

# Palladium-Catalyzed Carboxylation of Benzyl Chlorides with Atmospheric Carbon Dioxide in Combination with Manganese/Magnesium Chloride

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An efficient direct carboxylation of a series of benzyl chlorides with CO<sub>2</sub> catalyzed by Pd(OAc)<sub>2</sub>/dicyclohexyl (2',6'-dimethoxy-[1,1'-biphenyl]-2-yl)phosphine (SPhos) was developed to afford the corresponding phenylacetic acids in combination with Mn powder as a reducing reagent and MgCl<sub>2</sub> as an indispensable additive. The reaction proceeded smoothly under 1 atm CO<sub>2</sub>.

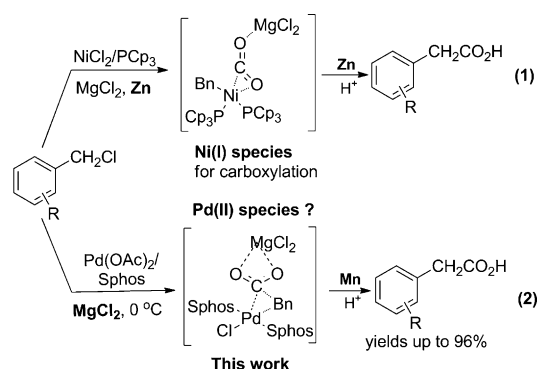
The application of Mn powder instead of a sensitive reducing reagent represents an operationally simple access to phenylacetic acids. Notably, MgCl<sub>2</sub> is able to stabilize the (SPhos)<sub>2</sub>Pd<sup>II</sup>(Bn)(Cl)(η<sup>1</sup>-CO<sub>2</sub>)(MgCl<sub>2</sub>) adduct and thus facilitates CO<sub>2</sub> insertion into the Pd<sup>II</sup>-C bond, which is supported by a DFT study.

## Introduction

CO<sub>2</sub> has attracted worldwide attention as an ideal C<sub>1</sub> source because of its high abundance, low cost, nontoxic nature, non-flammability, and renewability. In particular, the synthesis of carboxylic acids through C-C bond formation with CO<sub>2</sub> is highly promising in CO<sub>2</sub> fixation. However, the thermodynamic stability and kinetic inertness of CO<sub>2</sub> hinders its transformation processes. In this regard, transition metal complexes have been proven to be promising catalysts for efficient carboxylation reactions with CO<sub>2</sub> to furnish an excellent alternative to classical methods for carboxylic acids.<sup>[1-5]</sup> A series of reagents such as arenes,<sup>[1]</sup> alkenes,<sup>[2]</sup> allenes,<sup>[3]</sup> alkynes,<sup>[4]</sup> and organic halides/boronic esters<sup>[5]</sup> undergo smooth conversion with CO<sub>2</sub> in the presence of transition metal species.

Metal powder as a promising reductant has found wide application in reductive coupling<sup>[6]</sup> and reductive carboxylation reactions<sup>[5,7,8]</sup> thanks to its characteristics of low cost, lack of sensitivity, and ease of work-up. The carboxylation of active allylic halides mediated by Zn<sup>0</sup> or In<sup>0</sup> without the addition of catalysts displayed a high regioselectivity.<sup>[7c,d]</sup> Recently, Ni-catalyzed carboxylation reactions that start from aryl and benzyl halides as well as allyl esters with metal powder as a reductant have been established<sup>[5]</sup> and present a wide functional-group tolerance. Additionally, the formation of the Ni<sup>I</sup> intermediate is

crucial for successful carboxylation (Scheme 1). The Co-catalyzed carboxylation of propargyl acetates was also described by Tsuji et al. in the presence of Mn powder at room temperature.<sup>[8]</sup>



**Scheme 1.** Ni- or Pd-catalyzed carboxylation of benzyl chlorides in the presence of metal powder.

Ni- and Co-catalyzed carboxylation reactions mediated by a stoichiometric amount of metal have been well investigated, which inspired us to investigate the compatibility of metal powder in Pd-catalyzed carboxylation. Furthermore, numerous computational studies have focused on the mechanism of carboxylation with CO<sub>2</sub>,<sup>[9]</sup> whereas the Pd-catalyzed direct carboxylation and the CO<sub>2</sub> insertion mechanism into the Pd<sup>II</sup>-C bond remain a puzzle. We envisaged that CO<sub>2</sub> insertion into the Pd<sup>II</sup>-C bond probably depends on the choice of additive. Herein, we describe the Pd-catalyzed carboxylation of benzyl chloride with metal powder and additive under atmospheric CO<sub>2</sub> and tentatively explore the process of CO<sub>2</sub> insertion into the Pd<sup>II</sup>-C bond in a computational study (Scheme 1).

