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Palladium-catalysed reductive carbonylation of aryl halides with iron pentacarbonyl for synthesis of aromatic aldehydes and deuterated aldehydes

Nasser Iranpoor*, Habib Firouzabadi*, Elham Etemadi-Davan, Abed Rostami and Khashayar Rajabi Moghadam

The first use of iron pentacarbonyl is described for the novel and efficient conversion of aryl iodides, bromides and chlorides into their corresponding aryl aldehydes and/or aryl deuterated aldehydes. The reaction is catalysed with Pd(0) in aqueous *N,N*-dimethylformamide at atmospheric pressure. In this protocol, neither gaseous hydrogen nor any reducing agent is required for the formation of the carbonylated product. The reaction can be performed without a P(III) ligand for aryl iodides; however, employing a P(III) ligand is necessary to perform the reaction with aryl bromides and chlorides. Copyright © 2015 John Wiley & Sons, Ltd.

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Keywords: reductive carbonylation; Pd-catalysed; aromatic aldehyde; iron pentacarbonyl

Introduction

Palladium-catalysed carbonylative coupling reactions of aryl halides to produce esters, ketones, acids, amides and aldehydes have well been studied (Scheme 1).[1]

Among the cross-coupled carbonylative products, aldehydes are considered as important substrates due to their wide applications in organic synthesis, the aldehyde functional group being key intermediates in an array of synthetic reactions. Palladium-catalysed reductive carbonylation of aryl or vinyl halides to aldehydes is one of the most synthetically used carbonylation reactions.[2] However, only limited procedures have been developed for this synthetically important method. Schoenberg and Heck reported the first conversion of aryl and vinyl bromides or iodides to aldehydes in the presence of $[PdX_2(Ph_3P)_2]$ and CO/H_2.[1h] This reaction suffers from the necessity of high pressure and temperature and the application of gaseous H_2 as the external reducing agent, and also large amounts of Pd compound are required to achieve good yields.

Another catalytic reaction with Pd catalyst and CO/H_2 mixture for the efficient formylation of aryl and heteroaryl bromides has been reported at lower pressure.[3] Later on, other groups modified the reaction and conducted it with tin hydrides as the reducing agent in the presence of Pd catalyst and gaseous CO.[4] Due to the toxicity of tin hydrides, the application of organosilanes which are non-toxic was tested for this transformation.[5] Sodium formate was also used for the reductive carbonylation of aryl iodides and bromides as a source of hydrogen in conjunction with CO and Pd catalyst.[6] In order to avoid the use of gaseous CO with the difficulty of its handling, other groups conducted reductive carbonylation reactions employing CO-substitute reagents.[7] For example, Cacchi *et al.* used a mixture of R_3SiH as the reducing agent and acetic formic anhydride as the CO source to transform iodoarenes into the corresponding aldehydes.[8] Furthermore, Manabe *et al.* applied *N*-formylsaccharin as a solid CO source for the Pd-catalysed reductive carbonylation of aryl bromides at moderate temperatures.[9] Meanwhile, conversion of aryl triflates to aryl aldehydes was achieved using a Pd catalyst and a CO/H_2 mixture.[10] Recently, Liu and co-workers reported the Pd/C-catalysed direct formylation of aromatic iodides to aryl aldehydes using CO_2 in the presence of hydrosilane.[11]

As well as aryl aldehydes, synthesis of aromatic aldehydes bearing deuterium at the carbonyl functionality is of great interest, since deuterated aldehydes have found chemical and biochemical applications.[12] The classical method for the formation of deuterioaryl aldehydes requires strong bases and harsh reducing agents.[13] In 2004, Georg and co-workers reported the synthesis of deuterium-labelled aldehydes using commercially available $Cp_2Zr(D)Cl$ from a diversity of amides, including Weinreb amides.[14] In 2013, Skrystrup and co-workers demonstrated that D-isotope-labelled aldehydes can be achieved via Pd-catalysed carbonylation in a sealed two-chamber system applying 9-methylfluorene-9-carbonyl chloride as a source of externally delivered CO and DCO_2K for deuterium labelling.[15]

