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Palladium-Catalyzed Carboxylative Coupling of Allylstannanes and Allyl Halides

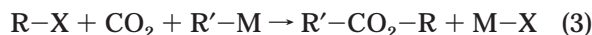
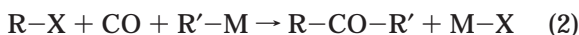
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Summary: A three-component carboxylative coupling between allyl halides, allylstannanes, and CO₂ to produce allyl esters is catalyzed by Pd and Pt phosphine complexes. Tentative mechanistic pathways for the catalytic reaction are proposed.

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 CO₂ 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 CO₂, 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 CO₂ in metal-catalyzed cross-coupling reactions provide processes for the formation of esters (eq 3)?



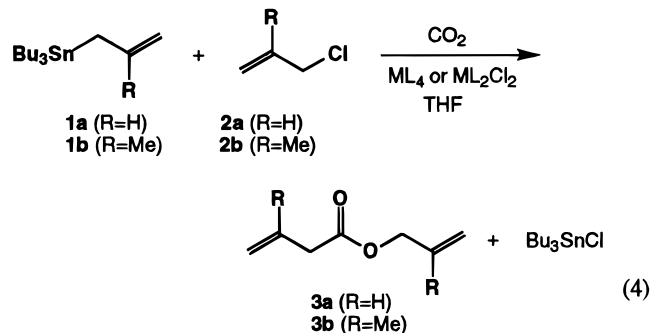
Such *carboxylative coupling* reactions might likely proceed via CO₂ insertion into the M–R' bond followed by substitution of R–X by the resulting metal carboxylate. Although insertions of CO₂ into metal–carbon bonds of electropositive main-group metals and many transition metals are common,¹ the resulting metal carboxylates (R–CO₂–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.

(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 CO₂ 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.

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 uncatalyzed⁵ and Pd-catalyzed⁶) led us first to test the viability of homocarbonylation of allyl halides and allylstannanes. Heating a 1:1 THF solution of allyltributyltin (**1a**) and allyl chloride (**2a**) under 30–50 atm of CO₂ with 10 mol % Pd(PPh₃)₄ produced the allyl butenoate **3a** in 50% isolated yield (eq 4).⁷ It is note-



worthy that under these conditions direct allyl–allyl (Stille-type) coupling^{2b,c} is completely suppressed; substantial carboxylation is even observed under 3 atm of CO₂. A catalyst survey under similar conditions (Table 1) revealed that both Pd(0) and Pd(II) complexes provide efficient carboxylation catalysts with PPh₃ or PBu₃ 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.

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

(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 CO₂ 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.

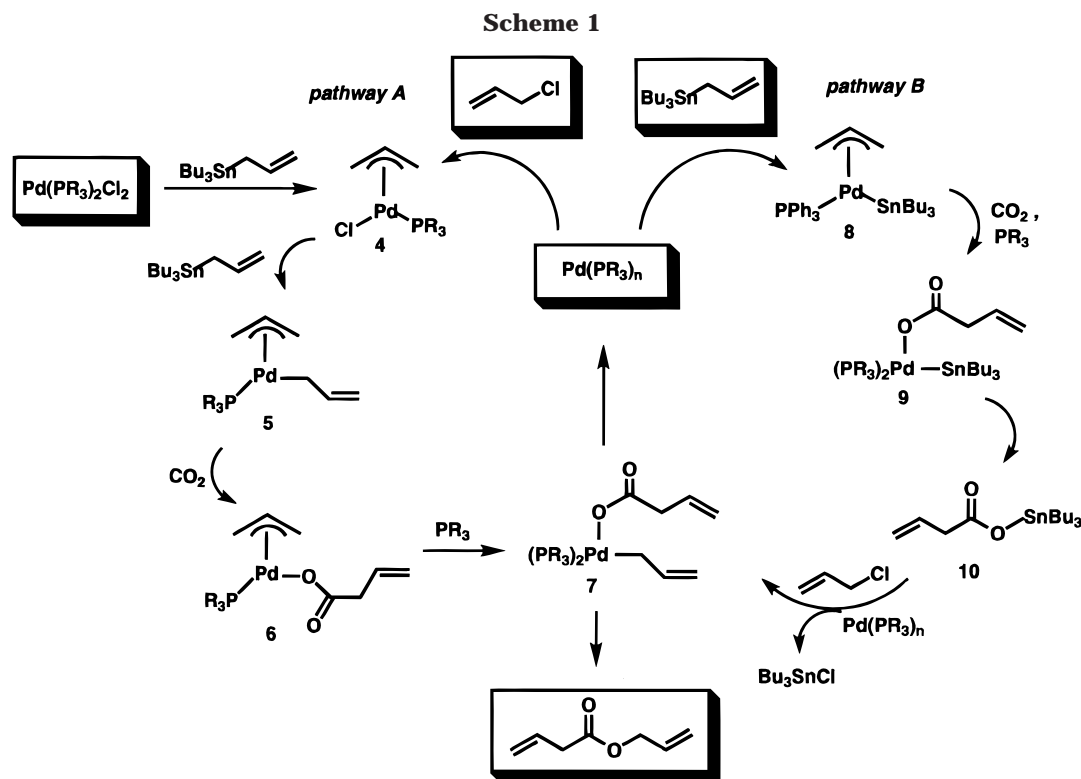


Table 1. Carboxylative Coupling of Allyltributylstannane (1a) and Allyl Chloride (2a)^a

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	dppf	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 CO₂, 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-methylallyl 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 RSnBu₃, in which R = PhCH₂, Ph, vinyl, PhC≡C-, or with R'Cl, in which R' = PhCH₂, 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(PPh₃)₄¹⁰ followed by transmetalation of the η³-allyl complex **4** with allylstannane,¹¹ reacts with CO₂ to afford the Pd carboxylate **6**,¹² which undergoes reductive elimination of the ester¹³ (regenerating Pd(0)). The accessibility of bis(allyl) complex **5** on starting from PdL₂Cl₂ and allylstannanes¹¹ 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),

(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.

