Bi-metallic Activation in Homogeneous Catalysis: Palladium-catalysed Carbonylation of Tricarbonyl(chloroarene)chromium Complexes to the Corresponding Aldehydes, Esters, Amides, and α-Oxo Amides

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Tricarbonyl(chloroarene)chromium complexes undergo palladium-catalysed carbonylation to give aromatic aldehydes, esters, amides, and α-oxo amides.

The palladium-catalysed carbonylation of aryl bromides or iodides to give aromatic carboxylic acids,[1] esters,[2] amides,[3] aldehydes,[4] α-oxo amides,[5] α-oxo esters,[6] and α-oxo acids[7] is well known. However, no reliable example of carbonylation of chlorobenzene has been reported; this would be of great industrial interest in view of the low cost of chloroaromatic compounds as compared with bromo or iodo analogues.

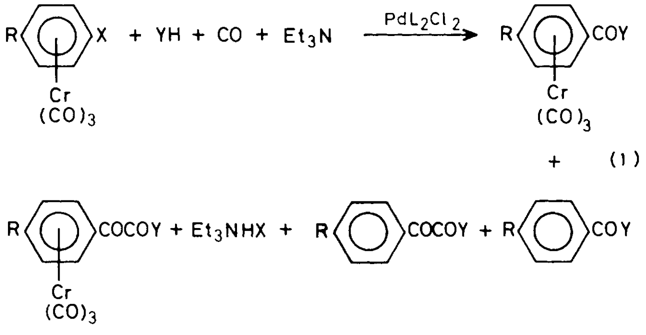
The difficulty of carrying out the carbonylation of chloroaromatic compounds is probably due to the high temperature required for the oxidative addition of the C–Cl bond to zerovalent palladium complex.[8,9] However, this elementary step is favoured when electron-withdrawing substituents are present on the aromatic ring.[9]

We have looked for an organometallic fragment which could act in the same way. The co-ordination of the $Cr(CO)_3$ group to an aromatic ring[10] is known to reduce the π-electron density;[11] we might therefore expect that it would also favour the oxidative addition of chlorobenzene to zerovalent palladium complexes and consequently promote the catalytic carbonylation reaction. We report here that tricarbonyl(chloro-

Table 1. Palladium-catalysed carbonylation of normal and *para*-substituted tricarbonyl(chlorobenzene)chromium complexes.[a,b]

Run	Haloarene	T/°C	Product	% Yield[c]	% Haloarene unconverted	N[d]
1	PhCl	170	$PhCO_2Me$	80		40
2[e]	PhCl	170	$PhCO_2Me$	68		34
3[f]	PhCl	170	$PhCO_2Me$	17		8.5
4	PhCl	130	$PhCO_2Me$	75	15	37.5
5[g]	PhCl	130	$PhCO_2Me$	60		300
6	PhCl	130	PhCHO	68	20	34
7[h]	PhCl	130	PhCHO	28		14
8[i]	PhCl	100	$PhCONEt_2$ $PhCOCONEt_2$	43 47	10	100
9	$4-CF_3C_6H_4Cl$	130	$4-CF_3C_6H_4CO_2Me$	80	15	40
10	$4-CF_3C_6H_4Cl$	130	$4-CF_3C_6H_4CHO$	20	13	10
11	$4-MeC_6H_4Cl$	130	$4-MeC_6H_4CO_2Me$	70	8	35
12	$4-MeC_6H_4Cl$	130	$4-MeC_6H_4CHO$	36	6	18
13	$4-MeOC_6H_4Cl$	130	$4-MeOC_6H_4CO_2Me$	55	40	27.5
14	$4-MeOC_6H_4Cl$	130	$4-MeOC_6H_4CHO$	30	20	15
15	$4-Me_2NC_6H_4Br$	130	$4-Me_2NC_6H_4CO_2Me$	50	30	25
16	$4-Me_2NC_6H_4Br$	130	$4-Me_2NC_6H_4CHO$	35	10	17.5

[a] Synthesized according to ref. 10; no tricarbonyl(haloarene)chromium could be obtained from 4-bromo- or 2-chloro-phenol or 4-bromoanisole. [b] Reagents: $PhClCr(CO)_3$ (1 mmol), Et_3N (1.2 mmol), $Pd(PPh_3)_2Cl_2$ (0.02 mmol), PPh_3 (0.1 mmol); methoxycarbonylation MeOH (20 ml), CO (25 bar); hydrocarbonylation toluene (20 ml), CO (15 bar), H_2 (15 bar). [c] Related to initial chromium compound. [d] Turnover number, related to palladium. [e] AcONa used instead of Et_3N. [f] Without base. [g] $PhClCr(CO)_3$ (10 mmol). [h] Only 1 bar of CO and 1 bar of H_2. [i] $PhClCr(CO)_3$ (1.2 mmol), $Pd(PMePh_2)Cl_2$ (0.011 mmol), Et_2NH (10 mmol), toluene (19 ml), CO (30 bar).



arene)chromium complexes undergo palladium-catalysed carbonylation† under mild conditions to give the corresponding free, or chromium-co-ordinated, esters, aldehydes, amides, or α-oxo amides according to the general equation (1). The results obtained for various chloroarenes are shown in Table 1.‡

The co-ordination of the tricarbonylchromium group to the various chloroarenes enables their carbonylation even in the presence of moderately electron-donating groups (runs 10—14), whereas the reaction does not occur with the chloroarenes alone under the same conditions. This suggests that the electron-withdrawing effect of tricarbonylchromium[11] promotes palladium insertion into the C–Cl bond.

