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Tandem one-pot CO₂ reduction by PMHS and silyloxy carbonylation of aryl/vinyl halides to access carboxylic acids†

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The present study discloses the synthesis of aryl/vinyl carboxylic acids from Csp²-bound halides (Cl, Br, I) in a carbonylative path by using silyl formate (from CO₂ and hydrosilane) as an instant CO-surrogate. Hydrosilane provides hydride for reduction and its oxidation product silanol serves as a coupling partner. Mono-, di-, and tri-carboxylic acids were obtained from the corresponding aryl/vinyl halides.

Aryl carboxylic acids are an important class of raw materials for the manufacturing of pharmaceuticals, fertilizers, polymers and nutritional products.¹ For example, *p*-phthalic acid and 2,6-naphthalenedicarboxylic acid are raw materials for PET and PEN respectively and BTC (benzene tricarboxylic acid) is the organic constituent of useful MOFs (Fig. 1).² Making aryl carboxylic acids through integration of CO₂ (carbon dioxide) is an ideal process. On that account, extensive carboxylation methods were developed.^{3,4}

Apart from direct use of CO₂ to install a carboxyl group,⁴ treating CO₂ as a CO-surrogate for carbonylation reactions has gained much attention in recent years^{5–7} and in certain cases, carboxylic acids or esters were obtained. For example, in 2013, Leitner and co-workers reported hydrocarboxylation of alkenes with CO₂ and H₂ to get carboxylic acids.⁶ In 2014, Beller *et al.* used alcohols as the reductant to reduce CO₂ forming CO *in situ* and then applied it in the following alkoxy carbonylation reaction giving esters as the product.⁷ The key point in these reactions of using CO₂ as a CO surrogate is to reduce CO₂ to CO with a suitable reductant. Hydrosilanes, as non-toxic and moisture stable leftover products of the silicone industry, were proved as cheap hydride sources for hydride transfer reductions.⁸ With hydrosilane, CO₂ can be transformed into silyl formate under mild conditions which can be hydrolysed to formic acid or further reduced to methanol or methane.⁹ Recently, silyl formate *in situ*

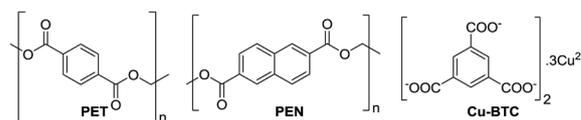


Fig. 1 Occurrence of carboxylic acids in polymers.

formed from CO₂ and hydrosilane has been explored as a CO surrogate for formylation of alkenes or aryl halides to form aldehydes (Scheme 1a and b).¹⁰ As a formate ester, we anticipated its applicability in C–C bond formation through alkoxy carbonylation type reactions like other formate esters,¹¹ and we are interested in developing a strategy to use silyl formate in carbonylation reactions for getting products other than aldehydes/alcohols. Here, we present our preliminary results about getting carboxylic acids through a Cu(II)–Pd(II) catalysed tandem CO₂ reduction-silyloxy carbonylation reaction of aryl halides (Scheme 1c).

In the reported process of formylating aryl halides or alkenes, the intermediate silyl formate was supposed to form CO and silanol by decomposition. The available hydride source (H₂ or Si–H) in the reaction system led to the hydrogenolysis of the acyl complex [R(C=O)ML], providing aldehyde as the final product and silanol as the byproduct.^{10b} We assumed that the silanol could act as a nucleophilic coupling partner and attack the acyl complex giving a silyl ester as the product.

