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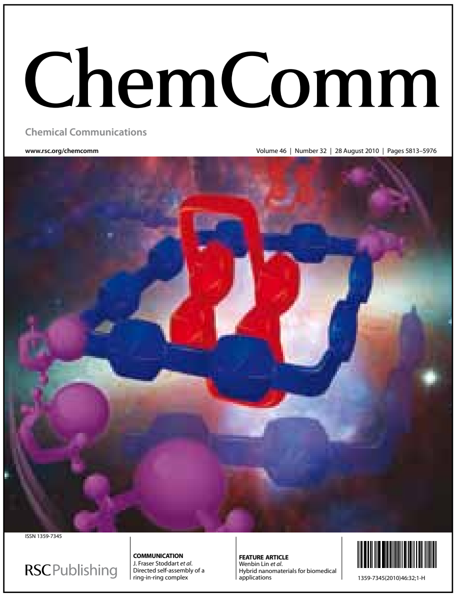

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ARTICLE TYPE

Silver(I)-catalyzed carboxylation of arylboronic esters with CO_2†

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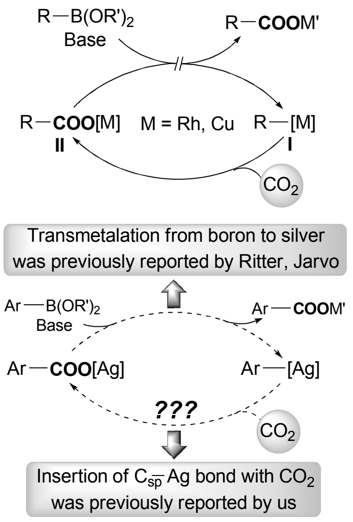
A variety of arylboronic esters were efficiently carboxylated with CO_2 using a simple AgOAc/PPh_3 catalyst, affording the corresponding carboxylic acids in good yield. This simple and efficient silver(I) catalytic system showed wide functional group compatibility.

The incorporation of CO_2 into organic substrates to provide high value-added chemicals has gained much attention, since CO_2 is an abundant, inexpensive, and renewable carbon resource.[1] In the presence of a suitable transition-metal catalyst, various carbon nucleophiles including organotin,[2] organoboron[3] and organozinc reagents,[4,5] unsaturated compounds,[6] terminal alkynes,[7] and activated C–H bonds[8] can be successfully carboxylated into carboxylic acids and derivatives[9] using CO_2 as carboxylative reagent. Among these nucleophiles, organoboronic acids and their derivatives are particularly attractive substrates due to their ease of handling, broad availability and functional group compatibility.[10,11] In 2006, Iwasawa and coworker reported that the carboxylation of aryl- and alkenylboronic esters could be smoothly carried out using $[Rh(OH)(cod)]_2$/dppp as catalyst and 3 equivalents of CsF as base.[3a] However, the rhodium catalytic system was proven to be inert toward bromo, nitro, alkynyl and vinyl substitutated organoboronic esters. This limitation was subsequently overcome by using CuI/bisoxazoline ligands catalytic system discovered by same group[3b] and *N*-heterocyclic carbene copper(I) catalysts developed by Hou et al.[3c] These copper(I) catalytic systems showed much higher chemoselectivity and wider substrate scope, epoxide, aldehyde groups were also tolerated.