Besides gaseous CO, metal carbonyls have also been used as the CO source for carbonylative insertion reactions such as amidation,[16] esterification,[17] alkenylcarbonylation,[18] Stille reaction[19] and carbonylative arylation.[20] In addition, carbonylation of iodoarenes

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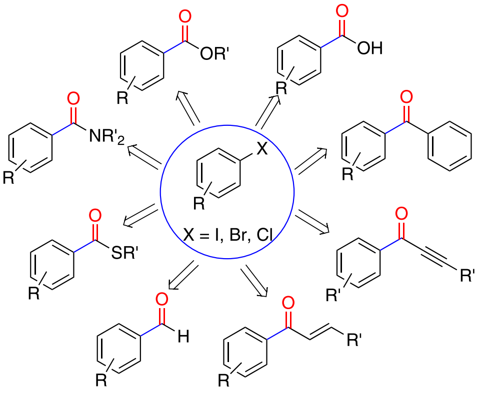
* *Correspondence to: Nasser Iranpoor or Habib Firouzabadi, Chemistry Department, College of Sciences, Shiraz University, Shiraz, Iran.*
E-mail: iranpoor@susc.ac.ir; firouzabadi@susc.ac.ir

Chemistry Department, College of Sciences, Shiraz University, Shiraz, Iran



Scheme 1. Pd-catalysed reductive carbonylation of aryl halides.

in the presence of gaseous CO has been done using bimetallic catalytic systems like $Fe(CO)_5$–$Co_2(CO)_8$ in which the metal carbonyl system was not the CO source for the reaction.[21] To the best of our knowledge, there is no report in the literature on the formylation of aryl halides in the presence of metal carbonyls without using any added reducing agent. With regard to this and also in continuation of our studies on carbonylation reactions,[22] we now report a new and novel phosphine-free Pd-catalysed method for the efficient conversion of iodoarenes to aryl carbaldehydes including their D-isotope-labelled derivatives using $Fe(CO)_5$ as CO source at 110 °C under atmospheric pressure in aqueous *N*,*N*-dimethylformamide (DMF). Moreover, we also extended this method to aryl bromides and chlorides in the presence of a P(III) ligand.

Experimental

^{1}H NMR (250 MHz) and ^{13}C NMR (62.9 MHz) spectra were recorded using a Bruker Avance spectrometer in $CDCl_3$ solutions with tetramethylsilane as the internal standard and were compared to those reported in the literature. Monitoring of the reaction was accomplished using TLC on silica gel PolyGram SILG/UV254 plates. UV–visible spectra were recorded using a PerkinElmer Lambda 25 spectrophotometer with temperature control using an EYELA NCB 3100 constant temperature bath. Purification of the products was carried out using columns of silica gel 60 (70–230 mesh).

General procedure for Pd-catalysed synthesis of aryl aldehydes/D-labelled aryl aldehydes from iodoarenes with $Fe(CO)_5$

In a three-necked flask, $PdCl_2$ (6.1 mg, 3.5 mol%), aryl iodide (1.0 mmol), $Fe(CO)_5$ (1.1 mmol, 0.147 ml) and Et_3N (3.0 mmol, 0.42 ml) in 1.3% v/v H_2O (D_2O)–DMF (0.04 ml of H_2O or D_2O in 3.0 ml of DMF) were added and stirred at 110 °C under argon atmosphere. The completion of the reaction was monitored using TLC or GC analysis. Cooling the reaction mixture to room temperature was followed by filtration. Then, H_2O (15.0 ml) was added to the filtrate. The aqueous layer was extracted with ethyl acetate (3 × 10 ml) and dried over anhydrous Na_2SO_4. Evaporation of the solvent and column chromatography of the crude mixture on silica gel using (*n*-hexane–ethyl acetate, 20:1) gave the corresponding aryl aldehydes in 75–92% yield. (Caution: since free carbon monoxide is generated in the thermal reaction of iron pentacarbonyl, the reaction should be conducted under an efficient hood.)

