Palladium-Catalyzed Hydroxycarbonylation of Aryl and Vinyl Bromides by Mixed Acetic Formic Anhydride

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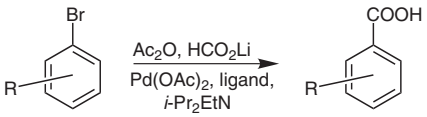
Abstract: The palladium-catalyzed hydroxycarbonylation of aryl and vinyl bromides in the presence of acetic anhydride and lithium formate as a carbon monoxide source has been developed. The combination of palladium(II) acetate with 1,1′-bis(diphenylphosphino)ferrocene (dppf) is an efficient catalytic system when the reaction is carried out at 120 °C.

Key words: hydroxycarbonylation, palladium, catalysis, aryl bromides, carboxylic acids

The transition-metal-catalyzed carbonylation of various organic substrates is important in industrial organic synthesis.[3] Hydroxycarbonylation of aryl and vinyl halides or triflates has received considerable attention.[4] Carbon monoxide is used as a substrate in such reactions. This inexpensive and readily available gas is highly toxic and must be stored in stainless steel containers.[5] The use of carbon monoxide in chemistry plants demands special equipment and expensive safety control. Thus, a new and safe technique where carbon monoxide is not introduced into the reaction mixtures, but instead is generated in situ, is highly desirable. There is additional interest in such techniques in the pharmaceutical industry. The wide use of automated combinatorial chemistry for the discovery of new drugs has led to a demand for the replacement of gaseous substrates by liquid and solid materials that are easier to handle.

In recent years, a few sources of carbon monoxide have been reported.[6] For example, carbonylation has been realized by the use of methyl formate.[7] Alper and Grushin performed the catalytic hydroxycarbonylation of aryl iodides and vinyl and benzyl halides by carbon monoxide generated in situ from chloroform and aqueous alkali.[8] Recently, Cacchi et al. reported on the use of acetic anhydride and lithium formate as precursors of carbon monoxide.[9] The mixed anhydride acetic formic anhydride was proposed as the source of carbon monoxide under these conditions. The hydroxycarboxylation of aryl iodides was carried out under mild conditions (palladium catalyst, *i*-Pr_2EtN, LiCl, DMF, 80 °C). However, aryl bromides, which are more interesting substrates for industrial applications, were sluggish to react under the reported conditions. In a limited number of examples [1,3-bis(diphenylphosphino)propane]dichloropalladium [$PdCl_2$(dppp)] was an efficient precatalyst but the reaction was very slow (64 h) and led to moderate yields of the desired products. Here we report a convenient protocol for the palladium-catalyzed hydroxycarbonylation of aryl bromides using Cacchi's source of carbon monoxide (Equation 1).



Equation 1

Our first attempt to carry out the hydroxycarbonylation of 4-bromobiphenyl under the conditions reported by Cacchi were disappointing. According to the reported procedure, lithium formate (2 equiv), acetic anhydride (3 equiv), and *N*,*N*-diisopropylethylamine (2 equiv) were reacted in *N*,*N*-dimethylformamide at room temperature for one hour, then 4-bromobiphenyl, lithium chloride, and the palladium catalyst were introduced; the reaction was performed at 80 °C. Even a simple replacement of the reported palladium catalyst [1,3-bis(diphenylphosphino)propane]dichloropalladium by a more readily available catalytic system such as tris(dibenzylideneacetone)dipalladium/1,3-bis(diphenylphosphino)propane and palladium(II) chloride/1,3-bis(diphenylphosphino)propane led to no production of the desired acid (Table 1, entries 1 and 2).

