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Efficient One-to-One Coupling of Easily Available 1,3-Dienes with Carbon Dioxide

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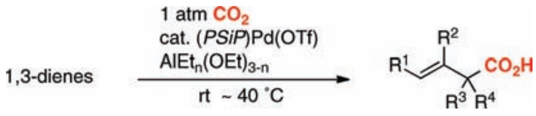
ABSTRACT



An efficient one-to-one coupling reaction of atmospheric pressure carbon dioxide with 1,3-dienes is realized for the first time through *PSiP*-pincer type palladium-catalyzed hydrocarboxylation. The reaction is applicable to various 1,3-dienes including easily available chemical feedstock such as 1,3-butadiene and isoprene. This protocol affords a highly useful method for the synthesis of β,γ-unsaturated carboxylic acid derivatives from CO_2.

One-to-one coupling of CO_2 with 1,3-dienes, some of which are easily available bulk chemicals, in the transition-metal-catalyzed CO_2-fixation reaction is a formidable challenge despite its high potential as a practical method for the preparation of carboxylic acid derivatives.[1] The reason for this scarcity is due to the facile dimerization of 1,3-dienes by palladium(0) or nickel(0) complexes which are commonly employed for such reactions. For example, Sasaki, Inoue, and Hashimoto reported in 1976 the first example of the Pd(0)-catalyzed coupling reaction of two molecules of butadiene and CO_2 to give a lactone along with butadiene dimers.[2] Since then, several research groups reported improvement in the yield and product selectivity by modifying the metal complexes,[3,4] and more recently, an intramolecular version of the reaction was developed employing a Ni catalyst.[5] All of these reactions include generation and carboxylation of bis-allyl metallic species generated by oxidative cyclization of two 1,3-butadiene units with low valent metals, and there still has been no report on the catalytic one-to-one coupling of CO_2 with 1,3-butadienes.[6]

We previously reported the *PSiP*-pincer type palladium-complex-catalyzed hydrocarboxylation reaction of allenes

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(1) For reviews on transition-metal-promoted CO_2-fixation reactions, see: (a) Braunstein, P.; Matt, D.; Nobel, D. *Chem. Rev.* **1988**, *88*, 747. (b) Yin, X.; Moss, J. R. *Coord. Chem. Rev.* **1999**, *181*, 27. (c) Sakakura, T.; Choi, J.-C.; Yasuda, H. *Chem. Rev.* **2007**, *107*, 2365. (d) Zevaca, T.; Dinjus, E. *Carbon Dioxide as Chemical Feedstock*; Aresta, M., Ed.; Wiley-VCH: Weinheim, 2010; p 89. (e) Riduan, S. N.; Zhang, Y. *Dalton Trans.* **2010**, *39*, 3347.

(2) (a) Sasaki, Y.; Inoue, Y.; Hashimoto, H. *J. Chem. Soc., Chem. Commun.* **1976**, 605. (b) Inoue, Y.; Sasaki, Y.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2375.

