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Nickel-Catalyzed Carboxylation of Aryl and Vinyl Chlorides Employing Carbon Dioxide

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Supporting Information

ABSTRACT: Nickel-catalyzed carboxylation of aryl and vinyl chlorides employing carbon dioxide has been developed. The reactions proceeded under a CO_2 pressure of 1 atm at room temperature in the presence of nickel catalysts and Mn powder as a reducing agent. Various aryl chlorides could be converted to the corresponding carboxylic acid in good to high yields. Furthermore, vinyl chlorides were successfully carboxylated with CO_2. Mechanistic study suggests that Ni(I) species is involved in the catalytic cycle.

Carbon dioxide is an ideal C1 source owing to its abundance, low cost, nontoxicity, and good potential as a renewable source.[1] However, it is not easy to activate such a thermodynamically and kinetically stable material. Therefore, efficient conversion of CO_2 with the aid of transition-metal catalysts is highly attractive.[2] In particular, hydrocarboxylation of carbon−carbon unsaturated compounds such as alkynes,[3a,b] alkenes,[3c] and 1,2- and 1,3-dienes[3d,e] is very promising. In addition, carboxylation reactions of arylzinc[4] and arylboronic esters[5] with CO_2 have been studied intensively, since in these reactions various functionalities that are not compatible with Grignard reagents were tolerated. However, these zinc and boron compounds must be prepared from the corresponding aryl halides prior to the catalytic reactions. Thus, direct carboxylation of the parent aryl halides is most desirable, as this is a more straightforward transformation.[6]

Catalytic carboxylation of aryl halides employing CO_2 was first developed as *electrochemical* reactions in the presence of nickel[7a−c] and palladium catalysts.[7d,e] Unfortunately, these were not efficient synthetic methods, and the scope of possible substrates was quite restricted. Later, nonelectrochemical carboxylation of aryl bromides and chlorides using CO_2 was carried out in the presence of *stoichiometric* amounts of Ni(0) complexes.[8] Recently, carboxylation of aryl bromides employing CO_2 was performed *catalytically* using a palladium complex as the catalyst.[9] However, in this reaction, the catalytic activity was not satisfactory, since (1) the more reactive aryl *bromides* should be employed as substrates, while the less reactive and more accessible aryl chlorides did not react at all; (2) the reaction must be carried out under a CO_2 pressure of 10 atm at 40 °C to achieve good yields; (3) the highly reactive and pyrophoric $ZnEt_2$ must be employed as the reducing agent; (4) large amounts (up to 17%) of arenes were inevitably formed as byproducts through hydrogenative debromination. Herein, we report a much more efficient catalytic reaction, in which a less noble nickel catalyst is highly active in carboxylation of aryl *chlorides* as well as vinyl chlorides under a CO_2 pressure of 1 atm at room temperature, with easy-to-handle Mn powder used as the reducing agent.

Reaction of 1-butyl-4-chlorobenzene (**1a**) was carried out using a mixture of $NiCl_2(PPh_3)_2$ (5.0 mol %) and added PPh_3 (10 mol %) as a catalyst with Mn powder (Aldrich, 99.99%, 3.0 equiv) as a reducing agent, in the presence of Et_4NI (10 mol %) in 1,3-dimethyl-2-imidazolidinone (DMI) at 25 °C under a CO_2 pressure of 1 atm (Table 1). The yield of 4-butylbenzoic acid (**2a**) was determined by gas chromatography (GC) analysis after derivatization to the corresponding methyl ester (**2a-Me**).[10] Under standard conditions, **2a-Me** was obtained in 95% yield. Unlike the Pd-catalyzed reaction,[9] only a small amount (<5%) of butylbenzene was afforded. Compound **2a** was isolated from the reaction mixture in 84% yield (entry 1). Without the added PPh_3 (i.e., with only $NiCl_2(PPh_3)_2$ as the catalyst), the yield of **2a-Me** was reduced to 53%, and the biaryl (**3a**) was obtained in 27% yield (entry 2). In the absence of $NiCl_2(PPh_3)_2$, **1a** was not converted, and **2a-Me** and **3a** were not obtained at all (entry 3). When the reaction was carried out under an Ar atmosphere, **1a** was not converted (entry 4).[11] These results clearly indicated that the arylmanganese species would not be formed through the reactions of aryl chlorides with Mn powder, either in the absence or in the presence of a nickel catalyst. The Mn powder was essential, and no reaction would proceed without it (entry 5). Et_4NI was also indispensable for the carboxylation (entry 6). When Et_4NBr and Et_4NCl were used in place of Et_4NI, no conversion of **1a** was observed. Employing a mixture of $NiCl_2\{P(4\text{-}MeOC_6H_4)_3\}_2$ (5.0 mol %) with added $P(4\text{-}MeOC_6H_4)_3$ (10 mol %) as a catalyst, the yield of **2a-Me** decreased considerably (entry 7). Other ligands such as tricyclohexylphosphine (PCy_3), 1,2-diphenylphosphinoethane (dppe), and 2,2′-bipyridine (bpy) suppressed the carboxylation completely (entries 8−10). Other reducing agents such as Zn powder or Mg turning gave either a low product yield or no product (entries 11 and 12). In DMF as the solvent, **2a-Me** was obtained in 64% yield with the formation of **3a** (9%). The reaction in THF afforded **2a-Me** and **3a** in 7% and 22% yields, respectively, while in toluene the reaction did not proceed at all.

