressed; substantial carboxylation is even observed under 3 atm of CO_2. A catalyst survey under similar conditions (Table 1) revealed that both Pd(0) and Pd(II) complexes provide efficient carboxylation catalysts with PPh_3 or PBu_3 as ligands, but no ester was produced using the chelating diphosphine 1,2-bis(diphenylphosphino)ethane (dppe). Both Pt(0) and Pt(II) precursors are also effective for catalysis, but the Ni complexes tested were inactive.



(4)

The carboxylative coupling reaction apparently is quite sensitive to the steric/electronic character of the substrates, since the corresponding reaction of the

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[1] Reviews: (a) Gibson, D. H. *Chem. Rev.* **1996**, *96*, 2063. (b) Kolomnikov, I. S.; Lysyak, T. V. *Russ. Chem. Rev. (Engl. Transl.)* **1990**, *59*, 344. (c) Behr, A. *Carbon Dioxide Activation by Metal Complexes*; VCH: Weinheim, Germany, 1988.

[2] Reviews: (a) Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*, 2nd ed.; University Science Books: Sausalito, CA, 1999; pp 78−92. (b) Farina, V.; Krishnamurthy, V.; Scott, W. J. *Org. React.* **1997**, *50*, 1. (c) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.

[3] Metal-catalyzed linear and cyclic couplings of CO_2 with 1,3-dienes and alkynes, which likely proceed via metal−carboxylate intermediates, often produce esters or lactones; for reviews and lead references, see ref 1c, pp 94−96 and 106−129.

[4] Shi, M.; Nicholas, K. M. *J. Am. Chem. Soc.* **1997**, *119*, 5057.

[5] March, J. In *Advanced Organic Chemistry*, 4th ed.; Wiley: New York, 1992; pp 341−342.

[6] Reviews: Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385. Tsuji, J. *Pure Appl. Chem.* **1982**, *54*, 197. Amatore, C.; Jutand, A.; Meyer, G.; Mother, L. *Chem. Eur. J.* **1999**, *5*, 466.

[7] The following procedure is representative. A stainless steel autoclave fitted with a glass liner containing a stir bar was charged with catalyst (0.1 mmol, 10 mol %), allyltributyltin (300 μL, 0.969 mmol), allyl chloride (100 μL, 1.23 mmol), and distilled THF (20 mL). The autoclave was purged with CO_2 three times and then pressurized to 750 psig. The system was then heated at 70 °C for 48 h. After cooling, the autoclave was vented, the solvent was removed by rotary evaporation, and the ester products were isolated by Kugelrohr distillation. In some runs naphthalene was added as an internal standard; samples were withdrawn periodically via a dip tube and analyzed by GC. Spectroscopic data for ester **3a** are included in the Supporting Information.