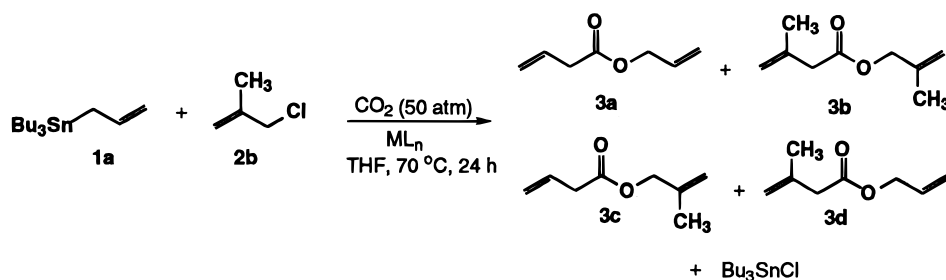
(12) (a) Hung, T.; Jolly, P. W.; Wilke, G. *J. Organomet. Chem.* **1980**, *190*, C5. (b) Hung, T. Dissertation, Ruhr-Universität, Bochum, Germany, 1980. (c) Santi, R.; Marchi, M. *J. Organomet. Chem.* **1979**, *182*, 117. (d) Ito, T.; Kindaichi, Y.; Takami, Y. *Chem. Ind. (London)* **1980**, *19*, 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 (η³-allyl)M(PR₃)₂SnR₂: Christofides, A.; Ciriano, M.; Spencer, J. L.; Stone, F. G. A. *J. Organomet. Chem.* **1979**, *178*, 273.

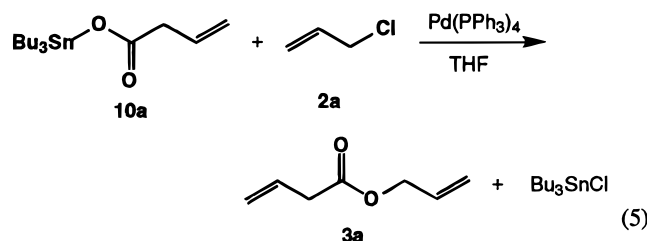
(8) Pd-catalyzed aryltin-vinyl halide coupling (without carboxylation) has recently been achieved using supercritical carbon dioxide as solvent: Morita, D. K.; Pesiri, D. R.; David, S. A.; Glaze, W. H.; Tumas, W. *J. Chem. Soc., Chem. Commun.* **1998**, 1397.

Scheme 2



catalyst	%3a	%3b	%3c	%3d
Pd(PPh ₃) ₄	20	30	21	29
Pd(PPh ₃) ₂ Cl ₂	24	25	29	20

quantitative conversion to the allyl ester **3a** occurred in the presence of Pd(PPh₃)₄ (17 mol %, eq 5). Presently,



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(PPh₃)₄ under 3–5 atm of CO₂ (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 CH₂=CHCH₂CO₂SnBu₃ (**10a**), is formed along with (Ph₃P)₂PdCl₂.¹⁵ 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 methylallyl chloride (**2b**) was investigated, with surprising results. Under catalysis by either Pd(PPh₃)₄ or Pd(PPh₃)₂Cl₂ 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

(15) ¹H NMR monitoring of a 1:1:1 mixture of **1a**, **2a**, and Pd(PPh₃)₄ under 3 atm of CO₂ 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 ¹³C NMR spectra with those of an authentic sample.⁴ Parallel ³¹P NMR monitoring also detected **4** and, subsequently, (Ph₃P)₂PdCl₂ and OPPh₃ as the major P-containing products. In a similar preparative scale experiment (at 8 atm) (Ph₃P)₂PdCl₂, OPPh₃, and **10a** were detected and isolated by selective extraction and precipitation; their identities were confirmed by comparison of their ¹H, ¹³C, ³¹P, and ¹¹⁹Sn NMR spectra with those of authentic samples.

3a,b.¹⁶ Since carboxylation of **1a** alone affords only the corresponding tin carboxylate⁴ 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 CO₂, 4 mol % Pd(PPh₃)₄, THF, 70 °C), indicating that the carboxylative coupling is reversible. Moreover, the observation that ester **3a** is consumed when heated with Pd(PPh₃)₄ (1:1, 4 atm CO₂) suggests that the reductive elimination equilibrium to form ester and Pd(PPh₃)_{*n*} is unfavorable (Scheme 1). Although the mechanism of allyl scrambling is presently uncertain, we suspect that a dipalladium species, with either bridging allyl¹⁷ or carboxylate¹⁸ 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.

Acknowledgment. We thank Dr. Peter Jolly for providing unpublished data on complexes of types **5** and **6**. We are also grateful for financial support provided by the U.S. Department of Energy, Office of Basic Energy Sciences.

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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(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.; Praet, A. P. *J. Organomet. Chem.* **1970**, *21*, 501.