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## Pd/C-catalyzed direct formylation of aromatic iodides to aryl aldehydes using carbon dioxide as a C1 resource<sup>†</sup>

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Pd/C-catalyzed direct formylation of aromatic iodides to aryl aldehydes using  $CO_2$  as a C1 resource was realized for the first time in the presence of hydrosilanes and base DBU under mild conditions, giving a series of aldehydes in good yields.

Catalytic conversion of  $CO_2$  into value-added chemicals has received significant attention in recent years because of its economical and nontoxic characteristics, and high potential as a renewable and environmentally friendly C1 resource alternative to toxic CO.<sup>1–9</sup> However, high-energy substrates, specific catalysts and harsh conditions are generally required for  $CO_2$  transformation due to the thermodynamic stability of  $CO_2$ . Recently, hydrosilylation of  $CO_2$  with hydrosilanes has made the  $CO_2$  conversion proceed under mild conditions, showing great promise in the synthesis of carbonyl compounds using  $CO_2$  as a C1 resource.<sup>10</sup> For example, direct formylation of amines with  $CO_2$  and hydrosilanes was achieved at 1 atm of  $CO_2$ .<sup>11</sup>

Aromatic aldehydes are important building blocks used as reactive intermediates in C–C, C–N and C–S coupling reactions, which have found wide applications in the synthesis of materials, pharmaceuticals, pesticides and agricultural chemicals.<sup>12</sup> Traditional methods for the synthesis of aromatic aldehydes include reduction of carboxylic acids or esters, Gattermann–Koch, Reimer–Tiemann, Duff and Vilsmeier reactions, which generally suffer from inherent drawbacks such as very low yields, poor selectivity, and requirement of toxic gas and harsh conditions.<sup>13</sup> The direct formylation synthesis of aromatic aldehydes from aromatic halides as a single-step alternative transformation has been developed using CO or CO alternatives as C1 sources (Scheme 1, left).<sup>14–16</sup> Such progress encourages us to explore the possibility for the direct formylation of aromatic halides into aromatic aldehydes using  $CO_2$  instead of CO as a C1 building block.



 $\label{eq:scheme1} \begin{array}{l} \mbox{Direct formylation of aromatic iodides with $CO_2$ and $PMHS$ (right) compared to previous reductive formylation methods (left). \end{array}$ 

In the course of our continual investigation on chemical conversion of  $CO_2$  into value-added chemicals *via* construction of C-N,<sup>17</sup>  $C-S^{18}$  and C-C bonds, we herein present the Pd/C-catalyzed direct formylation of aromatic iodides to aryl aldehydes using  $CO_2$  and silanes (*e.g.*, poly(methylhydrosiloxane), PMHS) as the resources for constructing C-C bonds in the presence of 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) (Scheme 1, right). In this protocol, the commercial Pd/C was used to activate aryl ioides, and DBU served as a catalyst for activating  $CO_2$  to react with silanes and as a base to neutralize the produced HI. The reported reactions were carried out under mild conditions and were successfully applied to a wide range of aryl iodides, affording aromatic aldehydes in moderate to excellent yields. To the best of our knowledge, this is the first work on the direct formylation of aromatic iodides to aldehydes using  $CO_2$  as a C1 resource.

The model substrate for the initial screening was iodobenzene (1), leading to benzaldehyde with the formation of biphenyl as a byproduct. The commercial Pd/C with a Pd particle size of around 3 nm was used as the catalyst in this work. The preliminary reaction of iodobenzene with  $CO_2$  and PMHS catalysed by Pd/C was performed in  $CH_3CN$  in the presence of DBU at 80 °C and  $CO_2$  pressure of 1 MPa for 12 h, and a benzaldehyde yield of 85% was obtained with biphenyl as the sole byproduct at 91% conversion of iodobenzene (Table 1, entry 1). Both Pd/C and DBU were essential for the formation of benzaldehyde confirmed by the fact that no benzaldehyde was obtained in the absence of either the Pd/C catalyst or base (Table 1, entries 2 and 3). The influence of the temperature and pressure on the reaction was investigated. As the reaction temperature was increased to 100 °C, both the

