Carbonylation of bromobenzene in a biphasic medium catalysed by water-soluble palladium complexes derived from tris(3-sulphophenyl)phosphine

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(Received December 10, 1993)

Abstract

The hydroxycarbonylation of bromobenzene has been explored in a biphasic medium. Water-soluble $[Pd(TPPTS)_3]$ (TPPTS = sodium salt of tris(3-sulphophenyl) phosphine) catalyses selectively this carbonylation reaction into benzoic acid. This complex is maintained intact in the presence of an excess of tris(3-sulphophenyl)phosphine salt. Even when a hydrogen donor is added, the reaction is limited to hydroxycarbonylation. The two complexes $[Pd(Ph)Br(TPPTS)_2]$ and $[Pd(COPh)Br(TPPTS)_2]$ have been synthesized. A catalytic cycle is proposed.

Key words: Palladium; Carbonylation; Biphatic medium Phosphines; Mechanism

1. Introduction

After the pioneering work of Heck and coworkers [1] on the alkoxycarbonylation of aryl, benzyl or vinyl halides, there has been much work devoted to the extension of this carbonylation reaction [2]. Compounds ArCONu can be prepared by reacting the NuH species with the aryl halide ArX under a CO pressure and in the presence of a base:

$$ArX + CO + NuH + base \xrightarrow{[Pd]} ArCONu + [base\ H]X \quad (1)$$

This reaction is catalysed by palladium complexes containing triphenylphosphine.

According to the nature of the nucleophilic group, various organic compounds such as aldehydes, esters, acids and amides can be prepared by reaction of H_2, ROH, H_2O and R_2NH respectively. Among the parameters which govern the reaction, the nature and the strength of the base are important in removing the HX produced [3]. Moreover, as the rate-determining step is often the oxidative addition of ArX to the palladium(0) active species, at least for hydroxycarbonylation and alkoxycarbonylation reactions [4], the nature of the phosphine is also of importance [5].

This carbonylation reaction is generally slow. Indeed, for aromatic bromides and chlorides, the catalytic activity remains under 10 h^{-1} [1,3,5b,6]. Only few exceptions were observed when molecular sieves were added to the medium (35 h^{-1}) [7], or when the aromatic ring was activated by a chromium tricarbonyl fragment (300 h^{-1}) [8].

We were interested in the hydroxycarbonylation of aromatic halides and we used water-soluble palladium complexes in order to improve the contact between the catalytic species and the nucleophilic agent. Bromobenzene was used as a representative compound of this class of molecule. Moreover, the palladium complex containing tris(3-sulphphenyl)phosphine prevents the precipitation of metallic palladium under the reaction conditions. The hydrogenocarbonylation reaction was also investigated. Finally a study of the mechanisms of the carbonylation was carried out.

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0022-328X/94/$7.00
SSDI 0022-328X(94)24649-4

2. Results and discussion

2.1. Generation of the water-soluble palladium complex

Usually a palladium(II) complex such as $[PdCl_2(PPh_3)_2]$ or a $Pd(OAc)_2$–PPh_3 mixture is used as starting material in the carbonylation of aryl halides [2]. Generally, the active species is a palladium(0) complex $[Pd(PPh_3)_x]$ [2a]. Recently it has been shown that addition of triphenylphosphine to $Pd(OAc)_2$ reduces of palladium(II) to $[Pd(PPh_3)_x]$ and forms triphenylphosphine oxide [9,10]. Recently, it was unambiguously demonstrated that palladium(II) complexes are reduced to a palladium (o) species by their own coordinated phosphine ligands which are oxidized to phosphine oxides in the presence of OH^- ions [2d].

We synthesized the complex $[Pd(TPPTS)_3]$ (1) (TPPTS ≡ sodium salt of tris(3-sulphophenyl)phosphine) by exchange with $[Pd(PPh_3)_4]$, as described by Herrmann et al. [11]. This complex is characterized by a broad singlet at 24.0 ppm in the ^{31}P NMR spectrum, and small amounts of TPPTS shift this signal towards high fields showing that exchange occurs. The observed chemical shift is the mean of $[Pd(TPPTS)_3]$, $[Pd(TPPTS)_2]$ and that of the free phosphine at −2.5 ppm, at 25°C. A similar phenomenon was observed when the PPh_3 analogue is added to an excess of free phosphine [10]. Thus, for a P-to-Pd ratio of 12.5, the mean phosphine signal appears at 3.2 ppm.

The addition of TPPTS to $Pd(OAc)_2$ (P-to-Pd ratio of 12.5) was monitored by ^{31}P NMR spectroscopy. Two signals are observed: a broad singlet centered at 4 ppm assigned to the mixture of $[Pd(TPPTS)_3]$, $[Pd(TPPTS)_2]$ and free TPPTS in dynamic equilibrium, and a sharp singlet at 36.3 ppm assigned to the oxide, OTPPTS.

