Palladium catalysed Carbonylation of Aryl Chlorides to the Corresponding Methyl Esters

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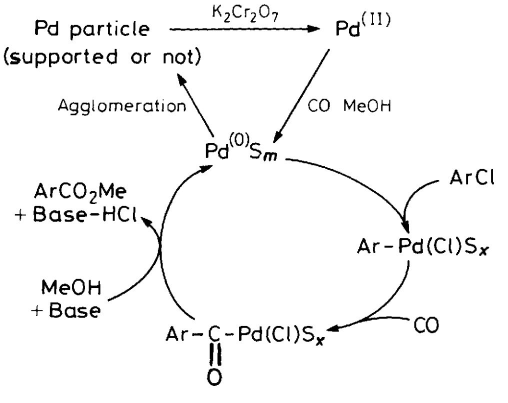
A series of aryl chlorides have been carbonylated at 200 °C to their corresponding methyl esters, in the presence of a 5% Pd/C catalyst; the addition of $K_2Cr_2O_7$ enhances the catalytic activity.

The carbonylation of aromatic halides, catalysed by palladium complexes, is a reaction of industrial interest leading to a wide range of products like esters,[1] aldehydes,[2] amides,[3] acids,[4] α-oxo-esters,[5] α-oxo-amides,[6] or α-oxo-acids.[7] These reactions proceed fairly well in the case of aryl iodides or bromides but remain generally uncontrolled in the case of aryl chlorides,† which are more attractive as starting materials in view of industrial application. This failure is partly due to the higher temperature required to perform the first step of the reaction, which is generally thought to be an oxidative addition of the C–Cl bond to a zerovalent palladium species.[12] At high temperature, zerovalent phosphine palladium complexes are usually short-lived and the separation of the metal in an inactive solid form is observed.

Recently, we reported that the co-ordination of a $Cr(CO)_3$ moiety to the aromatic ring of aryl chlorides enables their carbonylation to the corresponding esters, aldehydes, amides, or α-oxo-amides at mild temperature.[13] Activation of the C–Cl bond by the $Cr(CO)_3$ fragment favours its oxidative addition to zerovalent palladium. Unfortunately, it was not possible to find experimental conditions where the $Cr(CO)_3$ moiety could be recycled during the catalytic process, by exchange between the carbonylation product and chlorobenzene.

A method for direct catalytic carbonylation of aryl chlorides therefore remains desirable. The use of a temperature resistant supported zerovalent palladium catalyst is an approach which to our knowledge has not yet been described for these reactions.

We wish to report here that palladium supported on activated carbon catalyses the carbonylation of various aryl chlorides to the corresponding esters (Table 1) according to equation (1).‡



Scheme 1

$$\mathrm{ArCl + MeOH + CO + Base \xrightarrow{Pd/C} ArCO_2Me + Base\text{–}HCl} \qquad (1)$$

Good rotation numbers related to palladium are obtained with various aryl chlorides like chlorobenzene, *p*-dichlorobenzene, *p*-chloroanisol, or chloronaphthalene.§ Small amounts of hydrogenolysis (ArH) and coupling (Ar–Ar) products are also formed. Better results are obtained when a basic salt or oxide is added to trap HCl (compare runs 1 and 2); however, amines such as triethylamine, which is often used for that purpose,[14] exert an inhibiting effect on the reaction.

Rhodium or platinum supported on activated carbon do not show any activity in this reaction. Hydrocarbonylation of chlorobenzene to benzaldehyde was also observed in the presence of hydrogen pressure (run 11), but no aminocarbonylation occurred with diethylamine.

A remarkable promoting effect of oxidizing agents like $K_2Cr_2O_7$ or V_2O_5, on the initial turnover rate as well as the total turnover number, was also evidenced during these experiments (runs 12 and 13). The same effect is even observed when an unsupported homogeneous precursor such as $Pd(OAc)_2$ is used without the usual stabilizing phosphine ligands; in this case, carbonylation occurs only in the presence of the oxidizing agent (runs 14, 15, and 16). In the absence of oxidizing agent, no ester formation is observed and metallic palladium particles rapidly separate out.

The supported palladium catalyst deactivates during time. This phenomenum does not arise from an inhibition by the products, since the reaction proceeds again if a new charge of catalyst is introduced into the reactor. Deactivation is probably due to sintering since the average metal particle size (deduced from electron microscopy) increases from 40 Å for a fresh catalyst to 150 Å for a used one. This sintering process is likely to be related to the mechanism of the reaction. It may be assumed that oxidative addition of chlorobenzene to small particles of metallic palladium can occur and will result in the formation of a complex of palladium(II): (Ph)Pd(Cl)S_x (S = solvent or support) which will initiate a catalytic cycle of carbonylation similar to that proposed under homogeneous

