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**Preliminary communication**

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# Palladium(0)-catalyzed carbonylation of alkenyl- and arylborates and boronic acids with carbon monoxide

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## Abstract

Alkenyl- and aryl-borates and boronic acids react with CO under atmospheric pressure in methanol at 25 ° C in the presence of a catalytic amount of $Pd(PPh_3)_4$ to give the corresponding methyl carboxylates and ketones in moderate yields.

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During the study on catalytic or stoichiometric carbonylation of organometallic compounds we found that a zero-valent palladium ($Pd^0$) complex works as a catalyst for carbonylation of some organoboron derivatives. Although it is known that a divalent palladium ($Pd^{II}$) complex catalyzes the reaction in the presence of a suitable reoxidant [1], there are no reports on $Pd^0$-catalyzed carbonylation. This finding may support the assumption of $Pd^0$ insertion into the C–B bond which has been proposed in the $Pd(OAc)_2$-catalyzed protonolysis and allylation of alkenylboranes [2].

Treatment of (*E*)-1-styryl-1,3,2-benzodioxaborole (**1a**) with CO under atmospheric pressure in methanol at 25 ° C during 20 h in the presence of a catalytic amount of $Pd(PPh_3)_4$ (5 mol%) solely gave methyl cinnamate (**2a**) in 16% yield (314% yield on the basis of $Pd^0$). With a longer reaction time, 120 h, the yield of **2a** was slightly improved but no reaction occurred under 20 atm of CO, **1a** being almost completely recovered. A similar treatment of **1a** with 1 atm of CO in the presence of commercial Pd black (100 mol%) or triphenylphosphine (20 mol%) instead of $Pd(PPh_3)_4$ was not successful, but with various easily available organoboronic acids such as **1b**, **1c**, and **4** carbonylation products (**2**, **5**, and **6**) together with small amounts of coupling products (**3** and **7**) were formed. Typical results are shown in Table 1. With arylboronic acids (**4**) the main products were diaryl ketones (**6**), but the carbonylation of alkenylboronic acids (**1b** and **1c**) gave no ketones. On the other hand, the carbonylation of **1b** and **4** in the presence of a stoichiometric or catalytic amount of $Pd(OAc)_2$ only gave the corresponding esters. The addition of triethylamine or *m*-dinitrobenzene to $Pd^0$-catalyzed carbonylation of **4** improved the product yields and also affected the product distribution. The reaction did not occur using a catalytic amount of $PdCl_2$ or $PdCl_2(PPh_3)_2$.

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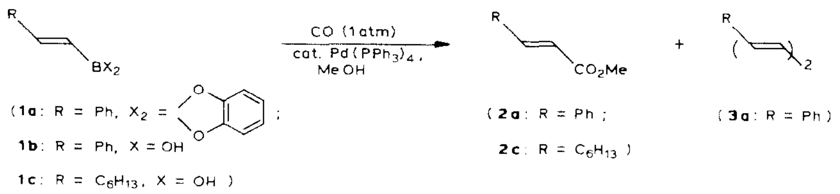

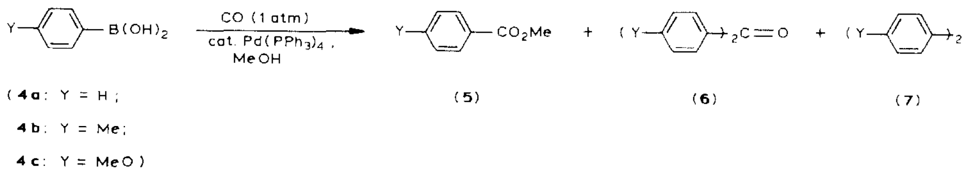

The different product distribution between Pd$^{II}$-mediated or -catalyzed carbonylation and Pd$^0$-catalyzed carbonylation suggests different reaction pathways. The former reaction may proceed via transmetallation giving a reactive organopalladium species (RPdZ) as proposed in many Pd$^{II}$-catalyzed carbonylations of organometallic compounds of several elements including boron [1,3]. Although more work is necessary to improve the product yield and to clarify the reaction scheme in this Pd$^0$-catalyzed reaction, the pathway involving the oxidative addition of Pd$^0$ to the C–B bond seems to be the most plausible for this catalytic process. Oxidative

Table 1

Carbonylation of organo-borates and -boronic acids [a]

| Organoboron compound (1 mmol) | Pd compound [b] (mmol) | | Reaction time (h) | Products and yield(%) [c] |
|---|---|---|---|---|
| **1a** | Pd**P**$_4$ | 0.05 | 20 | **2a**, 314(15.7) |
| **1a** | Pd**P**$_4$ | 0.05 | 120 | **2a**, 462(23.1) |
| **1b** | Pd**P**$_4$ | 0.01 | 20 | **2a**, 790(7.9); **3a**, trace |
| **1b** | Pd**P**$_4$ | 0.05 | 20 | **2a**, 614(30.7); **3a**, 29(2.9) |
| **1b** | Pd(OAc)$_2$ | 1 | 20 | **2a**, 77(77) |
| **1c** | Pd**P**$_4$ | 0.05 | 20 | **2c**, 288(14.4) |
| **4a** | Pd**P**$_4$ | 0.01 | 20 | **5a**, 370(3.7); **6a**, 340(6.8); **7a**, 25(0.5) |
| **4a** | Pd**P**$_4$ | 0.05 | 20 | **5a**, 206(10.3); **6a**, 264(26.4); **7a**, 15(1.5) |
| **4a** | Pd**P**$_4$ [d] | 0.05 | 20 | **5a**, 550(27.5); **6a**, 8(0.8); **7a**, 57(5.7) |
| **4a** | Pd(OAc)$_2$ | 1 | 2 | **5a**, 65(65) |
| **4a** | Pd(OAc)$_2$ | 0.05 | 20 | **5a**, 74(3.7) |
| **4b** | Pd**P**$_4$ | 0.01 | 20 | **5b**, 530(5.3); **6b**, 1010(20.2); **7b**, trace |
| **4b** | Pd(OAc)$_1$ | 1 | 2 | **5b**, 70(70) |
| **4c** | Pd**P**$_4$ | 0.05 | 20 | **5c**, 338(16.9); **6c**, 501(50.1); **7c**, trace |
| **4c** | Pd(OAc)$_2$ | 1 | 2 | **5c**, 72(72) |

[a] In methanol (10 ml) at 25 °C under 1 atm CO. [b] **P** denotes PPh$_3$. [c] Determined by GLC; the yield is calculated by (product (mmol)/Pd compound (mmol))×100. Yield based on the starting organoboron compound is shown in parentheses. [d] Et$_3$N (1 mmol) was added.

addition to a C–Hg bond of $Pd^0$ has been proposed in the $Pd(PPh_3)_4$-catalyzed carbonylation of some vinylmercury compounds [4].

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