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## Results and Discussion

The carboxylation of benzyl chloride (**1a**) as the model substrate was investigated initially in the presence of additives by using Pd(OAc)<sub>2</sub>/ligand system under 1 atm CO<sub>2</sub> in DMF (Table 1). To recycle the catalyst, easy-to-handle metal powder instead of sensitive reagent was used as a reductant. To the best of our knowledge, this is the first example of the use of metal powder in the Pd-catalyzed carboxylation reaction. Unsurprisingly, trace **2a** was observed in the absence of any additive (entry 1, Table 1), which suggests that an additive is crucial to perform the carboxylation. However, NBu<sub>4</sub><sup>+</sup>, which could assist electron transfer,<sup>[5b]</sup> was detrimental to the carboxylation and facilitated the dehalogenation (**3a**) and the cross-coupling reaction (**4a**)<sup>[10]</sup> (entry 2). The application of CsF, which could activate CO<sub>2</sub>,<sup>[4f]</sup> suppressed the conversion of **1a** significantly (entry 3).

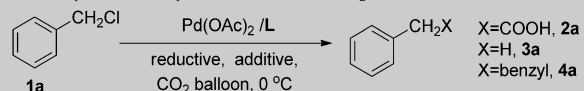
Interestingly, the presence of ZnCl<sub>2</sub> led to the formation of **2a** albeit with low conversion (entry 4). Finally, the addition of MgCl<sub>2</sub> resulted in a high yield of **2a** (77%) with a suppression of the formation of **3a** and **4a** (entry 5). It has been reported that magnesium halide could promote the CO<sub>2</sub> insertion into the Ni<sup>I</sup>-C bond,<sup>[9f]</sup> which suggests that MgCl<sub>2</sub> probably is also involved in the CO<sub>2</sub> insertion into the Pd<sup>II</sup>-C bond. These results stimulated us to further investigate the role of MgCl<sub>2</sub> in the Pd-catalyzed carboxylation by a DFT study. Additional control experiments with **1a** indicated that almost no **2a** was observed in the absence of ligand or metal powder (entries 6 and 7). Among the ligands tested, the use of dicyclohexyl-[2',6'-dimethoxy-[1,1'-biphenyl]-2-yl)phosphine (SPhos) facilitated the formation of phenylacetic acid (**2a**) with the inhibition of **3a** and **4a** (entries 5 and 8–10). Zn<sup>0</sup> and Fe<sup>0</sup> just gave a trace amount of **2a** (entries 11 and 12). Mn powder showed the best performance by giving a high yield of **2a** and a suppression of the formation of **3a** and **4a** (entry 5).

Encouraged by these results, we turned our attention to explore the scope of this carboxylation reaction. A variety of substituted benzyl chlorides delivered the corresponding phenylacetic acids in moderate to excellent yields (entries 1–10, Table 2). 2-(Chloromethyl)naphthalene also gave the desired product (**2k**) in good yield (entry 11). Interestingly, substrates that bear electron-withdrawing moieties gave higher yields than those that bear electron-donating moieties.

Clearly, this carboxylation protocol showed a good compatibility of functional groups such as ether (**2b**), alkyl (**2c**, **2d**, **2e**), and carbonyl (**2f**, **2g**). The *ortho* substituent (**2h**) did not hamper the carboxylation reaction. Furthermore, halo (**2h**, **2i**) and even vinyl groups (**2j**) remained intact, which allows further manipulation, for example, cross-coupling reactions.

As expected, no reaction occurred in the absence of Pd(OAc)<sub>2</sub> and SPhos, which indicates that Mn<sup>0</sup> itself could not insert into the C-Cl bond of benzyl chloride (Scheme S1a in the Supporting Information). Furthermore, a higher amount of **3a** was obtained in the absence of ligand (Scheme S1b),

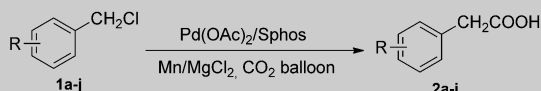
**Table 1.** Pd-catalyzed carboxylation of **1a** with CO<sub>2</sub>.<sup>[a]</sup>

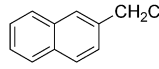


Entry	Ligand	Reductant [2.5 equiv.]	Additive [1.4 equiv.]	<b>2a</b> <sup>[b]</sup> [%]	<b>3a</b> <sup>[c]</sup> [%]	<b>4a</b> <sup>[c]</sup> [%]
1	SPhos	Mn	–	trace	12	32
2	SPhos	Mn	NBu <sub>4</sub> <sup>[e]</sup>	17	8	35
3	SPhos	Mn	CsF	5	2	2
4	SPhos	Mn	ZnCl <sub>2</sub>	22	16	1
5	SPhos	Mn	MgCl <sub>2</sub>	77	23	trace
6	–	Mn	MgCl <sub>2</sub>	0	76	1
7	SPhos	–	MgCl <sub>2</sub>	trace	0	0
8	PPh <sub>3</sub>	Mn	MgCl <sub>2</sub>	22	65	trace
9	PCy <sub>3</sub>	Mn	MgCl <sub>2</sub>	5	12	1
10	Xantphos <sup>[d]</sup>	Mn	MgCl <sub>2</sub>	4	47	13
11	SPhos	Zn	MgCl <sub>2</sub>	trace	66	10
12	SPhos	Fe	MgCl <sub>2</sub>	5	23	17