Carboxylation of various aryl chlorides (**1b−k**) was carried out (Table 2). Aryl chlorides bearing both electron-rich (entry

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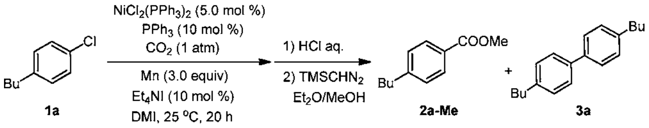
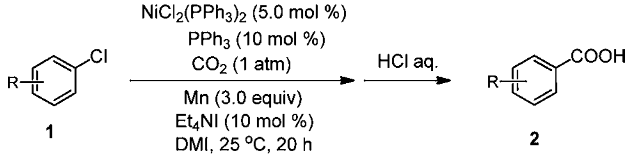
Table 1. Nickel-Catalyzed Carboxylation of 1a Employing Carbon Dioxide[a]

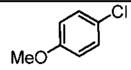
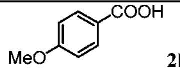
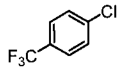
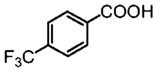
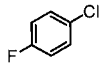
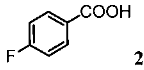
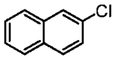
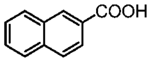
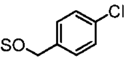
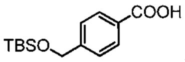
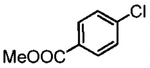
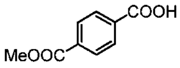
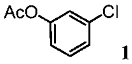
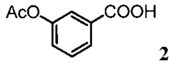
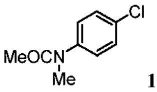
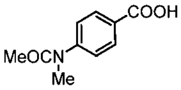
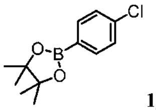
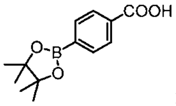
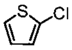
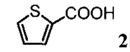
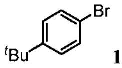
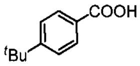
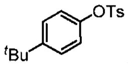
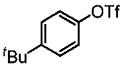
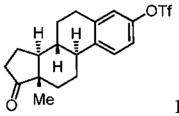
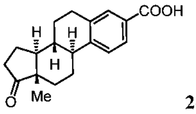


		yield (%)[b]	
entry	catalyst system: change from standard conditions	2a-Me	3a
1	standard conditions	95 (84)[c]	0
2	without added PPh_3	53	27
3	without $NiCl_2(PPh_3)_2$	0	0
4	without CO_2 (under Ar)	–	trace
5	without Mn powder	0	0
6	without Et_4NI	trace	trace
7	$P(4\text{-}MeOC_6H_4)_3$ in place of PPh_3[d]	53	0
8	PCy_3 in place of PPh_3[d]	0	0
9	dppe in place of PPh_3[e]	0	0
10	bpy in place of PPh_3[e]	0	0
11	Zn in place of Mn	9	27
12	Mg in place of Mn	0	0

[a] Reaction conditions: 1-butyl-4-chlorobenzene (**1a**, 0.50 mmol), $NiCl_2(PPh_3)_2$ (0.025 mmol, 5.0 mol %), PPh_3 (0.050 mmol, 10 mol %), Mn powder (1.5 mmol, 3.0 equiv), Et_4NI (0.050 mmol, 10 mol %), in DMI (0.75 mL), at 25 °C for 20 h. [b] Determined by GC analysis. [c] Isolated yield of **2a**. [d] A mixture of $NiCl_2L_2$ (0.025 mmol) and added L (0.050 mmol) was used as the catalyst: L = $P(4\text{-}MeOC_6H_4)_3$ or PCy_3. [e] A mixture of $NiCl_2L'$ (0.025 mmol) and L′ (0.025 mmol) was used as the catalyst: L′ = dppe or bpy.

