Electrosynthesis of Aromatic Aldehydes by Palladium-Catalyzed Carbonylation of Aryl Iodides in the Presence of Formic Acid

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The palladium-catalyzed electrocarbonylation of aryl halides performed in the presence of formic acid under one atmosphere of carbon monoxide affords aromatic aldehydes in good to high yields.

It has been recently reported that vinyl- and aryl halides or -triflates react under electroreducing conditions in the presence of palladium catalysts to produce biaryls,[1][2] aromatic[1][3] and α,β-unsaturated[4] carboxylic acids, alkenes, and arenes.[5] As part of our ongoing program devoted to the development of new applications of the palladium-catalyzed electrosynthesis, we now report our preliminary results on the preparation of aromatic aldehydes from aryl halides and carbon monoxide under electrochemical reducing conditions.

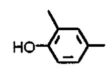
The synthesis of aryl aldehydes from aryl halides and CO is formally a hydride transfer.[6] We have reported that under electrochemical reduction (Eq. 1), the reactivity of aryl halides is reversed since the formation of aryl aldehydes results from a proton transfer. $n\mathrm{Bu_4NHSO_4}$ and $\mathrm{HClO_4}$ were used as proton sources.[7]

$$\mathrm{ArI + CO + 2e + H^+ \xrightarrow{Pd\ cat} ArCHO + I^-} \qquad (1)$$

The initial concept was based on electrochemical reduction of acylpalladium intermediates, [ArCOPdI], generated in situ from aryl iodides, palladium(0), and carbon monoxide, followed by the protonation of the resultant anionic species.[7] However, aromatic aldehydes were obtained in low yield.[7] For example, the electrolysis at −1.7 V vs. SCE of 4-iodoanisole (10^{-2} mol dm^{-3} in DMF containing $n\mathrm{Bu_4NBF_4}$ 0.2 mol dm^{-3}) in the presence of 10 mol-% of $\mathrm{PdCl_2(Ph_3P)_2}$, 1.5 equiv. of $n\mathrm{Bu_4NHSO_4}$ and one atmosphere of CO at 22°C gave anisole as the major product (46% yield), together with minor amount (14%) of the desired *p*-anisaldehyde. Apparently, when the potential is too negative, the reduction of the arylpalladium(II) complex (formed initially by the oxidative insertion of palladium(0) into the carbon−halogen bond) followed by a protonation step is faster than its reaction with CO to afford the corresponding acylpalladium complex (vide infra). A dramatic change occurred when performing the reaction at a less negative potential in the presence of formic acid (Eq. 2, Table 1).

$$\mathrm{ArI + CO + HCO_2H + e \xrightarrow[DMF,\ 60\ ^\circ C]{[Pd]\ cat} ArCHO + CO_2 + 1/2\,H_2 + I^-} \qquad (2)$$

Table 1. Palladium-catalyzed electrosynthesis of aromatic aldehydes from aryl iodides and carbon monoxide in the presence of formic acid (Eq. 2)

Entry	Aryl Iodides	Catalyst	E/V[a]	Aldehyde Yield %[b]
1	*p*-MeO-$\mathrm{C_6H_4}$-I	$\mathrm{PdCl_2(Ph_3P)_2}$	-1.5	78
2	*p*-Me-$\mathrm{C_6H_4}$-I	$\mathrm{Pd(Ph_3P)_4}$	-1.3	64
3	*o*-Me-$\mathrm{C_6H_4}$-I	$\mathrm{PdCl_2(Ph_3P)_2}$	-1.5	40
4	$\mathrm{C_6H_5}$-I	"	"	70
5		"	"	93
6	3,5-$\mathrm{Me_2}$-$\mathrm{C_6H_3}$-I	"	"	82
7	3,4-$\mathrm{Me_2}$-$\mathrm{C_6H_3}$-I	"	"	76
8	*p*-HO-$\mathrm{C_6H_4}$-I	$\mathrm{Pd(Ph_3P)_4}$	"	78
9	*p*-EtOCO-$\mathrm{C_6H_4}$-I	$\mathrm{PdCl_2(Ph_3P)_2}$	"	20

[a] Electrolysis potential vs. SCE. − [b] Relative to initial aryl iodide.