General procedure for synthesis of aryl aldehydes from aryl bromides and chlorides using $Fe(CO)_5$ catalysed with $PdCl_2$–Silicadiphenylphosphinite (SDPP)

A mixture of $PdCl_2$ (6.1 mg, 3.5 mol%), SDPP (9.0 mg), aryl halide (1.0 mmol), $Fe(CO)_5$ (1.1 mmol, 0.147 ml) and K_2CO_3 (2.0 mmol, 0.267 g) in 3.0 ml of 1.3% v/v H_2O–DMF was stirred for 2–14 h in a three-necked flask at 110 °C under argon atmosphere. The completion of the reaction was monitored with TLC using *n*-hexane–ethyl acetate (20:1) as eluent. The reaction mixture was cooled to room temperature and filtered. Adding H_2O (6.0 ml) to the organic residue and extracting the aqueous layer with ethyl acetate (3 × 10 ml) and drying over anhydrous Na_2SO_4 gave the crude mixture. Column chromatography of the crude organic mixture on silica gel (*n*-hexane–ethyl acetate, 20:1) afforded the desired product in 65–95% yield.

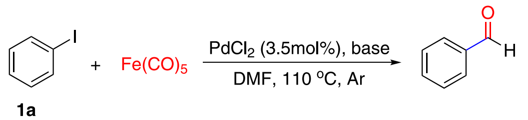
Results and discussion

In order to find the optimized reaction conditions for the reductive carbonylation of aryl halides, we performed the Pd-catalysed reaction of iodobenzene (**1a**) with $Fe(CO)_5$ under various reaction conditions under argon at 110 °C in DMF (Table 1).

When the reaction of **1a** is performed in the presence of $PdCl_2$ and K_2CO_3, the biphenyl as a homo-coupling product is obtained in 45% yield together with 50% of benzaldehyde (Table 1, entry 1). It is observed that changing the base from K_2CO_3 to Et_3N improves greatly the performance of the reaction and benzaldehyde is produced in high yield (90%) together with minor amounts of biphenyl (Table 1, entry 2). Lowering the temperature from 110 to 90 °C reduces the yield of aldehyde with an increase in biphenyl formation (Table 1, entry 4). The reaction proceeds well in DMF, but not in toluene, PEG400 or diglyme (Table 1, entries 5–7). After completion of the reaction, the iron carbonyl is converted to iron oxides residue and is separated from the reaction mixture by a simple filtration.

Since DMF from different suppliers contains different amounts of water, and in order to obtain reproducible results, we tried to determine the required amounts of water in DMF. Therefore, 0–6.6% v/v

Table 1. Optimization of phosphine-free Pd-catalysed reaction conditions for iodobenzene (**1a**)[a]



Entry	Base	Temperature (°C)	Time (h)	**2a** (%)
1	K_2CO_3	110	0.8	50
2	Et_3N	110	0.8	90
3	KOAc	110	4	50
4	Et_3N	90	4	70
5[b]	Et_3N	110	5	25
6[c]	Et_3N	110	5	30
7[d]	Et_3N	110	5	40

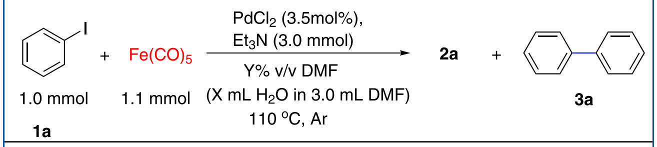
[a] Reaction conditions: **1a**: 1.0 mmol; base: 3.0 mmol; $Fe(CO)_5$: 1.1 mmol in DMF (3.0 ml).

[b] Toluene (3.0 ml) used as solvent.

[c] PEG400 (3.0 ml) used instead of DMF.