These results prompted us to search for a more efficient catalytic system for the hydroxycarbonylation reaction of aryl and vinyl bromides. A variety of phosphine ligands was examined using 4-bromobiphenyl (**1**) as a model substrate (Table 1). In this ligand screening, only 1,1′-bis(diphenylphosphino)ferrocene (dppf) (Table 1, entry 9) gave the desired product in good yield, where as tri-*tert*-butylphosphine, tri-2-tolylphosphine, triphenylphosphine, and 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) were less efficient or ineffective. Unfortunately, under these conditions 1-(4-bromophenyl)-*N*-(*tert*-butoxycarbonyl)ethylamine (**2**) provided the corresponding acid in only 35% yield (Table 2, entry 1). So we continued optimization using this less reactive substrate and varying the temperature, the palladium source, the solvent, and the amount of lithium chloride additive. The results are summarized in Table 2.

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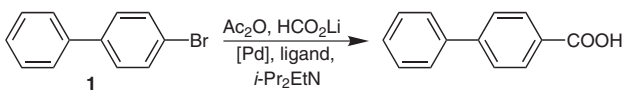
Table 1 Evaluation of Ligands for Hydroxycarbonylation of 4-Bromobiphenyl[a]

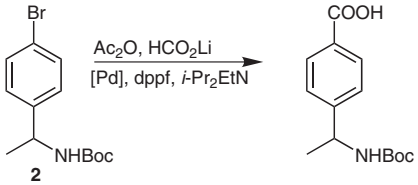


Entry	Palladium precatalyst (mol%)	Ligand (mol%)	Yield[b] (%)
1	$Pd_2(dba)_3$ (5)	dppp (10)	0
2	$PdCl_2$ (10)	dppp (10)	0
3	$Pd_2(dba)_3$ (5)	$(t\text{-Bu})_3P$ (10)	10
4	$Pd_2(dba)_3$ (5)	$(t\text{-Bu})_3P$ (20)	5
5	$Pd_2(dba)_3$ (5)	$(o\text{-Tol})_3P$ (30)	10
6	$Pd_2(dba)_3$ (5)	$(o\text{-Tol})_3P$ (60)	5
7	$Pd_2(dba)_3$ (5)	Ph_3P (30)	0
8	$Pd_2(dba)_3$ (5)	BINAP (20)	25
9	$Pd_2(dba)_3$ (5)	dppf (20)	70

[a] Reactions conditions: 4-bromobiphenyl (2 mmol), Ac_2O (2 equiv), HCO_2Li (3 equiv), *i*-Pr_2EtN (2 equiv), LiCl (3 equiv), DMF (9 mL), 80 °C, 24 h. After cooling, the mixture was diluted with EtOAc, washed with 2 M HCl, dried (Na_2SO_4) and concentrated under reduced pressure. The residue was analyzed by ^1H and ^{13}C NMR.
[b] By NMR.

We speculated that the temperature could be the crucial parameter for a successful hydroxycarbonylation reaction since both oxidative addition of bromide and thermal decomposition of intermediate acetic formic anhydride are determined by this factor. Indeed, dramatic improvement was observed by increasing the temperature (compare Table 2, entries 1, 3, and 4). When the reaction was carried out at 120 °C, a significant increase in the reaction rate was observed (86% HPLC yield after 3 h; Table 2, entry 4) and good conversion was achieved with a decreased amount of catalyst (Table 2, entries 5, 13 and 14). Contrary to Cacchi's data, no beneficial effect of lithium chloride was observed when 1,1′-bis(diphenylphosphino)ferrocene was used as a ligand at 80 °C or 120 °C (Table 2, entries 2 and 6 vs. 1 and 5). Changing the palladium source showed only a moderate effect, tris(dibenzylideneacetone)dipalladium, palladium(II) acetate, and palladium(II) chloride were effective precatalysts (Table 2, entries 4, 7 and 8). When the precatalyst/ligand ratio was changed, slightly better yields were obtained using an equimolar ratio of palladium(II) acetate and 1,1′-bis(diphenylphosphino)ferrocene (Table 2, entries 8–10). The choice of solvents was limited due to the high reactivity of the anhydrides. The reaction proceeded well in polar solvents, such as *N*,*N*-dimethylformamide and *N*-methylpyrrolidin-2-one (Table 2, entries 9 and 11). The yields decreased in dimethyl sulfoxide (Table 2, entry 12). Noteworthy was that the yield of the product was dramatically dependent on the aryl bromide concentration. The hydroxycarbonylation reaction proceeds smoothly only in dilute solutions of aryl bromide in *N*,*N*-dimethylformamide (Table 3). The hydrodebromination of bromide **2** plays a significant role when more concentrated solutions are used under these conditions.