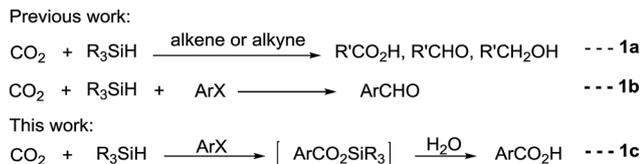
Among the available hydrosilanes, PMHS (polymethylhydrosiloxane) is the cheapest (1–5 \$ per kilogram) hydride donor and has low effective mass per hydride (60).^{8b} Silyl formate was prepared from CO₂ (balloon) and R₃SiH catalysed by Cu(OAc)₂/L1 (1,2-bis(diphenylphosphanyl)-benzene (BDP)) following a modified procedure (P1) from Baba *et al.*,^{9a} which was promptly utilized as a CO surrogate to examine the conditions for silyloxy carbonylation (P2). Using 2-bromo naphthalene **1a** as the substrate, we added Pd(OAc)₂/xanthphos (L2)/Et₃N into the silyl formate solution and progressed the reaction at 100 °C in a closed vessel. After normal workup, 2-naphthalene carboxylic acid **2a** was obtained in 60% yield along with some unidentified mixtures (Table 1, entry 1), supporting that, in the absence of

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Communication

Scheme 1 Carbonylations with CO₂ as a CO surrogate.

hydride, silanol can serve as the nucleophile to yield silyl ester. To improve the yield of **2a**, we screened solvents for silyloxycarbonylation reaction (Table 1 and Table S1, ESI[†]), and found that toluene is a better solvent. With a 1:2 ratio of dioxane–toluene, the yield was improved a little with incomplete conversion (Table 1, entry 2). With a 1:4 ratio of dioxane–decane, both conversion and yield were increased (Table 1, entry 3). When 1:4 dioxane–toluene was used, 98% isolated yield was obtained (Table 1, entry 4). At this stage, a parallel study of different silyl hydrides (Table 1, entries 4–6 and Table S2, ESI[†]) revealed that PMHS and (EtO)₃SiH are excellent reagents for the silyloxycarbonylation reaction.

With PMHS and 1:4 dioxane–toluene, the relative performance of various Pd(II)-catalysts was studied and endorsed that Pd(OAc)₂/L2 was the best for the reaction (Table S3, ESI[†]). Decreasing the loading of L2 or Pd(OAc)₂ resulted in a lower yield of **2a** (Table 1, entries 7 and 8). A comparative study affirmed that Et₃N was a preferable base as *N,N*-diisopropylethylamine (DIPEA) showed lower yield (Table 1, entry 9). Finally, 3 mol% Pd(OAc)₂ with 6 mol% L2 in a 1:4 ratio of dioxane–toluene was accepted as the optimized conditions for the silyloxycarbonylation process (Table 1, entry 4). Controlled experiments confirmed that all the reagents, the catalyst, the solvent ratio and the temperature are essential for the silyloxycarbonylation to produce carboxylic acid **2a** in higher yield (Table S4, ESI[†]).

Table 1 Reaction condition optimization^a

Entry	Dioxane/solvent (V/V)	R ₃ SiH	Conv ^b (%)	Yield ^b (2a %)
1	Dioxane (1:2)	PMHS	> 95	60
2	Toluene (1:2)	PMHS	78	65
3	^b Decane (1:4)	PMHS	> 95	67
4	Toluene (1:4)	PMHS	> 95	98 ^c
5	Toluene (1:4)	Ph ₂ SiH ₂	> 95	82
6	Toluene (1:4)	(EtO) ₃ SiH	> 95	93 ^c
7 ^d	Toluene (1:4)	PMHS	> 95	45
8 ^e	Toluene (1:4)	PMHS	> 95	90 ^c
9 ^f	Toluene (1:4)	PMHS	> 95	90 ^c

^a Reaction conditions: **P1**: CO₂ (balloon), Cu(OAc)₂·H₂O (1 mol%), L1 (1.5 mol%), R₃SiH (2.5 mmol); **P2**: **1a** (1.0 mmol); Pd(OAc)₂ (3 mol%), L2 (6 mol%), Et₃N (2.5 mmol), 100 °C, 3 h. ^b Calculated by ¹H NMR, > 95% conversion means no substrate can be detected. ^c Isolated yield. ^d Pd(OAc)₂/L2 = 1/1, 6 h. ^e Pd(OAc)₂ (1 mol%), 5 h. ^f DIEPA (2.5 mmol) as the base, 4 h.

