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Rhodium-Catalyzed Formylation of Aryl Halides with CO_2 and H_2

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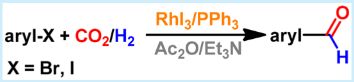
S Supporting Information

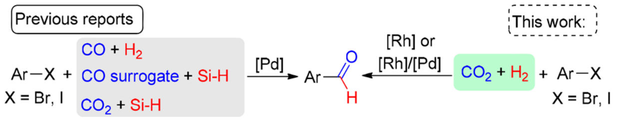


ABSTRACT: The reductive formylation of aryl iodides/bromides to aryl aldehydes using CO_2/H_2 is presented for the first time. It was realized over a catalytic system composed of RhI_3 or $RhI_3/Pd(dppp)Cl_2$ (dppp = 1,3-bis(diphenylphosphino)propane) and PPh_3 in the presence of Ac_2O/Et_3N at 100 °C, affording aromatic aldehydes in good to excellent yields, together with good functional-group tolerance and broad substrate scope. The reaction proceeds through three cascade steps, involving HCOOH formation, CO release, and formylation of aryl halides.

Carbon monoxide (CO) represents the most important C1 building block on an industrial scene in a myriad of industrial carbonylation processes.[1−3] However, the high toxicity, flammability, and production from fossil fuels make the handling and transportation of this gas complicated and limit its applications. Hence, the exploration of CO surrogates is of particular interest. As a sustainable and renewable C1 building block, the efficient conversion of carbon dioxide (CO_2) for the synthesis of value-added chemicals is of great significance in regard to reducing the predominant dependence on petrochemical feedstocks for the chemical supply chain.[4−8] Over the past decades, several approaches have been developed for CO_2 reduction using different types of reductants, such as H_2, hydrosilanes, and hydroboranes,[5,9,10] to afford CO, formic acid, formaldehyde, methanol, and methane successively.[11] Notably, although CO production from CO_2 hydrogenation could be achieved through a reverse water−gas shift pathway, the reaction is generally conducted at high temperature (>250 °C) together with low conversion and selectivity, in which the generated CO is difficult to use in the subsequent chemical conversion.[11] Therefore, development of efficient catalytic systems for the use of CO_2 as a surrogate for CO under mild conditions is attractive and challenging.

Formylation of aryl halides employing CO[12−14] or CO surrogates (e.g., *N*-formylsaccharin,[15] isocyanide,[16] paraformaldehyde[17]) (Scheme S1a−d, Supporting Information (SI)) is an efficient and complementary method to synthesize aromatic aldehydes, which are valuable intermediates in C−C bond-forming reactions. However, the inherent drawbacks of the reported approaches, such as the need for toxic CO or expensive CO surrogates and hydrosilanes, promote the continuous exploration of cleaner and less expensive routes for the synthesis of aromatic aldehydes. Our group realized the formylation of aryl iodides and bromides with CO_2 using poly(methylhydrosiloxane) (PMHS) as the reductant over Pd catalysts combined with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU),[18,19] leading to aryl aldehydes in moderate to excellent yields (Scheme S1e,f, SI). Skrydstrup et al. developed a protocol for the reduction of CO_2 to CO in the presence of CsF and disilane in dimethyl sulfoxide (DMSO) at room temperature, and the reduction could be coupled to an aminocarbonylation reaction using a two-chamber system (Scheme S1g, SI).[2,20] Later, they reported the conversion of CO_2 with diaryldisilanes and aryl halides to produce diarylketones through CO generation (Scheme S1h, SI).[21] In recent years, catalytic transformations involving CO_2 for carbonylative alkene functionalization have emerged to provide chemicals such as carboxylic acids,[22] esters,[23] and alcohols.[24] Ding and Xia et al. realized the one-pot hydroformylation of olefins with CO_2, hydrosilane, and H_2 to afford aldehydes through a tandem sequence of PMHS-mediated CO_2 reduction to CO and a conventional rhodium-catalyzed hydroformylation with CO/H_2 (Scheme S1i, SI).[25] From a sustainable point of view, H_2 is a far better choice of reductant than hydrosilanes or hydroboranes, and reduction of CO_2 to CO, as well as the subsequent utilization of CO_2 as C1 source in the formylation reaction of of aryl halides is highly desirable and has not been realized up to now (Scheme 1).