As OTPPTS, like $OPPh_3$, does not play any role in catalysis under rigorously homogeneous conditions, we preferred to introduce the non-air sensitive $Pd(OAc)_2$ salt and an excess of phosphine into the autoclave since we had shown that it is a good precursor for zero-valent palladium complexes.

Table 1
Hydroxycarbonylation of bromobenzene catalysed by **1**: influence of P-to-Pd ratio (PhBr, 25 mmol; $[Pd(OAc)_2]$, 0.5 mmol; NEt_3, 55 mmol; H_2O, 10 ml; toluene, 10 ml; $P(H_2) = P(CO) = 1.5$ MPa; $T = 150°C$; $t = 15$ h)

P-to-Pd ratio	Conversion (%)	Colour of aqueous phase
5	18	Black
7.5	97	Green
10	100	Green
12.5	100	Yellow
15	100	Yellow

2.2. Hydroxycarbonylation of bromobenzene

Carbonylation of bromobenzene under the conditions reported in Table 1 results selectively in benzoic acid according to:

$$PhBr + CO + H_2O + 2NEt_3 \longrightarrow [NHEt_3][PhCOO] + [NHEt_3]Br \quad (2)$$

In the presence of triethylamine, mainly ammonium benzoate is obtained, so that benzoic acid is isolated and quantified after acidification and extraction with diethyl ether.

This reaction was carried out at 1.5 MPa and 150°C, but, in the presence of a slight excess of phosphine, black palladium was invariably formed. For this reason the phosphorus-to-palladium ratio was examined. Table 1 displays the results of these experiments. For a low P-to-Pd ratio, deactivation of the palladium catalyst occurs, leading to extensive decomposition, as shown by black palladium on the walls of the autoclave and in the aqueous phase. The green colour observed after catalysis is due to the presence of small black particles which are deposited progressively. For a P-to-Pd value of 12.5 or more, the palladium complex is recovered intact. Indeed, ^{31}P NMR spectra show the presence of $[Pd(TPPTS)_x]$ complexes in equilibrium with the free TPPTS (1.9 ppm). Further experiments were done with a P-to-Pd ratio of 12.5.

The temperature is also a very important parameter

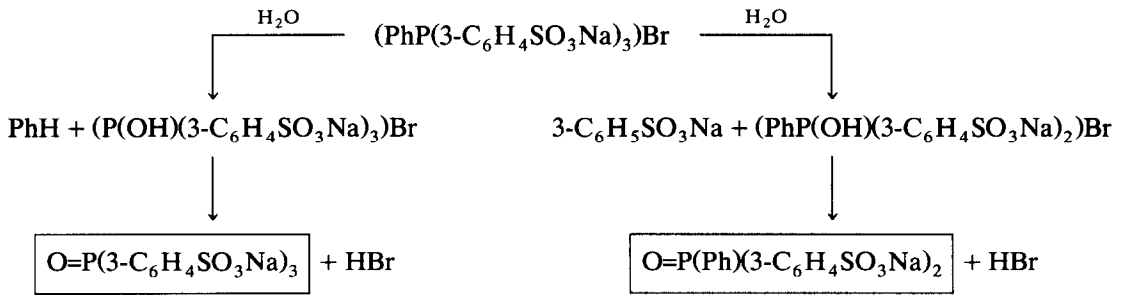


Fig. 1. Proposed pathway for the formation of OTPPTS and OTPPDS.

for this reaction. Below 120°C, there is no activity whereas, above 170°C, side reactions occur, especially the formation of $PhCONEt_2$ and related products due to decomposition of the triethylamine or of the triethylammonium salt. The best compromise between good chemoselectivity and a satisfactory reaction rate was found to be 150°C.

The catalytic reaction requires an induction period of 1 h and is complete after about 3 h, giving a turn-over frequency of 17 h^{-1}. Decantation of the reaction mixture allows a rapid separation of the organic and aqueous phases. Gas chromatography analyses have shown that the organic phase contains less than 2% of the total benzoic acid produced. The yellow aqueous phase was used in a second run. Carbonylation of the second aliquot of bromobenzene still recurred, but palladium was recovered as a black precipitate, affording an almost colourless aqueous phase. ^{31}P NMR spectroscopy reveals that only small amounts of TPPTS are still present in the medium and that the phosphine is transformed into OTPPTS (32.9 ppm) and $OPPh(3\text{-}C_6H_4SO_3Na)_2$ or OTPPDS (33.5 ppm). We have checked that these oxidation reactions occur only in the presence of palladium. These oxides could be formed via the phosphonium salt $[PhP(3\text{-}C_6H_4\text{-}SO_3Na)_3]Br$ according to Fig. 1. Indeed the two signals detected at 25.3 and 25.0 ppm are in the range characteristic of phosphonium salts [12]. They could result from an exchange reaction between the aryl group on the coordinated phosphine and the palladium-bound phenyl group, as already observed by Kong and Cheng [13]. In this case, the 3-sulphobenzoic acid resulting from the hydrolysis of the 3-sulphobenzoyl palladium species would have not been observed since its high polarity keeps it in water during the ether extraction.