[a] Reaction conditions: Pd(OAc)<sub>2</sub> (11.2 mg, 3.3 mol%), ligand (0.10 mmol, 6.6 mol%), benzyl chloride (186 mg, 1.47 mmol), reductant (2.5 equiv.), additive (1.4 equiv.), DMF 2 mL, 0 °C, CO<sub>2</sub> balloon, 12 h. [b] <sup>1</sup>H NMR yield with 1-chloro-2,4-dinitrobenzene as the internal standard. [c] GC yield with biphenyl as the internal standard. [d] Xantphos = (9,9-dimethyl-9H-xanthene-4,5-diyl)bis(diphenylphosphine); [e] NBu<sub>4</sub><sup>+</sup> (369 mg, 1 mmol).

**Table 2.** Pd-catalyzed carboxylation of various benzyl chlorides with CO<sub>2</sub>.<sup>[a]</sup>



Entry	R	Product (yield <sup>[b]</sup> [%])
1	<b>1a</b> , R = <i>p</i> -H	<b>2a</b> (77)
2	<b>1b</b> , R = <i>p</i> -OMe	<b>2b</b> (68)
3	<b>1c</b> , R = <i>p</i> -Me	<b>2c</b> (74)
4	<b>1d</b> , R = <i>m</i> -Me	<b>2d</b> (68)
5	<b>1e</b> , R = <i>p</i> -tBu	<b>2e</b> (66)
6	<b>1f</b> , R = <i>p</i> -ethoxycarbonyl	<b>2f</b> (88)
7	<b>1g</b> , R = <i>p</i> -acetyl	<b>2g</b> (86)
8	<b>1h</b> , R = <i>o</i> -Cl	<b>2h</b> (92)
9	<b>1i</b> , R = <i>m</i> -F	<b>2i</b> (96)
10	<b>1j</b> , R = <i>p</i> -vinyl	<b>2j</b> (49)
11	<b>1k</b> , 	<b>2k</b> (78)

[a] Unless otherwise stated, the reactions were performed with 1.47 mmol substrates in the presence of 0.05 mmol Pd(OAc)<sub>2</sub>, 0.10 mmol SPhos, 200 mg Mn powder, and 200 mg MgCl<sub>2</sub> at 0 °C, 1 atm CO<sub>2</sub>, 12 h in 2 mL DMF. [b] <sup>1</sup>H NMR yield with 1-chloro-2,4-dinitrobenzene as the internal standard.

which suggests that a small amount of nonligated Pd<sup>0</sup> species is generated in situ, which promotes the dehalogenation of benzyl chloride to give benzylmanganese chloride. Furthermore, **4a** is generated through the Pd<sup>0</sup>/SPhos-catalyzed cross-coupling reaction of benzyl chloride and benzylmanganese chloride (Scheme 2).<sup>[10]</sup> Then, to investigate whether the benzylmanganese chloride is the actual intermediate, benzylmanganese chloride generated in situ was exposed to CO<sub>2</sub> in