Table 2 Optimization of Hydroxycarbonylation of Bromide **2**[a]



Entry	Palladium precatalyst (mol%)	dppf (mol%)	Temp (°C)	Time (h)	Yield (%)
1[b]	$Pd_2(dba)_3$ (5)	20	80	20	35[c]
2	$Pd_2(dba)_3$ (5)	20	80	20	45[c]
3[b]	$Pd_2(dba)_3$ (5)	20	60	20	15[c]
4[b]	$Pd_2(dba)_3$ (5)	20	120	2 3	83[d] 86[d] (70)[e]
5[b]	$Pd_2(dba)_3$ (2.5)	10	120	5	61[d]
6	$Pd_2(dba)_3$ (2.5)	10	120	5	81[d]
7	$PdCl_2$ (5)	10	120	2.5	77[d]
8	$Pd(OAc)_2$ (5)	10	120	2.5	81[d]
9	$Pd(OAc)_2$ (5)	5	120	2.5	93[d]
10	$Pd(OAc)_2$ (5)	15	120	2.5	86[d]
11[f]	$Pd(OAc)_2$ (5)	5	120	2.5	96[d]
12[g]	$Pd(OAc)_2$ (5)	5	120	2.5	64[d]
13	$Pd(OAc)_2$ (2.5)	2.5	120	2.5	97[d]
14	$Pd(OAc)_2$ (1)	1	120	2.5	92[d]

[a] Reactions conditions: bromide **2** [1 (or 2) mmol], Ac_2O (2 equiv), HCO_2Li (3 equiv), *i*-Pr_2EtN (2 equiv), DMF [5 (or 10) mL].
[b] The reaction was run in the presence of LiCl (3 equiv).
[c] NMR yield. After cooling, the mixture was diluted with EtOAc, washed with 2 M HCl, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was analyzed by ^1H and ^{13}C NMR.
[d] HPLC yield.
[e] Isolated yield.
[f] NMP was used as the solvent.
[g] DMSO was used as the solvent.

Finally, among the formic acid salts and bases, a combination of lithium formate and *N*,*N*-diisopropylethylamine was the most efficient (Table 4).

To examine the scope of this reaction, a variety of bromides was then subjected to hydroxycarbonylation. In practice, the conditions we used when the procedure was applied to other aryl bromides are as follows: aryl bromide (1 equiv, 0.18 M), $Pd(OAc)_2$/dppf (3–5 mol%), *i*-Pr_2EtN (2 equiv), HCO_2Li (3 equiv), Ac_2O (2 equiv),

Table 3 Evaluation of Substrate Concentration for Hydroxycarbonylation of Bromide **2**[a]

Entry	Concentration of ArBr (M)	Isolated yield (%)
1	0.18	75
2	0.22	79
3	0.66	44
4	0.80	38

[a] Reactions conditions: bromide **2** (0.01–0.75 mol), Ac_2O (2 equiv), HCO_2Li (3 equiv), *i*-Pr_2EtN (2 equiv), 1 mol% $Pd(OAc)_2$, 1 mol% dppf, 120 °C, 7 h.

DMF, 120 °C. The results are summarized in Table 5. The amount of catalytic system was not optimized and 3–5 mol% was employed to achieve a full conversion of starting bromide.

