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Palladium(0)-catalyzed carbonylation of aryl and alkenyl boronic acids with carbon monoxide leading to esters and ketones. Transformation of a C–B bond to a C–CO bond

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Abstract

Arylboronic acids react with carbon monoxide (CO) at atmospheric pressure in methanol at 25°C in the presence of a catalytic amount (1–5 mol%) of tetrakis(triphenylphosphine)palladium(0) to give the corresponding methyl arenecarboxylates and diaryl ketones in moderate yield, where the addition of a base, especially sodium acetate, increases the selectivity for the esters. However, when the reactions are carried out in aprotic solvents such as tetrahydrofuran (THF), benzene, dichloromethane and dimethoxyethane, the ketones become the sole carbonylation products, THF being the solvent of choice. Alkenylboronic acids react similarly to afford selectively the corresponding methyl alkenecarboxylates in methanol and dialkenyl ketones in THF, respectively. A reaction pathway involving the oxidative addition of a carbon–boron bond to palladium(0) is proposed for this catalytic process.

Keywords: Palladium; Boron; Carbonylation; Oxidative addition

1. Introduction

It is well known that trialkylboranes react with carbon monoxide (CO) to afford alcohols, ketones and aldehydes after suitable treatment of carbonylborane intermediates initially formed by formal insertion of CO into a carbon–boron bond [1]. However, in the cases of alkenyl and aryl boron compounds, catalysis by transition-metals is necessary for such insertion as exemplified by the Pd(II)-catalyzed carbomethoxylation of alkenylboranes [2]. As part of our continuing studies on transition metal catalyzed carbon–carbon bond forming reactions using organoheteroatom compounds [3], we have now discovered that a zero-valent palladium complex works as a catalyst for carbonylation of aryl and alkenyl boronic acids; i.e. the transformation of a C(aryl and alkenyl)–B bond to a C–CO bond. This finding may support the assumption of Pd(0) insertion into a C–B bond which has been proposed in the palladium(II) acetate [$Pd(OAc)_2$]-catalyzed protonolysis and allylation of alkenylboranes [4] and the tetrakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$]-catalyzed cross-coupling of 1-alkenylboranes [5]. We report here the details of our results [6].

2. Results and discussion

2.1. Carbonylation of arylboronic acids

Treatment of benzeneboronic acid (**1a**) with CO at atmospheric pressure in methanol at 25°C for 20 h in the presence of a catalytic amount of $Pd(PPh_3)_4$ (5 mol%) gave methyl benzoate (**2a**) and benzophenone (**3a**) in 22% and 26% yields (440% and 520% yields on the basis of Pd(0)), respectively, together with 6% of biphenyl. The experiments were reproducible to give both **2a** and **3a** in the range of 15–23% and 18–26% yields, respectively (Scheme 1). Reaction conditions using a smaller amount of the catalyst, for a shorter reaction time, at a lower (5°C) or higher temperature (50°C) afforded lower yields of the products in every case. However, carbonylation of **1a** in the presence of a stoichiometric amount of $Pd(OAc)_2$ gave only the ester

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$$ArB(OH)_2 \xrightarrow[CO\ (1\ atm),\ MeOH]{cat.\ Pd\ compound} ArCO_2Me + ArCOAr + ArAr$$

1 2 3 4

a; Ar = Ph
b; Ar = 4-MeC_6H_4
c; Ar = 4-$MeOC_6H_4$
d; Ar = 4-ClC_6H_4
e; Ar = 4-BrC_6H_4
f; 3-$NO_2C_6H_4$
g; Ar = 1-naphthyl

Scheme 1.

