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Visible Light-Driven Carboxylation of Aryl Halides by the Combined Use of Palladium and Photoredox Catalysts

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Supporting Information Placeholder

ABSTRACT: A highly useful, visible light-driven carboxylation of aryl bromides and chlorides with CO_2 was realized using a combination of $Pd(OAc)_2$ as a carboxylation catalyst and $Ir(ppy)_2(dtbpy)(PF_6)$ as a photoredox catalyst. This carboxylation reaction proceeded in high yields under 1 atm of CO_2 with a variety of functionalized aryl bromides and chlorides without the necessity of using stoichiometric metallic reductants.

As a method to utilize CO_2 as a one-carbon source, the carboxylation reaction of organic halides via the Grignard reagents is one of the most basic reactions in organic synthesis. More recently, the transition metalcatalyzed carboxylation of organic halides such as aryl, alkenyl and alkyl halides with CO2 has attracted considerable attention and several reactions have been developed using Pd, Ni and Cu catalysts.^{1,2} However, these reactions necessitate the use of an excess amount of metallic reductants such as $ZnEt_2^{1a,1d,2e}$ and $Zn^{1c,2c}$ or $Mn^{1b,e-i,2a-d,f,g}$ powder, which is not desirable from the standpoint of the development of environmentallybenign processes (Scheme 1). Thus, it is highly desirable to develop a useful carboxylation reaction of organic halides, which does not necessitate the use of a stoichiometric metallic reductant. In this paper, we report a useful and general method for Pd-catalyzed carboxylation^{1a,g,2e,3,4} of aryl bromides and chlorides just by using Pd/photoredox dual catalysts^{5,6,7} in the presence of an amine as an electron donor instead of an excess amount of metallic reductants under visible light irradiation (Scheme 1).^{8,9}

We first examined the carboxylation of 3,4-(methylenedioxy)bromobenzene **1a** using catalytic amounts of Pd(OAc)₂, 2-dicyclohexylphosphino-2',4',6'triisopropylbiphenyl (Xphos)^{1a} and various photoredox Scheme 1. Transition metal-catalyzed carboxylation of aryl halides



catalysts under visible light irradiation in the presence of an excess amount of *i*Pr₂NEt as an electron-donor under a CO₂ atmosphere at room temperature (Table 1, entry $1 \sim 3$). Ru(bpy)₃(PF₆)₂ 4a, which was employed in the Rh-catalyzed hydrocarboxylation,⁹ was found to give the desired carboxylic acid 2a albeit in low yield, and the hydrogenated product 3a was also produced as a byproduct (entry 1). The conversion of substrate 1a and the vield of carboxylic acid 2a were improved with $Ir(ppy)_2(dtbpy)(PF_6)$ 4c having a higher reduction potential (entry 3). In this carboxylation reaction, palladium catalyst, photoredox catalyst, amine, light irradiation and CO_2 gas were all necessary, and lack of one component suppressed the reaction (Table S1). To further improve the yield of the carboxylation product, it was necessary to suppress the formation of the hydrogenated product 3a. As the ammonium salts of hydrogen bromide and carboxylic acid were thought to be produced with the progress of the reaction, addition of base was examined.¹⁰ And it was found that a better result was obtained by carrying out the reaction in the presence of Cs_2CO_3 as a base (entry 3 vs 4). The efficiency of the reaction was further improved by using 2-diphenylphosphino-2',4',6'triisopropylbiphenyl (PhXphos) as a less electrondonating ligand (entry $4 \sim 6$), and the carboxylic acid 2a was produced in 88% yield with 2.5 mol% each of $Pd(OAc)_2$ and $Ir(ppy)_2(dtbpy)(PF_6)$ 4c (entry 7).

Table 1. Screening of reaction conditions



entry	Ligand	Catalyst	Additive	Conv. /% ^a	Yield	
					2a	3a
1^b	Xphos	4 a	none	12	3	9
2^b	Xphos	4b	none	48	12	25
3 ^{<i>b</i>}	Xphos	4 c	none	100	48	45
4	Xphos	4 c	Cs_2CO_3	93	58	28
5	tBuXphos	4 c	Cs_2CO_3	100	65	13
6	PhXphos	4 c	Cs_2CO_3	93	75	10
7^c	PhXphos	4 c	Cs_2CO_3	100	88	6

^{*a*} Determined by ¹H-NMR spectra. ^{*b*} Using *i*Pr₂NEt (6.0 equiv.). ^{*c*} Using Ir catalyst **4c** (2.5 mol%).