Thus, since even in the first cycle phosphine oxide is formed, recycling the catalytic system requires the aqueous phase to be complemented with fresh TPPTS.

Using $[Pd(TPPTS)_3]$ as a catalyst affords a highly selective hydroxycarbonylation reaction. Moreover, provided that an excess of TPPTS is added, the integrity of the complex is maintained. However, the major drawback of this carbonylation reaction is the presence of increasing amounts of ammonium benzoate and ammonium bromide. As most of the reactions involving water-soluble complexes take place in the aqueous phase [14], this increase in salt concentration could decrease considerably the catalytic activity due to a salt effect. Moreover, in order to isolate the benzoic acid, it must be separated from the palladium catalyst and ammonium bromide.

For this reason we have explored the hydrogenocarbonylation reaction to produce benzaldehyde, soluble in the organic phase.

2.3. Hydrogencarbonylation vs. hydroxycarbonylation of bromobenzene

Dihydrogen was added to the reaction mixture under similar conditions. Whatever the dihydrogen pressure (1.5 and 3 MPa with $P_{CO} = 1.5$ MPa), less than 1% of benzaldehyde and 99% of benzoic acid (as benzoate) were formed. Since the solubility of dihydrogen is 8.45×10^{-4} mol^{-1} at 25°C in order to increase the concentration of the hydrogen source in water, sodium formate was used as hydrogen donor and basic reagent as well. One equivalent of formate per bromobenzene was introduced. The reaction proceeds more slowly and after 15 h the conversion was 92%. Even in these conditions no aldehyde appears (less than 1%) but 75% of benzoic acid and 16% of benzene are formed. Two reasons can account for the debromohydrogenation reaction observed. First, it may correlate with the large amounts of black palladium which were collected after the reaction. Indeed, in a separate run carried out with bromobenzene, dihydrogen, carbon monoxide, triethylamine and palladium on activated carbon (5 wt.%) under the same biphasic conditions, 3% of bromobenzene were hyrogenolysed into benzene, showing that palladium metal is a possible catalyst for the debromohydrogenation of bromobenzene. Secondly, benzene could be formed homogeneously as previously described by Helquist [15]. Decarbonylation of the species $[Pd(Ph)(HCO_2)L_2]$ and then reductive elimination would afford benzene. However, in this case, as insertion of carbonyl group in the phenyl–palladium bond is quite easy, we should have observed also the formation of benzaldehyde. Thus benzene is presumably formed by a heterogeneous pathway.

2.4. Mechanistic considerations

Moser, *et al.* [4] have reinvestigated the mechanism of the methoxycarbonylation of bromobenzene catalysed by triphenylphosphine-containing palladium complexes which had previously been described by Garrou and Heck [16]. It was shown that the active species is $[Pd(PPh_3)_2]$ and that the rate-determining step is the oxidative addition of bromobenzene to afford $[Pd(Ph)Br(PPh_3)_2]$ [16]. Carbonylation gives the benzoyl complex $[Pd(COPh)Br(PPh_3)_2]$; then a triethylamine-assisted attack of methanol regenerates the active palladium(0) species and leads to methylbenzoate and triethylammonium bromide [4].

For our part, we investigated the oxidative addition of bromobenzene to $[Pd(TPPTS)_3]$ in methanol. Below 35°C, no reaction occurs whereas, above 40°C, methanol itself reacts with the palladium complex to give a yellow precipitate, which shows IR bands characteristic of TPPTS and in the ^{31}P NMR spectrum a singlet at