The hydroxycarbonylation reaction shows broad substrate generality and afforded the expected acids with good yields starting from neutral, electron-poor, and electron-rich aryl bromides (Table 5, entries 1–8). For example, 4-(trifluoromethyl)benzoic acid, which has found a number of industrial applications,[10] was obtained in 74% yield (Table 5, entry 7). Of particular note is the tolerance of different functional groups, including ketones, esters, and ethers, to these conditions. Bromonaphthalenes were also transformed to the corresponding acids with good yields (Table 5, entry 9). This protocol can be used for the synthesis of dicarboxylic acids. Indeed, terephthalic acid was obtained from 1,4-dibromobenzene in 75% yield together with a 20% yield of benzoic acid (Table 5, entry 10). The methodology was further extended to vinylic bromides. 2-Bromo-1*H*-indene gave the corresponding acid in 83% yield under standard conditions (Table 5, entry 11).

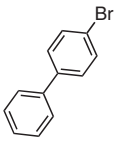
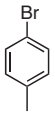
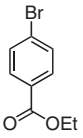
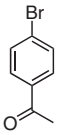
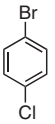
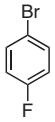
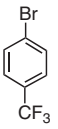
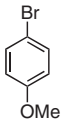
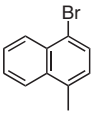
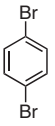
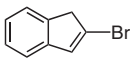
In summary, we have developed a general procedure for synthesis of carboxylic acids from aryl bromides using Cachi's source of carbon monoxide. Investigations are underway to utilize these conditions for gram- and kilogram-scale synthesis of pharmaceutical intermediates.

Table 4 Evaluation of Formate Counter Cation and Base for Hydroxycarbonylation of Bromide **2**[a]

Entry	M^+	Base	Time (h)	Yield[b] (%)
1	K^+	*i*-Pr_2EtN	15	9
2	Na^+	*i*-Pr_2EtN	15	2
3	Li^+	*i*-Pr_2EtN	2.5	92
4	Li^+	Et_3N	2.5 15	56 68

[a] Reactions conditions: bromide **2** (1 mmol), Ac_2O (2 equiv), HCO_2M (3 equiv), base (2 equiv), 1 mol% $Pd(OAc)_2$, 1 mol% dppf, 120 °C.
[b] By HPLC.

Table 5 Substrate Scope for Hydroxycarbonylation Reaction[a]

Entry	Substrate	$Pd(OAc)_2$ (mol%)	Time (h)	Yield (%)[b]
1		3	5	74[c]
2		5	2	89
3		5	1	79
4		5	1	71
5		5	3	76
6		5	1	82
7		5	1	74[d]
8		5	5	82
9		5	4	61
10		5	2	75[e]
11		5	1	83

[a] Reactions conditions: bromide (2–10 mmol), Ac_2O (2 equiv), HCO_2Li (3 equiv), *i*-Pr_2EtN (2 equiv), $Pd(OAc)_2$/dppf (1:1), DMF (5 mL/1 mmol of bromide), 120 °C.
[b] Isolated yield.
[c] 33% in the presence of 1 mol% $Pd(OAc)_2$.
[d] 36% in the presence of 3 mol% $Pd(OAc)_2$.
[e] Using Ac_2O (4 equiv), HCO_2Li (6 equiv), and *i*-Pr_2EtN (4 equiv), benzoic acid (20%) was also obtained.

Arenecarboxylic Acids; General Procedure

A soln of HCO_2Li (312 mg, 6 mmol), *i*-Pr_2EtN (697 μL, 4 mmol), and Ac_2O (377 μL, 4 mmol) in anhyd DMF (9 mL) was stirred at r.t. for 1 h under an inert atmosphere. Then, aryl bromide (2 mmol), $Pd(OAc)_2$ (22.5 mg, 0.10 mmol), and dppf (55.4 mg, 0.10 mmol) were added. The mixture was stirred at 120 °C until complete conversion of the bromide (by HPLC). After cooling, EtOAc (20 mL) and H_2O (20 mL) were added and the mixture was acidified to pH 1 with concd HCl. Two phases were separated and the aqueous layer was extracted with EtOAc (2 × 10 mL). Isolation of pure acid was achieved by extraction of the combined organic phase with 10% aq NaOH (3 × 10 mL), acidification of the aqueous phase to pH 1 with concd HCl, followed by reextraction with EtOAc (3 × 15 mL). The combined organic layers were dried (Na_2SO_4) and evaporate under reduced pressure at 80 °C. In a few cases (Table 5, entries 3, 4, 11) the pure acids were isolated by chromatography (silica gel, *n*-heptane–EtOAc, 50:50). The ^{1}H and ^{13}C NMR spectra of isolated acids (Table 5) were in accord with that reported in the literature.[11]