(3) (a) Musco, A.; Perego, C.; Tartiari, V. *Inorg. Chim. Acta* **1978**, *28*, L147. (b) Musco, A. *J. Chem. Soc., Perkin Trans. 1* **1980**, 693. (c) Behr, A.; Juszak, K.; Keim, W. *Synthesis* **1983**, 574. (d) Behr, A.; Juszak, K.-D. *J. Organomet. Chem.* **1983**, *255*, 263. (e) Behr, A.; He, R. *J. Organomet. Chem.* **1984**, *276*, C69. (f) Behr, A. *Bull. Soc. Chim. Belg.* **1985**, *94*, 671. (g) Behr, A.; He, R.; Juszak, K.-D.; Krüger, C.; Tsay, Y.-H. *Chem. Ber.* **1986**, *119*, 991. (h) Behr, A.; Kanne, U. *J. Organomet. Chem.* **1986**, *309*, 215. (i) Behr, A.; Heite, M. *Chem. Eng. Technol.* **2000**, *23*, 952. (j) Behr, A.; Becker, M. *Dalton Trans.* **2006**, 4607. (k) Behr, A.; Bahke, P.; Klinger, B.; Becker, M. *J. Mol. Catal. A: Chem.* **2007**, *267*, 149. (l) Braunstein, P.; Matt, D.; Nobel, D. *J. Am. Chem. Soc.* **1988**, *110*, 3207. (m) Hoberg, H.; Gross, S.; Milchereit, A. *Angew. Chem., Int. Ed.* **1987**, *26*, 571. (n) Hoberg, H.; Peres, Y.; Milchereit, A.; Gross, S. *J. Organomet. Chem.* **1988**, *345*, C17. (o) Pitter, S.; Dinjus, E. *J. Mol. Catal. A: Chem.* **1997**, *125*, 39. (p) Holzhey, N.; Pitter, S.; Dinjus, E. *J. Organomet. Chem.* **1997**, *541*, 243. (q) Holzhey, N.; Pitter, S. *J. Mol. Catal. A: Chem.* **1999**, *146*, 25.

(4) These reactions require high pressure CO_2 and still have some problems on the generality of substrates and product selectivity. Most of the reported reactions employ simple 1,3-dienes such as 1,3-butadiene and isoprene, and the products in these reactions are mainly five- or six-membered lactones, carboxylic acids, and esters as carboxylation products derived from the dimerized bis-allylmetallic intermediates. This diversity is due to not only the various reactivities of reaction intermediates (bis-allylmetal and its carboxylate complex) but also the existence of an isomerization pathway of the lactone products under reaction conditions. Selective formation of δ-lactone has been well investigated by Behr, and Ni-catalyzed selective formation of cyclopentanecarboxylic acid derivative was reported by Hoberg; see refs 1a, 3d, and 3m.

(5) (a) Takimoto, M.; Nakamura, Y.; Kimura, K.; Mori, M. *J. Am. Chem. Soc.* **2004**, *126*, 5956. (b) Takimoto, M.; Mori, M. *J. Am. Chem. Soc.* **2002**, *124*, 10008.

(6) There have been reported several examples of stoichiometric one-to-one coupling of 1,3-dienes with CO_2 using transition-metal complexes. For examples, see: (a) Bräunlich, G.; Walther, D.; Eibisch, H.; Schönecker, B. *J. Organomet. Chem.* **1993**, *453*, 295. (b) Takimoto, M.; Mori, M. *J. Am. Chem. Soc.* **2001**, *123*, 2895. (c) Hoberg, H.; Jenni, K. *J. Organomet. Chem.* **1987**, *322*, 193. (d) Gao, Y.; Iijima, S.; Urabe, H.; Sato, F. *Inorg. Chim. Acta* **1994**, *222*, 145 and references cited therein.

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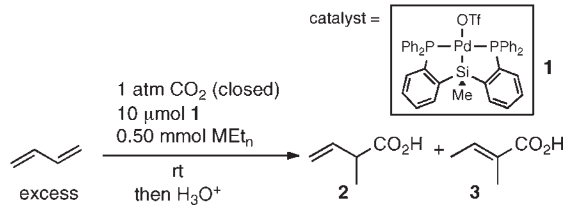
to give β,γ-unsaturated carboxylic acids through nucleophilic carboxylation of the σ-allyl palladium intermediates generated by hydropalladation of allenes.[7,8] We expected that such catalysis with palladium(II) bearing an anionic tridentate ligand would avoid the formation of the bis-allylmetal species from 1,3-dienes. In this paper, we report the first example of a catalytic one-to-one coupling reaction of CO_2 with easily available 1,3-dienes including 1,3-butadiene and isoprene as a useful CO_2-fixation by the palladium-catalyzed hydrocarboxylation reaction.[9,10]