2a in good yield. Its use as a catalyst was unsuccessful in the presence of a base such as sodium acetate, potassium carbonate or triethylamine although the formation of a naked palladium(0) would be expected, but when a suitable amount of triphenylphosphine was added, the catalytic system showed a reactivity similar to that of $Pd(PPh_3)_4$ and a mixture of **2a**, **3a**, and **4a** was obtained. However, the addition of tributylphosphine, 1,2-bis(diphenylphosphino)ethane, 1,3-bis(diphenylphosphino)propane or an excess of PPh_3 stopped the reaction almost completely. Typical results are shown in Table 1. Other palladium compounds such as bis[1,2-bis(diphenylphosphino)ethane]palladium[$Pd(dppe)_2$], tris(dibenzylideneacetone)dipalladium[$Pd_2(dba)_3$], palladium black, $PdCl_2$ and $PdCl_2(PPh_3)_2$, as well as $RhCl_3$ and $RhCl(PPh_3)_3$, were found to be completely ineffective.

For the purpose of improving the product yield and/or its selectivity and also of obtaining some clues for the reaction mechanism, the $Pd(PPh_3)_4$-catalyzed carbonylation was carried out in the presence of a variety of additives. As shown in Table 1, the addition of organic and inorganic bases such as triethylamine, pyridine, and sodium acetate improved the selectivity for the ester **2a**, especially in the NaOAc case, with a slight increase in the total yield of the carbonylated compounds. The addition of a radical scavenger such as hydroquinone or *m*-dinitrobenzene did not stop the reaction and the presence of excess oxygen did not have much effect on the reaction, suggesting that the carbonylation proceeds by an ionic mechanism in nature. In the $Pd(OAc)_2/PPh_3$-catalyzed case, selectivity for **2a** was also increased by addition of NaOAc (Table 1).

The $Pd(PPh_3)_4$-catalyzed carbonylation was applied to a variety of arylboronic acids (**1b–1g**) in both the presence and absence of NaOAc. The yields of the carbonylated products were in the range 17%–67%, and the ester became the major product in the presence of NaOAc, as in the case of **1a** (Table 2). With 1-naphthaleneboronic acid (**1g**) the favourable formation of binaphthyl was observed. CO insertion did not occur at the carbon–halogen bond of **1d** and **1e**, and neither 4-methoxycarbonylbenzeneboronic acids nor dimethyl terephthalate were produced. We confirmed separately that bromobenzene and chlorobenzene did not react at all under these conditions and were recovered almost completely, while **1a** was produced in 5% yield from iodobenzene (90% iodobenzene recovered).

Next, in order to find suitable condition, in which the ketone **3** is obtained as a major product and in good yield, we examined the effect of solvent type on the $Pd(PPh_3)_4$-catalyzed carbonylation of **1a**. As shown in Table 3, the use of aprotic solvents such as tetrahydrofuran (THF), CH_2Cl_2, 1,2-dimethoxyethane, toluene and benzene resulted in a sole formation of **3a**, with no benzoic acid produced. As THF was revealed to be the solvent of choice for this purpose, the carbonylation of a variety of arylboronic acids (**1b–1g**) was carried out in THF, typical results of which were also shown in

Table 1
Carbonylation of benzeneboronic acid **1a** in methanol under various conditions [a]

Pd compound (mmol)		Additive (mmol)	Conditions		Products and yield (%) [b]		
			temp (°C)	time (h)	**2a**	**3a**	**4a**
$Pd(PPh_3)_4$	0.05	–	25	20	15–23 [c]	18–26 [c]	1–6 [c]
$Pd(PPh_3)_4$	0.01	–	25	20	4	9	6
$Pd(PPh_3)_4$	0.05	–	25	5	7	8	2
$Pd(PPh_3)_4$	0.05	–	5	20	17	16	17
$Pd(PPh_3)_4$	0.05	–	50	5	2	3	2
$Pd(PPh_3)_4$	0.05	Et_3N (1)	25	20	28–39	1–2	6–11
$Pd(PPh_3)_4$	0.05	pyridine (1)	25	20	22	4	2
$Pd(PPh_3)_4$	0.05	NaOAc (1)	25	20	58	3	3
$Pd(PPh_3)_4$	0.05	O_2 [d]	25	20	11	36	10
$Pd(PPh_3)_4$	0.05	*p*-$C_6H_4(OH)_2$ (1)	25	20	18	11	trace
$Pd(PPh_3)_4$	0.05	*m*-$C_6H_4(NO_2)_2$ (1)	25	20	23	27	7
$Pd(OAc)_2$	1	–	25	2	64	0	0
$Pd(OAc)_2$	0.05	–	25	20	4	0	0
$Pd(OAc)_2$	0.05	PPh_3 (0.2)	25	20	21	11	1
$Pd(OAc)_2$	0.05	PPh_3 (0.1)/NaOAc (2)	25	20	51	2	0
$Pd(OAc)_2$	0.05	PPh_3 (0.1)	25	20	8	trace	4