Scheme 1. Formylation of Aryl Halides To Produce Aromatic Aldehydes



Herein, we developed a catalytic system composed of RhI_3 and PPh_3, which realized the reductive formylation of aryl iodides with CO_2/H_2 in the presence of acetic anhydride and Et_3N at 100 °C, affording aryl aldehydes in good to excellent yields, together with good functional-group tolerance and

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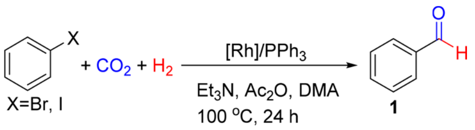
broad substrate scope. Moreover, with additional Pd(dppp)Cl_2, this catalytic system was also very effective for the formylation of aryl bromides. Detailed investigation on the reaction mechanism by isotope-labeling and control experiments showed that the reaction proceeded through three cascade steps involving initial HCOOH formation from CO_2 hydrogenation, subsequent CO release from the reaction of HCOOH with acetic anhydride, and final formylation of aryl halides by CO insertion and reductive elimination.

As part of our ongoing studies on CO_2 transformations,[19,26] we sought to develop a catalytic system for the formylation of aryl halides with CO_2 as the CO surrogate in the presence of H_2. For the reduction of CO_2 to CO, deoxygenative cleavage of the O═C═O bond is needed, which is difficult to realize owing to its high bond energy (532 kJ mol^{-1}).[27] In our preliminary study, acetic anhydride as a deoxygenation reagent was applied in the reaction of iodobenzene with CO_2/H_2 (1:1). A quick survey of the reaction conditions showed that 100% conversion of iodobenzene together with 61% yield of benzaldehyde (**1**) was obtained over RhI_3/PPh_3 in the presence of acetic anhydride, Et_3N as a base, and *N*,*N*-dimethylacetamide (DMA) as the solvent (Table 1, entry 1). Dehalogenation and direct coupling products (e.g., benzene and biphenyl) were detected as the main byproducts. It was indicated that all of the reagents were necessary, and the yield of **1** decreased to only 8% without solvent (entries 2–7, Table 1). Other rhodium salts including $RhCl_3$, $[RhCl(CO)_2]_2$, $Rh(PPh_3)_3Cl$, $RhCl(CO)(PPh_3)_2$, $[RhCl(COD)]_2$, $Rh(PPh_3)_3Br$, $Rh(acac)(CO)_2$, $Rh(OAc)_2·2H_2O$, $[Rh(CF_3COO)]_2$, and Rh/C were examined, and they exhibited low to moderate catalytic activities, affording **1** in yields of 6–55% (entries 2–11, Table S1, SI). In contrast, the reaction was sluggish using other solvents including 1,3-dimethyl-2-imidazolidinone (DMI), *N*-methyl-2-pyrrolidinone (NMP), tetrahydrofuran (THF), toluene, and 1,4-dioxane (entries 12–16, Table S1, SI). For base screening, Et_3N was found to be the most effective (entries 17–20, Table S1, SI). In addition, other bi-, tri-, and tetradentate phosphine ligands or nitrogen-containing ligands hardly afforded the formylated product (entries 21–30,Table S1, SI). Further detailed investigation on the reaction parameters (entries 31–48, Table S1, SI) showed that 100% conversion and 86% yield of **1** could be achieved under the optimum reaction conditions (entry 8, Table 1). In addition, large-scale formylation reaction of iodobenzene with CO_2/H_2 was carried out, affording benzaldehyde in 82% yield (entry 8, Table 1). Subsequently, formylation of bromobenzene with CO_2/H_2 was conducted under the above optimum conditions, but almost no conversion of bromobenzene occurred, probably due to the low activation ability of the rhodium species toward the C–Br bond (entry 9, Table 1). As previously reported, Pd(dppp)Cl_2 was able to effectively catalyze the formylation of aryl bromides with CO_2/hydrosilane.[19] Therefore, RhI_3/Pd(dppp)Cl_2/PPh_3 was applied in the reaction of bromobenzene with CO_2/H_2, and delightfully, 99% conversion of bromobenzene together with 87% yield of **1** was achieved (entry 10, Table 1). Moreover, it was shown that both PPh_3 and RhI_3 were necessary for high product yield (entries 11–13, Table 1). Addition of similar Pd complexes with different phosphorus ligands, including Pd(dppe)Cl_2, Pd(dppf)Cl_2, and $Pd(PPh_3)_2Cl_2$, also afforded moderate yields of **1** (65–73%) (entries 49–51, Table S1, SI). However, $PdCl_2$ and $Pd(OAc)_2$ gave **1** in relatively low yields (34% and 13%, respectively) (entries 52–53, Table S1, SI).