We first examined the hydrocarboxylation reaction employing 1,3-butadiene. When the reaction was carried out by using 10 μmol of *PSiP*-pincer type palladium triflate complex **1** and 0.5 mmol of $AlEt_3$ (50 molar amounts based on **1**) at ambient temperature in DMF in the presence of excess 1,3-butadiene under 1 atm of CO_2 in a closed system,[11] 2-methyl-3-butenoic acid **2** was obtained selectively in a TON of 100 (200% yield based on one mole of $AlEt_3$, Table 1, entry 1). The high efficiency of this reaction was demonstrated by the reaction in THF, where all three ethyls on aluminum were utilized as a reductant although isomerization of the initial product **2** to α,β-unsaturated carboxylic acid **3** occurred to some extent (entry 2). Importantly, the carboxylation occurred at the 2-position of 1,3-butadiene in good selectivity.[12] Use of $ZnEt_2$ instead of $AlEt_3$ afforded a complex mixture containing a small amount of **2** (entry 3).[13] The highest TON of 446 was realized by the reaction using 5 μmol of **1** and 5.0 mmol of $AlEt_3$ in DMF (entry 4).

Table 1. Hydrocarboxylation of 1,3-Butadiene

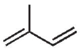
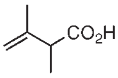
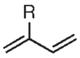
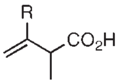
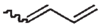
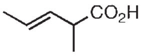
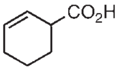
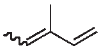
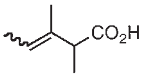


entry	MEt_n	solvent	time	**2** + **3**/ mmol	ratio of **2**:**3**	TON
1	$AlEt_3$	DMF	39 h	1.0[a]	>95:<5	100
2	$AlEt_3$	THF	40 h	1.5[a]	82:18	150
3	$ZnEt_2$	DMF	3 d	<0.05	–	–
4[b]	$AlEt_3$	DMF	3 d	2.23	48:52	446

[a] NMR yield. [b] Reaction was carried out using 5 μmol of **1** and 5.0 mmol of $AlEt_3$.

As summarized in Table 2, the reaction was applicable to other commercially available 1,3-dienes such as isoprene, myrcene, piperylene, 1,3-cyclohexadiene, and 3-methyl-1,3-pentadiene to afford corresponding β,γ-unsaturated carboxylic acids **4**–**8** in high regioselectivity and high TON (over 200) without being accompanied by isomerization of the double bond in most cases under similar reaction conditions. It should be noted that, in contrast to the

Table 2. Reaction of Commercially Available 1,3-Dienes[a]

entry	1,3-dienes	condiotions	products	
1	 isoprene	rt, 3 d	 **4**[b]	1.22 mmol TON = 245
2	 (R = $-(CH_2)_2CH{=}CMe_2$) myrcene[c]	40 °C, 24 h	 **5**	1.03 mmol TON = 206
3	 piperylene[d]	40 °C, 24 h	 **6**[e]	2.53 mmol TON = 506
4	 1,3-cyclohexadiene	40 °C, 30 h	 **7**	1.98 mmol TON = 396
5	 3-Me-1,3-pentadiene[f]	40 °C, 24 h	 **8**[g]	1.51 mmol TON = 302

[a] Reactions were carried out using 20 mmol of 1,3-dienes, 5.0 mmol of $AlEt_3$, and 5.0 μmol **1** in DMF. [b] Very small amounts of 2,3-dimethyl-2-butenoic acid (isomerization product) and 3-methyl-3-pentenoic acid (regioisomer of the carboxylation step) were included as judged by ^{1}H NMR (less than 3% of the carboxylation product). [c] 6.0 mmol of myrcene were used. [d] *E*/*Z* = 67:33. [e] *E*/*Z* = 93:7. [f] *E*/*Z* = 70:30. [g] *E*/*Z* = 67:33.

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(7) Takaya, J.; Iwasawa, N. *J. Am. Chem. Soc.* **2008**, *130*, 15254.