Table 2. Nickel-Catalyzed Carboxylation of Various Aryl Chlorides and Other Derivatives[a]



Entry	Substrate 1	Product 2	Yield (%)[b]
1[c]	 **1b**	 **2b**	90
2[c]	 **1c**	 **2c**	74
3	 **1d**	 **2d**	81
4	 **1e**	 **2e**	78
5	 **1f**	 **2f**	87
6[c]	 **1g**	 **2g**	76
7	 **1h**	 **2h**	82
8	 **1i**	 **2i**	72
9[d]	 **1j**	 **2j**	58
10[e]	 **1k**	 **2k**	52
11	 **1l**	 **2l**	80
12[f]	 **1m**	**2l**	73
13[f]	 **1n**	**2l**	72
14[f]	 **1o**	 **2o**	51

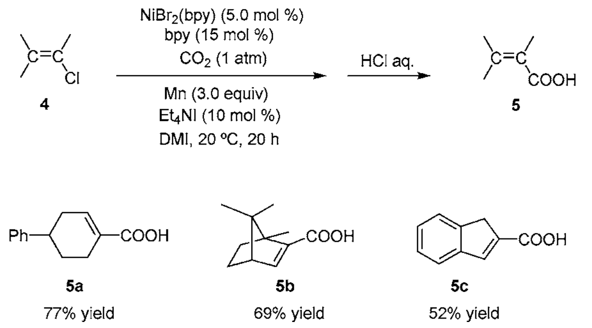
[a] Reaction conditions; **1** (0.50 mmol), $NiCl_2(PPh_3)_2$ (0.025 mmol, 5.0 mol %), PPh_3 (0.050 mmol, 10 mol %), Mn powder (1.5 mmol, 3.0 equiv), Et_4NI (0.050 mmol, 10 mol %), in DMI (0.75 mL), at 25 °C for 20 h. [b] Isolated yield. [c] A mixture of $NiCl_2\{P(4\text{-}MeOC_6H_4)_3\}_2$ (0.025 mmol, 5.0 mol %) and $P(4\text{-}MeOC_6H_4)_3$ (0.050 mmol, 10 mol %) was used as the catalyst at 40 °C for 24 h. [d] At 35 °C for 24 h. [e] At 35 °C for 30 h. [f] $NiCl_2(PPh_3)_2$ (0.050 mmol, 10 mol %), PPh_3 (0.10 mmol, 20 mol %), Mn powder (1.5 mmol, 3.0 equiv), Et_4NI (0.1 mmol, 20 mol %), in DMI (0.75 mL), at 60 °C for 20 h.

1) and electron-poor (entries 2 and 3) moieties gave the corresponding carboxylic acids (**2b–d**) in high yields. 2-Chloronaphthalene and an aryl chloride bearing a *tert*-butyldimethylsilyl (TBS) group provided the corresponding carboxylic acids in good yields (entries 4 and 5). Gratifyingly, ester (entries 6 and 7) and amide (entry 8) functionalities, which were not tolerated with organomagnesium and organolithium reagents, remained intact under the present reaction conditions. A boronic acid ester (entry 9) and a thiophene ring (entry 10) were also found to be compatible functionalities. An aryl bromide (**1l**) gave the corresponding carboxylic acid (**2l**) in 80% yield (entry 11). Aryl tosylate (**1m**) and triflates[13] (**1n** and **1o**) also provided the corresponding carboxylic acids at 60 °C (entries 12–14). Unfortunately, *ortho*-substituted aryl chlorides and aryl chlorides bearing hydroxyl or amino groups could not be used as substrates.

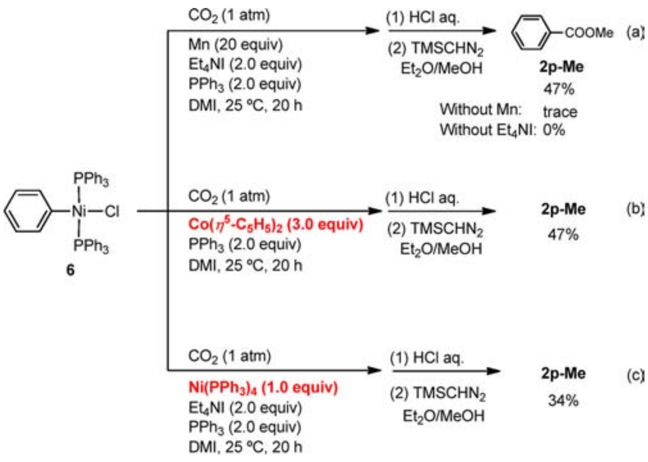
To date, vinyl chlorides[13] have not been successfully utilized in the carboxylation employing CO_2. In the presence of the nickel catalyst bearing bpy as the ligand, the aliphatic vinyl chlorides (**4a** and **4b**) afforded the corresponding *α*,*β*-unsaturated carboxylic acid in high yield (Scheme 1). The vinyl chloride conjugated with an aryl ring (**4c**) was also converted to the corresponding carboxylic acid in moderate yield.