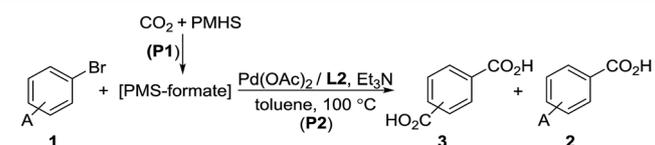
Table 2 Silyloxycarbonylation of bromoaryls^a

Entry	1, A =	Time (h)	Product 2 yield ^b (%)
1	1b , H	5	2b , 72
2	1c , 4-CO ₂ CH ₃	1.5	2c , 94
3	1d , 4-COCH ₃	4	2d , 72
4	1e , 4-CHO	2	2e , 97
5	1f , 4-NO ₂	7	2f , 96
6 ^c	1g , 4-Cl	0.5	2g , 77
7	1h , 4-OCH ₃	7	2h , 90
8	1i , 3,4-(methylenedioxy)	3	2i , 96
9	1j , 3-NO ₂	10	2j , 77
10	1k , 2-F	7	2k , 45
11	1l , 3-F-4-CH ₃	4	2l , 84
12	2m : 7 h, 94% 2n : 6 h, 75% 2o : 12 h, 54% 2p : 3-CO ₂ H, 7 h, 92% 2q : 6-CO ₂ H, 3 h, 78%		

^a Reaction conditions: **P1**, **P2**: see Table 1. ^b Isolated yield based on **1**. ^c 90 °C.

With the optimized conditions in hand, the substrate scope and generality of the reaction were explored. For the *para*-substituted bromobenzenes, regardless of the electron-withdrawing or -donating nature, the corresponding benzoic acids were obtained in good to excellent yields (Table 2) *via* a silyloxycarbonylation reaction starting from CO₂ and PMHS. For example, simple benzoic acid **2b** was obtained in 72% yield from bromobenzene **1b** (Table 2, entry 1). Functional groups such as ester, ketone, aldehyde, nitro, chloro and ether can all be tolerated in the reaction, giving yields in the range of 72–97% (Table 2, entries 2–8). For substrate **1g** with a Cl group at the *para*-position, two potential reaction sites lead to a mixture of two products, 4-chlorobenzoic acid **2g** and terephthalic acid. Therefore, after tuning the reaction time (30 min) we got **2g** in 77% yield at 90 °C. Compared with **1f** bearing a nitro group at the 4-position, **1j** having a nitro group at the 3-position under the same reaction conditions gave a lower yield of 77% (Table 2, entry 9). For substrate **1k** bearing fluoride at the *ortho*-position, the reaction provided **2k** in 45% yield because of the incomplete conversion (Table 2, entry 10). The low conversion is due to the steric hindrance of the fluoride. For 3-fluoro-4-methyl-bromobenzene **1l**, the silyloxycarbonylation reaction still proceeded smoothly, providing **2l** in 84% yield (Table 2, entry 11). Heterocyclic bromides **1m–q** were also good substrates for the reaction. Starting from CO₂ and PMHS, corresponding carboxylic acids **2m–q** were obtained in good to excellent yields (Table 2, entry 12).

From the reaction result of **1g**, we can deduce that: (1) multi carboxylic acids can be anticipated from aryl multi halides; (2) chlorobenzenes can also be feasible substrates for the silyloxycarbonylation reaction. So, we expected that, by increasing the amount of PMHS and Pd(II)/L2, iterative silyloxycarbonylation of dihalides could occur and yield dicarboxylated products. After a few trials, we found that 5 mol% Pd catalyst and four

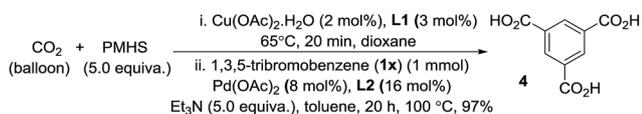
Table 3 Silyloxycarbonylation of aryl multi halides^a


Entry	1, A =	Time (h)	3, yield ^b (%)	2, yield ^c (%)
1	1g , 4-Cl	16	3a , 63	2g , 33
2 ^d	1r , 3-I	16	3b , 62	2r , 20
3	1s , 4-Br	8	3a , 93	0
4	1t , 4-Br-3-CH ₃	20	3c , 72	0
5				
		3d , 10 h, 93%	3e , 16 h, 91%	3f , 16 h, 84%

