

Palladium-Catalyzed Carboxylation of Allyl Stannanes

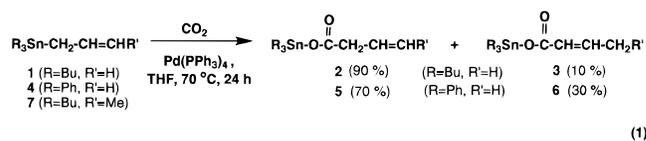
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Received November 18, 1996

The world's dwindling petroleum reserves and increasing atmospheric concentrations of carbon dioxide have stimulated considerable interest in the capture and chemical conversion of carbon dioxide. Among several approaches being examined toward this objective is the activation of carbon dioxide by transition metal complexes.¹ Efforts in our group have centered on defining and elucidating the reactivity patterns of coordinated carbon dioxide² and on the development of new catalytic reactions of this typically unreactive molecule.³ Especially synthetically attractive are reactions of CO₂ which result in carbon–carbon bond formation, e.g., the classic carboxylation of Grignard reagents.⁴ Indeed, insertions of CO₂ into the metal–carbon bonds of electropositive main group metals^{1b,5} and many transition metals¹ are common, but corresponding reactions with less polar organometallics, though still thermodynamically favorable,⁶ are rarer. Promoting such transformations would be highly desirable since the resulting metal carboxylates (RCO₂M) should be more amenable to subsequent transformation of the weaker M–O bond, enhancing the prospects for catalytic conversions to organic products. We report herein the first examples of a transition metal catalyzed insertion of CO₂ into otherwise unreactive tin–carbon bonds.

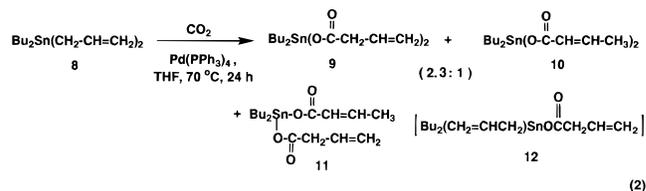
Allyltributyltin (**1**) does not react with CO₂ in THF even at 70 °C and 33 atm (24 h). However, under the same conditions in the presence of 8 mol % Pd(PPh₃)₄ or Pd(PBu₃)₄ stannane **1** is quantitatively converted to the carboxylates **2** (90%) and **3** (10%) (eq 1).^{7,8} The formation of isomer **3** must occur during the product-forming sequence because neither the starting material (**1**) nor the product (**2**) was isomerized in refluxing THF in the presence of Pd(PPh₃)₄. Under the same carboxylation conditions a 30% conversion of allyltriphenyltin (**4**, R = Ph) to insertion products **5** and **6** (7:3) was found,⁸ increasing



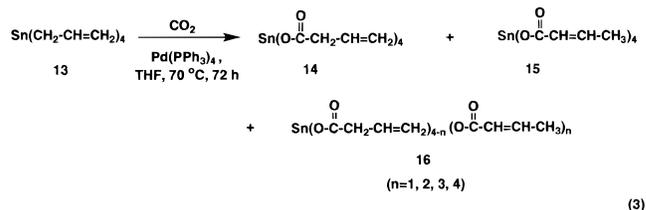
the reaction temperature (100 °C) and time (72 h) afforded no improvement. Surprisingly, crotyltributyltin (**7**, R' = Me) failed to undergo carboxylation entirely (70 °C, 33 atm, 8 mol % Pd(PPh₃)₄).

A number of other transition metal complexes, including Pd(CH₃CN)₂Cl₂, (Ph₃P)₃RhCl, and (Ph₃P)₃Ru(CO)H₂, were also tested for their ability to catalyze the carboxylation (70 °C, 33 atm) of allyl stannane **1**; in each case, however, **1** was recovered unchanged. The Lewis acid BF₃·Et₂O, an effective catalyst for the addition of allyl stannanes to aldehydes,¹⁰ likewise failed to induce the carboxylation of **1**. Thus, of the systems evaluated to date, only Pd(0) complexes have been found to be effective carboxylation catalysts.