4-Biphenylcarboxylic Acid (Table 5, Entry 1)

Prepared from 4-bromobiphenyl (466 mg, 2 mmol) following the general procedure; mp 224–225 °C; Lit.[12] mp 225–226 °C.

^{1}H NMR (DMSO-d_6): δ = 7.45 (m, 3 H), 7.71 (d, *J* = 6.6 Hz, 2 H), 7.78 (d, *J* = 8.2 Hz, 2 H), 8.01 (d, *J* = 8.2 Hz, 2 H), 11.5 (br s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 127.76, 127.90, 129.23, 130.02, 130.57, 130.92, 139.97, 145.25, 168.08.

4-[2-(*tert*-Butoxycarbonyl)ethyl]benzoic Acid (Table 3, Entry 2)

Prepared from 1-(4-bromophenyl)-*N*-(*tert*-butoxycarbonyl)ethylamine (3.00 g, 10 mmol) following the general procedure; mp 146–147 °C.

^{1}H NMR ($CDCl_3$): δ = 1.28 (t, *J* = 7.9 Hz, 3 H), 1.35 (s, 9 H), 4.56 (q, *J* = 7.9 Hz, 1 H), 4.81 (d, *J* = 7.5 Hz, 1 H), 7.39 (d, *J* = 7.8 Hz, 2 H), 7.89 (d, *J* = 7.8 Hz, 2 H), 10.5 (br s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 23.09, 28.70, 50.00, 78.30, 126.39, 129.56, 129.84, 151.10, 155.29, 167.68.

***p*-Toluic Acid (Table 5, Entry 2)**

Prepared from 4-bromotoluene (855 mg, 5 mmol) following the general procedure; mp 180–181 °C; Lit.[12] mp 180–182 °C.

^{1}H NMR (DMSO-d_6): δ = 2.18 (s, 3 H), 7.25 (d, *J* = 8.1 Hz, 2 H), 7.82 (d, *J* = 8.1 Hz, 2 H), 11.5 (br s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 22.37, 129.93, 131.37, 132.36, 138.80, 168.85.

Terephthalic Acid Monoethyl Ester (Table 5, Entry 3)

Prepared from ethyl 4-bromobenzoate (2.29 g, 10 mmol) following the general procedure; mp 169–170 °C; Lit.[13] mp 168–170 °C.

^{1}H NMR (DMSO-d_6): δ = 1.32 (t, *J* = 7.9 Hz, 3 H), 4.32 (q, *J* = 7.9 Hz, 2 H), 8.03 (br s, 4 H), 11.5 (br s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 19.83, 66.90, 135.02, 135.17, 139.10, 140.60, 170.84, 172.32.

4-Acetylbenzoic Acid (Table 5, Entry 4)

Prepared from 4-bromoacetophenone (796 mg, 4 mmol) following the general procedure; mp 208–209 °C; Lit.[12] mp 208–210 °C.

^{1}H NMR (DMSO-d_6): δ = 2.60 (s, 3 H), 8.02 (s, 4 H), 13.2 (br s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 28.15, 129.47, 130.71, 135.71, 141.04, 167.81, 198.87.

4-Chlorobenzoic Acid (Table 5, Entry 5)

Prepared from 1-bromo-4-chlorobenzene (383 mg, 2 mmol) following the general procedure; mp 238–240 °C; Lit.[12] mp 239–241 °C.