For example, when the electrochemical reduction of 4-iodoanisole was carried out at −1.5 V vs. SCE under one atmosphere of CO in the presence of 10 mol-% of $[\mathrm{PdCl_2(Ph_3P)_2}]$ and 2 equiv. of $\mathrm{HCO_2H}$, *p*-anisaldehyde was isolated in 78% yield. These conditions were applied to a variety of aryl iodides and the preparative results are summarized in Table 1.[8] Aryl iodides bearing electron-donating substituents gave the best results, with a slight decrease of the yields when they contain *ortho*-substituents (Table 1, compare entries 2 and 3). Lower yields were obtained with aryl iodides containing electron-withdrawing substituents (Table 1, entry 9), most probably because of competitive overreduction. This view seems to be supported by the cyclic voltammetry of *p*-EtOCO−$\mathrm{C_6H_4}$−CHO, which shows that it is more easily reduced than the starting aryl iodide.

The reduction of $[\mathrm{PdCl_2(Ph_3P)_2}]$ at the very beginning of the electrolysis affords a palladium(0) complex which acti-

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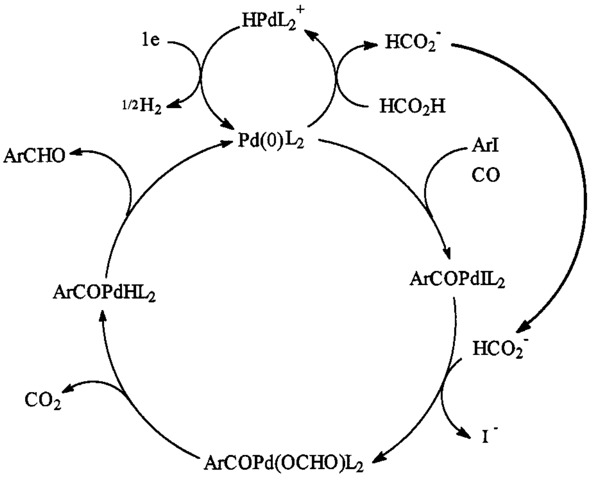
vates aryl iodides by an oxidative addition. Kinetic investigation showed that the rate of the oxidative addition of $[Pd^0(Ph_3P)_4]$ with PhI was considerably slower in the presence of CO (e.g.: for $[PhI] = 20\ mmol\ dm^{-3}$, $t_{1/2} = 2$ s in the absence of CO; $t_{1/2} = 310$ s in the presence of CO at atmospheric pressure). This fact suggests that the nature of the usual reactive species in the oxidative addition, viz. $[Pd^0(Ph_3P)_2]$, changes in the presence of carbon monoxide, very likely because of the formation of a palladium(0) complex ligated to carbon monoxide (Eq. 3).

$$Pd^0(Ph_3P)_2 + CO \rightleftharpoons Pd^0(Ph_3P)_2(CO) \qquad (3)$$

Thus the oxidative addition overall rate decreases either because $[Pd^0(Ph_3P)_2]$ is less available, or because $[Pd^0(Ph_3P)_2(CO)]$ is less reactive owing to its lower nucleophilicity, or both. This could not be kinetically discriminated because the too low solubility of CO at atmospheric pressure in DMF (ca. 3−4 $mmol\ dm^{-3}$) prevented any fine quantitative investigation of the kinetics of the oxidative addition. Indeed, our amperometric method used to monitor the kinetics requires concentrations of $[Pd^0(Ph_3P)_4]$ of at least 2 $mmol\ dm^{-3}$ to allow precise currents measurements. Therefore, at this stage, we cannot decide whether the CO group is already present on the palladium(0) center when the oxidative addition takes place or the oxidative addition to $[Pd^0(Ph_3P)_2]$ precedes the coordination of carbon monoxide. Whatever the real mechanism may be, it remains that acylpalladium(II) intermediates are formed in the palladium-catalyzed reaction of aryl iodides with carbon monoxide.[7] It is worthwhile to note that the electrolysis potentials are less negative that the reduction potential of acylpalladium(II) complexes.[7] Consequently, these complexes cannot be reduced to anionic species as it was established in our previous work (Eq. 1).[7] Under the present conditions, they can be converted into the corresponding aldehydes only through the intermediacy of σ-acyl−σ-formate palladium(II) complexes formed by the nucleophilic attack of formate on the acylpalladium(II) complexes[6] (Scheme 1). Subsequent elimination of CO_2,[6] followed by the reductive elimination of palladium(0) species from the resultant acylpalladium hydride affords the aldehyde and regenerates the palladium(0) complex.