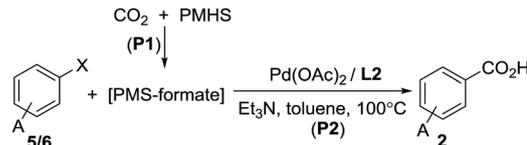
^a Reaction conditions: **P1**: CO₂ (balloon), Cu(OAc)₂·H₂O (2 mol%), **L1** (3 mol%); **P2**: **1** (1.0 mmol), Pd(OAc)₂ (5 mol%), **L2** (10 mol%), Et₃N (4.0 mmol), PMHS (4.0 mmol), 100 °C. ^b Isolated yield based on **1**. ^c Calculated from ¹H NMR. ^d **2r** = 3-bromo benzoic acid.

equivalents of PMHS were effective enough for successful dicarboxylation. So, under these conditions, dihalo benzene **1g** produced a mixture of terephthalic acid **3a** (63%) along with **2g** (33%) (Table 3, entry 1). Similarly, **1r** resulted in a mixture of **3b** (62%) and 3-Br-benzoic acid **2r** (20%) (Table 3, entry 2) (*vide infra*). Encouragingly, exclusive dicarboxylic acids **3a**, **3c** and **3d-f** were obtained from the corresponding aryl di-bromides **1s-w** (Table 3, entries 3–5). Utilization of CO₂ to make these dicarboxylic acids was not reported in the literature, and for the first time we made these dicarboxylic acids through CO₂ incorporation using the present method. To check the extent of iterative silyloxycarbonylation, tribromobenzene **1x** was subjected to tricarboxylation with an excess of PMHS and catalyst, and trimesic acid **4** (BTC) was obtained in almost quantitative yield (97%, Scheme 2).

Enlightened from the dicarboxylation of **1g** and **1r** that chloro and iodo aryls can also participate in the carboxylation process, we next focused on the conversion of iodo and chloro aryls. Under the same conditions of bromo aryls, iodoaryls **5a-d** yielded the carboxylic acids **2b**, **2d**, **2f**, and **2h** in comparable yields with their bromo-congeners (Table 4, entries 1–4). Similarly, *meta*-substituted iodoaryl **5e** gave **2s** in 76% yield (Table 4, entry 5). In the case of **1r**, having I and Br at the 1,3-position, the mono silyloxycarbonylation produced 3-Br-benzoic acid **2r** in 52% yield indicating that the reaction of iodide is favored over bromide (Table 4, entry 6). Only activated chloroaryls **6a-d** with electron withdrawing groups at the *para* position underwent the silyloxycarbonylation reaction and produced the corresponding acids **2c-f** (Table 4, entries 7–10) in good yields but with relatively long reaction times owing to their lower reactive profiles. But chloro aryl **6e** produced **2t** only in 20% yield (Table 4, entry 11). Also, 2,6-dichloropyridine **6f** and 2-chloroquinoline **6g** yielded the



Scheme 2 Silyloxycarbonylation of 1,3,5-tribromobenzene.

Table 4 Silyloxycarbonylation of chloro and iodo aryls^a


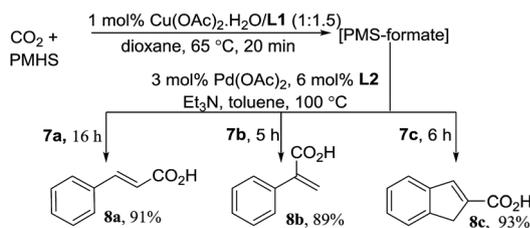
Entry	5 or 6, X/A	Time (h)	2, yield ^a (%)
1	5a , I/H	5	2b , 84
2	5b , I/4-COCH ₃	4	2d , 85
3	5c , I/4-NO ₂	10	2f , 85
4	5d , I/4-OCH ₃	5	2h , 60
5	5e , I/3-COCH ₃	2	2s , 76 ^b
6	1r , I/3-Br	2	2r , 52
7	6a , Cl/4-CO ₂ CH ₃	16	2c , 83
8	6b , Cl, 4-COCH ₃	14	2d , 45
9	6c , Cl/4-CHO	5	2e , 93
10	6d , Cl/4-NO ₂	14	2f , 60
11	6e , Cl/3-CO ₂ CH ₃	20	2t , 20
12	6f , 2,6-dichloropyridine	10	2u , 45
13	6g , 2-chloroquinoline	5	2v , 45

^a The same as that in Table 2. ^b Treated with MeOH/H⁺ and isolated as methyl ester.