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Scheme 1

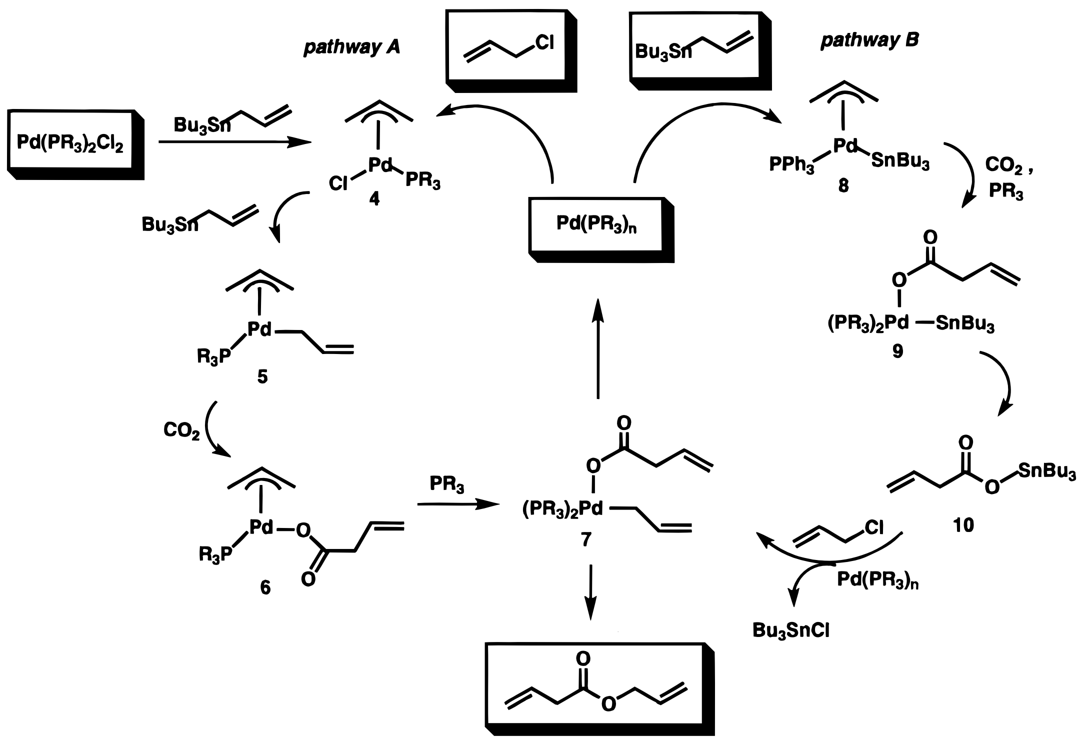

Table 1. Carboxylative Coupling of Allyltributylstannane (1a) and Allyl Chloride (2a)[a]

precatalyst	added ligand	ester yield[b]	TON[c]
none	none	0	0
Pd(PPh$_3$)$_4$	none	46	4.0
PdCl$_2$(PPh$_3$)$_2$	none	55	3.5
PdCl$_2$(PPh$_3$)$_2$	PPh$_3$ (2 equiv)	96	8.1
PdCl$_2$(PhCN)$_2$	PBu$_3$ (2 equiv)	97	10.3
PdCl$_2$(PhCN)$_2$	dppe	0	0
Pt(PPh$_3$)$_4$	none	87	6.6
PtCl$_2$(PPh$_3$)$_2$	none	71	6.7
PtCl$_2$(PPh$_3$)$_2$	PPh$_3$ (2 equiv)	39	3.9
Ni(1,5-COD)$_2$	PPh$_3$ (4 equiv)	0	0
NiCl$_2$(PPh$_3$)$_2$	none	0	0

[a] All reactions employed 1.0 mmol of **1**, 1.0 mmol of **2**, 50 atm of CO$_2$, and ca. 0.10 mmol of catalyst in 25 mL of THF at 70 °C for 48 h. [b] Determined as the percentage by GC with naphthalene as internal standard. [c] TON (turnover number) = mmol of product/(mmol of precatalyst).

2-methallyl derivatives **1b** and **2b** proceeded more slowly and less selectively under the standard conditions, affording only a 25% yield of **3b** (87% conversion). Furthermore, preliminary investigation of the substrate scope indicates that with the present catalytic system both partners must be allylic to achieve significant conversion. Thus, under the above conditions no carboxylation products were detected with RSnBu$_3$, in which R = PhCH$_2$, Ph, vinyl, PhC≡C−, or with R′Cl, in which R′ = PhCH$_2$, Ph.[8]

The above observations, especially the specificity of the reaction for allylic substrates, the demonstrated Pd-catalyzed carboxylation of allylstannanes,[4] literature precedents (vide infra), and preliminary experiments, suggest the likely operation of either (or both) of two catalytic pathways (**A** and **B**; Scheme 1), differing essentially according to which intermediate is carboxylated. In pathway **A** the bis(allyl) Pd complex **5**,[9] derived from oxidative addition of allyl halide to Pd(PPh$_3$)$_4$[10] followed by transmetalation of the η^3-allyl complex **4** with allylstannane,[11] reacts with CO$_2$ to afford the Pd carboxylate **6**,[12] which undergoes reductive elimination of the ester[13] (regenerating Pd(0)). The accessibility of bis(allyl) complex **5** on starting from PdL$_2$Cl$_2$ and allylstannanes[11] could account for the carboxylation activity of both Pd(0) and Pd(II) complexes. Alternatively, in pathway **B** PdL$_n$ first catalyzes the carboxylation of the allylstannane[4,14] and then the resulting tin carboxylate **10** undergoes Pd-catalyzed substitution with allyl halide to give the ester. The viability of this pathway was separately demonstrated. Although no reaction was observed between the tin carboxylate **10** and allyl chloride (**2a**) alone (65 ° C, THF, 18 h),

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[8] Pd-catalyzed aryltin−vinyl halide coupling (without carboxylation) has recently been achieved using supercritical carbon dioxide as solvent: Morita, D. K.; Pesiri, D. R.; David, S. A.; Glaze, W. H.; Tumas, W. *J. Chem. Soc., Chem. Commun.* **1998**, 1397.