[a] **1a** (1 mmol), MeOH (10 ml) and CO (1 atm); [b] Based on **1a**: 1 mmol of **2a** and 0.5 mmol of **3a** and **4a** correspond to 100% yield, respectively: [c] Results of several runs. [d] Oxygen was passed through methanol for 1 h.

Table 2
Carbonylation of arylboronic acids **1** in methanol in the presence or absence of NaOAc [a]

1 (1 mmol)	Additive (1 mmol)	Products and yield (%) [b]		
		2	**3**	**4**
1a	–	15–23 [c]	18–26 [c]	1–6 [c]
1a	NaOAc	51	5	1
1b	–	17	30	1
1b	NaOAc	42	9	2
1c	–	7	29	2
1c	NaOAc	34	14	2
1d	–	6–7 [c]	22–32 [c]	0–2 [c]
1d	NaOAc	41	4	4
1e	–	9	6	0
1e	NaOAc	30	2	0
1f	–	30	22 [d]	7 [d]
1f	NaOAc	15	2	0
1g	–	4	24 [d]	19 [d]
1g	NaOAc	19	5 [d]	30 [d]

[a] Methanol (10 ml), $Pd(PPh_3)_4$ (0.05 mmol), and CO (1 atm); at 25°C for 20 h. [b] GLC yield, see the footnote of Table 1. [c] Results of several runs. [d] Isolated yield.

Table 3. In all cases the corresponding ketones were obtained in fair to good yields together with small amounts of biaryls, except for the naphthyl compound **1g** which afforded mainly binaphthyl, as observed with methanol as solvent.

When the $Pd(PPh_3)_4$-catalyzed crossover carbonylation was attempted with equimolar amounts of **1a** and **1b** in THF, a mixture of **3a**, 4-methylbenzophenone, and **3b** (ca. 1:2:1) was obtained, together with small amounts of biaryls (see Section 3). Similarly, from a mixture of **1a** and **1d**, were obtained three different ketones **3a**, 4-chlorobenzophenone, and **3d** (ca. 1:4.6:4.0) in which an unsymmetrical ketone (crossover reaction product) was also the main product.

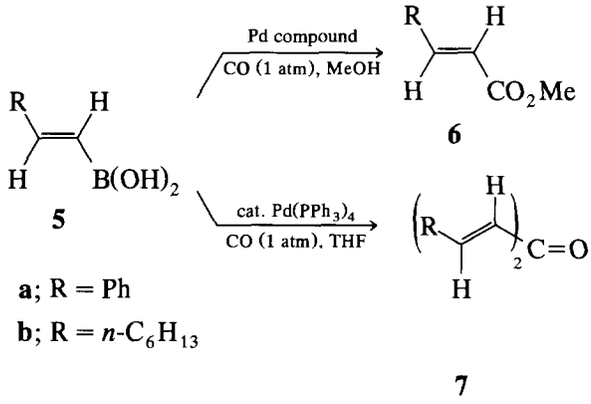
2.2. Carbonylation of alkenylboronic acids