25.8 ppm. At 35°C, the reaction proceeds slowly to afford quantitatively after 15 h [Pd(Ph)Br(TPPTS)$_2$] (**2**) as a white precipitate. Elemental analysis and IR spectra are consistent with this. In particular, the characteristic palladium-bound phenyl C–C stretch was found at 1562 cm^{-1}. This complex reacts quickly with water, since a deep-garnet colour develops when it is dissolved in water. ^{1}H NMR spectra recorded in D_2O are consistent with a [Pd(Ph)(TPPTS)$_2$] fragment, as shown by the signal intensities. In ^{31}P NMR spectrum there is a singlet at 27.8 ppm. We assign to this garnet complex a formula [Pd(Ph)X(TPPTS)$_2$]. After evaporation of the solution the υ(CC) band shifted from 1562 for **2** to 1556 cm^{-1} for the resulting garnet solid. We believe that the bromide has been replaced by OH or OH_2. Moreover, any attempt to prepare [Pd(Ph)Br(TPPTS)$_2$] by an exchange reaction from the PPh_3 analogue in water–chloroform mixtures failed. Indeed we obtained the complex [Pd(TPPTS)$_3$] in equilibrium with free TPPTS (0.6 ppm), OTPPTS (37.1 ppm) and presumably a phosphonium salt (26.3 ppm) in the aqueous phase while benzene is produced simultaneously. In Fig. 2 a pathway is proposed to account for our observations.

Finally, when performed in water, the direct addition of bromobenzene to [Pd(TPPTS)$_3$] leads to [Pd(Ph)X(TPPTS)$_2$] as shown by its ^{31}P NMR signal at 27.9 ppm and its υ(CC) band at 1556 cm^{-1}.

Thus the complex [Pd(Ph)Br(TPPTS)$_2$] can be prepared by oxidative addition of bromobenzene to [Pd(TPPTS)$_3$], provided that the reaction is carried out in methanol. When this compound is dissolved in water or when the oxidative addition is made in water, the bromide is presumably replaced by a hydroxide or an aqua ligand. The complex [Pd(TPPTS)$_3$] is ultimately produced by ligand exchange from [Pd(Ph)Br(PPh$_3$)$_2$].

On the contrary the addition of an aqueous phase containing TPPTS to a chloroform solution of [Pd(COPh)Br(PPh$_3$)$_2$] leads at 50°C after 1 h to the corresponding complex [Pd(COPh)Br(TPPTS)$_2$] (**3**). In the ^{31}P NMR spectrum this complex is characterized by a singlet at 24.7 ppm, as well as the signal of free TPPTS at −2.5 ppm. The ^{13}C NMR spectrum is not informative enough, since the spectra show a phenyl group and two palladium-bound TPPTS but not the CO benzoyl signal. In the IR spectrum the υ(CO) band is masked by the broad δ(OH) band of water at 1636 cm^{-1}. However, the presence of the benzoyl group is shown by the carbonyl-bound phenyl C–C stretch at 1579 cm^{-1}, which compares correctly with the analogous υ(CC) at 1578 cm^{-1} for the complex [Pd(COPh)Br(PPh$_3$)$_2$]. In addition, the presence of COPh is confirmed by the quantitative formation of triethylammonium benzoate and **1** when the water-soluble complex resulting from ligand exchange reacts with water in the presence of triethylamine. The absence of triethylamine does not allow this reaction to proceed. As we also observed in catalysis, reductive elimination of the carbonylated compound needs to be assisted by a basic agent.

Moreover, carbonylation of [Pd(Ph)X(TPPTS)$_2$] under ambient conditions leads to [Pd(COPh)X(TPPTS)$_2$], showing a singlet in the ^{31}P NMR spectrum at 24.7 ppm and, after evaporation, a υ(CC) band at 1579 cm^{-1}. Thus, the carbonylation of the palladium phenyl bond into a palladium benzoyl bond is rather easy and in any case more rapid than the oxidative addition of bromobenzene to **1**.

As **1–3** have been characterized, a catalytic cycle can been proposed which recalls that initially published by Garrou and Heck [16] and then modified by Moser *et al.* [4]. We consider that in water a nucleophilic attack of a hydroxide ion assisted by triethylamine occurs on the benzoyl species. This proposed mechanism is supported by the fact that sodium hydroxide affords the same result. Figure 3 displays the four main steps, including a pentacoordinated carbonyl species which has not been observed.

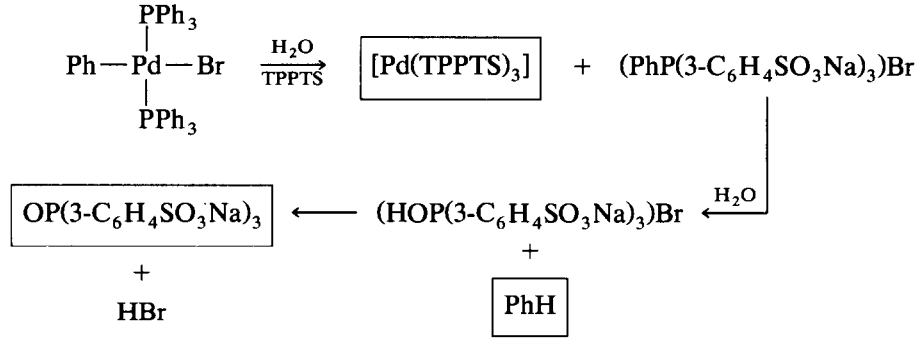


Fig. 2. Proposed pathway for the formation of **1**, OTPPTS and benzene in an attempt to replace the PPh_3 in [Pd(Ph)Br(PPh$_3$)$_2$] by TPPTS.