[d] Diglyme (3.0 ml) used instead of DMF.

Table 2. Effect of various amounts of water in DMF on reductive carbonylation of **1a** with $Fe(CO)_5$



Entry	H_2O (X mL)	Y (% aq. DMF)	Time (h)	**2a** (%)
1	0	0	0.8	0[a]
2	0.02	0.66	1	60[b]
3	0.03	1	1	85
4	0.04	1.3	4	90
5	0.05	1.6	4	89
6	0.1	6.6	5	62[b]

[a] Biphenyl obtained as a major product.
[b] Biphenyl obtained in 30% yield.

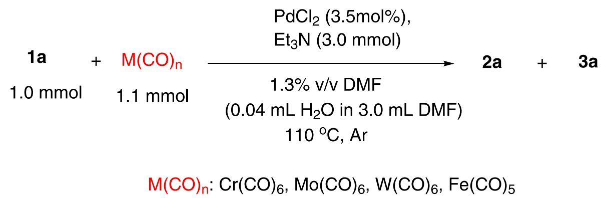
water–DMF mixtures were prepared from dry DMF and the model reaction was performed in each of them. As the results of Table 2 show, when the amount of water in DMF is 1.0–1.7%, the maximum yield of aldehyde is obtained. Lowering or increasing the amounts of water increases the amounts of biphenyl side-product.

To investigate the applicability of other metal carbonyls, we carried out the reaction of **1a** in the presence of $W(CO)_6$, $Cr(CO)_6$ and $Mo(CO)_6$ under our optimized reaction conditions. It is observed that $Fe(CO)_5$ gives a much higher yield of benzaldehyde for shorter reaction time (Table 3).

Next, we analysed the scope of the reductive carbonylation reaction of aryl halides under phosphine-free conditions. The obtained results are summarized in Table 4. The phosphine-free condition for aryl iodides gives high yields of the corresponding carbaldehydes with relatively short reaction times. Since the reactions of bromobenzene and chlorobenzene under this condition were not successful, we assumed that the presence of a P(III) ligand might be crucial for the successful formation of the desired aldehydes from these substrates. All products are known compounds and are identified by their spectral data and their comparison with authentic samples.[14,15,23]

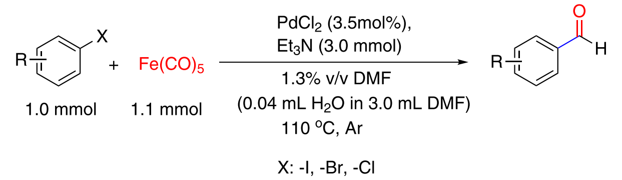
Since the obtained conditions for conversion of aryl iodides to their corresponding carbaldehydes were not suitable for aryl bromides and chlorides, we decided to study the effect of adding a phosphine ligand on the progress of the reaction. Therefore the effect a P(III) ligand such as Ph_3P or $Ph_2PCH_2CH_2PPh_2$ and also the recently reported SDPP[24] as a heterogeneous ligand on the reaction of bromobenzene as a model was investigated (Table 5). As we have reported previously, from the *in situ* reaction of SDPP and Pd(II), the heterogeneous nano-Pd(0)–SDPP[24] is obtained. Transmission and scanning electron microscopies and X-ray diffraction as reported previously by our group show the nanostructure morphology of the Pd-supported SDPP.[24]

Table 3. Pd-catalysed reductive carbonylation of **1a** with various metal carbonyls



Entry	$M(CO)_n$	Time (h)	**2a** (%)	**3a** (%)
1	$Cr(CO)_6$	12	10	50
2	$Mo(CO)_6$	12	5	20
3	$W(CO)_6$	12	0	25
4	$Fe(CO)_5$	4	90	5

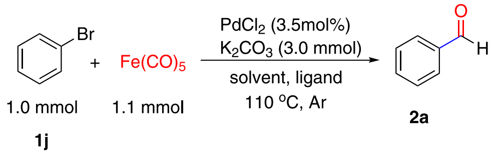
Table 4. Pd-catalysed reductive carbonylation of aryl halides under phosphine-free conditions