Table 1. Rhodium-Catalyzed Formylation of Iodobenzene/Bromobenzene with CO_2/H_2 To Afford Benzaldehyde 1[a]

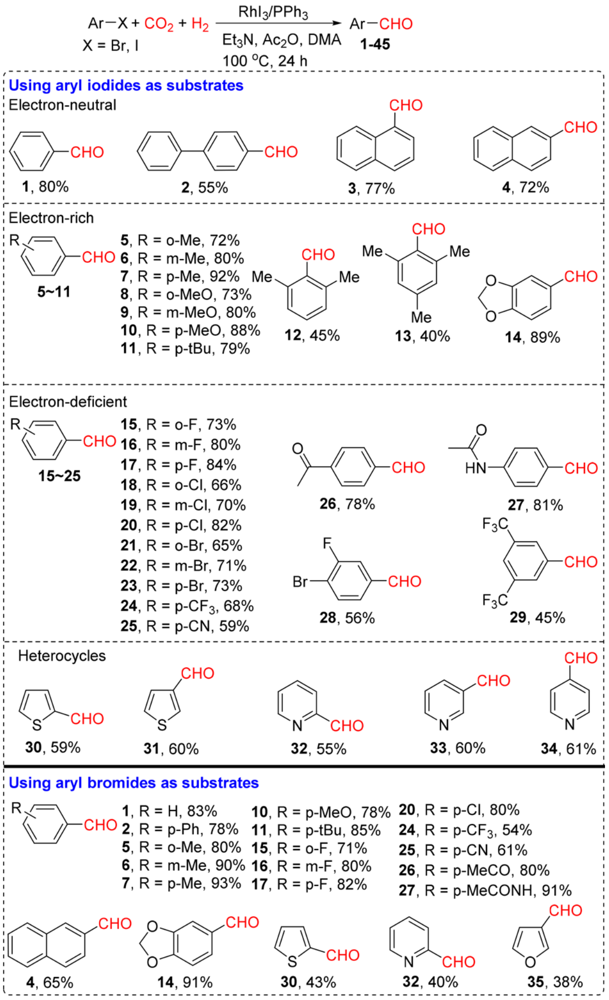


entry	substrate	deviation from standard conditions	conversion[b] (%)	yield[b] (%)
1	PhI	none	100	61
2	PhI	no PPh_3	97	0
3	PhI	no Et_3N	99	0
4	PhI	no Ac_2O	99	0
5	PhI	no CO_2	100	0
6	PhI	no H_2	100	0
7	PhI	no DMA	43	8
8[c]	PhI	none	100	86 (82[e])
9[c]	PhBr	none	33	<1
10[c,d]	PhBr	none	99	87
11[c,d]	PhBr	no PPh_3	62	26
12[c,d]	PhBr	no RhI_3	26	6
13[c,d]	PhBr	no RhI_3 and PPh_3	33	4

[a] Standard conditions: PhI (1 mmol), RhI_3 (5 mol %), PPh_3 (15 mol %), Et_3N (5 mmol), Ac_2O (2 mmol), DMA (2 mL), CO_2 (3 MPa) + H_2 (3 MPa), 100 °C, 24 h. [b] Determined by GC using dodecane as an internal standard. [c] Ac_2O (4.5 mmol), Et_3N (1.2 mmol), CO_2 (4 MPa) + H_2 (4 MPa). [d] Additional Pd(dppp)Cl_2 (5 mol %) was added. [e] PhI (10 mmol), RhI_3 (5 mol %), PPh_3 (15 mol %), Et_3N (12 mmol), Ac_2O (45 mmol), DMA (20 mL), CO_2 (4 MPa) + H_2 (4 MPa), 100 °C, 24 h, conducted in an autoclave with the inner volume of 100 mL.