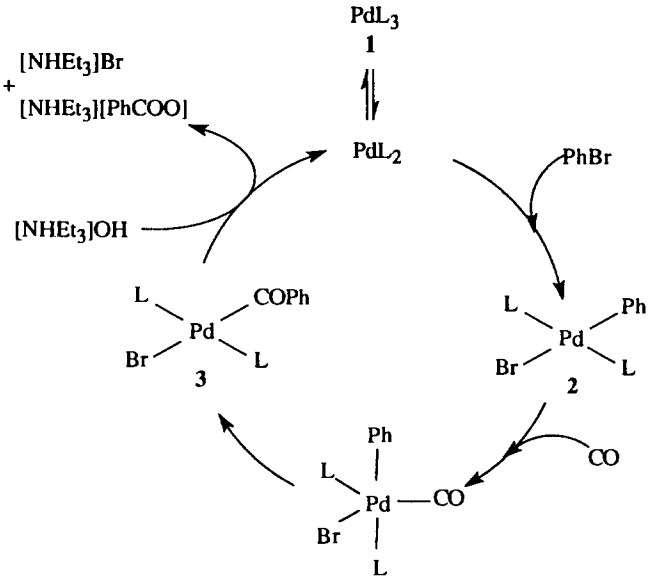


Fig. 3. Proposed catalytic cycle for the hydroxycarbonylation of bromobenzene in water.

3. Experimental details

3.1. Equipment

NMR spectra were recorded on a Bruker WH 90 spectrometer (^{31}P {^1H} (36.43 MHz); 30°C; external reference, H_3PO_4; 85%), a Bruker AC 200 spectrometer (^1H (200.13 MHz); external reference tetramethylsilane (TMS)) and a Bruker WM 250 spectrometer (^{13}C (62.90 MHz); external reference, TMS): d, doublet; t, triplet; "t"; apparent triplet; m, multiplet; dd, doublet of doublets; dt, doublet of triplets, dm, doublet of multiplets, tt, triplet of triplets, dtd, doublet of triplets of doublets, dtt, doublet of triplets of triplets.

All the experiments were carried out under argon. IR spectra were collected on a Perkin–Elmer 1710 Fourier transform spectrometer: m, medium; s, strong; vs, very strong. The elemental analyses were performed at the Service Central d'Analyse du CNRS in Vernaison (France). Gas chromatography analyses were carried out on a Carlo Erba HR GCS 160 instrument equipped with an Econo Cap FFAP capillary column, using diphenylether as an internal standard.

3.2. Materials

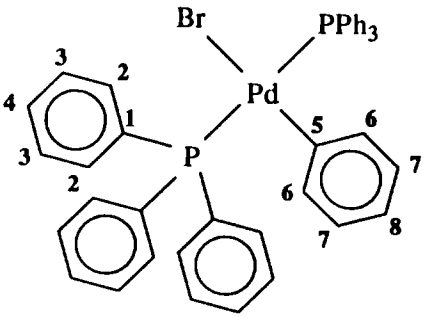
All reagents were used as supplied by the manufacturers: chlorobenzene, hydrazine, triphenylphosphine (Aldrich), bromobenzene (Lancaster), diphenylether (Prolabo), triethylamine (SDS). Argon, dinitrogen, carbon monoxide and dihydrogen were from Prodair (purity, greater than 99%) and were used as received without further purification. TPPTS was provided by Rhône-Poulenc Chimie as a solution in water. Solvents such as benzene, chloroform, dimethyl formamide, dimethyl sulphoxide, ethanol, methanol and toluene were obtained from SDS. They were used without further purification. All the solvents were saturated with argon prior to use.

3.3. $[Pd(PPh_3)_4]$

This complex was prepared according to the literature [17].

3.4. $[Pd(Ph)(Br)(PPh_3)_2]$

Only the work-up of this previously published synthesis has been modified [4,18]. After filtration and washing with 50 ml of ether, the resulting solid was dissolved in 5 ml of chloroform, and 40 ml of methanol were added to give a cream precipitate of [Pd(Ph)(Br)$(PPh_3)_2$]. The product was recovered by filtration and dried under vacuum (98% yield). IR and ^{31}P NMR spectra agree with the data given in the literature.

