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# Palladium-catalyzed cycloaddition of carbon dioxide with methoxyallene

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## Abstract

A palladium catalyst generated from $Pd_2(dba)_3 \cdot CHCl_3$ and $^nBu_2PCH_2CH_2Py$ (Py = 2-pyridyl) has effected novel cycloaddition of methoxyallene with $CO_2$ to afford (*E*)-5-methoxy-2-(methoxymethylene)-4-methylene-5-pentanolide regio- and stereospecifically, where a methoxy functional group plays an important role.

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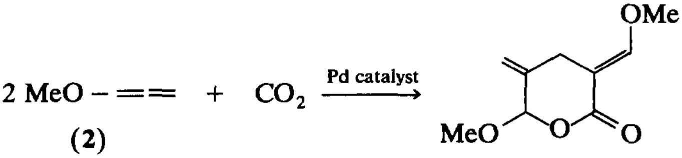
Transition metal-catalyzed $CO_2$ fixation into unsaturated hydrocarbons [1] is an attractive approach to chemical utilization of $CO_2$, which is of great concern at the present time in relation to carbon resources and environment problems. As to transition metal-catalyzed $CO_2$ fixation into allene, a few works using Pd [2], Rh [3], and Ni [4] complexes have been reported. Yields of $CO_2$ fixation products, however, were not more than 20%.

The palladium-catalyzed reaction of allene with $CO_2$ [2] has not been efficient and selective; an acyclic ester (**1**) has been obtained in 16% yield along with formation of its regioisomer, 4,6-dimethyl-2-pyrone, and allene oligomers. Here we report the unprecedented palladium-catalyzed cycloadddition of methoxyallene (**2**) with $CO_2$, which affords (*E*)-5-methoxy-2-(methoxymethylene)-4-methylene-5-pentanolide (**3**) (eq. 1). This reaction is characterized by a decisive role of a methoxy functional group.



(**2**) (**3**) (1)

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Table 1

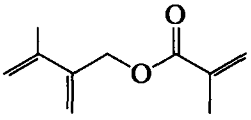
Palladium-catalyzed cycloaddition of $CO_2$ with methoxyallene (**2**) [a]

| Pd compound | Ligand (L) | L/Pd | Temp. (°C) | **3** [b], Yield (%) | **6** [b], Yield (%) |
|---|---|---|---|---|---|
| $Pd(acac)_2$ | $PCy_3$ | 3 | 100 | 28 | trace |
| | | 4 | | 33 | trace |
| | | 5 | | 25 | trace |
| | | 4 [d] | | 25 | 11 |
| | | 2 [e] | | 0 | 28 |
| | **4** | 1 | | 45 | 0 |
| | | 2 | | 39 | trace |
| | | 3 | | trace | trace |
| | | 1 | 120 | 55[33] [c] | trace |
| | $^nBu_2PCH_2Py$ | | 100 | 41 | 0 |
| | $P^nBu_3$-Pyridine (1:1) | | 120 | 23 | trace |
| $Pd(OAc)_2$ | $PCy_3$ | 4 | 100 | 26 | 0 |
| $Pd_2(dba)_3 \cdot CHCl_3$ | $PCy_3$ | | | 24 | 0 |
| | **4** | 1 | 120 | 64[41] [c] | 0 |

[a] The reaction was carried out under nitrogen in a 50 mL autoclave. **2** (0.50 mmol); Pd/**2** = 0.05; $CO_2$ (initial pressure at room temperature 50 kg $cm^{-2}$); solvent MeCN (10 mL); 20 h. [b] Yield determined by GC using an internal standard. Products **3**, **6** showed spectroscopic data and elemental composition in accord with the proposed structures. [c] The value in square brackets is the isolated yield (%) determined by PLC. [d] Pd/**2** = 0.10. [e] Pd/**2** = 0.10, MeCN (5 mL).

When **2** [5] was treated with $CO_2$ under pressure in MeCN at 120°C, in the presence of a palladium catalyst (5 mol%) generated from $Pd_2(dba)_3 \cdot CHCl_3$ (dba = dibenzylideneacetone) and one equivalent of 1-(2-pyridyl)-2-(di-n-butylphosphino)ethane ($^nBu_2PCH_2CH_2Py$) (**4**) [6], the lactone **3** was produced in 64% yield regio- and stereospecifically (Table 1). Effectiveness of the ligand **4** in the palladium-catalyzed reaction is noteworthy. Acyclic co-oligomers were not detected. An acetal moiety of **3** was readily converted into an aldehyde group by hydrolysis; $^1H$ NMR spectroscopy revealed that treatment of **3** in MeCN-$d_3$ at room temperature with a small amount of 5% HCl aqueous solution gave **5** quantitatively.

Effect of the ligand on the formation of **3** was examined using $Pd(acac)_2$. Tricyclohexylphosphine ($PCy_3$) was less efficient than **4**. Other tertiary phosphine ligands such as $P^iPr_3$, $P^nBu_3$, $P(C_8H_{17}\text{-n})_3$, $Cy_2P(CH_2)_4PCy_2$, and $Ph_2P(CH_2)_nPPh_2$ ($n$ = 2,3) produced **3** in *ca.* 10–20% yields. Increase of the palladium catalyst concentration and decrease of the ligand/Pd ratio effected formation of **6**, which suggests that **6** may be formed from **3** via isomerization catalysed by a palladium-hydride species. Under the reaction condition of $Pd(acac)_2$ (20 mol%)-2 $PCy_3$/MeCN (5 mL)/100°C/20 h with $CO_2$ (60 kg/$cm^2$) and without $CO_2$, **3** was actually isomerized to **6**, in 90 and 86% yields, respectively. Use of MeCN as a solvent is necessary for the reaction; the reactions using $PCy_3$ in DMF and THF produced small and trace amounts of **3** and **6**, respectively.



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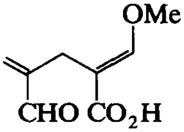

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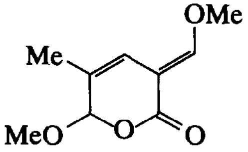

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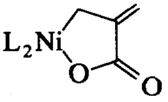

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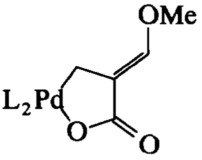

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1,2-Pentadiene did not produce a co-oligomer with $CO_2$ in the presence of the $Pd_2(dba)_3 \cdot CHCl_3$–4 catalyst. This finding indicates that the methoxy-substituent plays a crucial role in the present reaction. With regard to the formation of a nickel metallacycle (7) [7] from allene, $CO_2$, and a $Ni^0$ complex *, one possible explanation for the effect of the methoxy group can be that the electron-donating methoxy group promotes formation of a palladium matallacycle intermediate (8) by its conjugation with an electron-withdrawing carbonyl group.

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* Nickel(0)-catalyzed cycloaddition reaction of $CO_2$ with allene has been reported to form 3-methyl-4-methylene-2-pentene-5-olide in 20% yield [4], which shows a different regiochemistry from the present reaction.