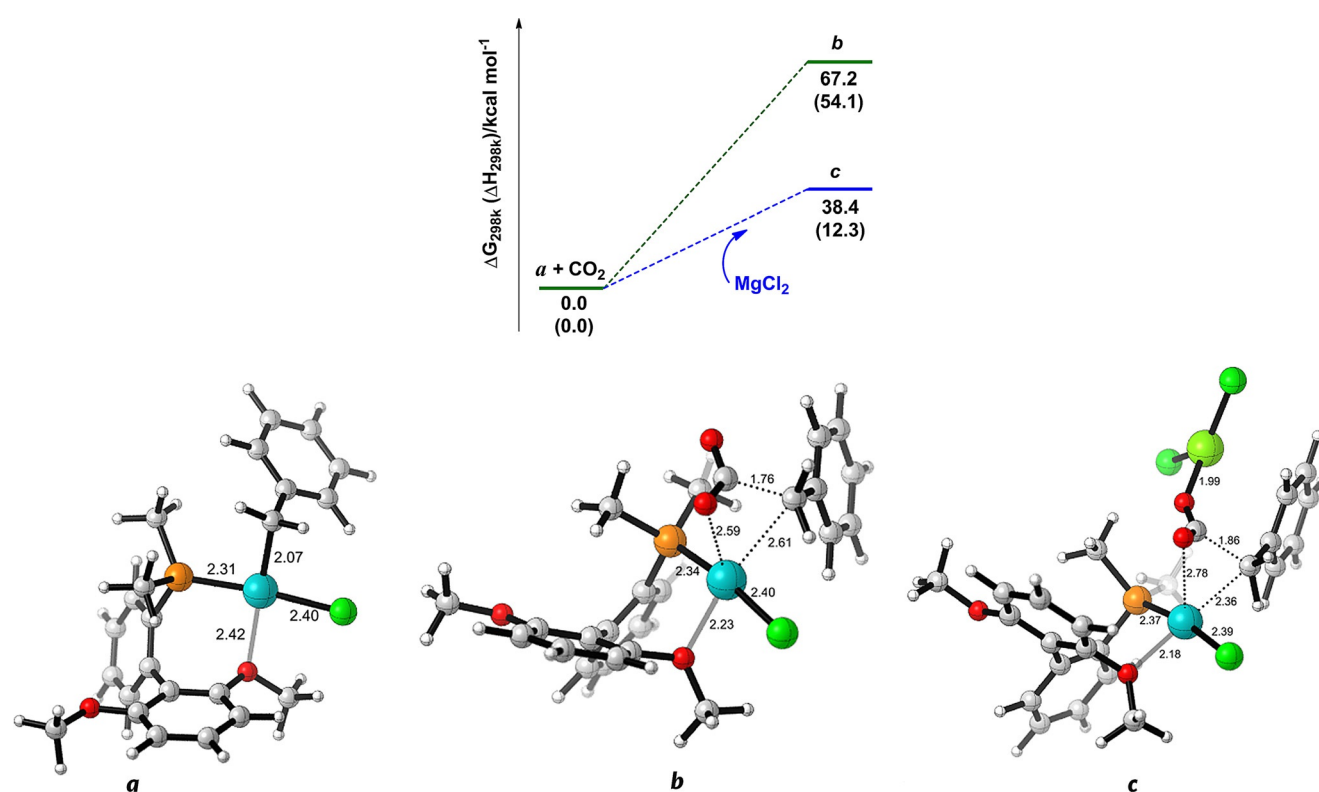
both the presence and absence of Pd(OAc)<sub>2</sub>/SPhos (Scheme S1 c and d). Indeed, no **2a** was observed, even with further prolonging the reaction time, which implies that benzylmanganese chloride as the reaction intermediate can be ruled out and that a challenging CO<sub>2</sub> insertion into the Pd–C bond occurred in this catalytic system.

Based on previous reports<sup>[5a,11]</sup> and the experimental results, a Pd<sup>0</sup>/Pd<sup>II</sup> mechanism was proposed, which contradicts the well-established Ni<sup>I</sup> mechanism. A DFT study was performed to investigate CO<sub>2</sub> insertion into the Pd<sup>II</sup>–C bond with replacement of the cyclohexyl group by a methyl group for simplification. It is well known that monoligated (SPhos)Pd<sup>0</sup> complexes give a high catalytic activity in the Suzuki coupling reaction.<sup>[12]</sup> However, the Gibbs activation energy ( $\Delta G^\ddagger$ ) for the CO<sub>2</sub> insertion into the monoligated Pd<sup>II</sup>–C bond was calculated to be 67.2 or 38.4 kcal mol<sup>-1</sup> in the absence and presence of MgCl<sub>2</sub>, respectively. In the optimized transition state **b** and **c**, the positively charged Pd atom interacts with the O atom of CO<sub>2</sub> and the Bn moiety interacts with the C atom of CO<sub>2</sub> (Figure 1). Such large  $\Delta G^\ddagger$  values imply that this monoligated (SPhos)BnPdCl complex can hardly account for the CO<sub>2</sub> insertion process in view of the mild reaction conditions used in the experiment.