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Procedures for formylation of iodobenzenes to aryl aldehydes, the results of formylation of iodobenzene using CO<sub>2</sub> and various hydrosilanes, control experiments, <sup>1</sup>H and <sup>13</sup>C NMR data and spectra of intermediates and products. See DOI: 10.1039/c3cc49365b

 Table 1
 Pd/C-catalyzed direct formylation of 1 with carbon dioxide and

 PMHS under different conditions<sup>a</sup>

	Х + CO <sub>2</sub> + РМНS -	Pd/C	0	
L	1	2400	2	
Entry ArX	Base	$T/^{\circ}\mathbf{C}$	Conv./%	Yield <sup>b</sup> /%
1 C <sub>6</sub> H <sub>5</sub> I	DBU	80	91	85(70) <sup>c</sup>
$2^d$ C <sub>6</sub> H <sub>5</sub> I	DBU	80	0	nd <sup>e</sup>
3 C <sub>6</sub> H <sub>5</sub> I	—	80	0	nd
$4 C_6H_5I$	DBU	100	94	$87(73)^{c}$
5 C <sub>6</sub> H <sub>5</sub> I	DBU	50	60	42
6 <sup>f</sup> C <sub>6</sub> H <sub>5</sub> I	DBU	80	100	$93(77)^{c}$
$7^g$ C <sub>6</sub> H <sub>5</sub> I	DBU	80	28	11
$8^h$ C <sub>6</sub> H <sub>5</sub> I	$Cs_2CO_3$	80	95	nd
$9^h$ C <sub>6</sub> H <sub>5</sub> I	$K_2CO_3$	80	90	nd
10 C <sub>6</sub> H <sub>5</sub> I	DBU/Cs <sub>2</sub> CO <sub>3</sub>	80	80	58
11 C <sub>6</sub> H <sub>5</sub> Br	DBU	100	0	nd
12 C <sub>6</sub> H <sub>5</sub> Cl	DBU	100	0	nd

<sup>*a*</sup> Reaction conditions: **1** (5 mmol), Pd/C catalyst (2.5 mol%), PMHS (Si–H 15 mmol), base (1.1 equiv.), pressure of CO<sub>2</sub> (1 MPa), CH<sub>3</sub>CN (10 ml), 12 h. <sup>*b*</sup> Yields determined by NMR analysis using mesitylene as internal standard. <sup>*c*</sup> Yields of isolated products. <sup>*d*</sup> In the absence of the Pd/C catalyst. <sup>*e*</sup> Not detected. <sup>*f*</sup> Reaction time, 20 h. <sup>*g*</sup> CO<sub>2</sub> pressure (0.1 MPa), 24 h. <sup>*h*</sup> The product was biphenyl.

iodobenzene conversion and the yield of benzaldehyde slightly increased accordingly (Table 1, entry 4), while lowering the temperature to 50 °C still resulted in a yield of 42% at the conversion of 60% (Table 1, entry 5). Prolonging the reaction time to 20 h afforded 93% yield of the product with complete conversion of the substrate (Table 1, entry 6). Lowering the CO<sub>2</sub> pressure to 0.1 MPa still afforded a yield of 11% after 24 h (Table 1, entry 7). These results indicated that the direct formylation of aryl iodides with CO<sub>2</sub> into aldehydes could be achieved under mild conditions.

The influence of different bases on the direct formylation of iodobenzene was studied. The tested inorganic bases like Cs2CO3 and K<sub>2</sub>CO<sub>3</sub> were ineffective in the formation of benzaldehyde, affording biphenyl in high yields instead (Table 1, entries 8 and 9). This suggests that Ullmann reactions of iodobenzene to produce diphenyl occurred under the experimental conditions, in which the bases promoted the iodobenzene conversion and neutralized the produced HI. Interestingly, when Cs<sub>2</sub>CO<sub>3</sub> (1.0 equiv.) together with DBU (0.1 equiv.) was used as the base, the formylation reaction proceeded well, giving 58% yield of benzaldehyde (Table 1, entry 10). From these findings, it can be deduced that DBU played a crucial role in the formation of benzaldehyde though all the tested bases including DBU, Cs<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> could promote the conversion of iodobenzene. In the case of DBU as the base, [DBU][HI] was detected as an ionic liquid, suggesting that one role of DBU in the reaction process was to neutralize the produced HI similar to those of the inorganic bases. Another role of DBU was deduced to activate CO2, consistent with that reported,<sup>9b</sup> thus resulting in the formylation of iodobenzene finally.