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† Carbonylation of 1-chloronaphthalene catalysed by nickel complexes with low turnover numbers has been reported;[8] cobalt catalysed carbonylation of some aryl chlorides has also been mentioned,[9] sometimes with photostimulation.[10] While this paper was submitted, the use of bis(diisopropylphosphino)propane was claimed to stabilize zerovalent palladium and enable the carbonylation of various aryl chlorides.[11]

‡ In a typical experiment, the aryl chloride (22.5—147 mmol), methanol (5 ml), sodium acetate (184.5 mg; 2.25 mmol), 5% Pd/C (from Aldrich) (95 mg; 0.045 mmol), and eventually toluene (10 ml) are charged under argon in a 100 ml stainless steel glass coated autoclave. The reactor is pressurized with 3 bar of CO and then heated with stirring at 200 °C for 50 h. The products are analysed by GC on a 25 m Cp Sil 5 capillary column (dodecane is used as internal standard) and characterized by GC-MS techniques.

§ No reaction was observed in the case of *p*-chlorotoluene or *p*-chloroaniline. 2-Chloropyridine led quantitatively to *N*-methylpyridone. Only nitrobenzene and *p*-chloroaniline were obtained from *p*-nitrochlorobenzene; anisol and *o*-chloroanisol were formed from *o*-chlorophenol.

Table 1. Palladium catalysed carbonylation of aryl chlorides.[a]

Run	ArCl	ArCl/Pd	$K_2Cr_2O_7$/Pd	Products	Initial turnover rate[b]/h^{-1}	Turnover number[b]
1	PhCl	3000	0	$PhCO_2Me$	4	120
2[c]	PhCl	3000	0	$PhCO_2Me$	—	35
3	$4\text{-}CF_3C_6H_4Cl$	800	0	$4\text{-}CF_3C_6H_4CO_2Me$	—	5
4	$4\text{-}HOC_6H_4Cl$	500	0	$4\text{-}HOC_6H_4CO_2Me$	—	20
5	$4\text{-}MeOC_6H_4Cl$	900	0	$4\text{-}MeOC_6H_4CO_2Me$	—	87
6	$4\text{-}ClC_6H_4Cl$	500	0	$4\text{-}ClC_6H_4CO_2Me$	—	45
7	$3\text{-}ClC_6H_4Cl$	1000	0	$3\text{-}ClC_6H_4CO_2Me$	—	30
8[d]	$C_{10}H_7Cl$	1000	0	$C_{10}H_7CO_2Me$	—	186
9	$4\text{-}MeCOC_6H_4Cl$	1000	0	$4\text{-}MeCOC_6H_4CO_2Me$	—	80
10	$4\text{-}HOCOC_6H_4Cl$	1000	0	$4\text{-}HOCOC_6H_4CO_2Me$	—	60
11[e]	PhCl	4000	0	PhCHO	—	80
12	PhCl	3000	50	$PhCO_2Me$	15	260
13	PhCl	3000	200	$PhCO_2Me$	25	350
14[f]	PhCl	3000	50	$PhCO_2Me$	5	95
15[f]	PhCl	3000	200	$PhCO_2Me$	5	240
16[f,g]	PhCl	3000	50	$PhCO_2Me$	5	90

[a] General conditions: ArCl (22.5—147 mmol), methanol (5 ml), AcONa (184.5 mg; 2.25 mmol), CO (3 bar), 5% Pd/C (95 mg; 0.045 mmol), toluene (10 ml for runs 3 to 10); 200 °C for 50 h. [b] Related to palladium. [c] Without base. [d] 1-Chloronaphthalene. [e] PhCl (20 ml), AcONa (184.5 mg; 2.25 mmol), CO (3 bar), H_2 (3 bar), 5% Pd/C (95 mg; 0.045 mmol). [f] $Pd(OAc)_2$ (10 mg, 0.045 mmol) instead of Pd/C. [g] V_2O_5 instead of $K_2Cr_2O_7$.

conditions.[14] No palladium could be detected in the solution during the course of an experiment nor any loss of metal on the used catalyst. The catalytic intermediates involved in this process are therefore either in low concentration in the liquid phase or remain physisorbed on the support. At the end of a catalytic cycle of carbonylation, the active palladium species may reinitiate a new one or agglomerate into an inert particle of higher size (Scheme 1).

This hypothesis is further supported by the strong effect of oxidizing agents such as $K_2Cr_2O_7$ which increases the initial rate of the reaction as well as the turnover number. The role of $K_2Cr_2O_7$ is very likely to reoxidize large particles of metallic palladium into a highly dispersed palladium(II) species which can be reduced again under CO into an active zerovalent palladium complex. Deactivation of the catalyst by sintering would then be retarded. The same procedure is assumed to occur in solution when an unsupported homogeneous precursor such as $Pd(OAc)_2$ is used without phosphine, in the presence of $K_2Cr_2O_7$ or V_2O_5. The oxidizing agent retards separation of zerovalent palladium particles and enables the carbonylation to proceed (Scheme 1).

In conclusion, it then appears possible to perform the carbonylation of chlorobenzene with a 'naked' zerovalent palladium catalyst in the absence of phosphine.

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