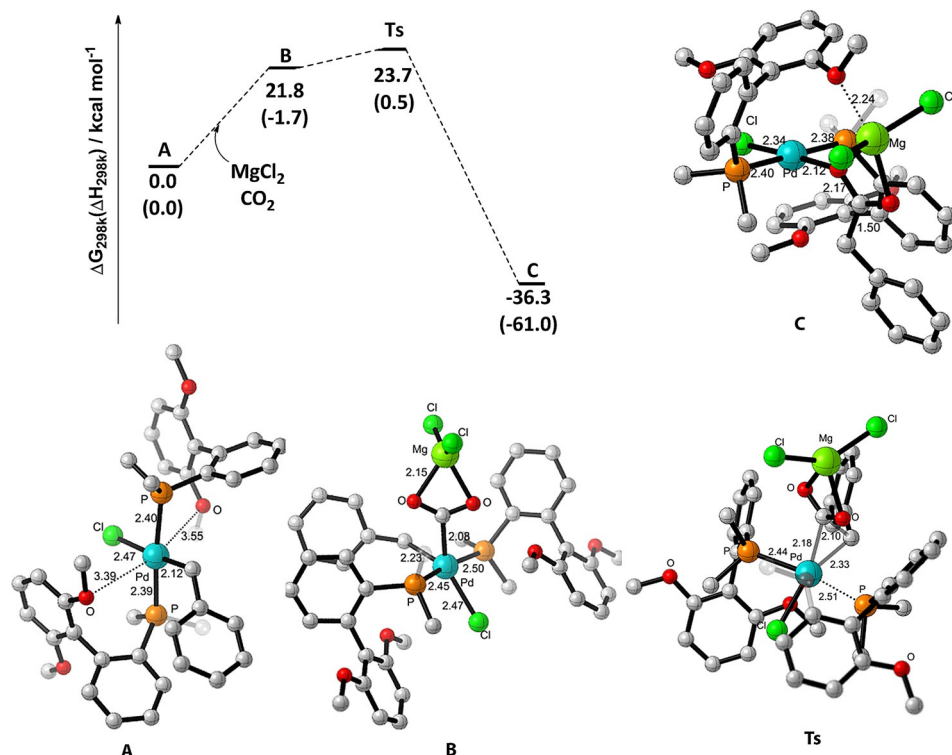
The CO<sub>2</sub> insertion into the L<sub>2</sub>Pd<sup>II</sup>–C bond in the presence of MgCl<sub>2</sub> was calculated. Inspiringly, in the presence of CO<sub>2</sub> and MgCl<sub>2</sub>, intermediate **A** coordinates with CO<sub>2</sub> and MgCl<sub>2</sub> to afford the Pd<sup>II</sup>–( $\eta^1$ -CO<sub>2</sub>)–MgCl<sub>2</sub> adduct **B** with a  $\Delta G^\ddagger$  value of

21.8 kcal mol<sup>-1</sup> (Figure 2). However, the CO<sub>2</sub> molecule fails to react with intermediate **A** to afford the Pd<sup>II</sup>–CO<sub>2</sub> adduct in the absence of MgCl<sub>2</sub>, which is in agreement with the observation that almost no phenylacetic acid was observed without MgCl<sub>2</sub> (entry 1, Table 1). The electrostatic interaction between the positively charged Mg atom and the negatively charged O atom of CO<sub>2</sub> stabilizes the CO<sub>2</sub> coordination bond with the Pd<sup>II</sup> center to generate the Pd<sup>II</sup>( $\eta^1$ -CO<sub>2</sub>)(MgCl<sub>2</sub>) adduct **B**. Starting from **B**, the CO<sub>2</sub> inserts easily into the Pd<sup>II</sup>–C bond via the transition state **Ts** to afford the carboxylic intermediate **C** (Figure 2). Notably, the structure of **Ts** is quite different to those of **b** and **c**. In the structure of **Ts**, the C atom of CO<sub>2</sub> interacts with both the Pd center and benzyl group simultaneously, and MgCl<sub>2</sub> shows relatively strong interaction with the two oxygen atoms of CO<sub>2</sub>, which delivers CO<sub>2</sub> to the benzyl group. Therefore, MgCl<sub>2</sub> presumably promotes the carboxylation reaction by stabilizing the Pd<sup>II</sup>–CO<sub>2</sub> adduct and thus accelerating the CO<sub>2</sub> insertion into the Pd<sup>II</sup>–C bond, which is fully consistent with the experimental results presented in Table 1.

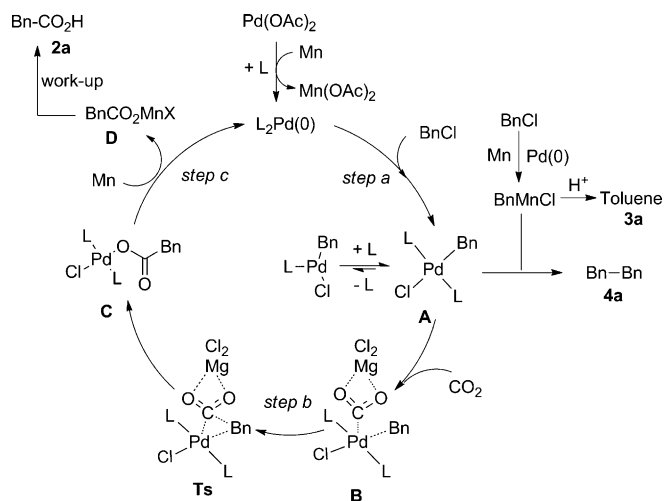
Therefore, we proposed a catalytic Pd<sup>0</sup>/Pd<sup>II</sup> cycle for the carboxylation of benzyl chloride in combination with Mn/MgCl<sub>2</sub> (Scheme 2). Firstly, the Pd<sup>II</sup> complex is reduced to the L<sub>2</sub>Pd<sup>0</sup> species. Then oxidative addition of benzyl chloride takes place to form the intermediate **A** (step a). Subsequently, the Pd<sup>II</sup>–CO<sub>2</sub>–MgCl<sub>2</sub> adduct **B** is generated, and CO<sub>2</sub> insertion into the Pd–C bond via the transition state **Ts** occurs easily with the aid of MgCl<sub>2</sub>, as proved by the DFT study (step b). A final one-step,