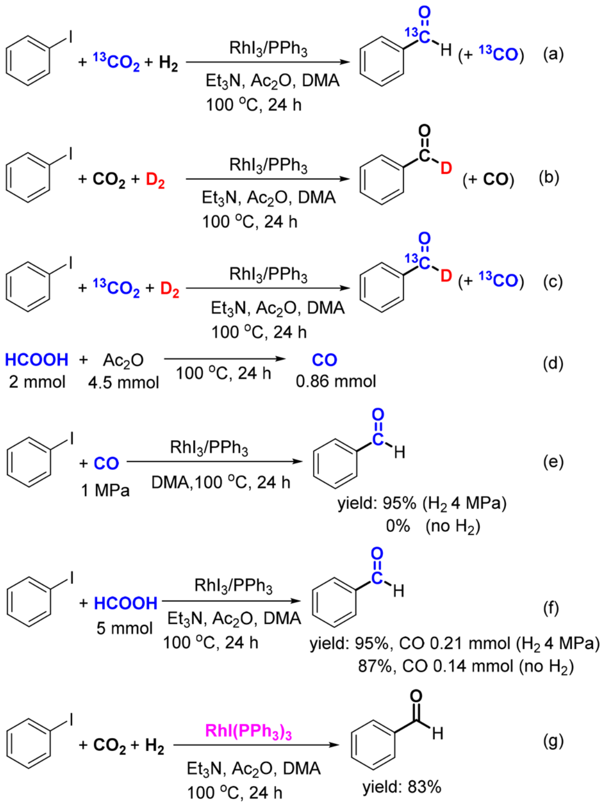
Having demonstrated the feasibility of benzaldehyde synthesis from iodobenzene with CO_2/H_2 as the building block for the formyl group, the scope of this transformation was then explored (Scheme 2). Neutral iodoarenes including iodobenzene, 4-iodobiphenyl, 1-iodonaphthalene, and 2-iodonaphthalene provided the corresponding aromatic aldehydes **1–4** in moderate to high yields (55–80%). For iodobenzene derivatives with electron-donating groups (Me, OMe), the product yields (**5–10**, 72–92%) were influenced by the position of the substituent groups, following the order of *o*- < *m*- < *p*-, probably owing to the steric hindrance effect. Employing 4-*tert*-butyliodobenzene as the substrate afforded a product (**11**) yield of 79%. Notably, other electron-rich iodoarenes with two or three methyl groups reacted well, providing 45% (**12**), 40% (**13**), and 89% (**14**) yields of the aromatic aldehydes, respectively. Aryl iodides with other halide substitutes (F, Cl, Br) were also compatible under our reaction conditions, with 65–84% (**15–23**) yields of the formylated products being obtained. In addition, the influence of the substituent group position followed the order of *o*- < *m*- < *p*- due to steric hindrance effects. Other aryl iodides with electron-withdrawing groups such as trifluoromethyl, cyano, acetyl, acetyl amino groups also provided acceptable yields (59–81%, **24–27**), demonstrating the compatibility of this catalytic system to reducible groups even under high H_2 pressure. Generally, dehalogenation and direct coupling reaction easily occurred for electron deficient aryl halides.[19] Aryl aldehydes with two electron-withdrawing groups could be obtained in moderate yields (56% and 45% for **28** and **29**, respectively). Heterocyclic iodides were amenable to the

Scheme 2. Substrate Scope for the Rh-Catalyzed Formylation of Aryl Iodides/Bromides Using CO_2/H_2[a]



[a] The reaction was conducted under the condition of entry 8 (aryl iodides) and 10 (aryl bromides) in Table 1. Isolated yields of the products are given and the structures were determined by GC−MS and NMR. For details, see the SI.