In addition, bromobenzene or chlorobenzene was examined as the substrate. Unfortunately, the direct formylation reaction of these two compounds did not occur under similar reaction conditions (Table 1, entries 11 and 12).

Various hydrosilanes were also examined in the formylation reaction of iodobenzene with CO<sub>2</sub> (Table S1, see ESI†). It was found that PMHS and phenylsilanes were effective for the formylation reaction, and PMHS showed the best performance (Table S1, entries 2–6, ESI<sup>†</sup>). However, in the cases of Et<sub>3</sub>SiH and Et<sub>2</sub>SiH<sub>2</sub>, only biphenyl was formed without any detectable benzaldehyde. In addition, in the case of PhSiH<sub>3</sub>, Ph<sub>2</sub>SiH<sub>2</sub> and Ph<sub>3</sub>SiH as hydrides, the iodobenzene conversion and benzaldehyde yield followed the order: PhSiH<sub>3</sub> < Ph<sub>2</sub>SiH<sub>2</sub> < Ph<sub>3</sub>SiH (Table S1, entries 2–4, ESI<sup>†</sup>).

In the cases of  $Ph(CH_3)_2SiH$  and  $Ph_2CH_3SiH$ , similar phenomena were observed (Table S1, entries 5 and 6, ESI†).

Encouraged by the results described above, various iodobenzenes substituted with electron-donating and electron-withdrawing groups were examined to react with CO2 and PMHS catalyzed by Pd/C and DBU, and the results are listed in Table 2. To our delight, all the tested substrates produced the corresponding aryl aldehydes in moderate to excellent yields under the standard conditions, and coupling or deiodinated products were obtained as byproducts depending on the nature of the used substrates. The reactions of iodobenzene derivatives with electron-donating groups, for example, Me and MeO groups proceeded efficiently in high aldehyde yields comparable to that of iodobenzene formylation, and the byproducts were the corresponding coupling products and no deiodinated products were detectable (Table 2, entries 2-6). Substituents at the ortho position affected the formylation reactions, leading to slightly decreased yields of the corresponding aldehydes, presumably due to steric hindrance (Table 2, entries 2, 5 and 7). Reactions of substrates with weakly electron-withdrawing groups, such as F-, Cl- and Br-substituents, also proceeded well. Because chlorobenzene and bromobenzene were proved not to react with CO2 and PMHS under the experimental conditions (Table 1, entries 11 and 12), the selective formylation at the iodide position of the F-, Cl-, Br-substituted iodobenzenes occurred as expected, thus giving the corresponding benzaldehydes in good isolated yields (Table 2, entries 8-10). The formylation of 1,4-diiodobenzene occurred well, giving the mixture of phenyl iodide, benzaldehyde and terephthaldehyde as illustrated in Scheme 2. The formylation reactions of iodobiphenyl and 1-iodonaphthalene took place; however, more deiodinated products were produced (Table 2, entry 11 and 12). The formylation reactions also proceeded with substrates bearing strongly electron-withdrawing groups, such as NO2, CN and CHO (Table 2, entries 13-15). However, in these cases, the corresponding products were obtained in decreased yields, and the dehalogenation products became the major products determined by NMR analysis. The direct formylation reaction was also applied to substituted S- and N-containing heteroaromatic compounds (Table 2, entries 16-19). The protocol was found to work well with iodothiophenes to produce the corresponding aldehydes in good yields. It is noteworthy that in the cases of the substrates bearing electron-withdrawing substitutes, the competitive side reaction of deiodination proceeded, thus giving corresponding aldehydes in declined yields.