**Figure 1.** Gibbs energy profile and geometries for CO<sub>2</sub> insertion into the monoligated Pd<sup>II</sup>–C bond of **a** calculated by the M06/6-311 + G(d,p)/LANL2DZ//M06/6-31G(d)/LANL2DZ method. Values given in brackets are the enthalpy energy change. Intermediate **a** is formed through the oxidative addition of monoligated Pd<sup>0</sup> species with benzyl chloride. All the energies are given in kcal mol<sup>-1</sup>, and the bond lengths in Å. H: white, C: gray, O: red, Mg: light green, P: orange, Cl: deep green, Pd: cyan.



**Figure 2.** Gibbs energy profile and geometries for CO<sub>2</sub> insertion into the Pd<sup>II</sup>-C bond of **A** calculated by the M06/6-311 + + G(d,p)/LANL2DZ//M06/6-31G(d)/LANL2DZ method. Values given in brackets are the enthalpy energy change. Intermediate **A** is formed through the oxidative addition of L<sub>2</sub>Pd<sup>0</sup> species with benzyl chloride. All the energies are given in kcal mol<sup>-1</sup>, and the bond lengths in Å. C: gray, O: red, Mg: light green, P: orange, Cl: deep green, Pd: cyan.



**Scheme 2.** Proposed catalytic cycle.

two-electron reduction with Mn powder regenerates the active L<sub>2</sub>Pd<sup>0</sup> species and provides the manganese carboxylate **D** (step c), which delivers the expected carboxylated product upon hydrolytic work-up.

## Conclusions

An effective Pd-catalyzed carboxylation of functionalized benzyl chlorides with CO<sub>2</sub> by employing Mn powder as a reductant has been developed. We believe this protocol represents an operationally simple access to phenylacetic acids under mild conditions without the use of sensitive reducing reagents. Notably, our computational study suggests that MgCl<sub>2</sub> is presumably involved in the process of CO<sub>2</sub> insertion into the (SPhos)<sub>2</sub>Pd<sup>II</sup>-C bond by stabilizing the Pd<sup>II</sup>-CO<sub>2</sub> adduct and thus accelerates the CO<sub>2</sub> insertion. An extensive investigation on the Pd-catalyzed carboxylation with CO<sub>2</sub> is currently underway.

## Experimental Section

### General

Commercially available materials were used without further purification. CO<sub>2</sub> with a purity of 99.999% was commercially available. Mn powder (200 mesh, 98% trace metal basis) was purchased from Aladdin Industrial Corporation. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded by using a Bruker 400 MHz NMR spectrometer. Chemical shifts are relative to those of CDCl<sub>3</sub> (7.26 ppm, <sup>1</sup>H and 77.16 ppm, <sup>13</sup>C) as an internal standard. ESI-MS was recorded by using an LCQ-Advantage instrument from Thermo-Finnigan Analytical methods. GC was performed by using a Shimadzu GC-2014, equipped with a capillary column (RTX-17, 30 m × 0.25 μm) using a flame ionization detector. Mass spectra were recorded by using a Shimadzu GCMS-QP2010 equipped with a RTX-5 MS capillary column at an ionization voltage of 70 eV.

### General procedure for the carboxylation of benzyl chlorides with CO<sub>2</sub>

All operations were performed under an N<sub>2</sub> atmosphere by using standard Schlenk and vacuum line techniques. An oven-dried Schlenk tube that contained a magneton was charged with a Pd source, ligand, reducing agent, and additive, if applicable. The Schlenk tube was then evacuated and back-filled under a CO<sub>2</sub> flow, and an atmospheric pressure of CO<sub>2</sub> was established. The solvent and the corresponding chlorides (1.47 mmol) were added subsequently by syringe, and the resulting solution was cooled to the desired temperature and stirred for the indicated time. The mixture was then allowed to warm to RT, and the reaction was quenched carefully with 1 N HCl to hydrolyze the resulting carboxylate, and the product was extracted several times with AcOEt. A sample of the obtained solution was analyzed to determine the conversions and byproducts by GC using biphenyl as the internal

standard, and the yield of phenylacetic acid derivatives was determined by  $^1\text{H}$  NMR spectroscopy using 1-chloro-2,4-dinitrobenzene as the internal standard. If required, the resulting carboxylic acid was purified by conventional flash chromatography.