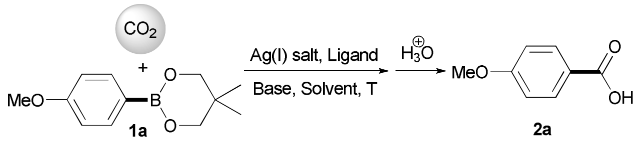
With regard to the mechanism of rhodium- or copper-catalyzed carboxylation of organoboronic esters with CO_2 (Scheme 1), active species **I** bearing a new metal–carbon bond was initially formed by transmetalation reaction of metal catalyst with organoboronic ester, subsequent insertion of CO_2 into metal–carbon bond afforded metal carboxylate **II**, which further underwent one or two transmetalation reaction regenerating **I** and simultaneously forming the new carboxylate product. It is well-known that besides rhodium and copper catalyst, silver complexes can also serve as effective catalysts for the reaction using allenyl- and arylboronic acids or esters as nucleophiles. In this reaction, transmetalation from boron to silver can easily proceed in the presence of suitable base, thus highly reactive species bearing sp^2-hybridized carbon–silver bond is thought to be formed.[12] Given that CO_2 could insert into the sp^2-hybridized carbon–silver bond to afford silver carboxylate, silver would be another metal candidate which shows expectant activity toward the carboxylation of arylboronic reagents with CO_2.[13] Indeed, in our recently developed silver(I)-catalyzed carboxylation of terminal alkynes with CO_2,[7g] the insertion of CO_2 into sp-hybridized carbon–silver bond can be easily achieved. This result leads us to ask the following question: does the smooth performance also occur in the insertion of CO_2 into sp^2-hybridized carbon–silver bond? On the basis of above mechanistic and experimental insights, we envisioned that with wise choice of ligand and base, silver complexes could be promising catalysts for the carboxylation of arylboronic esters with CO_2 (Scheme 1). Herein, we report the realization of this hypothesis, in which a variety of arylboronic esters were efficiently carboxylated with CO_2 using a simple and efficient silver(I)-based catalyst. This catalytic system showed wide substrate scopes and various functionalized carboxylic acids could be obtained in good yield.



Scheme 1 Transition-metal-catalyzed carboxylation of organoboronic esters with CO_2

Initially, the carboxylation reaction of 4-methoxyphenylboronic acid 2,2-dimethyl-1,3-propanediol ester (**1a**) with CO_2 was chosen as a model reaction to screen the optimized silver catalytic system (Table 1). A poor (25%) but encouraging yield of 4-methoxybenzoic acid (**2a**) was obtained using 10 mol % AgOAc alone as catalyst and 2 equiv of KO^{t}Bu as base (Table 1, entry 1). To our surprise, the addition of a simple PPh$_3$ ligand resulted in a remarkable increase in yield (91%) of **2a** (Entry 2). It is noteworthy that no carboxylative product was observed in the absence of any transition-metal catalyst (Entry 3). In the further ligand screening, more bulky PCy$_3$ ligand gave 85% yield (Entry 4), while strikingly decreased yield was observed for the bidentate ligand dppe (Entry 5). Compared with cheap and readily available PPh$_3$ ligand, *N*-heterocyclic carbene ligands, which were obtained by multistep synthesis, also gave lower yield (Entries 6–9).

Table 1 Silver(I)-catalyzed carboxylation of organoboronic ester **1a** with CO$_2$[a]

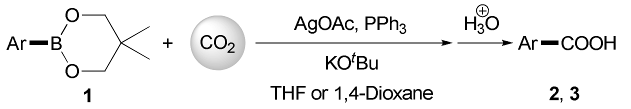


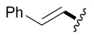
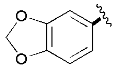
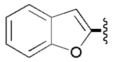
Entry	Ag(I) salt	Ligand	Base	Yield (%)[b]
1	AgOAc	-	KO^{t}Bu	25
2	AgOAc	PPh$_3$	KO^{t}Bu	91
3	-	PPh$_3$	KO^{t}Bu	-
4	AgOAc	PCy$_3$	KO^{t}Bu	85
5	AgOAc	dppe	KO^{t}Bu	35
6	AgOAc	IMes	KO^{t}Bu	55
7	AgOAc	SIMes	KO^{t}Bu	67
8	AgOAc	IPr	KO^{t}Bu	87
9	AgOAc	SIPr	KO^{t}Bu	84
10	AgF	PPh$_3$	KO^{t}Bu	83
11	AgBF$_4$	PPh$_3$	KO^{t}Bu	86
12	AgPF$_6$	PPh$_3$	KO^{t}Bu	87
13	AgNO$_3$	PPh$_3$	KO^{t}Bu	85
14	AgOAc	PPh$_3$	CsF	30
15	AgOAc	PPh$_3$	K$_2$CO$_3$	-
16[c]	AgOAc	PPh$_3$	KO^{t}Bu	80
17[d]	AgOAc	PPh$_3$	KO^{t}Bu	85
18[e]	AgOAc	PPh$_3$	KO^{t}Bu	90
19[c,e]	AgOAc	PPh$_3$	KO^{t}Bu	89
20[c,f]	AgOAc	PPh$_3$	KO^{t}Bu	57
21[c,e,g]	AgOAc	PPh$_3$	KO^{t}Bu	37
22[g]	AgOAc	PPh$_3$	KO^{t}Bu	60