In order to gain an insight into the mechanism of the Pd-catalyzed direct formylation of aromatic iodides to aldehydes, several control experiments were performed. First, the reaction of iodobenzene (1 mmol) with  $CO_2$  (1 MPa) catalyzed by Pd/C (2.5 mol%) in the presence of DBU (1.1 equiv.) and without PMHS was

Table 2 Synthesis of various aromatic aldehydes<sup>a</sup>

		2.5mol% Pd/C					
	Ar1 + CO <sub>2</sub> + PMHS 1	DBU CH <sub>3</sub> CN 80°C	+ Ar-	ar-CHU + Ar-Ar + Ar-H 2 3 4			
				Products yield <sup>b</sup> /%			
Entry	Substrate	Product		ArCHO	Ar–Ar	Ar-H	
1	l 1a	CHO	A	77	5	nd <sup>c</sup>	
2	t tb		В	71	8	nd	
3	10	2	С	67	11	nd	
4	Id Id	СНО	2D	81	Trace	nd	
5	1e		2E	66	13	nd	
6	MeO 1f	MeO	O 2F	80	Trace	nd	
7	OMe 1g	СНО	2G	62	nd	12	
8	F 1h	F CHO	2H	64	nd	24	
9	CI 1i	СІСІСНО	) 21	60	nd	25	
10	Br 1j	Br	) 2J	57	nd	27	
11	Ph 11	Ph	2L	30	nd	58	
12	1m	СНО	2М	60	nd	25	
13	0 <sub>2</sub> N 1	O <sub>2</sub> N	2N	12	nd	80	
14	NC 10	NC	20	20	nd	75	
15	OHC 1p	онс	10 2P	29	nd	63	
16 <sup><i>d</i></sup>	⟨ 1q	СНО	2Q	57	nd	nd	
17	√ 1r	S 2	?R	64	nd	27	
18	N I Is	N CHO	S	29	33	20	
19	I 1t	CHO N 2	!T	43	nd	35	

<sup>*a*</sup> Reaction conditions: substrate (5 mmol), PMHS (Si–H 15 mmol), DBU (1.1 equiv.), CH<sub>3</sub>CN (10 ml), 80  $^{\circ}$ C, CO<sub>2</sub> (1 MPa), 20 h. Conversion was 100%. <sup>*b*</sup> Yields of isolated products. <sup>*c*</sup> Not detected. <sup>*d*</sup> Conversion was 73%.



Scheme 2 Formylation of 1,4-diiodobenzene with CO<sub>2</sub> and PMHS.

carried out (Scheme S1A, see ESI<sup>†</sup>). It was indicated that only a trace amount of biphenyl was obtained and no benzoic acid was detected. The reaction of benzoic acid with PMHS was performed in the presence of Pd/C (2.5 mol%) and DBU (1.1 equiv.) under the same other conditions; however, no benzaldehyde was obtained (Scheme S1B, ESI<sup>†</sup>). These results suggested that the formylation of aromatic iodides to aldehydes with  $CO_2$  and PMHS may not proceed through benzoic acid as an intermediate.

It was reported that CO<sub>2</sub> could react with organosilanes to produce silvl formate.<sup>19</sup> In this work, silvl formate was also formed from CO<sub>2</sub> and PMHS in the presence of DBU, confirmed by <sup>1</sup>H NMR analysis. In the <sup>1</sup>H NMR spectrum (Fig. S1b, ESI<sup>†</sup>) the signal assigned to the methyl proton of PMHS shifted from  $\delta = 0.22$ to 0.36 ppm and a new signal appeared at  $\delta$  = 8.07 ppm, ascribed to silvl formate. This silvl formate might be the key intermediate in the formation of aldehydes. In order to prove this hypothesis, we added iodobenzene and Pd/C to the silvl formate solution from CO<sub>2</sub> reacting with PMHS catalyzed by DBU, and stirred it at 80 °C for 12 h. In the <sup>1</sup>H NMR spectrum of the reaction solution (Fig. S1c, ESI<sup>†</sup>) a new signal appeared at 10.02 ppm, attributed to benzaldehyde. These results indicated that silvl formate formed from PMHS with CO<sub>2</sub> was the key intermediate in the direct formylation reaction of iodobenzene with CO2, which further reacted with iodobenzene catalyzed by Pd/C to form benzaldehyde.

