Ligandless Palladium Catalyzed Reductive Carbonylation of Aryl Iodides under Ambient Conditions

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# 1. General information

**Reagent Information.** All the organohalides were purchased from Alfa Aesar, Energy Chemical, Beijing InnoChem Science & Technology Co., Ltd., and Accela ChemBio Co., Ltd. and were used as received. PEG-400 (bought from Acros and Energy Chemical) was pre-dried (toluene azeotrope) and deoxygenated. Pd(OAc)$_2$ was purchased from Accela ChemBio Co.. The following Et$_3$SiH and bases were used: Et$_3$SiH (Alfa Aesar), anhydrous Na$_2$CO$_3$ and anhydrous NaHCO$_3$ (Alfa Aesar).

**Physical Methods.** $^1$H and $^{13}$C NMR spectra of solutions in CDCl$_3$ were recorded on a Bruker Avance 400 instrument. Chemical shifts were expressed in parts per million (ppm) downfield from tetramethylsilane and refer to the solvent signals (CDCl$_3$: H 7.24 and C 77.0 ppm). The signal of water was observed at about 1.58 ppm. Abbreviations for signal couplings are: br, broad; s, singlet; d, doublet; t, triplet; m, multiplet; dd, doublet of doublets; dt, triplet of doublets; td, doublet of triplets; tt, triplet of triplets; ddd, doublet of doublet of doublets; tdd, doublet of doublet of triplets. Coupling constants, $J$, were reported in hertz unit (Hz). TEM was performed on a JEM-2100F.

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2. General procedures

**General Procedure A for reductive carbonylation of aryl iodide to aromatic aldehyde under ambient conditions.** A flask was charged with aryl iodide 1 (0.5 mmol), Pd(OAc)$_2$ (2.4 mg, 0.01 mmol), Na$_2$CO$_3$ (53.1 mg, 0.5 mmol), NaHCO$_3$ (42.0 mg, 0.5 mmol), and PEG-400 (2 g) before standard cycles evacuation and backfilling with dry and pure carbon monoxide. Triethylsilane (162.8 µl, 1.0 mmol) was added successively. Then, the mixture was stirred at room temperature for the indicated time. At the end of the reaction, the reaction mixture was extracted with diethyl ether (3 × 10 mL). The organic phases were combined, and the volatile components were evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether / diethyl ether).

In the recycling experiment, the residue was subjected to a second run by charging it with the same substrates as mentioned above without further addition of Pd(OAc)$_2$ and PEG 400. In the fourth, sixth, and eighth runs, another 0.5 g of PEG-400 was added to the reaction mixture.

**General procedure B for reductive carbonylation of diiodobenzene to aromatic dialdehyde under ambient conditions.** A flask was charged with diiodobenzene (0.5 mmol), Pd(OAc)$_2$ (2.4 mg, 0.01 mmol), Na$_2$CO$_3$ (106.2 mg, 1.0 mmol), NaHCO$_3$ (84.0 mg, 1.0 mmol), and PEG-400 (2 g) before standard cycles evacuation and backfilling with dry and pure carbon monoxide. Triethylsilane (325.6 µl, 2.0 mmol) was added successively. Then, the mixture was stirred at room temperature for the indicated time. At the end of the reaction, the reaction mixture was extracted with diethyl ether (3 × 10 mL). The organic phases were combined, and the volatile components were evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether / diethyl ether).

3. Analytical data of products

4-Nitrobenzaldehyde (2a): Following general procedure A, 2a was isolated as a light yellow solid (66 mg, 87%). Known compound; the NMR spectroscopic data agree with those described in ref. [S1] ¹H NMR (400 MHz, CDCl$_3$): δ 10.13 (s, 1H), 8.36 (d, $J = 8.9$ Hz, 2H), 8.05 ppm (d, $J = 8.9$ Hz, 2H); ¹³C NMR (100 MHz, CDCl$_3$): δ 190.3, 151.1, 140.0, 130.4, 124.3 ppm; mp 105.9–106.4 °C.