[9] (a) Henc, B.; Jolly, P. W.; Salz, R.; Wilke, G.; Benn, R.; Hoffman, E. G.; Mynott, R.; Schroth, G.; Seevogel, K.; Sekutowski, J. C.; Kruger, C. *J. Organomet. Chem.* **1980**, *191*, 425. (b) Henc, B.; Jolly, P. W.; Salz, R.; Stobbe, S.; Wilke, G.; Benn, R.; Mynott, R.; Seevogel, K.; Goddard, R.; Kruger, C. *J. Organomet. Chem.* **1980**. *191*, 449.

[10] (a) Fitton, P.; Johnson, M. P.; McKeon, J. E. *J. Chem. Soc., Chem. Commun.* **1968**, 6. (b) Powell, J.; Shaw, B. L. *J. Chem. Soc. A* **1968**, 774. (c) Cotton, F. A.; Faller, J. W.; Musco, A. *Inorg. Chem.* **1967**, *6*, 179.

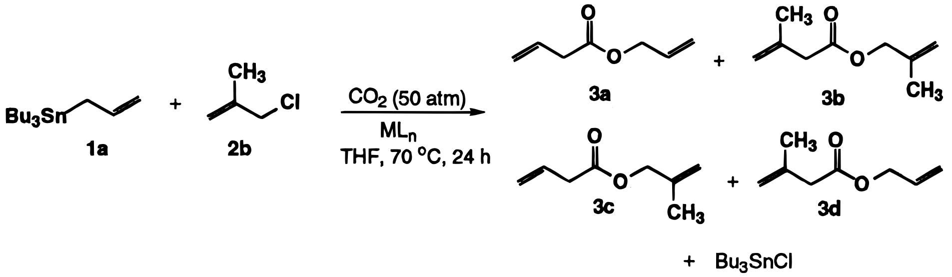
[11] Nakamura, H.; Iwama, H.; Yamamoto, Y. *J. Am. Chem. Soc.* **1996**, *118*, 6641.

[12] (a) Hung, T.; Jolly, P. W.; Wilke, G. *J. Organomet. Chem.* **1980**, *190*, C5. (b) Hung, T. Dissertation, Ruhr-Universitat, Bochum, Germany, 1980. (c) Santi, R.; Marchi, M. *J. Organomet. Chem.* **1979**, *182*, 117. (d) Ito, T.; Kindaichi, Y.; Takami, Y. *Chem. Ind. (London)* **1980**, *19*, 83.

[13] A similar scheme has been proposed for the recently reported Pd-catalyzed three-component coupling of allylstannanes, allyl halides, and electrophilic alkenes: Nakamura, H.; Shim, J.-G.; Yamamoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 8113.

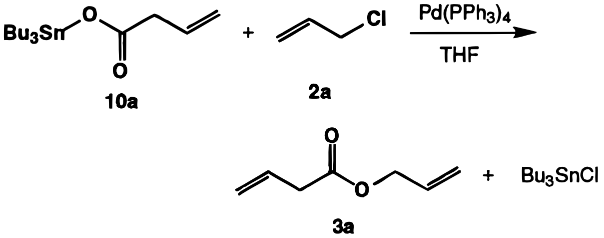
[14] Allyltin compounds have been reported to react with Pt(0) phosphine complexes to produce (η^3- allyl)M(PR$_3$)SnR$_3$: Christofides, A.; Ciriano, M.; Spencer, J. L.; Stone, F. G. A. *J. Organomet. Chem.* **1979**, *178*, 273.