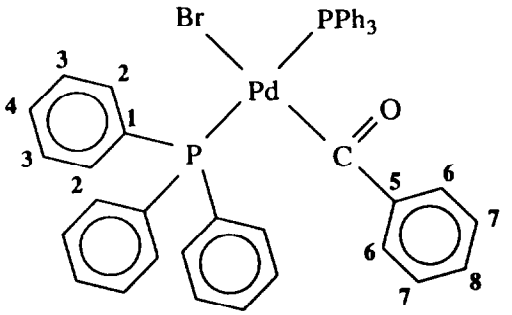


^1H NMR ($CDCl_3$, 27°C): δ 6.96 (2H, t, $J(H_7H_6) = J(H_7H_8) = 7.2$ Hz, H_7); 7.1–7.3 (1H, m, H_8); 7.28 (18H, m, $H_3 + H_4$); 7.53 (2H, dd, $J(H_6H_7) = 7.7$ Hz, $J(H_6H_8) = 1.4$ Hz, H_6); 7.65 (12 H, dd, $J(H_2H_3) = 6.0$ Hz, $J(H_2P) = 11.9$ Hz, H_2) ppm.

^{13}C NMR ($CDCl_3$, 24°C); δ 121.73 (dt, $J(C_8H_8) = 159.0$ Hz, $J(C_8H_6) = 7.1$ Hz, C_8); 127.66 (d, $J(C_7H_7) = 162.4$ Hz, C_7); 127.73 (dtd, $J(C_3H_3) = 162.6$ Hz, $J(C_3P) = 5.1$ Hz, $J(C_3H'_3) = 5.5$ Hz, C_3); 129.64 (dt, $J(C_4H_4) = 160.7$ Hz, $J(C_4H_2) = 7.4$ Hz, C_4); 131.50 (tt, $J(C_1P) = 22.6$ Hz, $J(C_1H_3) = 7.2$ Hz, C_1); 134.57 (dt"t", $J(C_2H_2) = 163.4$ Hz, $J(C_2P) = 6.2$ Hz, $J(C_2H_4) \approx J(C_2H_2) = 6.7$ Hz, C_2); 136.21 (dm, $J(C_6H_6) = 157.9$ Hz, C_6); 156.02 (tt, $J(C_5P) = 3.1$ Hz, $J(C_5H_7) < 5$ Hz, C_5) ppm.

3.5. $[Pd(COPh)(Br)(PPh_3)_2]$

This complex was prepared according to the literature [4]. IR and ^{31}P NMR are in agreement with the literature.



^{1}H NMR ($CDCl_3$, 27°C); δ 6.19 (2H "t", $J(H_7H_6) \approx (H_7H_8) = 7.4$ Hz, H_7); 6.33 (1H, t, $J(H_8H_7) = 7.5$ Hz, H_8); 6.59 (2H, dm, $J(H_6H_7) = 7.9$ Hz, H_6); 7.28 (m, 18H, $H_3 + H_4$), 7.65 (12H, "t", $J(H_2H_3) \approx J(H_2P) = 6.2$ Hz, H_2) ppm.

^{13}C NMR ($CDCl_3$, 24°C): δ 127.23 (dd, $J(C_7H_7) = 160.8$ Hz, $J(C_7H_{7'}) = 7.6$ Hz, C_7); 127.92 (dtd, $J(C_3H_3) = 161.4$ Hz, $J(C_3P) = 5.1$ Hz, $J(C_3H_{3'}) = 5.5$ Hz, C_3); 129.08 (d "t", $J(C_6H_6) = 159.6$ Hz, $J(C_6H_{6'}) \approx J(C_6H_8) = 6.7$ Hz, C_6); 130.05 (dt, $J(C_4H_4) = 160.8$ Hz, $J(C_4H_2) = 7.5$ Hz, C_4); 131.12 (tt, $J(C_1P) = 22.3$ Hz, $J(C_1H_3) = 7.7$ Hz, C_1); 131.29 (dt, $J(C_8H_8) = 160.1$ Hz, $J(C_8H_6) = 7.7$ Hz, C_8); 134.78 (dt "t", $J(C_2H_2) = 162.1$ Hz, $J(C_2P) = 6.4$ Hz, $J(C_2H_4) \approx J(C_2H_{2'}) = 6.2$ Hz, C_2); 140.06 (tt, $J(C_5P) = 15.8$ Hz, $J(C_5H_7) = 7.9$ Hz, C_5); 231.15 (t, $J(C_9P) = 4.1$ Hz, C_9) ppm.

3.6. [Pd(TPPTS)$_3$] (1)

This complex was prepared according to the first procedure of Herrmann et al. [11].

^{31}P {1H} NMR (H_2O–D_2O, 30°C): δ 24.00 (s) ppm.

IR (KBr): ν(CC) 1464 (m); ν(CP) 1397 (m), 1095 (s); ν(SO) 1191 (vs) 1039 (vs), 693 (vs); δ (CH) 788 (s), 692 (s) cm^{-1}.