Isophthalaldehyde (2b): Following general procedure A, 2b was isolated as a light yellow solid (66 mg, 87%). Known compound; the NMR spectroscopic data agree with those described in ref. [S2] ¹H NMR (400 MHz, CDCl$_3$): δ 10.09 (s, 1H), 8.35 (t, $J = 1.4$ Hz, 1H), 8.13 (dd, $J = 7.6$, 1.7 Hz, 1H), 7.71 ppm (t, $J = 7.7$ Hz, 1H); ¹³C NMR (100 MHz, CDCl$_3$) δ 191.0, 137.0, 134.6, 131.0, 129.9 ppm; mp 86.2–86.5 °C.
Methyl 4-formylbenzoate (2c): Following general procedure A, 2c was isolated as a white solid (66 mg, 87%). Known compound; the NMR spectroscopic data agree with those described in ref.[S3] 1H NMR (400 MHz, CDCl₃) δ 10.00 (s, 1H), 8.08 (d, J = 8.0 Hz, 2H), 7.85 (d, J = 8.0 Hz, 2H), 3.86 ppm (s, 3H); 13C NMR (100 MHz, CDCl₃) δ 191.4, 165.8, 139.0, 134.9, 129.9, 129.3, 52.4 ppm. mp 60.2–61.5°C.

Phenyl 4-iodobenzoate (2d): Following general procedure A, 2d was isolated as a white solid (91 mg, 81%). Known compound; the NMR spectroscopic data agree with those described in ref.[S4] 1H NMR (400 MHz, CDCl₃): δ 10.13 (s, 1H), 8.35 (d, J = 8.4 Hz, 2H), 8.01 (d, J = 8.4 Hz, 2H), 7.44 (t, J = 8.0 Hz, 2H), 7.29 (t, J = 7.4 Hz, 1H), 7.21 ppm (d, J = 7.6 Hz, 2H); 13C NMR (100 MHz, CDCl₃): δ 191.5, 164.1, 150.6, 139.5, 134.4, 130.7, 129.64, 129.60, 126.2, 121.5 ppm. mp 107.1–108.0°C.

4-Chlorobenzaldehyde (2e): Following general procedure A, 2e was isolated as a white solid with low melting point (60 mg, 85%). Known compound; the NMR spectroscopic data agree with those described in ref.[S1] 1H NMR (400 MHz, CDCl₃): δ 9.96 (s, 1H), 7.80 (d, J = 8.7 Hz, 2H), 7.49 ppm (d, J = 8.7 Hz, 2H); 13C NMR (100 MHz, CDCl₃): δ 190.9, 140.9, 134.7, 130.9, 129.4 ppm. mp 47.3–48.5°C.

4-(Trifluoromethyl)benzaldehyde (2g): Following general procedure A, 2g was isolated as a colorless oil (78 mg, 90%). Known compound; the NMR spectroscopic data agree with those described in ref.[S2] 1H NMR (400 MHz, CDCl₃): δ 10.08 (s, 1H), 7.99 (d, J = 8.6 Hz, 2H), 7.79 ppm (d, J = 8.4 Hz, 2H); 13C NMR (100 MHz, CDCl₃): δ 191.1, 138.7, 135.6 (d, J = 32 Hz), 129.9, 126.1 (q, J = 4 Hz), 123.4 ppm (q, J = 271 Hz).

3-Fluoro-4-methylbenzaldehyde (2h): Following general procedure A, 2h was isolated as a light yellow liquid (66 mg, 87%). Known compound; the NMR spectroscopic data agree with those
described in ref.\cite{S5} $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.90 (s, 1H), 7.54 (dd, $J = 7.7, 1.5$ Hz, 1H), 7.48 (d, $J = 9.4$ Hz, 1H), 7.33 (t, $J = 7.8$ Hz, 1H), 2.33 ppm (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 190.8 (d, $J = 2$ Hz), 161.5 (d, $J = 248$ Hz), 136.3 (d, $J = 6$ Hz), 132.6 (d, $J = 18$ Hz), 132.1 (d, $J = 5$ Hz), 125.9 (d, $J = 3$ Hz), 114.9 (d, $J = 23$ Hz), 15.1 ppm (d, $J = 4$ Hz).

3-Methylbenzaldehyde (2k): Following general procedure A, 2k was isolated as a colorless oil (54 mg, 90%). Known compound; the NMR spectroscopic data agree with those described in ref.\cite{S1} $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.96 (s, 1H), 7.67–7.65 (m, 2H), 7.42–7.39 (m, 2H), 2.41 ppm (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 192.6, 138.9, 136.5, 135.3, 130.0, 128.9, 127.2, 21.2 ppm.

4-Methylbenzaldehyde (2l): Following general procedure A, 2l was isolated as a light yellow oil (66 mg, 87%). Known compound; the NMR spectroscopic data agree with those described in ref.\cite{S6} $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.94 (s, 1H), 7.75 (d, $J = 8.1$ Hz, 2H), 7.31 (d, $J = 8.1$ Hz, 2H), 2.42 ppm (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 192.0, 145.5, 134.2, 129.8, 129.7, 129.9, 127.2, 21.9 ppm.