Generality of the reaction was examined using various functionalized aryl bromides (Table 2). A wide range of substrates bearing alkyl 1c, alkoxy 1d, halide 1e~g, internal alkyne 1k and alkene 1l at 4-position gave the corresponding methyl ester derivatives in good yield after the methyl esterification with trimethylsilyldiazomethane (TMSCHN₂).¹¹ In particular, with 4chlorobromobenzene 1g as a substrate, 4-chlorobenzoate 5g was selectively obtained. Cobalt- and nickelcatalyzed carboxylations of sterically hindered aryl triflates was reported by the Tsuji's group,^{2d} but 2,6diisopropylphenyl triflate did not give the carboxylic acid under their conditions. On the contrary, the carboxvlation of equally congested 2.4.6triisopropylbromobenzene **1n** proceeded in 76% yield by the combined use of Pd and photoredox catalysts probably because the electron-transfer step was not affected by steric congestion so much. The bromides of electronrich heteroarenes such as thiophene **10** and indole **1p**,**q** also gave the methyl esters **50~q**. On the other hand, the reaction of bromobenzenes containing ester 1i, ketone 1r and nitrile 1j gave the carboxylic acids 2i,j,r in low to

moderate yields and the hydrogenated products were produced more than other bromobenzenes under the conditions using PhXphos (Table S14). This result was attributed to the direct reduction of bromobenzene derivatives by a photoredox catalyst,¹² and in these cases, the desired carboxylic acids were obtained in good yield by using tBuXphos as an electron-rich phosphine ligand (Table S13). These results also showed that carbonyl and cyano groups were compatible in this reaction. Thus, by the appropriate choice of the Xphos type ligands, the carboxylation of a variety of bromobenzenes proceeded just by using catalytic amounts of the Pd catalyst and the photoredox catalyst under atmospheric pressure of CO₂ using amine as an electron donor. It is also noted that the yields were improved compared to the reaction using ZnEt₂ in most cases probably because the side reaction of arylpalladium bromide intermediate with Et₂Zn was avoided in this reaction.^{1a}

Table 2. Substrate scope of aryl bromides

	2. Substrat	e scope e	/1 al yl i	0101	mues	
A . D.	CO Pd(OAc PhXphc Ir(ppy) ₂ (dtbpy)					
Ar—Br 1a-r	Cs ₂ CO <i>I</i> Pr ₂ NE DMA, rt, <i>h</i>	Аг-СО ₂ іме 5а-г				
		R =				
R	CO ₂ Me	5b H	85%	5h NHBoc		77% ^b
		5c Me	88%	5i COOMe		76% ^b
		5d OMe	91%	5j CN		76% ^b
		5e CF ₃ 5f F	83% 96%	5k	-}ті	PS 85%
		5g Cl	90% ^a	51	2 de la companya de l	82%
 O 	CO ₂ Me	Ĉ	,CO₂Me `Me		iPr iPr	CO ₂ Me /Pr
	5a 91%	5m 80%		5n 76% ^{<i>c</i>}		
Ľ,	CO ₂ Me	R = Boo	CO ₂ M	e		CO ₂ Me
		H	5q 45%		51 67	70

^{*a*} Reaction time is 4 hour. ^{*b*} Using *t*BuXphos instead of PhXphos. ^{*c*} Reaction time is 8 hour.

Next, we examined the reaction of aryl chlorides. The carboxylation of aryl chlorides was reported using a Ni catalyst,^{1b} but the reaction using a Pd catalyst has not been reported yet. Under the reaction conditions of aryl bromides using PhXphos, 4-trifluoromethylchlorobenzene **6e** gave the corresponding carboxylic acid **2e** in 31% yield, and the unreacted **6e** was partially recovered. However, by using *t*BuXphos as an electron-rich ligand, the carboxylic acid **2e** was obtained in 96% yield probably due to the acceleration of

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59 60 the oxidative addition step (Table S15). Various aryl chlorides gave the corresponding methyl esters in good yield after the methyl esterification with TMSCHN₂ (Table 3). In the Pd-catalyzed carboxylation reaction using ZnEt₂, the aryl chlorides did not give the carboxylic acids.^{1a} On the contrary, the present reaction proceeded with a wide variety of substrates, and the carboxylation of various functionalized aryl chlorides proceeded in good yield by using the photoredox catalyst and *i*Pr₂NEt.