However, the dissociation constant of formic acid in DMF is too low to enable it to be the direct source of formate ions. Accordingly, 4-iodoanisole was recovered in 90% yield when it was treated in DMF (containing nBu_4NBF_4 0.2 $mol\ dm^{-3}$) for 24 h at 60 °C with formic acid, 10 mol-% of $[Pd^0(PPh_3)_4]$ under one atmosphere of carbon monoxide. *p*-Anisaldehyde was obtained in only 6% yield.

Nor could formic acid be the indirect source of formate ions by electrochemical reduction of its protons. Indeed, the electrolyses were carried out at a potential of −1.5 V, whereas the electrochemical reduction of formic acid under the same conditions, in the absence of palladium, occurred at −2.0 V (Eq. 4).



Scheme 1

$$\begin{tikzcd} HCO_2H \arrow[r, leftrightharpoons] & H^+ \arrow[d, "+e\ (at\ -2.0\ V)"] & + HCO_2^- \\ & 1/2H_2 & \end{tikzcd} \qquad (4)$$

Therefore, it is apparent that under our electrolytic conditions, the palladium must play a second crucial role in supplying the reaction medium with formate ions. This prompted us to investigate the role of palladium(0) complexes in the generation of formate ions from formic acid. $[Pd^0(Ph_3P)_4]$ was found to react with formic acid in DMF at room temperature. The reaction was monitored by conductimetry as well as by cyclic voltammetry and ^{31}P-NMR spectroscopy. Conductivity increased with time so as to reach a plateau whose value depended on the amount of formic acid (Figure 1). Thus ionic species were formed by this reaction which is an equilibrium.

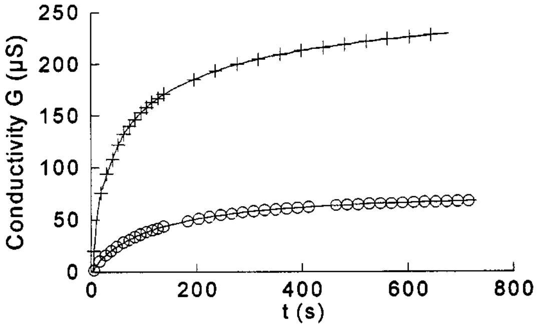


Figure 1. Conductance measurements of solutions of $[Pd(Ph_3P)_4]$ (2 $mmol\ dm^{-3}$) and *n* equivalents of HCO_2H in DMF, at 20 °C. (O) $n = 1$; (+) $n = 100$

Concomitantly, cyclic voltammetry indicated that a reducible palladium(II) complex was formed ($E_p = -0.99$ V vs. SCE, compare Figures 2a−c).[9a] The same species could be characterized by its ^{31}P-NMR signal at $\delta = 24.27$ vs. H_3PO_4 (external standard).[9b] Since the equilibrium concentrations of the ionic species were lower in the presence of excess PPh_3, this suggests a reaction between $Pd^0(Ph_3P)_3$ and formic acid presumably via the low ligated complex $[Pd^0(Ph_3P)_2]$ to afford a formate anion and a cationic palladium(II) hydride (Eq. 5). The equilibrium constant *K* has