Scheme 3. Isotope-Labeling Experiments and Control Experiments



formylation reaction as well, leading to the corresponding aldehydes **30−34** with yields of 55−61%.

Subsequently, formylation of aryl bromides with CO_2/H_2 was conducted over $RhI_3/Pd(dppp)Cl_2/PPh_3$. Various aromatic aldehydes were obtained in good to excellent yields, including benzaldehyde **1** (83%) and its derivatives bearing electron-neutral (**2**, 78% and **4**, 65%), electron-rich (**5**, **6**, **7**, **10**, **11**, **14**, 78−93%), and electron-deficient groups (**15−17**, **20**, **24−27**, 54−91%). Formylation of heterocyclic aromatic bromides also performed well, affording the target aldehydes (**30**, **32**, **35** in moderate yields (38−43%).

To gain insight into the details of aryl iodide formylation with CO_2/H_2, isotope-labeling experiments were performed under the conditions of entry 8 in Table 1 using $^{13}CO_2$ and D_2 instead of CO_2 and H_2, respectively, to verify the sources of the carbon and hydrogen in the formyl group. The molecular ion peaks of *m*/*z* 107, 107, and 108 in the GC−MS spectrum of the reaction solution (Figure S1, SI), can be assigned to $C_6H_5{}^{13}CHO$, C_6H_5CDO, and $C_6H_5{}^{13}CDO$, respectively, confirming that both CO_2 and H_2 are involved the formation of the formyl group (Scheme 3a−c). Moreover, CO was detected by GC in the gas phase after the reaction (Figure S2, SI), and in the case of using $^{13}CO_2$, the molecular ion peak of *m*/*z* 29 for ^{13}CO was detected by GC−MS (Figure S3, SI). The ^1H NMR spectrum of the reaction mixture indicated the formation of HCOOH and CH_3COOH during the reaction process of entry 8 in Table 1, which were also detected by GC−MS (Figure S4 and S5, SI). From the above results, it can be deduced that HCOOH may be generated from the CO_2 hydrogenation catalyzed by a Rh-based catalytic system similar to the reported results,[28] and the subsequent reaction of HCOOH with Ac_2O led to the release of CO and the formation of CH_3COOH.[29] Actually, it was found that HCOOH could react with Ac_2O to release CO at 100 °C without any catalyst (Scheme 3d). Subsequently, several control experiments were conducted. It was indicated that in the case of using CO instead of CO_2 a high yield of **1** (95%) was obtained in the presence of H_2 (4 MPa), while no **1** was detected in the absence of H_2 (Scheme 3e), suggesting that H_2 played an important role probably in the reductive elimination step (Scheme 4, step **III**, **E** to **F**). In the control experiment using HCOOH instead of CO_2, 95% and 87% yields of **1** were obtained in the presence and absence of H_2, respectively, and CO was detected in the gas phase (Scheme 3f). Hence, it can be deduced that HCOOH could also act as a hydrogen source for the reductive elimination process.[29]

Kinetic study results showed that at the beginning of the reaction, no CO or HCOOH was detected within the first 2 h (Figure S6, SI). At 3 h, 0.19 mmol of CO was detected in the gas phase and no HCOOH was detectable, together with 9% yield of **1**, suggesting that in this case the generated CO was excess while the generated HCOOH was completely consumed. As the reaction proceeded, both CO and