Concerning the mechanism of this reaction, the following results have been obtained. As the resting state of this reaction, PhPdBr(Xphos) was observed by a ³¹P-NMR spectrum under the catalytic reaction conditions (Figure S1).¹³ It was also found that the first reduction potential of the isolated PhPdBr(Xphos) was -2.28 V (vs Fc/Fc^{+}), which was much lower than the reduction potential of the reductant Ir(II) (Figure S4).^{14,15} Interestingly, CV measurement of this complex under CO₂ atmosphere showed a new peak at about -1.4 V.¹⁶ From these data, two major possibilities are thought to exist for the actual palladium species reduced during the reaction (Scheme 2). The first one is (ArCOO)PdX(Xphos) C generated in a small amount in equilibrium with ArPdX(Xphos) **B** under CO_2 (path a).¹³ Photoredoxcatalyzed one-electron reduction of C would give (ArCOO)Pd(I)(Xphos) **D** and X⁻, and the generated **D** would undergo further one-electron reduction to give Ar(0)(Xphos) and $ArCOO^{-}$. In this case, the reduction of the carboxylate complex C would shift the equilibrium and the carboxylation reaction would proceed catalytically.¹⁷ The other possibility of the reducible species is a CO₂-coordinated ArPd(II)X(Xphos) E, again generated in a small amount, and this species would be able to undergo one-electron reduction to give a CO₂-coordinated ArPd(I)(Xphos) species F, which would have higher ability to undergo addition to CO₂ to give (ArCOO)Pd(I)(Xphos) **D** (path b). This would then undergo the similar process as described above.¹⁸

In our previous Rh/photoredox dual catalysis for hydrocarboxylation reaction, the key Rh(I) hydride complex was generated by two-electron and two-proton transfers to Rh(I) carboxylate complex to give dihydride Rh(III) carboxylate complex, which eliminated the carboxylic acid salt with the assistance of a base.⁹ On the contrary, in the present system, it is likely that the direct reduction of Pd(II) species to Pd(0) through successive two-electron transfer proceeded by the photoredox catalysis.

Scheme 2. Proposed mechanism



In conclusion, we have developed a novel direct carboxylation of aryl halides by the combined use of a carboxylation $Pd(OAc)_2$ as catalyst and $Ir(ppy)_2(dtbpy)(PF_6)$ 4c as a photoredox catalyst using *i*Pr₂NEt as an easily available, non-metallic electrondonor. This carboxylation of aryl bromides and chlorides does not necessitate the use of a stoichiometric metallic reductant, and proceeded in good yield with various functionalized aryl bromides and chlorides by using appropriate ligands, PhXphos or tBuXphos. In particular, the transition metal-catalyzed carboxylation of a very sterically hindered 2,4,6-triisopropylbromobenzene 1n and the Pd-catalyzed carboxylation of aryl chlorides were realized for the first time. Application of this carboxylation reaction to other transition metal catalysts and expansion of the substrate scope such as alkenyl and alkyl halides are now in progress.

ASSOCIATED CONTENT

Supporting Information. Detailed experimental procedures, spectral data, analytical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Reduction of aryl halides could proceed by the photoredox catalyst and an amine under photo-irradiation conditions in the absence of Pd catalyst. However, there would also be a Pd-catalyzed reduction process because the amount of the hydrogenated product was increased under the same conditions in the presence of Pd(OAc)₂ amd Xphos. For more discussions on the formation of the reduction product, see SI.

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(13) No detectable formation of (PhCOO)PdBr(Xphos) was observed when PhPdBr(Xphos) was subjected to a CO₂ atmosphere, and it is possible that there is an equilibrium between PhPdBr(Xphos) and (PhCOO)PdBr(Xphos), the former of which is thermodynamically more stable. The decarboxylation of palladium carboxylates is a well-known process, although usually higher temperature is required. See: (a) Myers, A. G.; Tanaka, D.; Mannion, M. R. J. Am. Chem. Soc. 2002, 124, 11250. (b) Tanaka, D.; Romeril, S. P.; Myers, A. G. J. Am. Chem. Soc. 2005, 127, 10323. (c) Dickstein, J. S.; Mulrooney, C. A.; O'Brien, E. M.; Morgan, B. J.; Kozlowski, M. C. Org, Lett. 2007, 9, 2441. (d) Wang, Z.; Ding, Q.; He, X.; Wu, J. Org. Biomol. Chem. 2009, 7, 863. (e) Shang, R.; Xu, Q.; Jiang, Y. Y.; Wang, Y.; Liu, L. Org. Lett. 2010, 12, 1000. See SI for more detailed discussions on the mechanism of this reaction.

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(16) This new peak was rather weak, but repeated experiments confirmed its presence. See SI for details.

(17) The counter cations of the halide and carboxylate anions are both protons generated from the oxidized amine, and these two acids are neutralized with the excess Cs_2CO_3 and/or amine.

(18) Prior additional one-electron reduction of CO₂-coordinated ArPd(I)(Xphos) to $[ArPd(0)(Xphos)]^-$ to work as the actual carboxylation species is also conceivable.

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