Multiple carboxylation of poly(allyl)stannanes also can be effected with Pd(0) catalysis. Thus, diallyldibutyltin (**8**) reacted completely with CO₂ under the standard conditions to afford allyl dicarboxylates **9**, **10** (2.3:1),⁸ and, presumably, **11** (overall yield >90%, eq 2).¹¹ Surprisingly, no singly inserted product,



i.e., **12**, was detected. In the Pd-catalyzed reaction of tetraallyltin (**13**) with CO₂ a complex mixture of carboxylates (allyl)_{4-n}Sn(O₂C-allyl)_n (n = 1–4) was produced after 24 h judging by ¹H NMR analysis. However, if the reaction time was extended to 72 h, the major products (ca. 80 % yield) were the isomeric tetracarboxylates **14**, **15**, and **16**,¹¹ i.e., all four Sn–allyl bonds had inserted CO₂ (eq 3). Under these conditions double bond isomerized products (**15**, **16** n = 3, 4) dominated ca. 4:1.



(8) Authentic samples of previously unreported carboxylates **2**, **3**, **5**, **6**, **9** and **10** were prepared from the reaction of 3- or 2-propenoic acid with bis(tributyltin) oxide, bis(triphenyltin) oxide, or dibutyltin oxide, respectively (ref 9, toluene/110 °C/H₂O azeotrope). These were identical spectroscopically with products from the reactions of **1**, **4**, and **8** with CO₂. Spectral data (IR, ¹H and ¹³C NMR, and MS) for all products are compiled in the Supporting Information.

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(11) Precise product ratios in eqs 2 and 3 could not be determined because the ¹H and ¹³C NMR spectra of the “mixed” isomers **11** and **16** are indistinguishable from mixtures of the “symmetrical” isomers, **9** + **10** and **14** + **15**. Thus, NMR spectra (¹H and ¹³C) of a presumably authentic mixture of **9**, **10**, and **11** obtained by reaction of Bu₂SnO with a 1:1 mixture of 2- and 3-propenoic acid were the same as a 1:1 mixture of **9** and **10**. Integration of the ¹H NMR spectra of the product mixtures from eqs 2 and 3, however, allowed determination of the reported allyl to crotyl isomer ratios. The hydrolytic and thermal lability of the stannyl esters precluded separation of the isomers by flash or gas chromatography.

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(6) Bond enthalpy considerations for M–CR₃ + CO₂ → M–OC(=O)–CR₃ indicate an exothermic process for virtually all metals since a strong M–O bond is formed at the expense of a weaker M–C bond and a C–C σ-bond is formed at the expense of a comparably strong C–O π-bond.

(7) The following procedure is representative. Allyltributyltin (0.33 g, 1.0 mmol), Pd(PPh₃)₄ (0.093 g, 0.08 mmol), 20 mL of dry THF, and a magnetic stir bar were placed in the 50 mL glass liner of a stainless steel autoclave under a nitrogen purge. After the autoclave was purged several times with CO₂, it was pressurized with CO₂ (33 atm), sealed, and heated at 70 °C for 24 h with stirring. After cooling and release of the pressure, the solvent was removed under reduced pressure, and the residue was passed through a short column of flash silica (1:1 ethyl acetate/hexane) to afford a spectroscopically pure mixture of the tin carboxylates **2** and **3**.

Of the various stannanes tested only those possessing allyl-tin bonds were found to undergo carboxylation. Hence, tetrabutyltin, tetraphenyltin, vinyltributyltin, and benzyltributyltin each were recovered unchanged after contact with CO₂/Pd(PPh₃)₄ under the usual conditions; propargyltriphenyltin appeared to undergo polymerization. Various allyl silanes, e.g., allyltrimethylsilane, allyltriphenylsilane, and allyltrimethoxysilane, were likewise found to be unreactive. While these reactivity findings generally correlate with the strength of the C–M (M = Sn, Si) bond,¹² the failure of the crotyl- and benzyltin derivatives to react with CO₂ and the diminished reactivity of allyltriphenyltin (**4**) suggests that a specific Pd–allyl interaction may play an important role in catalysis.