To gain insight into the catalytic mechanism, we carried out stoichiometric reactions using $NiPhCl(PPh_3)_2$ (**6**), which was prepared by oxidative addition of chlorobenzene to $Ni(PPh_3)_4$.[14] In the presence of CO_2 (1 atm), Mn powder, Et_4NI, and PPh_3 (similar conditions to the catalytic reaction), **6** afforded the carboxylated product (**2p-Me**) in 47% yield after derivatization to the corresponding methyl ester (Scheme 2a). However, upon removal of either Mn powder or Et_4NI from the reaction systems, either a trace amount of **2p-Me** or no product at all was obtained (Scheme 2a). Thus, both Mn and Et_4NI were found to be indispensable for the carboxylation of **6**. Interestingly, a typical homogeneous reducing agent $Co(\eta^5\text{-}C_5H_5)_2$ ($E^{\circ\prime}$ = −1.33 V vs Fc/Fc^+ in CH_2Cl_2)[15] can replace the Mn/Et_4NI system to afford **2p-Me** in the same yield (Scheme 2b). Therefore, the Mn/Et_4NI system may operate to reduce Ni(II) to Ni(I). Electrochemical measurements showed that Ni(II) complexes could be reduced to the corresponding Ni(I)

Scheme 1. Nickel-Catalyzed Carboxylation of Vinyl Chlorides[a]



Scheme 2. Stoichiometric Reactions Relevant to Mechanism

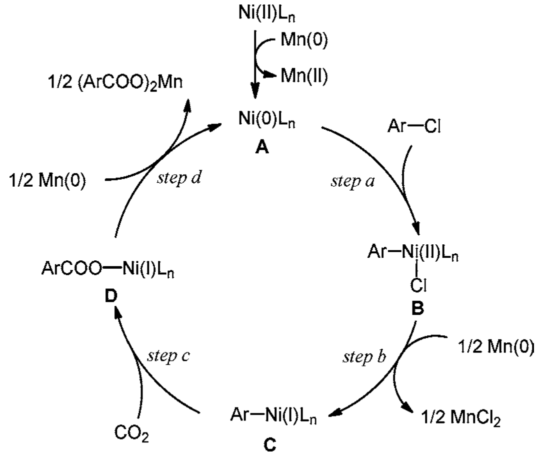


species around −0.8 V (vs SCE in DMF).[7c] Et$_4$NI could assist the electron transfer from Mn to the nickel catalyst center via the bridging of the iodide ion.[12b,16] On the other hand, it was reported that Ni(PPh$_3$)$_4$ reacted with NiCl$_2$(PPh$_3$)$_2$ to provide the Ni(I) species.[17] As shown in Scheme 2c, Ni(PPh$_3$)$_4$ could replace Mn to afford **2p-Me** in 34% yield. These results strongly indicate that the Ni(I) species[18] plays an important role in the present catalytic carboxylation. Such Ni(I) species were also postulated in the electrochemical carboxylation.[7c]

With the observations in Schemes 2, a possible catalytic cycle for the nickel-catalyzed carboxylation of aryl chlorides with CO$_2$ is proposed, as shown in Scheme 3. First, the Ni(II) complex must be reduced to a Ni(0) species (**A**). Then, oxidative addition of the aryl chloride (**1**) takes place to give a Ni(II) intermediate (**B**) (step a). As suggested by the stoichiometric reaction in Scheme 2, Ni(II) would be reduced by the Mn/Et$_4$NI system to afford Ni(I) intermediate (**C**) (step b). The generation of Ni(I) species was observed in electrochemical reactions.[7c] Then, nucleophilic Ni(I) (**C**) reacts with CO$_2$ to give the carboxylatonickel intermediate (**D**) (step c). Finally, reduction of **D** by Mn gives the corresponding manganese carboxylate, and the Ni(0) catalyst species is regenerated (step d).

In conclusion, a nickel-catalyzed, highly efficient carboxylation of aryl and vinyl chlorides employing CO$_2$ has been developed. The present reactions proceeded under a CO$_2$ pressure of 1 atm at room temperature. The Ni(I) species is involved in the catalytic cycle with the aid of the Mn/Et$_4$NI system as an efficient reducing agent. Further studies on the reaction are now in progress.

Scheme 3. Plausible Reaction Mechanism



■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and characterization of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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