From the above experiments, it is clear that DBU had dual roles: catalyzing the formation of silyl formate from  $CO_2$  with hydrosilanes and neutralizing HI produced in the reaction process, while Pd/C catalyzed the formation of benzaldehyde *via* the reaction of silyl formate with iodobenzene. On the basis of the experimental results and the previous reports,<sup>19</sup> a possible reaction mechanism was proposed, as shown in Scheme 3. The first step of the catalytic cycle is an already accepted process: the rapid oxidative addition of aryl iodide to Pd(0) **A** to genetate arylpalladium halide **B**, which acted as a nucleophilic agent to



Scheme 3 Proposed mechanism.

react with the key intermediate silyl formate C *via* adding the aryl group to the carbon atom of formate to form the product and silyloxylpalladium halide **D**, followed by the reaction with PMHS to genetate the polysiloxane **E** and HPdI species. Finally, with the help of the base DBU, Pd(0) was regenerated and the catalytic cycle finished.

In summary, we have demonstrated for the first time a novel and practical method for Pd/C-catalyzed direct conversion of aromatic iodides into benzaldehyde derivatives using  $CO_2$  as a C1 resource under mild conditions. Notably, various functional groups are tolerated under the experimental conditions, and a series of aromatic aldehydes were obtained in moderate to excellent yields. Compared to CO-involved direct formylation of aromatic halides to aromatic aldehydes, this approach is simpler, more environment friendly, and less costly, which also widens the applications of  $CO_2$  in chemical synthesis.

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## Notes and references

- (a) Carbon Dioxide as Chemical Feedstock, ed. M. Aresta, Wiley-VCH, Weinheim, 2010; (b) D. J. Darensbourg, *Chem. Rev.*, 2007, **107**, 2388; (c) M. Y. He, Y. H. Sun and B. X. Han, *Angew. Chem., Int. Ed.*, 2013, **52**, 9620.
- W. Leitner, Coord. Chem. Rev., 1996, 153, 257; (b) M. Peters,
   B. Kohler, W. Kuckshinrichs, W. Leiner, P. Markewitz and
   T. E. Muller, ChemSusChem, 2011, 4, 1216; (c) M. Cokoja,
   C. Bruchmeier, B. Rieger, W. A. Herrmann and F. E. Kuhn, Angew.
   Chem., Int. Ed., 2011, 50, 8510; (d) A. H. Liu, R. Ma, C. Song,
   Z. Z. Yang, A. Yu, Y. Cai, L. N. He, Y. N. Zhao, B. Yu and
   Q. W. Song, Angew. Chem., Int. Ed., 2012, 51, 11306.
- 3 (a) S. Wesselbaum, T. vom Stein, J. Klankermayer and W. Leitner, Angew. Chem., Int. Ed., 2012, 51, 7499; (b) C. Huff and M. Sanford, J. Am. Chem. Soc., 2011, 133, 18122.
- 4 (a) P. G. Jessop, T. Ikariya and R. Noyori, *Chem. Rev.*, 1995, 95, 259;
  (b) C. Federsel, R. Jackstell and M. Beller, *Angew. Chem., Int. Ed.*, 2010, 49, 6254; (c) B. Chatelet, L. Joucla, J. P. Dutasta, A. Martinez, K. C. Szeto and V. Dufaud, *J. Am. Chem. Soc.*, 2013, 135, 5348.
- 5 (a) K. Sasano, J. Takaya and N. Iwasawa, J. Am. Chem. Soc., 2013, 135, 10954; (b) T. León, A. Correa and R. Martin, J. Am. Chem. Soc., 2013, 135, 1221.