These observed structure/reactivity features in combination with the established reactivity of Pd–allyl complexes with CO₂¹³ lead us to propose Scheme 1 as a *tentative* catalytic mechanism: (i) oxidative addition of allylstannane to Pd(0)L_n gives η³- and η¹-allyl palladium complexes **17** and **18**; (ii) insertion of CO₂ into the η¹-allyl palladium bond of **18** (or the Pd–Sn bond); and (iii) reductive elimination of the carboxylate and organotin groups to give the product and regenerate Pd(0). The sensitivity of the reaction to substitution on or adjacent to the Sn–allyl unit suggests that an initial η²-complex may precede the oxidative addition step; however, no indication of complexation of **1** by Pd(PPh₃)₄ was provided by ¹H NMR analysis (C₆D₆). Although transmetalation from Sn to Pd(II) complexes¹⁴ and the activation of allyl electrophiles (e.g., halides, carbonates) by Pd(0) complexes¹⁵ are both well documented, Pd(0) activation of allyl tin reagents has little precedent.¹⁶ However, the viability of an (η³-allyl)Pd(stannyl) intermediate such as **17** is supported by formation of a Pt analog in the reaction of Pt(ethylene)₂(PPh₃) with (allyl)SnMe₃.¹⁷ The viability of CO₂ insertion into the Pd–C bond of **17** or **18** is bolstered by prior examples of CO₂ insertion reactions of η¹- and η³-allyl-Pd complexes.¹³ Since neither starting material nor product isomerization occurs under the reaction conditions (*op cit*), isomerization of the intermediate CO₂ inserted species, e.g., **19**, apparently occurs prior to product release.¹⁸ An alternative mechanistic pathway involving reaction of an intermediate Pd-

(12) Average bond dissociation energies (kcal/mol) are Si–O (ca. 112), Si–C (ca. 76), Sn–C (ca. 46), and Sn–O (ca. 100). *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: London, G.B., 1992; Vol. 1, p 5. Purcell, K.; Kotz, J. C. *Inorganic Chemistry*; Saunders: Philadelphia, PA, 1977; p 272.

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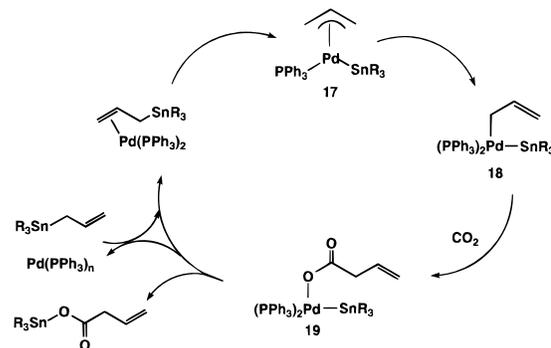
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Scheme 1



(η²-CO₂) complex with the allyl stannane¹⁹ cannot be excluded at this time. However, IR spectra of Pd(PPh₃)₄/CO₂ solutions (1 atm, THF) showed no absorptions in the 1625–1700 cm⁻¹ region expected for such a species,²⁰ and the mismatched nucleophilic character of both the allyl stannane¹⁰ and such CO₂ complexes^{1,2,20} mitigate against this possibility. Finally, we note that although allyl stannanes are well established participants in radical allyl transfer reactions,²¹ the catalytic carboxylation of **1** was unaffected by the addition of the radical inhibitors TEMPO and 2,6-dimethyl phenol (0.1 equiv), rendering unlikely the intervention of a radical pathway.

In conclusion we have discovered a new catalytic reaction of carbon dioxide in which a metal–carbon bond is activated toward CO₂ insertion. The product organotin carboxylates, especially diorganotin esters, have a wide range of commercial applications.²² Efforts are underway to elucidate the mechanistic details of this reaction and to identify systems enabling the carboxylation of other unreactive metal–carbon bonds and subsequent transformation thereof.

Acknowledgment. We are grateful for financial support provided by the U.S. Department of Energy, Office of Basic Energy Sciences.

Supporting Information Available: IR, ¹H and ¹³C NMR, and MS spectral and physical data for **2**, **3**, **5**, **6**, **9**, **10**, **14**, and **15** (2 pages). See any current masthead page for ordering and Internet access instructions.

JA9639832

(18) Extensive double bond isomerization has been found in the reactions of (η³-allyl)Pd complexes with CO₂; ref 13c–f.

(19) A reviewer's thoughtful comments on this point were appreciated.

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