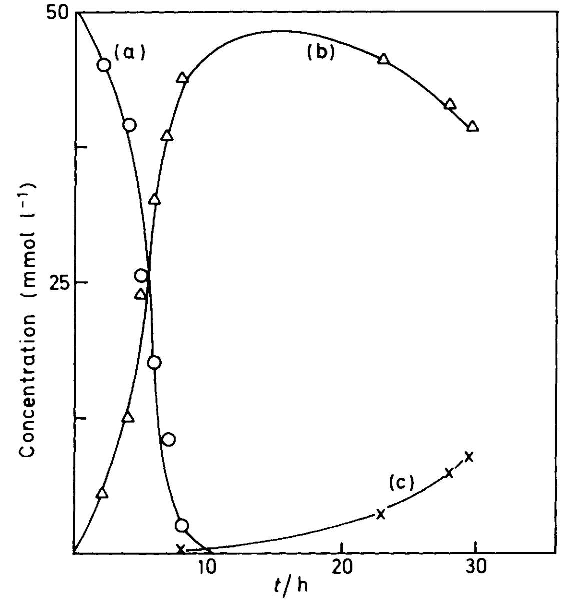


Figure 1. Methoxycarbonylation of tricarbonyl(chlorobenzene)-chromium at 100 °C: (a) $PhClCr(CO)_3$, (b) $PhCO_2MeCr(CO)_3$, (c) $PhCO_2Me$; $PhClCr(CO)_3$ (1 mmol), Et_3N (1.2 mmol), $Pd(PPh_3)_2Cl_2$ (0.02 mmol), PPh_3 (0.1 mmol), MeOH (1 ml), PhCl (19 ml), CO (3 bar).

As already observed with other aromatic halides, methoxycarbonylation leading to aromatic esters is more efficient than hydrocarbonylation leading to the corresponding aldehydes.

Sodium acetate can be used instead of triethylamine, but the presence of a base is always necessary to capture the hydrochloric acid liberated (runs 1—3).

There was no attempt at optimisation, but turnover numbers as high as 300 were obtained (run 5).

A good yield of double carbonylation product was obtained when diethylamine was used as nucleophile (run 8).

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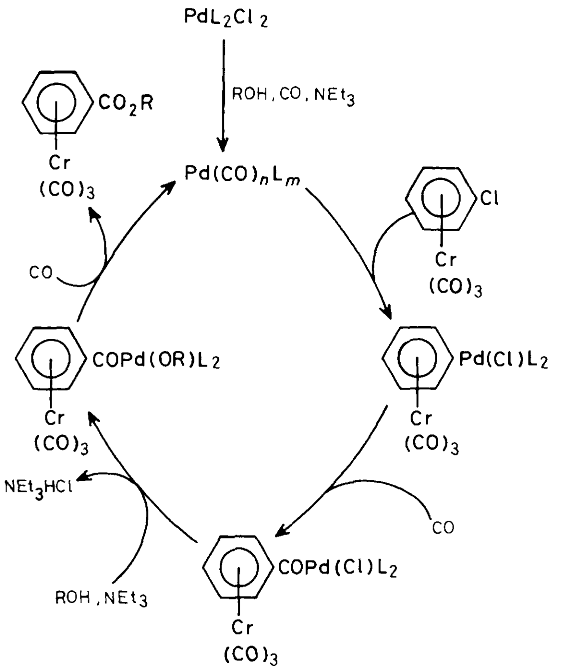
† This work was patented in 1985 (BF 85 09675 and BF 85 09676). At the same time a palladium-catalysed coupling reaction of tricarbonyl(chloroarene)chromium complexes with terminal alkynes[12] was reported, and more recently a similar reaction with alkenes or tetra-alkyltin was described.[13]

‡ The reaction is carried out in a 100 ml stainless steel, Teflon-coated autoclave. The tricarbonyl(chloroarene)chromium complex (1 mmol) and the palladium catalytic system (0.02 mmol) are loaded and the autoclave is subjected three times to a cyclic vacuum–argon purge. The liquid reagent [methanol, diethylamine, or triethylamine (20 ml)] is introduced pure or diluted in toluene. Dodecane (0.5 ml) is added as g.l.c. internal standard. The reactor is pressurised with the required gas and then heated with stirring to 100—170 °C for 20—70 h. The products are analysed by g.l.c. on a 25 m Cp SiL 5 capillary column, with flame ionisation detector.



Scheme 1. Y = RO, Et_2N, H.

Some mechanistic information could be obtained from the effect of temperature on product distribution. At 170 °C methoxycarbonylation of tricarbonyl(chlorobenzene)chromium leads to free methyl benzoate and various chromium compounds such as $Cr(CO)_6$ and $Cr(CO)_5PPh_3$, whereas at 100 °C tricarbonyl(methyl benzoate)chromium can be obtained with a selectivity of 95% (Figure 1). Deco-ordination of the $Cr(CO)_3$ group occurs subsequently to give the corresponding free ester. This result strongly suggests that the catalytic cycle involves intermediates in which the $Cr(CO)_3$ fragment remains bonded to the aromatic ring (Scheme 1). In the first step at least of the probable catalytic cycle (derived from a recent publication)[14] bi-metallic activation of the chlorobenzene must occur, whereby the benzene ring is σ-co-ordinated to palladium and π-co-ordinated to chromium.

In the hydro- and amino-carbonylation reactions no attempt was made to obtain chromium-co-ordinated products; however we would assume that in both cases oxidative addition of the C–Cl bond to zerovalent Pd proceeds with the $Cr(CO)_3$ group co-ordinated to the benzene ring.

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