Elemental anal. Found: C, 32.9, H, 2.7. Calc. C, 33.1, H, 2.6%.

3.7. [Pd(Ph)(Br)(TPPTS)$_2$] (2)

0.59 g (0.3 mmol) of **1** and 0.32 ml (3.0 mmol) of bromobenzene were added to 50 ml of chloroform. The orange solution was stirred at 35°C for 15 h to give a white precipitate of **2**. This was filtrated and dried under vacuum (0.29 g; yield, 65%).

IR (KBr): ν(CC) 1562 (m), 1467 (m); ν(CP), 1398 (m), 1099 (s); ν(SO) 1196 (vs), 1040 (vs), 624 (vs); δ (CH) 790 (s), 731 (s), 691 (s), 676 (s) cm^{-1}.

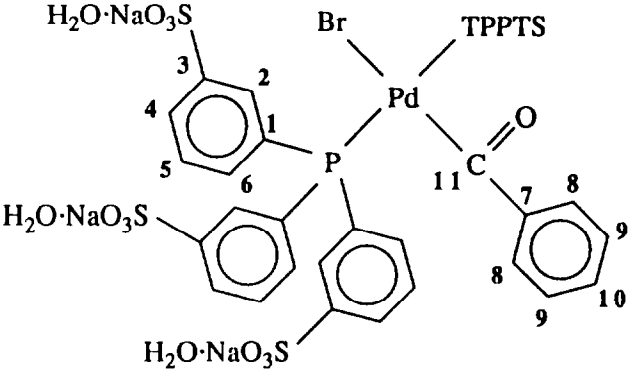
Elemental anal. Found: C, 33.4, H, 2.7, S, 12.8, Br, 5.3, Na, 9.1, Pd, 7.1. Calc. C, 33.8, H, 2.7, S, 12.0, Br, 5.3, Na, 9.0, Pd, 6.8%.

3.8. [Pd(COPh)(Br)(TPPTS)$_2$] (3)

A solution of 0.41 g (0.5 mmol) of [Pd(COPh)-Br(PPh_3)$_2$] in 15 ml of chloroform was mixed with an aqueous solution of TPPTS (1 mmol in 10 ml) at 50°C for 3 h. The aqueous phase became yellow but exchange was not complete and the organic phase was still coloured. After decanting, the aqueous phase was washed with chloroform and dried under vacuum. Complex **3** was obtained as a mixture with TPPTS in excess.

IR (KBr): ν(CC) 1578 (m), 1467 (m); ν(CP) 1398 (m), 1099 (s); ν(SO) 1196 (vs), 1040 (vs), 623 (vs); δ (CH) 790 (s), 688 (s) cm^{-1}.

^{31}P {1H} NMR (H_2O–D_2O, 30°C); δ 24.74 (s) ppm.



^{1}H NMR (D_2O, 20°C); δ 6.96 ("t", 2H, $J(H_9H_8) \approx J(H_9H_{10}) = 7.6$ Hz, H_9); 7.16 (t, 1H, $J(H_{10}H_9) = 7.2$ Hz, H_{10}); 7.3–8 (m, 26H, $H_2 + H_4 + H_5 + H_6 + H_8$) ppm.

^{13}C NMR (D_2O, 24°C): δ 131.1 (d, $J(C_9H_9) = 163.3$ Hz, C_9); 131.17 (dm, $J(C_4,H_4) = 166.0$ Hz, C_4); 132.03 (dm, $J(C_8H_8) = 161.2$ Hz, C_8); 132.22 (t, $J(C_1P) = 22.4$ Hz, C_1); 132.49 (dt, $J(C_5H_5) = 167.5$ Hz, $J(C_5P) = 5.4$ Hz, C_5); 133.44 (dt, $J(C_6H_6) = 165.8$ Hz, $J(C_6P) = 6.5$ Hz, C_6); 136.4 (dt, $J(C_{10}H_{10} = 162.7$ Hz, $J(C_{10}H_8) = 7.4$ Hz, C_{10}); 139.91 (m, C_7); 140.24 (dt, $J(C_2H_2) = 165.8$ Hz, $J(C_2P) = 7.2$ Hz, C_2);145.9 (m, $J(C_3P) = 4.9$ Hz, C_3) ppm.

3.9. General procedure for carbonylation of bromobenzene

The mixture of products was prepared in a Schlenk tube. To 10 ml of water and 10 ml of toluene were added 0.11 g (0.5 mmol) of palladium diacetate, 2.63 ml (25 mmol) of bromobenzene, 3.87 g (6.25 mmol) of TPPTS and 7.7 ml (55 mmol) of triethylamine. The mixture was stirred for 5 min in order to dissolve the solid catalyst and was introduced in a stainless steel autoclave previously purged with argon. The autoclave was heated to 150°C under carbon monoxide at 0.3 MPa. Then it was pressurized to 1.5 MPa and stirred at a constant pressure. After 15 h, the autoclave was cooled to room temperature and slowly depressurized. The solution was collected under argon in a separatory funnel and after decanting the two phases were analysed independently.