Entry	Aryl halide	Time (h)	Product	Yield (%)[a]
1	C_6H_5–I (**1a**)	4	**2a**	90
2	4-$CH_3C_6H_4$–I (**1b**)	5.4	**2b**	92
3	4-$MeOC_6H_4$–I (**1c**)	5.6	**2c**	83
4	4-OHC_6H_4–I (**1d**)	3.5	**2d**	80
5	4-$NO_2C_6H_4$–I (**1e**)	3	**2e**	0
6	4-ClC_6H_4–I (**1f**)	4	**2f**	0
7	1-Naphthyl–I (**1g**)	4.5	**2g**	78
8	3,4-Di-ClC_6H_3–I (**1h**)	4	**2h**	83
9	2-$CH_3C_6H_4$–I (**1i**)	3.5	**2i**	75
10	C_6H_5–Br (**1j**)	36	**2a**	10
11	C_6H_5–Cl (**1k**)	36	**2a**	0

[a] Isolated yield. All products are known compounds and are identified by their spectral data and comparison with authentic samples.[14, 15, 23b] Due to the reduction of nitro group, a mixture of unidentified products together with the homo-coupling product was obtained.

Table 5. Effect of solvents and ligands on reductive carbonylation of bromobenzene with iron pentacarbonyl



Entry	Solvent	Ligand	**2a** (%)	**3a** (%)
1	DMF[a]	Ph_3P[b]	65	30
2	DMF[a]	SDPP[c]	83	9
3	DMF[a]	SDPP[d]	55	40
4	DMF[a]	$(Ph_2PCH_2)_2$[e]	60	35
5	Toluene	SDPP[c]	15	60
6	DMSO	SDPP[c]	60	20
7	PEG400	SDPP[c]	50	20
8	Diglyme	SDPP[c]	40	50
9	H_2O	SDPP[c]	40	50
10	DMF (dry)	SDPP[c]	0	70

[a] 1.3% v/v DMF (0.04 ml H_2O in 3.0 ml DMF) was used as solvent.
[b] Ph_3P (14 mol%).
[c] SDPP (9.0 mg).
[d] SDPP (6.0 mg).
[e] $(Ph_2PCH_2)_2$ (7.0 mol%).

The obtained results show that SDPP as a ligand is more suitable than either Ph_3P or $Ph_2PCH_2CH_2PPh_2$ and its use delivers the highest yield of benzaldehyde (Table 5, entry 2). By changing the solvent to toluene, dimethylsulfoxide (DMSO), H_2O, PEG400 and diglyme, we observe that 1.3% v/v DMF (0.04 ml of H_2O in 3.0 ml of DMF) as the reaction solvent is the most suitable one which delivers benzaldehyde (**2a**) in 83% yield (Table 5, entry 2). In solvents such as DMSO, diglyme and PEG400, the major product is found to be biphenyl (**3a**). Neat water is not an appropriate solvent because $Fe(CO)_5$ is decomposed rapidly and iron oxides are precipitated in the reaction mixture (Table 5, entry 9). The reaction was also carried out in dry DMF, but the carbonylated product is not formed (Table 5, entry 10). With regards to the obtained results, 1.3% aq. DMF was selected as the appropriate solvent for this transformation in which the biphenyl side-product formation is lower than 10%.

In order to determine the appropriate amounts of palladium and SDPP, we conducted the reaction of bromobenzene in the presence of $Fe(CO)_5$ with various amounts of $PdCl_2$ and SDPP and also in their absence under controlled conditions (Table 6). In addition to explore the effect of pre-prepared nano-Pd(0)–SDPP and the *in situ* generated one, the reaction was also studied in the presence of the pre-prepared catalyst (Table 6, entry 9). However, no significant difference in the isolated yield of the benzaldehyde and the reaction time is observed (Table 6, entries 6 and 9). It is concluded that the progress of the reaction is similar using either the pre-prepared nano-Pd(0)–SDPP or the *in situ* generated one. The effects of temperature and base were also explored and the best results are obtained at 110 °C in the presence of K_2CO_3.