(8) Hydrocarboxylation of styrene derivatives were reported using Ni-catalyst, see: Williams, C. M.; Johnson, J. B.; Rovis, T. *J. Am. Chem. Soc.* **2008**, *130*, 14936.

(9) Sequential reactions of allylmetal species generated by hydrozincation or -magnesation of 1,3-diene with electrophiles including CO_2 were reported; see: (a) Gao, Y.; Urabe, H.; Sato, F. *J. Org. Chem.* **1994**, *59*, 5521. (b) Viktorov, N.; Zubritskii, L. *Russ. J. Gen. Chem.* **2001**, *71*, 1773.

(10) There are numerous reports on the catalytic intermolecular reductive coupling of 1,3-dienes with carbonyl compounds such as aldehyde. For examples of Ni-catalyzed reaction with aldehyde, see: (a) Kimura, M.; Tamaru, Y. *Top. Curr. Chem.* **2007**, *279*, 173 and references cited therein. (b) Yang, Y.; Zhu, S.-F.; Duan, H.-F.; Zhou, C.-Y.; Wang, L.-X.; Zhou, Q.-L. *J. Am. Chem. Soc.* **2007**, *129*, 2248. (c) Sato, Y.; Hinata, Y.; Seki, R.; Oonishi, Y.; Saito, N. *Org. Lett.* **2007**, *9*, 5597. For examples of Rh and Ir-catalyzed reactions, see:(d) Jang, H.-Y.; Huddleston, R. R.; Krische, M. J. *Angew. Chem., Int. Ed.* **2003**, *42*, 4074. (e) Bower, J. F.; Patman, R. L.; Krische, M. J. *Org. Lett.* **2008**, *10*, 1033. (f) Kimura, M.; Nojiri, D.; Fukushima, M.; Oi, S.; Sonoda, Y.; Inoue, Y. *Org. Lett.* **2009**, *11*, 3794. (g) Zbieg, J. R.; Fukuzumi, T.; Krische, M. J. *Adv. Synth. Catal.* **2010**, *352*, 2416. For examples of Ru-catalyzed reactions, see:(h) Shibahara, F.; Bower, J. F.; Krische, M. J. *J. Am. Chem. Soc.* **2008**, *130*, 6338. (i) Smejkal, T.; Han, H.; Breit, B.; Krische, M. J. *J. Am. Chem. Soc.* **2009**, *131*, 10366. (j) Han, H.; Krische, M. J. *Org. Lett.* **2010**, *12*, 2844. For an example of a Ti-catalyzed reaction, see:(k) Bareille, L.; Gendre, P. L.; Moïse, C. *Chem. Commun.* **2005**, 775.

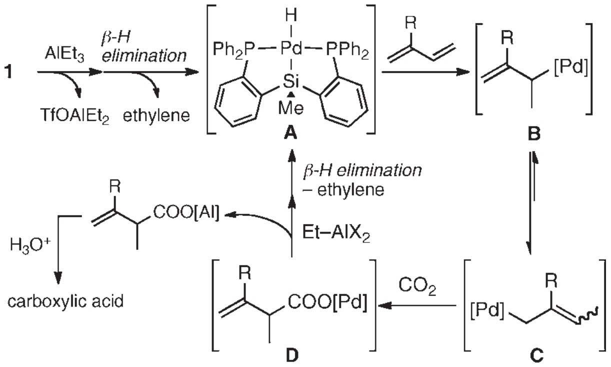
(11) Gaseous 1,3-butadiene (ca. 30 mmol) was bubbled into a DMF solution containing **1** under 1 atm of CO_2 in a 30 mL two-necked flask equipped with a three-way stopcock with a balloon. After $AlEt_3$ was added to a mixture, the system was cut off from the balloon to keep the flask closed.

(12) A very small amount of 3-pentenoic acid, which is the regioisomer of the carboxylation step, was detected by ^{1}H NMR (less than 3% of the carboxylation product).