Scheme 2



catalyst	%3a	%3b	%3c	%3d
$Pd(PPh_3)_4$	20	30	21	29
$Pd(PPh_3)_2Cl_2$	24	25	29	20

quantitative conversion to the allyl ester **3a** occurred in the presence of $Pd(PPh_3)_4$ (17 mol %, eq 5). Presently,



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we cannot determine which of these two catalytic pathways (**A** or **B**) is operative. ^1H NMR monitoring and preparative experiments on 1:1:1 mixtures of **1a**, **2a**, and $Pd(PPh_3)_4$ under 3−5 atm of CO_2 (65 °C) over several hours revealed that, initially, allyl complex **4** is produced as the major Pd species; subsequently **4** gradually disappears and a new species, apparently the tin butenoate derivative $CH_2{=}CHCH_2CO_2SnBu_3$ (**10a**), is formed along with $(Ph_3P)_2PdCl_2$.[15] Efforts to determine the catalytic relevance of these observations are continuing.

To assess the reaction selectivity and to probe the mechanism further, a mixed carboxylation reaction between allylstannane **1a** and methallyl chloride (**2b**) was investigated, with surprising results. Under catalysis by either $Pd(PPh_3)_4$ or $Pd(PPh_3)_2Cl_2$ a nearly statistical mixture of *four* esters was produced (Scheme 2), which included the expected mixed ester **3c** as well as the isomeric **3d** and the two homocoupled esters **3a**,**b**.[16] Since carboxylation of **1a** alone affords only the corresponding tin carboxylate[4] **10** and **2b** alone is not carboxylated at all under the standard conditions, the homoesters **3a**,**b** are not the result of self-carboxylative coupling of the stannane and the organic halide, respectively. Hence, the esters **3a**,**b**,**d** are apparently derived from a crossover process in which the ancestry of the allyl fragment (i.e., from **1a** or **2b**) is erased. Comparable statistical allyl scrambling was also observed when mixtures of the esters **3a**,**b** or **3c**,**d** were heated together under the catalytic conditions (50 atm of CO_2, 4 mol % $Pd(PPh_3)_4$, THF, 70 °C), indicating that the carboxylative coupling is reversible. Moreover, the observation that ester **3a** is consumed when heated with $Pd(PPh_3)_4$ (1:1, 4 atm CO_2) suggests that the reductive elimination equilibrium to form ester and $Pd(PPh_3)_n$ is unfavorable (Scheme 1). Although the mechanism of allyl scrambling is presently uncertain, we suspect that a dipalladium species, with either bridging allyl[17] or carboxylate[18] ligands, may be involved.

Efforts are underway to elucidate further the mechanistic details of this new catalytic reaction of carbon dioxide and to extend its scope.

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Supporting Information Available: Text giving preparative details and characterizational data for authentic esters and stoichiometric NMR tube and preparative carboxylation reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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[15] ^1H NMR monitoring of a 1:1:1 mixture of **1a**, **2a**, and $Pd(PPh_3)_4$ under 3 atm of CO_2 in d_8-THF at 65 °C over several hours revealed the initial consumption of allyl chloride with formation of η^3-allyl complex **4**. Gradually **4** was superseded by a new species tentatively identified as the tin butenoate **10a**, on the basis of comparison of its ^1H and ^{13}C NMR spectra with those of an authentic sample.[4] Parallel ^{31}P NMR monitoring also detected **4** and, subsequently, $(Ph_3P)_2PdCl_2$ and $OPPh_3$ as the major P-containing products. In a similar preparative scale experiment (at 8 atm) $(Ph_3P)_2PdCl_2$, $OPPh_3$, and **10a** were detected and isolated by selective extraction and precipitation; their identities were confirmed by comparison of their ^1H, ^{13}C, ^{31}P, and ^{119}Sn NMR spectra with those of authentic samples.

[16] The identities of esters **3a**−**d** were established by GC/MS and NMR analysis of the mixture and by comparison with authentic samples of each ester, which were prepared by DCC−DMAP-promoted reactions of the respective carboxylic acids and alcohols. Spectral data for **3a**−**d** are available in the Supporting Information.

[17] Werner, H.; Kuhn, A. *J. Organomet. Chem.* **1979**, *179*, 439.

[18] van Leeuwen, P. W. N. M.; Praat, A. P. *J. Organomet. Chem.* **1970**, *21*, 501.