4. Conclusion

This study has shown that the active species [Pd(TPPTS)$_2$] can be maintained intact during the carbonylation reaction of bromoaromatic compounds, provided an excess of TPPTS is present. The water-soluble palladium tris(3-sulphophenyl)phosphine complex which catalyses this reaction works in a biphasic system, but the benzoic acid produced remains in the aqueous phase, thus avoiding the direct recycling of the catalyst. This work has also shown that water reacts so quickly that any hydrogen source cannot produce an aldehyde and that the reaction is quite limited exclusively to the hydroxycarbonylation of bromobenzene. The mechanism follows the classical steps initially proposed by Garrou and Heck and involves a zero-valent palladium species.

Acknowledgments

We thank Rhône-Poulenc for a gift of TPPTS. Comptoir Lyon–Alemand–Louyot is gratefully acknowledged for a loan of palladium salts.

References

1 A. Schoenberg, I. Bartoletti and R.F. Heck, *J. Org. Chem., 39* (1974) 3318.
2 (a) R.F. Heck, in A.R. Katritzky, O. Meth-Cohn and C.W. Rees (eds.), *Reagents in Organic Synthesis*, Academic Press, New York 1985.
(b) J. Gauthier-Lafaye and R. Perron, in A. Mortreux and F. Petit (eds.), *Industrial Applications of Homogeneous Catalysis*, Reidel, Dordrecht 1988, p. 19.
(c) L. Krumenacker, Ph. Leconte, F. Metz and R. Perron, *Industrial Aspects of Molecular Activation by Metals, Comett III, Carry-le-Rouet*, April 23–27 1990 H. Arzovmanian and I. Tkatchenko (eds.), Marseille, Vol. II.
(d) V.V. Grushin and H. Alper, *Organometallics, 12* (1993) 1890.
3 I. Pri-Bar and O. Buchman, *J. Org. Chem., 53* (1988) 624.
4 W.R. Moser, A.W. Wang and N.K. Kildahl, *J. Am. Chem. Soc., 110* (1988) 2816.
5 (a) Y. Ben-David, M. Portnoy and D. Milstein, *J. Chem. Soc., Chem. Commun.*, (1989) 1816.
(b) Y. Ben-David, M. Portnoy and D. Milstein, *J. Am. Chem. Soc., 111* (1989) 8742.
(c) M. Huser, M.T. Youinou and J.A. Osborn, *Angew. Chem., Int. Edn. Engl., 101* (1989) 1427.
6 (a) A. Schoenberg and R.F. Heck, *J. Am. Chem. Soc., 96* (1974) 7761.
(b) J.K. Stille and P.K. Wong, *J. Org. Chem., 40* (1975) 532.
(c) I. Pri-Bar and O. Buchman, *J. Org. Chem., 49* (1984) 4009.
(d) V.P. Baillargeon and J.K. Stille, *J. Am. Chem. Soc., 108* (1986) 452.
(e) B. El Ali and H. Alper, *J. Mol. Catal., 67* (1991) 29.
7 H. Urata, N.X. Hu, H. Maekawa and T. Fuchikami, *Tetrahedron Lett., 23* (1991) 4733.
8 R. Mutin, C. Lucas, J. Thivolle-Cazat, V. Dufaud, F. Dany and J.M. Basset, *J. Chem. Soc., Chem. Commun.*, (1988) 896.
9 F. Ozawa, A. Kubo and T. Hayashi, *Chem. Lett.*, (1992) 2177.
10 C. Amatore, A. Jutand and M.A. M'Barki, *Organometallics, 11* (1992) 3009.
11 W.A. Herrmann, J. Kellner and H. Riepel, *J. Organomet. Chem., 389* (1990) 103.
12 C. Larpent, G. Meignan and H. Patin, *Tetrahedron, 18* (1990) 6381.
13 K.C. Kong and C.H. Cheng, *J. Am. Chem. Soc., 113* (1991) 6312.
14 Ph. Kalck and F. Monteil, *Adv. Organomet. Chem., 34* (1992) 219.
15 P. Helquist, *Tetrahedron Lett.*, (1978) 1913.
16 P.E. Garrou and R.F. Heck, *J. Am. Chem. Soc., 98* (1976) 4115.
17 D.R. Coulson, *Inorg. Synth., 13* (1972) 121.
18 P. Fitton and E.A. Rick, *J. Organomet. Chem., 28* (1971) 287.