The amount of $Fe(CO)_5$ has a crucial effect on the yield of the carbonylated product. Lowering the amount of $Fe(CO)_5$ from 1.1 to 0.55 equimolar reduces the product yield to 50% (Table 6, entry 10).

With a defined protocol in hand, the feasibility of the formation of aryl aldehydes from aryl bromides and chlorides was studied (Table 7). It is found that aryl halides carrying cyano and nitro groups are not suitable substrates for this reaction and produce the corresponding aldehydes in low yields. In these cases, the possibility of reduction of nitro and cyano groups with $Fe(CO)_5$ together with the homo-coupling reaction produce a mixture of unidentified products (Table 7, products **2f** and **2e**). The steric effects of aryl halides appear to be insignificant since sterically hindered 1-iodonaphthalene and 1-bromonaphthalene afford good yields of their corresponding products.

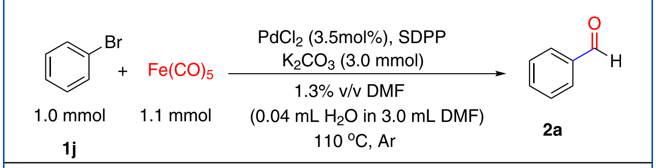
With the purpose of studying the pathway of Pd(II) to Pd(0) reduction under phosphine-free conditions, we performed the following reactions and studied the UV–visible spectra. Initially, a solution of $PdCl_2$ in DMF was stirred at 110 °C. The UV–visible spectrum of the solution shows a broad band around 425 nm (Fig. 1) which indicates the presence of Pd(II) in the solution. Then, a mixture of $PdCl_2$ and $Fe(CO)_5$ was heated in DMF at 110 °C and, after 30 min, the UV–visible spectrum of the mixture was obtained (Fig. 1). Disappearance of the broad band at about 425 nm is indicative of the formation of Pd(0) species. This observation is consistent with a literature report for the reduction of Pd(II) to Pd(0) in CO detectors.[25] This latter spectrum also has a broad band at about 550 nm which is similar to the UV–visible spectrum of a solution of $Fe(CO)_5$ in DMF at 110 °C after stirring for 30 min (Fig. 1).

From the above results, we can conclude that $Fe(CO)_5$ or liberated CO can reduce Pd(II) to Pd(0) when the reaction is conducted under phosphine-free conditions using aryl iodides.

To verify the hypothesis that either $Fe(CO)_5$ or DMF is the source of carbonyl in this reaction, we performed the reaction of iodobenzene, $PdCl_2$ and Et_3N in DMF in the absence of $Fe(CO)_5$ at 110 °C under our optimized conditions. After 24 h, no aldehyde is obtained and instead the homo-coupled product is isolated (Scheme 2). Consequently, we can conclude that CO liberated from $Fe(CO)_5$ is the carbonyl source for the reaction and DMF is not decomposed under our conditions to produce CO for the reaction.

Subsequently, to study the reaction mechanism, the reaction of 3,4-dichloroiodobenzene as a higher molecular weight iodoarene

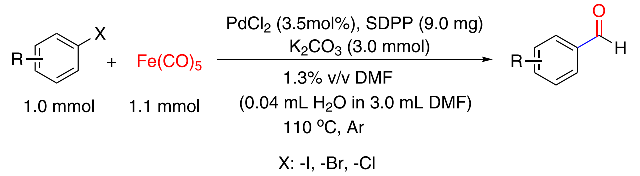
Table 6. Effect of temperature and amount of SDPP, $PdCl_2$ and $Fe(CO)_5$ on carbonylation of bromobenzene[a]