Treatment of (*E*)-styrylboronic acid (**5a**) with CO at atmospheric pressure in methanol at 25°C for 20 h in the presence of a catalytic amount of $Pd(PPh_3)_4$ (5 mol%) gave methyl cinnamate as the sole product (**6a**) in 21–31% yields (420–620% yields based on Pd(0)). Similarly, from (*E*)-1-octenylboronic acid (**5b**), (*E*)-methyl 1-nonenoate (**6b**) was obtained in 14–28% yields (280–560% yields based on Pd(0)) (Scheme 2). An increase of the amount of catalyst led to an increase of the ester yield, but the yield on the basis of Pd(0) was not much improved. Carbonylation using a stoichiomet-

Table 3
Carbonylation of arylboronic acids **1** in various solvents [a]

1	Solvent	Products and yield (%) [b]		
		2	**3**	**4**
1a	MeOH	15–23 [c]	18–26 [c]	1–6 [c]
1a	THF	0	52–61 [c]	0–1 [c]
1a	CH_2Cl_2	0	39	1
1a	DME [d]	0	36	1
1a	toluene	0	32	2
1a	benzene	0	46	1
1a	MeCN	0	1	0
1b	THF	0	61	8
1c	THF	0	56	9
1d	THF	0	42–58 [c]	0–8 [c]
1e	THF	0	47	7
1f	THF	0	8 [e]	0
1g	THF	0	32 [e]	51 [e]

[a] **1** (1 mmol), $Pd(PPh_3)_4$ (0.05 mmol), solvent (10 ml), and CO (1 atm); at 25°C for 20 h. [b] GLC yield, see the footnote of Table 1. [c] Results of several runs. [d] 1,2-Dimethoxyethane. [e] Isolated yield.

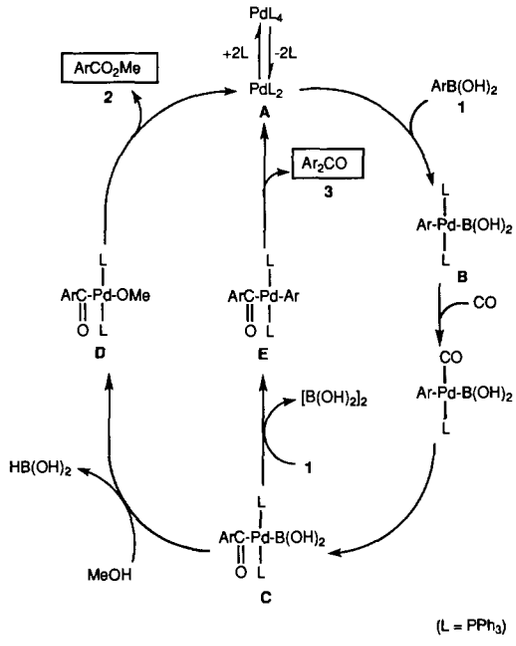


Scheme 2.

Table 4
Carbonylation of alkenylboronic acid **5** [a]

5 (1 mmol)	Palladium compound (mmol)		Solvent	Products and yield (%) [b]	
5a	$Pd(PPh_3)_4$	0.05	MeOH	**6a**	21–31 [c]
5a	$Pd(PPh_3)_4$	0.1	MeOH	**6a**	59
5a	$Pd(OAc)_2$	1	MeOH	**6a**	77
5a	$Pd(OAc)_2$ [d]	0.1	MeOH	**6a**	24
5a	$Pd(PPh_3)_4$	0.05	THF	**7a**	24 [e]
5b	$Pd(PPh_3)_4$	0.01	MeOH	**6b**	10
5b	$Pd(PPh_3)_4$	0.05	MeOH	**6b**	14–28 [c]
5b	$Pd(PPh_3)_4$	0.2	MeOH	**6b**	43
5b	$Pd(OAc)_2$	1	MeOH	**6b**	94

[a] CO (1 atm) at 25°C for 20 h. [b] GLC yield: 1 mmol of **6** and 0.5 mmol of **7** correspond to 100% yield, respectively. [c] Results of several runs. [d] PPh_3 (0.2 mmol) was added. [e] Isolated yield. The other product is (*E,E*)-1,4-diphenylbutadiene (24%).