[a] Reaction conditions: **1a** (0.6 mmol), silver(I) salt (0.06 mmol), ligand (0.09 mmol), base (1.2 mmol), 4 mL THF, 20 atm, 70 °C, 16 h. [b] Isolated yield. [c] 1,4-Dioxane as solvent. [d] 5 mol % AgOAc, 7.5 mol % PPh$_3$. [e] 1 mol % AgOAc, 1.5 mol % PPh$_3$, 100 °C, 8 h. [f] 0.1 mol % AgOAc, 0.15 mol % PPh$_3$, 100 °C, 8 h. [g] 2 atm of CO$_2$. dppe: 1,2-bis(diphenylphosphino)ethane. IMes: 1,3-dimesityl-imidazol-2-ylidene. SIMes: 1,3-dimesityl-imidazolin-2-ylidene. IPr: 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene. SIPr: 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene.

Combination of PPh$_3$ with other silver sources such as AgF, AgBF$_4$, AgPF$_6$ or AgNO$_3$ could also serve as effective catalysts for the carboxylation reaction (Entries 10–13). In the rhodium- or copper-catalyzed carboxylation of organoboronic esters reported by Iwasawa,[3a,3b] CsF was established as the most efficient base. However, when CsF was used as base in the AgOAc/PPh$_3$ catalytic system, only 30% yield was obtained (Entry 14). Potassium carbonate was found to be unsuitable base for this reaction system (Entry 15). The decreased catalyst loading (5 mol % Ag) resulted in a slightly lower yield of product (Entry 17). Notably, 1 mol % loading of silver catalyst at 100 °C gave good yield of **2a** in the shorter time (Entries 18 and 19). The silver catalytic system proved to be sensitive to the CO$_2$ pressure, and relatively high CO$_2$ pressure (20 atm) is beneficial to enhancing the reaction rate (Table 1, entries 2 and 22, entries 19 and 21).

Table 2 AgOAc/PPh$_3$-catalyzed carboxylation of various organoboronic esters with CO$_2$



Entry	Ar	Yield (%)[a]	
		Method A[b]	Method B[c]
1	4-MeOC$_6$H$_4$	91	89 (**2a**)
2	3-MeOC$_6$H$_4$	85	83 (**2b**)
3	4-PhOC$_6$H$_4$	75	75 (**2c**)
4	C$_6$H$_5$	90	86 (**2d**)
5	4-MeC$_6$H$_4$	83	82 (**2e**)
6	4-^{t}BuC$_6$H$_4$	85	86 (**2f**)
7	4-FC$_6$H$_4$	80	82 (**2g**)
8	2-ClC$_6$H$_4$	89	88 (**2h**)
9	3-ClC$_6$H$_4$	87	84 (**2i**)
10	4-ClC$_6$H$_4$	84	83 (**2j**)
11	4-BrC$_6$H$_4$	70	71 (**2k**)
12	4-IC$_6$H$_4$	79	76 (**2l**)
13	2-CF$_3$C$_6$H$_4$	88	84 (**2m**)
14	3-CF$_3$C$_6$H$_4$	73	79 (**2n**)
15	4-CF$_3$C$_6$H$_4$	70	74 (**2o**)
16	3-NO$_2$C$_6$H$_4$	77	75 (**2p**)
17	4-CNC$_6$H$_4$	74	77 (**2q**)
18	4-(CH$_2$=CH)C$_6$H$_4$	82	79 (**2r**)
19	4-PhC$_6$H$_4$	70	80 (**2s**)
20	1-naphthyl	72	76 (**2t**)
21	2-naphthyl	77	75 (**2u**)
22	2-furanyl	83	78 (**2v**)
23	2-thienyl	84	81 (**2w**)
24	3-thienyl	80	83 (**2x**)
25	4-HCOC$_6$H$_4$	76	72 (**2y**)
26	4-MeCOC$_6$H$_4$	65	65 (**2z**)
27	4-MeOOCC$_6$H$_4$	60	61 (**3a**)
28	4-(PhC≡C)C$_6$H$_4$	84	82 (**3b**)
29		81	80 (**3c**)
30		80	85 (**3d**)
31		64	67 (**3e**)