Entry	$PdCl_2$ (mol%)	SDPP (mg)	Base	**2a** (%)
1	—	—	K_2CO_3	0
2	2.5	6.0	K_2CO_3	60
3	3.5	9.0	Et_3N	50
4	3.5	9.0	KOAc	58
5	3.5	9.0	Et_3N	55
6	3.5	9.0	K_2CO_3	83
7[b]	3.5	9.0	K_2CO_3	50
8	3.5	—	K_2CO_3	55
9[c]	—	—	K_2CO_3	80
10[d]	3.5	9.0	K_2CO_3	55

[a] Reaction time is 12 h and temperature is 110 °C.
[b] Temperature is 90 °C.
[c] Pre-prepared nano-Pd(0)–SDPP was used (4.0 mg).
[d] Amount of $Fe(CO)_5$ is 0.55 mmol instead of 1.1 mmol.

Table 7. Reductive carbonylation of aryl halides in the presence of $PdCl_2$–SDPP



Entry	Aryl halide	Time (h)	Product	Yield (%)
1	C_6H_5–I (**1a**)	1.7	**2a**	95
2	C_6H_5–Br (**1j**)	12	**2a**	83
3	C_6H_5–Cl (**1k**)	15	**2a**	65
4	4-$CH_3C_6H_4$–Br (**1l**)	14	**2b**	80
5	4-$CH_3C_6H_4$–Cl (**1m**)	20	**2b**	60
6[a]	4-CNC_6H_4–Br (**1n**)	7	**2f**	8
7[a]	4-$NO_2C_6H_4$–Br (**1o**)	8	**2e**	10
8	1-Naphthyl–Br (**1p**)	17	**2g**	70
9	4-OHC_6H_4–Br (**1q**)	15	**2d**	75
10	4-$CH_3OC_6H_4$–Br (**1r**)	15	**2c**	80
11	2-$CH_3C_6H_4$–Br (**1s**)	19	**2i**	75

[a] Due to the reduction of nitro and cyano group, a mixture of unidentified products together with the homo-coupling product was obtained.

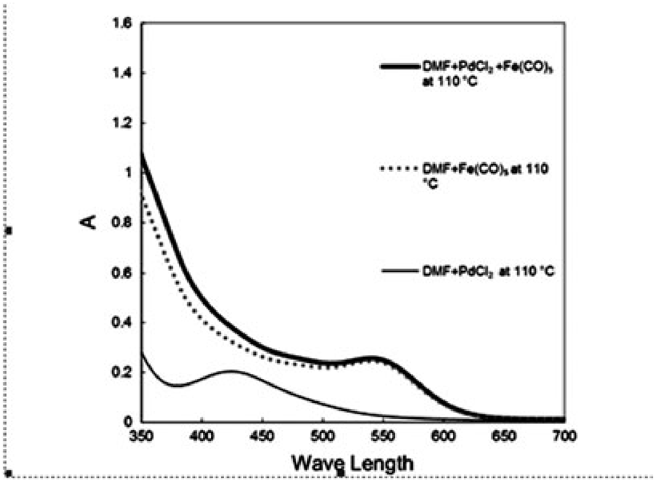
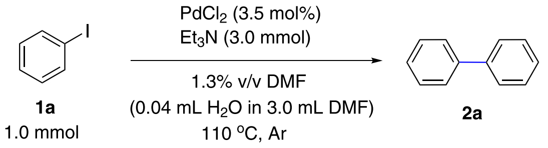


Figure 1. UV–visible spectra.