**2-Phenylacetic acid (2a):** Yield 77%; m.p. 77–78 °C (lit.<sup>[5d]</sup> 77–79 °C);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 3.65 (s, 2H), 7.25–7.45 ppm (m, 5H);  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 177.85, 133.38, 129.52, 128.80, 127.51, 41.16 ppm; HRMS (ESI):  $m/z$ : calcd for  $\text{C}_8\text{H}_8\text{O}_2$ : 136.0524 [ $\text{M}-\text{H}^+$ ] $^-$ ; found 135.0456.

**2-(4-Methoxyphenyl)acetic acid (2b):** Yield 68%; m.p. 83–85 °C (lit.<sup>[5d]</sup> 83–85 °C);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 3.58 (s, 2H), 3.79 (s, 3H), 6.86 (d, 2H), 7.19 ppm (d, 2H);  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 178.26, 158.99, 130.55, 125.45, 114.21, 55.40, 40.26 ppm; HRMS (ESI):  $m/z$ : calcd for  $\text{C}_9\text{H}_{10}\text{O}_3$ : 166.0630 [ $\text{M}-\text{H}^+$ ] $^-$ ; found 165.0548.

**2-(*p*-Tolyl)acetic acid (2c):** Yield 74%; m.p. 90–92 °C (lit.<sup>[13a]</sup> 90–91 °C);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.33 (s, 3H), 3.61 (s, 2H), 7.12–7.20 (d, 2H), 7.24–7.30 ppm (d, 2H);  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 178.24, 137.19, 130.31, 129.49, 129.37, 40.72, 21.24 ppm; HRMS (ESI):  $m/z$ : calcd for  $\text{C}_9\text{H}_{10}\text{O}_2$ : 150.0681 [ $\text{M}-\text{H}^+$ ] $^-$ ; found 149.0610.

**2-(*m*-Tolyl)acetic acid (2d):** Yield 68%; m.p. 62–63 °C (lit.<sup>[13a]</sup> 63–64 °C);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.34 (s, 3H), 3.61 (s, 2H), 3.79 (s, 3H), 7.05–7.20 (m, 3H), 7.22–7.28 ppm (m, 1H);  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 177.81, 138.50, 133.24, 130.25, 128.69, 128.27, 126.51, 41.07, 21.49 ppm; HRMS (ESI):  $m/z$ : calcd for  $\text{C}_9\text{H}_{10}\text{O}_2$ : 150.0681 [ $\text{M}-\text{H}^+$ ] $^-$ ; found 149.0609.

**2-[4-(*tert*-Butyl)phenyl]acetic acid (2e):** Yield 66%; m.p. 82–84 °C (lit.<sup>[5d]</sup> 83–85 °C);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.34 (s, 9H), 1.97 (s, 2H), 4.37 (q,  $^3J$  = 7.1 Hz, 2H), 7.20–7.28 (m, 2H), 7.34–7.40 ppm (m, 2H);  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 177.88, 150.32, 130.40, 129.15, 125.73, 40.67, 31.44 ppm; HRMS (ESI):  $m/z$ : calcd for  $\text{C}_{12}\text{H}_{16}\text{O}_2$ : 192.1150 [ $\text{M}-\text{H}^+$ ] $^-$ ; found 191.1080.

**2-[4-(Ethoxycarbonyl)phenyl]acetic acid (2f):** Yield 88%; m.p. 100–102 °C (lit.<sup>[13b]</sup> 101 °C);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.39 (t,  $^3J$  = 7.1 Hz, 2H), 3.71 (s, 2H), 4.37 (q,  $^3J$  = 7.1 Hz, 2H), 7.68–7.19 (m, 1H), 8.59–7.65 ppm (m, 1H);  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 176.83, 166.49, 161.71, 138.30, 130.04, 129.78, 129.57, 61.17, 41.03, 14.45 ppm; HRMS (ESI):  $m/z$ : calcd for  $\text{C}_{11}\text{H}_{12}\text{O}_4$ : 208.0736 [ $\text{M}-\text{H}^+$ ] $^-$ ; found 207.0652.

