

Preliminary communication

Palladium(0)-catalyzed carbonylation of alkenyl- and aryl-borates and boronic acids with carbon monoxide

Toshiyuki Ohe, Kouichi Ohe, Sakae Uemura* and Nobuyuki Sugita

Institute for Chemical Research, Kyoto University, Uji, Kyoto (Japan)

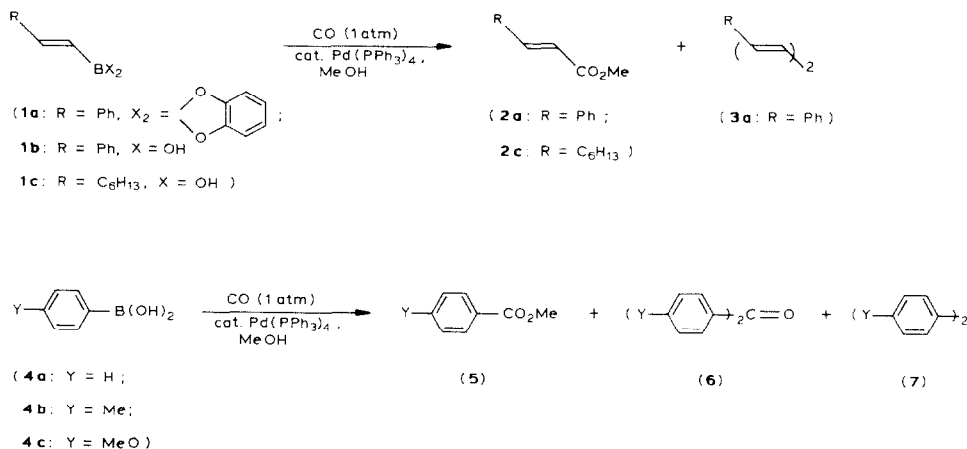
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Abstract

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 $\text{Pd}(\text{PPh}_3)_4$ to give the corresponding methyl carboxylates and ketones in moderate yields.

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 $\text{Pd}(\text{OAc})_2$ -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 $\text{Pd}(\text{PPh}_3)_4$ (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 $\text{Pd}(\text{PPh}_3)_4$ 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 $\text{Pd}(\text{OAc})_2$ 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 $\text{PdCl}_2(\text{PPh}_3)_2$.



The different product distribution between Pd^{II}-mediated or -catalyzed carbonylation and Pd⁰-catalyzed carbonylation suggests different reaction pathways. The former reaction may proceed via transmetalation 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 Pd⁰-catalyzed reaction, the pathway involving the oxidative addition of Pd⁰ 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	PdP ₄	0.05	20	2a, 314(15.7)
1a	PdP ₄	0.05	120	2a, 462(23.1)
1b	PdP ₄	0.01	20	2a, 790(7.9); 3a, trace
1b	PdP ₄	0.05	20	2a, 614(30.7); 3a, 29(2.9)
1b	Pd(OAc) ₂	1	20	2a, 77(77)
1c	PdP ₄	0.05	20	2c, 288(14.4)
4a	PdP ₄	0.01	20	5a, 370(3.7); 6a, 340(6.8); 7a, 25(0.5)
4a	PdP ₄	0.05	20	5a, 206(10.3); 6a, 264(26.4); 7a, 15(1.5)
4a	PdP 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	PdP ₄	0.01	20	5b, 530(5.3); 6b, 1010(20.2); 7b, trace
4b	Pd(OAc) ₁	1	2	5b, 70(70)
4c	PdP 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 PPh₃. ^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 Et₃N (1 mmol) was added.

addition to a C–Hg bond of Pd^0 has been proposed in the $\text{Pd}(\text{PPh}_3)_4$ -catalyzed carbonylation of some vinylmercury compounds [4].

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