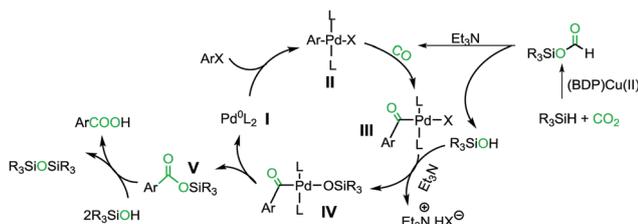
corresponding acids **2u** and **2v** respectively in 45% yield (Table 4, entries 12 and 13). Overall, in the present carboxylation process, the iodo congeners showed similar reactivity while the chloro congeners showed suppressed yields and took longer reaction times.

We found that the present strategy also functioned on vinyl bromides. Alkenoic acids **8a-c** were obtained in excellent yields from the corresponding bromides **7a-c** under the standard conditions of mono carboxylation. The products maintained retention of geometry from the corresponding bromoalkenes (Scheme 3).

During the mechanism study, to rule out the role of formic acid in the reaction,¹² prior hydrolysis of silyl formate and then carbonylation was performed and no product was formed (see Table S5, ESI[†]). Here, under our conditions, CO gas was detected by GC upon heating the silyl formate in the presence of Et₃N,¹³ which implied the possibility of CO involved



Scheme 3 Silyloxycarbonylation of vinyl bromides.



Scheme 4 Proposed mechanism of silyloxycarbonylation.

carbonylation. After releasing CO, silanol R_3SiOH was left and it was supposed to participate in the reaction to form the silyl ester. To check the silyl ester, the reaction mixture before hydrolyzing was analyzed by NMR (Fig. S1–S5, ESI[†]). The results of 1H NMR showed the presence of $(EtO)_3SiOSi(EtO)_2OH$ and a little up field shift for Ar-protons of **2a** (Fig. S1 and S2, ESI[†]). In ^{13}C NMR spectra (Fig. S3 and S4, ESI[†]), chemical shifts at δ 165.0 and δ 171.3 ppm were ascribed to **2a'** ($ArCO_2Si(OEt)_3$) and **2a** respectively. Also, ^{29}Si NMR showed two peaks at δ –85.3 and –85.5 ppm attributed to $(EtO)_3SiOSi(EtO)_2OH$. The third peak at δ –92.5 ppm implied the signal for **2a'** (Fig. S5, ESI[†]). Based on these results, we proposed the mechanism shown in Scheme 4. The formation of free acid could be possible by dimerization of silanol while hydrolysing the silyl ester. Usual water work-up hydrolyses the silyl ester and liberates the carboxylic acid.

In conclusion, we have developed an efficient silyloxycarbonylation strategy to make carboxylic acids from CO_2 utilizing PMHS as a source of both non-metallic reductant and nucleophilic coupling partner. The strategy works in one-pot tandem Cu(II)-catalysed reduction–Pd(II)-mediated silyloxycarbonylation reaction involving silyl formate as a CO-surrogate. The method is applicable to produce mono-, di-, and tricarboxylic acids from iodo/bromo/chloro aryls and vinyl bromides, in good to excellent yields. This work provides a novel strategy of utilizing CO_2 as a CO-surrogate to get carboxylic acids. Further application of this strategy to other carbonylative reactions is underway.

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Conflicts of interest

There are no conflicts to declare.

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- In a separate experiment formic acid was used as a CO surrogate and the carbonylation reaction was checked (see Table S6, ESI[†]).
- Enhanced CO production was found compared to simple thermal decomposition.