(13) Use of common palladium catalysts such as $Pd(PPh_3)_4$ or $PdCl_2(PPh_3)_2$ instead of **1** resulted in no formation of the desired one-to-one adduct.

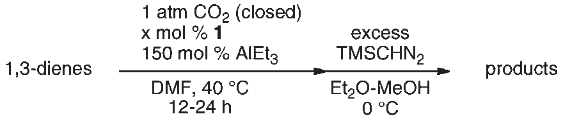
previously reported CO_2-fixation reactions with 1,3-dienes,[14] this reaction proceeded successfully with 1,3-dienes with several substitution patterns including 1- or 2-monosubstituted, 1,2-disubstituted, and cyclic ones.[15] These results demonstrate the first example of a one-to-one coupling reaction of 1 atm of CO_2 with 1,3-butadiene and other easily available 1,3-dienes, providing a useful method for the synthesis of β,γ-unsaturated carboxylic acids by CO_2-fixation.

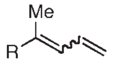
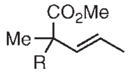
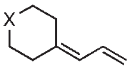
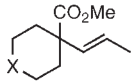
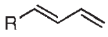
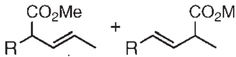
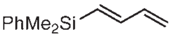
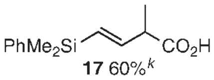
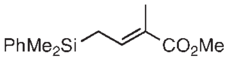
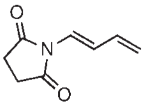
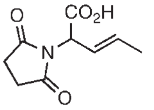
Scheme 1. Proposed Reaction Mechanism



The reaction is thought to proceed with generation of *PSiP*-pincer type palladium hydride complex **A** by β-hydride elimination after transmetalation of $AlEt_3$ to **1** (Scheme 1). Hydrometalation of 1,3-dienes occurs at the less hindered alkene moiety to give σ-allylpalladium intermediates **B**, which isomerize to the other, less sterically crowded σ-allylpalladium intermediates **C**.[16] Then, nucleophilic addition of σ-allylpalladium intermediates **C** to CO_2 occurs at the γ-position of the palladium regioselectively to give palladium carboxylate complexes **D**,[17] which are reconverted to the catalytically active palladium hydride **A** by subsequent transmetalation with $AlEt_3$ followed by β-hydride elimination.

Table 3. Generality of 1,3-Dienes



entry	1,3-dienes	x / mol %	products
			
1	R = Ph **9a**[a]	0.5	**10a** 91%
2[n]	**9a**	0.1	**10a** 61%[e]
3	R = -$(CH_2)_2$Ph **9b**[b]	2.5	**10b** 79%
4	R = -$(CH_2)_2CH{=}CMe_2$ **9c**[c]	5	**10c** 87%
5	R = -$(CH_2)_3$OTBDPS **9d**[d]	3	**10d** 84%
			
6	X = CHPh **11a**	2.5	**12a** 92%[f]
7	X = NBoc **11b**	2.5	**12b** 79%
8[h]	X = $C(OCH_2)_2$ **11c**	2.5	**12c** 97%
9[g,h]	 R = *p*-$MeOC_6H_4$ **13**	2.5	 **14**[i] + **15** 79% (**14**:**15** = 48:52)
10[j]	 **16**	2.5	 **17** 60%[k]
11[l]	**16**	5	 **18** 52%
12[l,m]	 **19**	2.5	 **20** 81%[e]

[a] E/Z = 9:1. [b] E/Z = 7:3. [c] E/Z = 9:1. [d] E/Z = 8:2. [e] Isolated as a carboxylic acid without esterification. [f] dr = 78:22. [g] In THF at rt for 2 days. [h] $AlEt_2(OEt)$ was employed instead of $AlEt_3$. [i] E/Z = 95:5. [j] 105 mol % of $AlEt(OEt)_2$. [k] NMR yield. [l] In THF. [m] 105 mol % of $AlEt_2(OEt)$. [n] The reaction was carried out for 40 h.