^{1}H NMR (DMSO-d_6): δ = 7.54 (d, *J* = 8.4 Hz, 2 H), 7.92 (d, *J* = 8.4 Hz, 2 H), 7.93 (br s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 129.37, 130.38, 130.65, 144.29, 168.66.

4-Fluorobenzoic Acid (Table 5, Entry 6)

Prepared from 1-bromo-4-fluorobenzene (875 mg, 5 mmol) following the general procedure; mp 183–184 °C; Lit.[12] mp 182–184 °C.

^{1}H NMR (DMSO-d_6): δ = 7.54 (d, *J* = 8.4 Hz, 2 H), 7.92 (d, *J* = 8.4 Hz, 2 H), 7.93 (br s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 116.95 (d, *J* = 22.6 Hz), 129.10, 133.65 (d, *J* = 10.3 Hz), 166.65 (d, *J* = 250.6 Hz), 168.14.

4-(Trifluoromethyl)benzoic Acid (Table 5, Entry 7)

Prepared from 1-bromo-4-(trifluoromethyl)benzene (900 mg, 4 mmol) following the general procedure; mp 218–220 °C; Lit.[12] mp 219–220 °C.

^{1}H NMR (DMSO-d_6): δ = 7.85 (d, *J* = 8.2 Hz, 2 H), 8.12 (d, *J* = 8.2 Hz, 2 H), 12.3 (br s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 124.97 (q, *J* = 270.5 Hz), 126.69 (q, *J* = 3.2 Hz), 131.25, 133.34 (q, *J* = 31.5 Hz), 135.82, 167.35.

***p*-Anisic Acid (Table 5, Entry 8)**

Prepared from 4-bromoanisole (748 mg, 4 mmol) following the general procedure; mp 183–184 °C; Lit.[12] mp 182–185 °C.

^{1}H NMR (DMSO-d_6): δ = 3.81 (s, 3 H), 7.01 (d, *J* = 8.1 Hz, 2 H), 7.88 (d, *J* = 8.1 Hz, 2 H), 12.61 (br s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 56.60, 114.98, 124.17, 132.50, 164.03, 168.15.

4-Methyl-1-naphthoic Acid (Table 5, Entry 9)

Prepared from 1-bromo-4-methylnaphthalene (442 mg, 2 mmol) following the general procedure; mp 179–181 °C; Lit.[12] mp 179–180 °C.

^{1}H NMR (DMSO-d_6): δ = 2.71 (s, 3 H), 7.45 (d, *J* = 8.1 Hz, 1 H), 7.65 (m, 2 H), 8.06 (d, *J* = 8.1 Hz, 1 H), 8.09 (m, 1 H), 8.94 (m, 1 H), 12.9 (br s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 22.82, 125.85, 126.88, 127.31, 128.38, 131.05, 132.17, 133.63, 140.98, 170.01.

Terephthalic Acid (Table 5, Entry 11)

Prepared from 1,4-dibromobenzene (472 mg, 2 mmol) following the general procedure along with benzoic acid (20%); mp >300 °C; Lit.[12] mp >300 °C.

^{1}H NMR (DMSO-d_6): δ = 8.15 (s, 4 H), 13.41 (s, 2 H).

^{13}C NMR (DMSO-d_6): δ = 130.76, 135.93, 167.15.

1*H*-Indene-2-carboxylic Acid (Table 5, Entry 10)

Prepared from 2-bromo-1*H*-indene (780 mg, 4 mmol) following the general procedure; mp 233–235 °C; Lit.[14] mp 234–235 °C.

^{1}H NMR (DMSO-d_6): δ = 3.62 (d, *J* = 1.6 Hz, 2 H), 7.32 (m, 2 H), 7.53 (m, 2 H), 7.68 (m, 1 H), 12.9 (br s, 1 H).

^{13}C NMR (DMSO-d_6): δ = 39.06, 122.85, 123.88, 126.49, 126.83, 137.95, 139.69, 142.12, 144.18, 165.23.

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