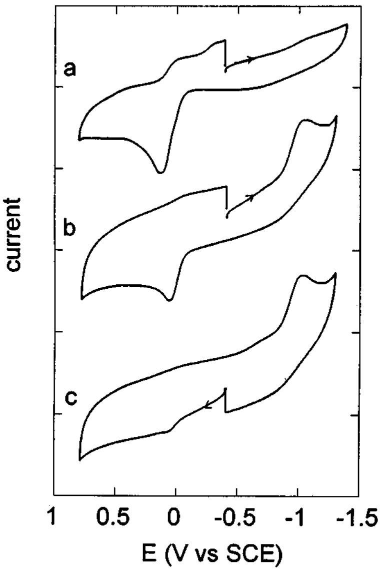


Figure 2. Cyclic voltammetry performed in DMF (containing $n\mathrm{Bu_4NBF_4}$, 0.3 mol dm^{-3}) at a steady glassy carbon disk electrode (i.d. = 2 mm) with a scan rate of 0.2 V s^{-1}. 20 °C. a) $[\mathrm{Pd^0(Ph_3P)_4}]$ (2 mmol dm^{-3}) alone. b) $[\mathrm{Pd(Ph_3P)_4}]$ (2 mmol dm^{-3}) and $\mathrm{HCO_2H}$ (0.4 mol dm^{-3}): reduction after one hour reaction. c) $[\mathrm{Pd^0(Ph_3P)_4}]$ (2 mmol dm^{-3}) and $\mathrm{HCO_2H}$ (0.4 mol dm^{-3}): oxidation after one hour reaction.

$$\mathrm{Pd^0(Ph_3P)_3 + HCO_2H \rightleftharpoons HPd^{II}(Ph_3P)_2^+ + HCO_2^- + PPh_3} \quad K \tag{5}$$

been estimated from conductivity measurements: $K = 5{\cdot}10^{-5}$ mol dm^{-3}, at 0 °C.

On the basis of its reduction potential (−0.99 V vs. SCE), $[\mathrm{HPd(Ph_3P)_2}]^+$ is reducible under our electrolytic conditions to palladium(0) complex (Eq. 6, Figure 2b).

$$\mathrm{HPd^{II}(Ph_3P)_2^+ + 1e \longrightarrow Pd^0(Ph_3P)_2 + 1/2H_2} \quad \text{(at -0.99 V)} \tag{6}$$

Consequently, the equilibrium sketched in Eq. 5 is continuously displaced to the right side to generate a small but constant flux of formate in the reaction medium. The result is that formate ions are generated at an adequate rate by this combination of chemical and electrochemical steps, at a potential where the direct reduction of formic acid to formate (Eqs. 4) cannot occur.

To sum up, the palladium catalyst plays a triple role: i) activation of the aryl iodide by oxidative addition, ii) activation of CO to form an acylpalladium complex and iii) activation of formic acid to generate formate ions. The tentative mechanism of the electrosynthesis of aldehydes is outlined in Scheme 1

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[8] The electrosynthesis of aldehydes was performed in a three-electrode cell containing 40 mL of anhydrous DMF and $n\mathrm{Bu_4NBF_4}$ (0.2 mol dm^{-3}) as supporting electrolyte. The cathode was a glassy carbon electrode and the anode a platinum wire. The reference electrode was a saturated calomel electrode. The cell was charged with 0.5 mmol of aryl iodide, 10 mol-% of the catalyst and 2 equivalents of formic acid. Electrolyses were performed at constant potential (see Table 1) under one atmosphere of CO at 60°C. After acidic hydrolysis, the mixture was extracted with diethyl ether. Crude reaction mixtures were then analyzed by GC analysis and yields were calculated by using authentic samples as external standards.

[9] [9a] The identical reduction peak was observed in the reaction of acetic acid and $[\mathrm{Pd^0(Ph_3P)_4}]$]. − [9b] The identical ^{31}P-NMR signal was observed in the reaction of acetic acid and $[\mathrm{Pd^0(Ph_3P)_4}]$.

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