We next applied this hydrocarboxylation reaction to variously substituted and functionalized 1,3-dienes. Treatment of 1-methyl-1-phenyl-1,3-butadiene **9a** and $AlEt_3$ with 0.5 mol % of **1** in DMF at 40 °C afforded α-quaternary (E)-β,γ-unsaturated ester **10a** in 91% yield regio- and stereoselectively after esterification of the crude product by $TMSCHN_2$ (Table 3, entry 1). The catalyst loading could be reduced to 0.1 mol % and the TON reached 610 (entry 2). Furthermore this reaction showed wide compatibility with functional groups such as silyl ether (**9d**), alkene moiety (**9c**), carbamate (**11b**), and ketal (**11c**) without affecting these functionalities. Importantly, this carboxylation is highly stereoselective to give (E)-β,γ-unsaturated esters even by using a mixture of stereoisomers of the starting dienes **9a**−**d** (E/Z = 9:1−7:3). Carboxylation products bearing synthetically useful alkenylsilane and allylsilane moieties (**17** and **18**) were obtained selectively depending on the choice of solvent and aluminum reagent when dienylsilane **16** was used as the substrate (entries 10 and 11). The reaction is highly regioselective except for the reaction of 1-monosubstituted diene **13** probably because the regioisomeric σ-allylpalladium intermediates existed in equal amounts by equilibration (entry 9). Interestingly, the reaction of dienamide **19** was found to give α-amino (E)-β,γ-unsaturated acid **20** as a single

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(14) Some examples of a Pd-catalyzed reaction of CO_2 with isoprene were reported to give several CO_2-incorporated products in low selectivity. See: (a) Hoberg, H.; Minato, M. *J. Organomet. Chem.* **1991**, *406*, C25. (b) Dinjus, E.; Leitner, W. *Appl. Organomet. Chem.* **1995**, *9*, 43. See also refs 1a, 3f, and 3g.

(15) At present, the reaction is limited to terminal dienes (vinyl-substituted olefins) except for 1,3-cyclohexadiene.

(16) σ-Allylpalladium complexes bearing a *PSiP*-pincer backbone have been prepared. See: (a) Takaya, J.; Iwasawa, N. *Organometallics* **2009**, *28*, 6636. (b) Mitton, S., J.; McDonald, R.; Turculet, L. *Angew. Chem., Int. Ed.* **2009**, *48*, 8568.

(17) For examples of allylation of CO_2 by σ-allyl palladium complexes, see: (a) Hung, T.; Jolly, P.; Wilke, G. *J. Organomet. Chem.* **1980**, *190*, C5. (b) Shi, M.; Nicholas, K. M. *J. Am. Chem. Soc.* **1997**, *119*, 5057. (c) Johansson, R.; Wendt, O. F. *Dalton Trans.* **2007**, *36*, 488. (d) Johnson, M. T.; Johansson, R.; Kondrashov, M. V.; Steyl, G.; Ahlquist, M. S. G.; Roodt, A.; Wendt, O. F. *Organometallics* **2010**, *29*, 3521. (e) Wu, J.; Green, J. C.; Hazari, N.; Hruszkewycz, D. P.; Incarvito, C. D.; Schmeier, T. J. *Organometallics* **2010**, *29*, 6369. See also ref 16a.

regioisomer, and this reaction would be a useful method for α-amino acid synthesis by CO_2-fixation (entry 12).

In conclusion, we have developed an efficient one-to-one coupling reaction of atmospheric pressure CO_2 with 1,3-butadiene and other easily available 1,3-dienes by the *PSiP*-pincer type palladium-catalyzed hydrocarboxylation. This protocol affords a highly useful method for the synthesis of β,γ-unsaturated carboxylic acid derivatives from CO_2.

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Supporting Information Available. Preparative methods and spectral and analytical data of compounds **2**−**20**. This material is available free of charge via the Internet at http://pubs.acs.org.