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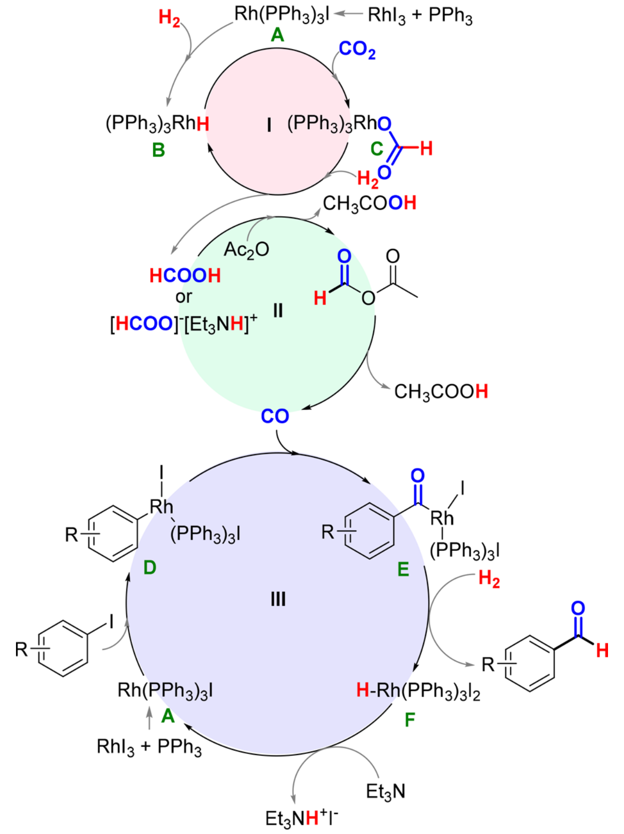
Scheme 4. Proposed Reaction Mechanism for the Rh-Catalyzed Formylation of Aryl Iodides Using CO_2/H_2



HCOOH began to accumulate, and the yield of **1** increased rapidly from 9% (3 h) to 66% (12 h). Finally, when the reaction finished, 1.06 mmol of HCOOH and 1.50 mmol of CO was obtained, and it were estimated that 0.82 mmol of CO was involved in the formylation reaction to afford 82% yield of **1**.

The investigation results of the influence of PPh_3 amount on the catalytic activity showed that under the otherwise identical conditions, the maximum yield of **1** (70%) was achieved with the molar ratio of RhI_3/PPh_3 as 1:3, while more or less PPh_3 all led to decreased yields of **1** (entry 18 vs 23−25, Table S1, SI). This indicates that molar ratio of [Rh]:PPh_3 in the actual catalytic species was 1:3, which was probably $Rh(PPh_3)_3I$. Thus, $Rh(PPh_3)_3I$ was synthesized and used as the catalyst instead of RhI_3 and PPh_3, and 83% yield of **1** was afforded under otherwise identical reaction conditions.

On the basis of the experimental results and previous reports, a cascade reaction mechanism for the formylation of aryl iodides is proposed (Scheme 4). Initially, in step I, HCOOH (or $[HCOO]^-[Et_3NH]^+$ in the presence of Et_3N) is formed through hydrogenation of CO_2 catalyzed by $Rh(PPh_3)_3I$ species (**A**), which involves the formation of $(PPh_3)_3Rh{-}H$ (**B**) in the presence of H_2, CO_2 insertion into the Rh−H bond (**C**) and metathesis with H_2 to release HCOOH and regenerate $(PPh_3)_3Rh{-}H$ (**B**).[30] Subsequently, in step II, the produced HCOOH reacts with acetic anhydride to afford the $HC(O)OC(O)CH_3$ intermediate, which then decomposes to CH_3COOH with simultaneous release of CO. Finally, in step III, the reaction starts with the oxidative addition of $Rh(PPh_3)_3I$ (**A**) to aryl iodide, affording the corresponding arylrhodium complex (**D**). Then, the benzoylrhodium complex (**E**) is obtained after the coordination and insertion of CO. The aldehyde product is obtained after metathesis with H_2 and the active Rh species are regenerated from the rhodium hydroiodide (**F**) complex by reaction with Et_3N.[14] For aryl bromides, the **Step III** is catalyzed by $Pd(dppp)Cl_2$ in a CO insertion and reductive elimination pathway as previously reported.[14]

In conclusion, we have demonstrated the catalytic formylation of aryl iodides/bromides using CO_2/H_2. The use of commercially available RhI_3/PPh_3 together with Ac_2O as a deoxygenation reagent afforded the aryl aldehydes in good to excellent yields. This transformation provides an atom-efficient alternative to traditional formylation methodologies and utilizes CO_2 as a C1 source. In particular, if hydrogen is provided from renewable sources, the new synthetic route clearly has the potential to significantly reduce the dependence on petrochemical feedstocks for the chemical supply chain.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b02027.

Experimental procedures, supplementary scheme and figures, NMR and MS spectra (PDF)

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§Z.L. and Z.Y. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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