Scheme 3.

ric amount of $Pd(OAc)_2$ afforded the ester in high yield as expected [2]. The corresponding borate of **5a** ((*E*)-1-styryl-1,3,2-benzodioxaborole) reacted similarly to give **6a** [4]. Carbonylation of **5a** in THF gave the divinyl ketone **7a**. Typical results are shown in Table 4.

2.3. Possible reaction scheme

The different product distribution between $Pd(OAc)_2$-mediated carbonylation and Pd(0)-catalyzed carbonylation suggests different reaction pathways for the two reactions. The former reaction may proceed via transmetallation, giving a reactive organopalladium species (RPdOAc) similar to that proposed for Pd(II)-catalyzed carbonylation of organometallic compounds of many elements, including boron [2,7]. However, in the latter reaction, the pathway involving the oxidative addition of a C–B bond to Pd(0) seems to be the most plausible considering the fact that carbonylation of iodobenzene also proceeds under the same conditions, though slowly, where an oxidative addition of a C–I bond to Pd(0) would be expected. Although the exact mechanism of the reaction is not certain, the most plausible catalytic cycle of $Pd(PPh_3)_4$-catalyzed carbonylation of arylboronic acids **1** seems to be that shown in Scheme 3. A carbon–boron bond of **1** adds oxidatively to Pd of the coordinatively unsaturated Pd-triphenylphosphine complex (**A**) to give an arylpalladium compound (**B**), whereupon substitution of the phosphine ligand with CO followed by aryl migration from Pd to the CO carbon occurs to produce an aroylpalladium compound (**C**). The presence of an excess PPh_3 or stronger ligand such as Bu_3P and 1,2-bis(diphenylphosphino)ethane may retard the formation of coordinatively unsaturated complex. With methanol as solvent, substitution of a $B(OH)_2$ moiety with a methoxy group may occur to give the compound **D** which reductively eliminates the product ester **2**. The presence of a base may help these processes by neutralizing the acidic $HB(OH)_2$ produced. Compound **C** can also react with another molecule of **1** to give the ketone **3** via an aroylarylpalladium compound **E**. As shown in Table 2, the major products from **1c** (*p*-methoxy substituent) and **1f** (*m*-nitro substituent) in methanol are the ketone **3c** and the ester **2f**, respectively. This may be explained by considering that substitution of the anionic $B(OH)_2$ moiety of **C** with an electron-rich arylboronic acid is faster than with an electron-deficient one. In aprotic solvents only the pathway from **C** to **E** can be operative. The formation of three different ketones, including an unsymmetrical one in the crossover carbonylation of a mixture of different arylboronic acids can be explained by considering the intermolecular reactions between the intermediate **C** and arylboronic acids, as shown in Scheme 3. Unfortunately, however, all attempts to obtain spectral evidence (IR and ^1H NMR) for the presence of the complex **B** and/or some aroylpalladium compounds and also to isolate them have so far been unsuccessful [8].

3. Experimental details

^1H NMR spectra were recorded on JEOL VXR 200 (200 MHz) and JEOL GSX-270 (270 MHz) spectrometers using Me_4Si as the internal standard in $CDCl_3$. IR spectra were recorded on JASCO IR-810 and Perkin Elmer 521 IR spectrophotometers. Melting points were determined on a Yanaco MP-J3 micro melting point apparatus and were uncorrected. Mass spectra were obtained on a Shimadzu QP-5000S spectrometer at an ionizing voltage of 70 eV. GLC analyses were carried out with a Yanaco G2800 instrument equipped with a EGSS-X (3% on Chromosorb W, 1 m), PEG 6000 (25% on Chromosorb W, 1 m) and Silicone DC QF-1 (5% on Chromosorb W, 1m) columns and a Shimadzu GC-14A instrument equipped with CBP 10-S25-050 (Shimadzu, fused silica capillary column, 0.33 mm × 25 m, 5.0 μm film thickness) column using dinitrogen as carrier gas. GLC yields were determined using suitable hydrocarbons as internal standards. Isolation of pure products was carried out with column chromatography on SiO_2 (Wakogel C200, 100–200 mesh, Wako Pure Chemical Ind. Ltd.).