2-(3-Formylphenyl)acetonitrile (2m): Following general procedure A, 2m was isolated as a light yellow solid (66 mg, 87%). Known compound (CAS: 864674-53-3); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.00 (s, 1H), 7.84 – 7.82 (m, 2H), 7.64 – 7.53 (m, 2H), 3.83 ppm (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 191.4, 137.0, 133.7, 131.2, 129.9, 129.6, 128.7, 117.1, 23.4 ppm.

3,5-Dimethylbenzaldehyde (2n): Following general procedure A, 2n was isolated as a colorless oil (58 mg, 87%). Known compound; the NMR spectroscopic data agree with those described in ref.\cite{S7} $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.93 (s, 1H), 7.46 (s, 2H), 7.24 (s, 1H), 2.37 ppm (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 192.8, 138.7, 136.6, 136.2, 127.5, 21.0 ppm.
1-Naphthaldehyde (2o): Following general procedure A, 2o was isolated as a light yellow oil (66 mg, 85%). Known compound; the NMR spectroscopic data agree with those described in ref. [58].

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 10.38 (s, 1H), 9.24 (d, $J$ = 8.6 Hz, 1H), 8.07 (d, $J$ = 8.2 Hz, 1H), 7.96 (dd, $J$ = 7.1, 1.3 Hz, 1H), 7.90 (d, $J$ = 8.2 Hz, 1H), 7.67 (ddd, $J$ = 8.5, 6.9, 1.4 Hz, 1H), 7.62–7.55 ppm (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 193.5, 136.6, 135.2, 133.7, 131.4, 130.5, 129.0, 128.4, 126.9, 124.8 ppm.

Terephthalaldehyde (2r): Following general procedure B, 2r was isolated as a white solid (42 mg, 62%). Known compound; the NMR spectroscopic data agree with those described in ref. [52].

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 10.10 (s, 2H), 8.01 ppm (s, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 191.5, 140.0, 130.1 ppm; mp 114.8–115.4°C.

4. TEM image

Scheme S1. TEM image of *in situ* generated palladium nanoparticles (Scale: 50 nm).

5. Hg(0) poisoning test
As general procedure A, a reaction of 1-iodo-4-nitrobenzene 1a (0.5 mmol, 127.0 mg), Pd(OAc)$_2$ (0.01 mmol, 2.4 mg), Na$_2$CO$_3$ (0.5 mmol, 53.1 mg), NaHCO$_3$ (0.5 mmol, 42.0 mg), and triethylsilane (1.0 mmol, 162.8 µl) in PEG-400 (2.0 g), with the addition of elemental mercury (1 mmol, 100 equiv, 200.6 mg) (relative to palladium) was conducted. Following the reaction for 12 h under ambient temperature and pressure, the isolated yield of the desired product 2a was 79%, suggesting that the reaction is not inhibited by the introduction of Hg(0) (Equation 1).

6. CS$_2$ poisoning test

As general procedure A, four reactions of 1-iodo-4-nitrobenzene 1a (0.5 mmol, 127.0 mg), Pd(OAc)$_2$ (0.01 mmol, 2.4 mg), Na$_2$CO$_3$ (0.5 mmol, 53.1 mg), NaHCO$_3$ (0.5 mmol, 42.0 mg), and triethylsilane (1.0 mmol, 162.8 µl) in PEG-400 (2.0 g) were carried out, one as a control. Carbon disulfide: 0.70 equiv., 1.0 equiv., and 1.5 equiv. (relative to palladium) were introduced to the other reactions, respectively. All reaction mixtures were stirred under ambient temperature and pressure for 12 h. Subsequent analysis of the reaction yields suggests that reaction is completely inhibited when employing ≥1.0 equiv. of the added CS$_2$ (Table S1).

Table S1. Results of CS$_2$ poisoning test.

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<tr>
<th>Entry</th>
<th>CS$_2$(equiv.)</th>
<th>Yield/%</th>
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</tr>
<tr>
<td>2</td>
<td>0.70</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
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<td>&lt;5</td>
</tr>
<tr>
<td>4</td>
<td>1.5</td>
<td>-</td>
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</table>

7. References

8. Copies of NMR Spectra

2a

$^1$H NMR (400 MHz, CDCl$_3$)

2a

$^{13}$C NMR (100 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)

$^1$C NMR (100 MHz, CDCl$_3$)
\[ \text{H}_3\text{COOC} - \text{CHO} \]

\[ \text{H}_3\text{COOC} - \text{CHO} \]

\[ ^1H \text{ NMR (400 MHz, CDCl}_3) \]

\[ ^{13}C \text{ NMR (100 MHz, CDCl}_3) \]
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)

2e

$^1$H NMR (400 MHz, CDCl$_3$)

Cl

CHO

2e

Cl

CHO
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)