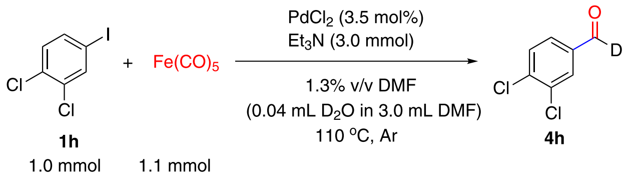
was studied in DMF that contains 1.3% of D_2O. After the reaction is completed, the ^1H NMR spectrum of the isolated product reveals the absence of the peak at 10.2 ppm which is present when the reaction is performed in DMF containing the same amount of H_2O. Thus, use of D_2O in dry DMF leads to deuterium instead of hydrogen being placed in the aldehyde functionality and affords deuterioaryl aldehyde. The iron oxides formed at the end of the reaction are the by-products of $Fe(CO)_5$ (Scheme 3).

This reaction is found to be an easy and efficient method for D-labelling of aldehydes in which deuterium is substituted for hydrogen. We therefore examined the scope of this reaction for deuterioaryl aldehyde synthesis from aryl iodides (Table 8). This delicately designed reductive carbonylation method shows that it is suitable for the synthesis of deuterioaryl aldehydes from iodoarenes under phosphine-free conditions.

A detailed description of a plausible mechanism for the reductive carbonylation of aryl halides is outlined in Scheme 4. In this mechanism, liberation of CO converts the intermediate (I) to (II) by CO insertion. Reaction of $Fe(CO)_X$ ($X = 4, 5$) with water under basic conditions is a well-known reaction to produce $H(D)–Fe–(CO)_{X-1}$.[26] Reaction of this reducing agent with the intermediate (II) produces intermediate (III) which is responsible for the generation of the aryl carbaldehyde. Iron carbonyl intermediates are converted to iron residues such as iron oxides which are separated from the reaction mixture.

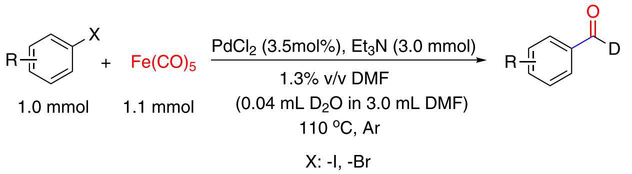


Scheme 2. Reaction in the absence of $Fe(CO)_5$.



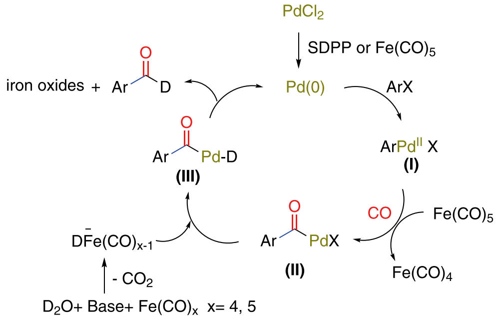
Scheme 3. Role of D_2O in the reaction pathway.

Table 8. Synthesis of deuterioaryl aldehydes from iodoarenes in the presence of $Fe(CO)_5$[a]



Entry	Aryl halide	Time (h)	Product	Yield (%)
1	C_6H_5–I (**1a**)	5	**4a**	90
2	4-$CH_3C_6H_4$–I (**1b**)	6	**4b**	87
3	4-$CH_3OC_6H_5$–I (**1c**)	8	**4c**	78
4	3,4-Di-ClC_6H_3–I (**1h**)	9	**4h**	79
5	C_6H_5–Br (**1j**)	36	**4a**	10

[a] All products are known compounds and are identified by their spectral data and comparison with the authentic samples.[23]



Scheme 4. Plausible mechanism of reductive carbonylation of aryl halides.

Conclusions

In summary, we have developed a novel Pd-catalysed methodology for the reductive carbonylation of iodoarenes under phosphine-free conditions in which $Fe(CO)_5$ acts as the CO source, without the use of H_2 or adding any reducing agent at atmospheric pressure in wet DMF. In addition, conducting the reaction of aryl bromides and chlorides in the presence of a P(III) ligand afforded aryl aldehydes in good to high yields. This methodology excludes the direct use of CO gas with the difficulty in its handling. In addition, we also introduced a very simple method to synthesize aromatic aldehydes with D-isotope labelling using dry DMF containing trace amounts of D_2O.

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