[a] Isolated yield. [b] Reaction conditions: **1** (0.6 mmol), AgOAc (0.06 mmol), PPh$_3$ (0.09 mmol), KO^{t}Bu (1.2 mmol), 4 mL THF, 20 atm, 70 °C, 16 h. [c] Reaction conditions: **1** (0.6 mmol), AgOAc (0.006 mmol), PPh$_3$ (0.009 mmol), KO^{t}Bu (1.2 mmol), 4 mL 1,4-dioxane, 20 atm, 100 °C, 8 h.

Once established that AgOAc/PPh$_3$ can function as efficient catalyst for carboxylation of 4-methoxyphenylboronic esters with CO$_2$, the substrate scope of arylboronic esters was then

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investigated under two optimized reaction conditions: Method A: 10 mol % AgOAc, 15 mol % PPh_3, 2 equiv. KO^tBu, THF, 20 atm, 70 °C, 16 h. Method B: 1 mol % AgOAc, 1.5 mol % PPh_3, 2 equiv. KO^tBu, 1,4-dioxane, 20 atm, 100 °C, 8 h (Table 2). These silver(I) catalytic systems showed high level of generality and a wide range of functional groups were tolerated, from electron-rich aryl ethers (Table 2, entries 1–3, and 30) to electron-withdrawn aryltrifluoromethyl, arylnitro, , arylcyano, arylaldehyde, arylketone and arylester functionalities (Table 2, entries 13–17, 25–27). Chloro and trifluoromethyl groups at *ortho*, *meta*, and *para* positions were all compatible with the reaction conditions (Table 2, entries 8–10, and 13–15). Boronic esters with heteroaromatic derivatives were also found to be suitable substrates (Table 2, entries 22–24, and 31). Notably, similar to copper catalytic systems, the silver(I) catalytic system proved applicable for bromo, iodo, nitro, vinyl and alkynyl substituted organoboronic esters which are inactive toward rhodium catalytic systems (Table 2, entries 11, 12, 16, 18 and 28). Another advantage of the presented silver(I) catalytic system is that AgOAc and PPh_3 are all inexpensive and commercially available, which make it more attractive for the potentially practical applications.

In summary, we report a simple and efficient AgOAc/PPh_3 catalyst for the carboxylation of arylboronic esters with CO_2. The catalytic system shows wide functional group compatibility and a variety of functionalized carboxylic acids can be obtained in good yield. Efforts on the detailed mechanism and expansion of this silver catalytic system are currently ongoing in our laboratory.

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† Electronic Supplementary Information (ESI) available: Experimental procedures, analytical data and copies of NMR spectra. See DOI: 10.1039/b000000x/

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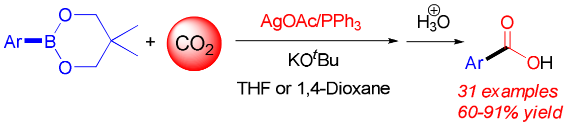
Silver(I)-catalyzed carboxylation of arylboronic esters with CO_2

Xiao Zhang, Wen-Zhen Zhang,* Ling-Long Shi, Chun-Xiao Guo, Ling-Ling Zhang and Xiao-Bing Lu*



Carboxylation of arylboronic esters with CO_2 was achieved using a simple and efficient AgOAc/PPh_3 catalyst, affording various functionalized carboxylic acids in good yield.