Solvents were freshly distilled prior to use: methanol was distilled from $Mg(OMe)_2$ prepared in situ ($Mg + I_2$); THF was distilled from benzophenoneketyl; 1,2-dimethoxyethane was distilled from lithium aluminium hydride; dichloromethane, acetonitrile, benzene, and

toluene were distilled from calcium hydride. Arylboronic acids (**1b**, **1c**, **1d**, **1e** and **1g**) [9] and alkenylboronic acids (**5a** [10] and **5b** [11]) were prepared by reported methods. The two arylboronic acids (**1a** and **1f**) were commercial products. All methyl esters, ketones and biaryls, as well as 1,4-diphenyl-1,3-butadiene and benzalacetone (**7a**), but excluding 1,1′-dinaphthyl (**4g**), were purchased commercially and used for GLC determination. The compounds **3f**, **4f**, **3g** and **4g** were isolated by column chromatography and identified spectroscopically. Asymmetrical ketones, such as 4-methylbenzophenone (mp 56–57°C, Ref. [12] 59.5°C) and 4-chlorobenzophenone (mp 74–75°C, Ref. [13] 75–76°C), were prepared separately in 65–80% yield by the treatment of the corresponding acid chlorides with sodium tetraphenylborate in the presence of $Pd(PPh_3)_4$ [3c] and were used as authentic samples for GLC determination.

3.1. General procedure for $Pd(PPh_3)_4$-catalyzed carbonylation of arylboronic acids 1 with carbon monoxide

In a two-necked 30 ml round-bottom flask, equipped with a septum inlet and a three-way stopcock, were placed arylboronic acid **1** (1 mmol), tetrakis(triphenylphosphine)palladium(0) (0.058 g, 0.05 mmol) and a suitable amount of an internal standard for GLC determination. The system was then flushed with CO from a CO-filled balloon connected to the flask, and dry solvent (10 ml) was injected by a syringe. The mixture was stirred for an appropriate time at 25°C, poured into brine (50 ml) and extracted with dichloromethane (30 ml × 2). The extract was washed with water and dried over anhydrous Na_2SO_4. GLC analysis revealed the presence of methyl benzoates, diarylketones and biaryls. Some products were isolated by column chromatography using ethyl acetate–hexane as an eluent.

3.1.1. 3,3′-Dinitrobenzophenone (3f)

A yellow solid, mp. 150–151°C (Ref. [14] 153.4–153.8°C), ^{1}H NMR (270 MHz): δ 7.78 (2H, t, J = 8.1 Hz), 8.13–8.17 (2H, m), 8.50–8.54 (2H, m), 8.63 (2H, t, J = 1.8 Hz). ^{13}C NMR (50 MHz): 124.6, 127.6, 130.1, 135.2, 137.7, 148.3, 191.8. IR (KBr): 3070, 1665, 1610, 1525, 1350 cm^{-1}. MS m/z (rel. intensity): 272 (M^+, 20), 150 (100), 104 (33), 76 (36).

3.1.2. 3,3′-Dinitrobiphenyl (4f)

A pale yellow solid, mp. 194.2–196°C (Ref. [15] 201–202°C), ^{1}H NMR (270 MHz): 7.71 (2H, t, J = 8.1 Hz), 7.96–8.00 (2H, m), 8.29–8.33 (2H, m), 8.50–8.51 (2H, m). ^{13}C NMR (50 MHz): 122.1, 123.3, 130.3, 133.0.