**2-(4-Acetylphenyl)acetic acid (2g):** Yield 86%; m.p. 110–112 °C (lit.<sup>[5d]</sup> 111–112 °C);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.60 (s, 3H), 3.74 (s, 2H), 7.40 (d,  $^3J$  = 8.6 Hz, 2H), 7.96 ppm (d,  $^3J$  = 8.3 Hz, 2H);  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 197.8, 176.3, 138.6, 136.2, 129.7, 128.7, 40.8, 26.6 ppm; HRMS (ESI):  $m/z$ : calcd for  $\text{C}_{10}\text{H}_{10}\text{O}_3$ : 178.0630 [ $\text{M}-\text{H}^+$ ] $^-$ ; found 177.0560.

**2-(2-Chlorophenyl)acetic acid (2h):** Yield 92%; m.p. 93–95 °C (lit.<sup>[5d]</sup> 91–93 °C);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 3.81 (s, 2H), 7.20–7.42 ppm (m, 4H);  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 177.27, 134.77, 131.76, 131.68, 129.68, 129.12, 127.10, 38.96 ppm; HRMS (ESI):  $m/z$ : calcd for  $\text{C}_8\text{H}_7\text{ClO}_2$ : 170.0135; found [ $\text{M}-\text{H}^+$ ] $^-$  169.0055, [ $\text{M}-\text{CO}_2-\text{H}^+$ ] $^-$  125.0166.

**2-(3-Fluorophenyl)acetic acid (2i):** Yield 96%; m.p. 42–44 °C (lit.<sup>[13a]</sup> 42–43 °C);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 3.65 (s, 3H), 6.98–7.08 (m, 3H), 7.25–7.32 ppm (m, 1H);  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 177.55, 164.16, 161.71, 135.54, 135.46, 130.28, 130.20, 125.26,

125.23, 116.72, 116.50, 114.65, 114.44, 40.79 ppm; HRMS (ESI):  $m/z$ : calcd for  $\text{C}_8\text{H}_7\text{FO}_2$ : 154.0430 [ $\text{M}-\text{H}^+$ ] $^-$ ; found 153.0351.

**2-(4-Vinylphenyl)acetic acid (2j):** Yield 49%; m.p. 83–85 °C (lit.<sup>[5d]</sup> 83–86 °C);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 3.64 (s, 2H), 5.24 (d,  $J$  = 10.9 Hz, 1H), 5.73 (d,  $J$  = 17.6 Hz, 1H), 6.70 (dd,  $J$  = 17.6, 10.9 Hz, 1H), 7.26–7.21 (m, 2H), 7.38 ppm (d,  $J$  = 8.1 Hz, 2H);  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 177.59, 136.91, 136.47, 132.84, 129.69, 126.61, 114.16, 40.82 ppm; HRMS (ESI):  $m/z$ : calcd for  $\text{C}_{10}\text{H}_{10}\text{O}_2$ : 162.0681 [ $\text{M}-\text{H}^+$ ] $^-$ ; found 161.0610.

**2-(Naphthalen-2-yl)acetic acid (2k):** Yield 78%; m.p. 140–142 °C (lit.<sup>[5d]</sup> 140–142 °C);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 3.81 (s, 2H), 7.36–7.50 (m, 3H), 7.71–7.86 ppm (m, 4H);  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 177.78, 133.53, 132.68, 130.81, 128.48, 128.33, 127.82, 127.44, 126.39, 126.10, 41.31 ppm; HRMS (ESI):  $m/z$ : calcd for  $\text{C}_{12}\text{H}_{10}\text{O}_2$ : 186.0681 [ $\text{M}-\text{H}^+$ ] $^-$ ; found 185.0603.

**1,2-Diphenylethane (4a):** M.p. 48–50 °C (lit.<sup>[13c]</sup> 48–51 °C);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.92 (s, 4H), 7.16–7.22 (m, 4H), 7.24–7.30 ppm (m, 4H);  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 141.92, 128.59, 128.47, 126.05, 38.10 ppm; GC-MS calcd for  $\text{C}_{14}\text{H}_{14}$  182.11; found 182.15 (25.86%), 91.10 (100%).

## Computational details

All the calculations were performed by the DFT method<sup>[14]</sup> by using the GAUSSIAN 09 package.<sup>[15]</sup> All the structures reported in this research were optimized by the M06 method in conjunction with BSI basis sets, in which BSI signifies basis set LANL2DZ<sup>[16a]</sup> performed for the Pd atom and basis set 6-31G<sup>\*[16b]</sup> for the other C, H, O, P, Cl, and Mg atoms. Furthermore, all the final structures were confirmed by frequency calculations to be energy minima. Energy calculations were performed at M06/6-311 + + G<sup>\*\*[16b-j]</sup>/LANL2DZ//M06/BSI level, in which basis set 6-311 + + G<sup>\*\*</sup> was employed for C, H, O, P, Cl, and Mg atoms and basis set LANL2DZ was employed for the Pd atom. All energy data reported are in kcal mol<sup>-1</sup>, and the length data were in Å. Structures were generated using CYLview.<sup>[17]</sup>

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