- 6 (a) T. Sakakura, J. C. Choi and H. Yasuda, *Chem. Rev.*, 2007, 107, 2365; (b) M. S. Jeletic, M. T. Mock, A. M. Appel and J. C. Linehan, *J. Am. Chem. Soc.*, 2013, 135, 11533.
- 7 T. Sakakura and K. Kohno, Chem. Commun., 2009, 1312.
- 8 K. Huang, C. L. Sun and Z. J. Shi, Chem. Soc. Rev., 2011, 40, 2435.
- 9 (a) F. C. Liu, M. B. Abrams, R. T. Baker and W. Tumas, *Chem. Commun.*, 2001, 433; (b) P. Munshi, D. J. Heldebrant, E. P. Mckoon, P. A. Kelly, C. C. Tai and P. G. Jessop, *Tetrahedron Lett.*, 2003, 44, 2725; (c) Y. Kayaki, Y. Shimokawatoko and T. Ikariya, *Adv. Synth. Catal.*, 2003, 345, 175.
- (a) B. Marciniec, *Coord. Chem. Rev.*, 2005, 249, 2374; (b) D. Addis, S. Das, K. Junge and M. Beller, *Angew. Chem., Int. Ed.*, 2011, 50, 6004; (c) A. F. Holleman, E. Wiberg and N. Wiberg, *Lehrbuch der Anorganischen Chemie*, Walter de Gruyter, Berlin, 1995.
- (a) C. D. Gomes, O. Jacquet, C. Villiers, P. Thuery, M. Ephritikhine and T. Cantat, *Angew. Chem., Int. Ed.*, 2012, 51, 187; (b) O. Jacquet, C. D. Gomes, M. Ephritikhine and T. Cantat, *J. Am. Chem. Soc.*, 2012, 134, 2934.
- 12 L. N. Ferguson, Chem. Rev., 1946, 38, 227.
- (a) J. Fetter, F. Bertha, L. Poszavacz and G. Simig, J. Heterocycl. Chem., 2005, 42, 137; (b) F. Aldabbagh, Compr. Org. Funct. Group Transform. II, 2005, 3, 99; (c) L. P. Crawford and S. K. Richardson, Gen. Synth. Methods, 1994, 16, 37; (d) R. C. Larock, Comprehensive Organic Transformation: A Guide to Functional Group Preparation, Wiley-VCH, New York, 2nd edn, 1999; (e) H. Wynberg, Chem. Rev., 1960, 60, 169; (f) L. N. Ferguson, Chem. Rev., 1946, 38, 227; (g) O. Meth-Cohn and S. P. Stanforth, Comp. Org. Syn., 1991, 2, 777.
- (a) V. P. Baillargeon and J. K. Stille, *J. Am. Chem. Soc.*, 1986, 108, 452;
  V. P. Baillargeon and J. K. Stille, *J. Am. Chem. Soc.*, 1983, 105, 7175;
  (b) I. Pri-Bar and O. Buchman, *J. Org. Chem.*, 1984, 49, 4009;
  (c) A. S. Singh, B. M. Bhanage and J. M. Nagarkar, *Tetrahedron Lett.*, 2011, 52, 2382.
- 15 (a) H. Neumann, R. Kadyrov, X. F. Wu and M. Beller, *Chem.-Asian J.*, 2012, 7, 2213; (b) A. G. Sergeev, A. Spannenberg and M. Beller, *J. Am. Chem. Soc.*, 2008, **130**, 15549.
- 16 (a) S. Cacchi, G. Fabrizi and A. Goggiamani, Org. Lett., 2003, 5, 4269;
  (b) T. Ueda, H. Konishi and K. Manabe, Angew. Chem., Int. Ed., 2013, 52, 8611.
- 17 B. Yu, H. Y. Zhang, Y. F. Zhao, S. Chen, J. L. Xu, C. L. Huang and Z. M. Liu, *Green Chem.*, 2013, **15**, 95.
- 18 B. Yu, H. Y. Zhang, Y. F. Zhao, S. Chen, J. L. Xu, L. D. Hao and Z. M. Liu, ACS Catal., 2013, 3, 2076.
- (a) A. Jansen and S. Pitter, J. Mol. Catal. A: Chem., 2004, 217, 41;
  (b) P. Deglmann, E. Ember, P. Hofmann, S. Pitter and O. Walter, Chem.-Eur. J., 2007, 13, 2864; (c) W. Sattler and G. Parkin, J. Am. Chem. Soc., 2012, 134, 17462; (d) S. Itagaki, K. Yamaguchi and N. Mizuno, J. Mol. Catal. A: Chem., 2013, 366, 347; (e) L. Zhang, J. H. Cheng and Z. M. Hou, Chem. Commun., 2013, 49, 4782.