3.1.3. 1,1′-Dinaphthylketone (3g)

A white solid, mp. 99–100°C (Ref. [16] 99–100°C), ^{1}H NMR (270 MHz): 7.38–7.44 (2H, m), 7.51–7.60 (6H, m), 7.89–8.02 (4H, m), 8.53–8.57 (2H, m). ^{13}C NMR (67.8 MHz): 124.4, 125.9, 126.6, 127.9, 128.5, 130.4, 131.2, 132.5, 133.9, 137.2, 199.8. IR ($CHCl_3$): 1665 (C=O) cm^{-1}. MS m/z (rel. intensity): 282 (M^+, 55), 155 (73), 127 (100).

3.1.4. 1,1′-Dinaphthyl (4g)

A white solid, mp. 145–148 and 158–159°C (Ref. [17] 144–146 and 157–159°C), ^{1}H NMR (270 MHz): 7.24–7.30 (2H, m), 7.38–7.50 (6H, m), 7.56–7.61 (2H, m), 7.94 (4H, dd, J = 8.1 and 1.1 Hz). ^{13}C NMR (50 MHz): 125.4, 125.9, 126.0, 126.6, 127.8, 127.9, 128.2, 132.9, 133.6, 138.5. MS m/z (rel. intensity): 254 (M^+, 95), 253 (100), 126 (71), 113 (45).

3.2. Typical procedure for $Pd(PPh_3)_4$-catalyzed cross-over carbonylation

In a two-necked 30 ml round-bottom flask, equipped with a septum inlet and a three-way stopcock, were placed benzeneboronic acid (0.061 g, 0.5 mmol), 4-methylbenzeneboronic acid (0.068 g, 0.5 mmol), $Pd(PPh_3)_4$ (0.058 g, 0.05 mmol) and bibenzyl (an internal standard for GLC determination). The system was then flushed with CO from a CO-filled balloon connected to the flask and dry THF (10 ml) was injected by a syringe. The mixture was stirred at 25°C for 24 h, poured into brine (50 ml) and extracted with dichloromethane (30 ml × 2). The organic phase was washed with water and dried over anhydrous Na_2SO_4. GLC analysis revealed the presence of benzophenone (**3a**) (0.042 mmol), 4-methylbenzophenone (0.094 mmol), 4,4′-dimethylbenzophenone (**3b**) (0.040 mmol), biphenyl (**4a**) (0.023 mmol), 4-methylbiphenyl (0.017 mmol) and a trace amount of 4,4′-dimethylbiphenyl (**4b**).

3.3. ^{1}H NMR monitoring procedure for the mixture of benzeneboronic acid (1a) and $Pd(PPh_3)_4$ in $CDCl_3$

In 10 ml flask, were placed benzeneboronic acid (9.6 mg, 0.079 mmol) and $Pd(PPh_3)_4$ (47.3 mg, 0.041 mmol). After 0.5 ml of $CDCl_3$ had been added to the mixture under a dinitrogen atmosphere, the decanted solution was injected into a nitrogen substituted NMR tube equipped with a septum cap by a syringe. ^{1}H NMR monitoring was carried out at irregular intervals (15 min, 1 h, 4 h, 10 h, 24 h) and at room temperature after the injection. After 26 h the tube was opened and CO was bubbled through the $CDCl_3$ solution using a glass capillary for 2 min and ^{1}H NMR monitoring was again started. Determination in CD_3OD was carried out in a similar fashion.

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[8] The ^{1}H NMR spectrum of a mixture of **1a** and $Pd(PPh_3)_4$ in CD_3OD under N_2 (in an ^{1}H NMR tube) did not show any signals other than those for the above two compounds, and new peaks due to biphenyl only appeared gradually. However, under the same conditions in $CDCl_3$ as solvent new signals at 8.02 ppm (doublet) appeared after 15 min, together with signals at 8.23 ppm (doublet) due to **1a**, both signals remaining even after 24 h with CO bubbling, but the signals at 8.02 ppm almost disappeared after 68 h. At the same time, the intensity of the multiplet peak at 7.78 ppm increased during 1–4 h and remained unchanged after that. However, we do not yet know whether these new signals can be ascribed to protons of complex **B**.

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