Carbonylation of benzyl bromide to benzeneacetic acid and its esters catalysed by water-soluble palladium complexes

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Abstract

A catalytic system containing $PdCl_2(cod)$ (cod = 1,5-cyclooctadiene) and a water-soluble phosphine PNS (PNS = $Ph_2PCH_2CH_2C(O)NHC(CH_3)_2CH_2SO_3Li$) in water/toluene solution exhibits activity in the carbonylation of benzyl bromide to benzeneacetic acid (87% yield) at 130°C and 10 atm of CO. In a reaction carried out in water/alcohol solution, corresponding esters were obtained in yields dependent on the kind of alcohol used: 24% for BuOH, 62% for ^{i}PrOH, 78% for EtOH, and 85% for MeOH. In the synthesis of benzeneacetic acid methyl ester $C_6H_5CH_2C(O)OCH_3$ at 50–100°C under 5–10 atm of CO, TOF ca. 300 was achieved. The contribution of palladium(0) phosphine complexes was proved using the $^{31}P\{^1H\}$ NMR and IR methods. The complex $Pd(PNS)_4$, obtained in the reaction of $PdCl_2(cod)$ with PNS and $NaBH_4$, reacts with $C_6H_5CH_2Br$ yielding an oxidative addition product, $PdBr(C_6H_5CH_2)(PNS)_2$, identified using the $^{31}P\{^1H\}$ NMR method. In CD_3OD solution containing $Pd(PNS)_4$ and $C_6H_5CH_2Br$ saturated with CO, the ester described by the formula $C_6H_5CH_2C(O)OCD_3$ was identified. This suggests that the reaction of CO-insertion into Pd−C bonding is relatively fast. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Palladium; Water soluble catalyst; Carbonylation; Benzyl bromide; Benzeneacetic acid

1. Introduction

The aryl halides, PhX (X = Cl, Br, I), used as substrates for the carbonylation reaction (Scheme 1), were found to be excellent substrates for the synthesis of very valuable carbonyl compounds used next as medicines or fragrances [1,2].

The synthesis of benzeneacetic acid via the carbonylation reaction was found to be a less expensive and troublesome method in comparison to the traditional synthesis based on two-step process — conversion of benzyl chloride to benzyl cyanide and subsequent hydrolysis of cyanide with sulphuric acid [1,2]. The kind of carbonylation reaction product depends on the kind of nucleophilic agent used; namely, carboxylic acids are produced in water solution, esters are obtained in alcohol, whereas amides are produced when amines are applied. The carbonylation reaction of aryl halides to obtain

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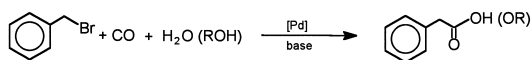
Scheme 1.

carboxylic acids is usually carried out in mixed solvents, e.g., water and toluene, which does not favour sufficient reagent miscibility and therefore causes a low reaction rate. The organic phase (toluene) contains a substrate and a catalyst with coordinated hydrophobic phosphines. In the water phase the reaction product, carboxylic acid, is collected as a sodium salt (when NaOH is used). Due to increased reaction effectivity, some phase transfer (PT) agents, like glycols [3] or 18 crown-6-ether [4], are added. In some cases, relatively good results have been obtained without the use of PT agents, as in the case of the carbonylation of aryl halides with $PdCl_2(PR_3)_2$ (R = Ph, Cy, Me, Bu) complexes [4].

Polyethylene glycol (PEG) used as a PT agent in the carbonylation of phenyl halides to phenylacetic acids not only transfers a catalyst $(Co(CO)_4^-)$ from water to the organic phase but also accelerates the hydrolysis of the cobalt–acyl complex [3].

To improve the yield of phenylacetic acid in synthesis catalysed with palladium complexes, some zeolites [5] or alcoholates of titanium or zirconium [6] have been applied. In some reactions, a cobalt complex with basic Al_2O_3 and sodium or potassium alcoholates has been applied [7].

The replacement of hydrophobic phosphines by water-soluble ones significantly increases the effectivity of the mutual contacts of catalyst transient forms with nucleophilic agents. Additionally, the advantage of that system is demonstrated by the easy separation of organic products from the catalyst [8]. Recently, several catalytic systems for aryl halides carbonylation based on water-soluble catalysts have been described. A palladium complex described by the formula $PdCl_2[PPh_2(m\text{-}C_6H_4SO_3Na)]_2$ has been applied as a catalyst for the carbonylation

of benzyl chloride and an 89–93% yield of phenylacetic acid at 1 atm of CO was achieved [9]. A palladium catalyst with TPPTS (TPPTS = $P(m\text{-}C_6H_4SO_3Na)_3$), which is formed in situ from $Pd(OAc)_2$ and TPPTS, catalyses the carbonylation of bromobenzene to benzoic acid. Spectroscopic studies have confirmed the participation of water-soluble palladium complexes like $Pd(TPPTS)_3$ in that catalytic process [10]. The palladium complex with TPPTS applied to the carbonylation reaction of aryl halides demonstrates very high TON, over 1500 [11,12]. Good results have also been obtained in the carbonylation of benzyl chloride with a system containing palladium compounds and the water-soluble phosphine BINAS, which has been found to be active even in acidic medium [11]. Precipitation of metallic palladium was not observed but activity decreased in time. Applying $Pd(TPPTS)_3$ as a catalyst for carbonylation in water solution, benzeneacetic acid has been obtained from benzyl alcohol [13], and benzenepropionic acid from the styrene [14]. Other carboxylic acids are also the products of alcohol carbonylation, e.g., ibuprofen (2-(4-isobutylphenyl)propionic acid) has been obtained from 1-(4-isobutylphenyl)ethanol when $Pd(TPPTS)_3$ has been applied as a catalyst [15,16].

2. Aim of the studies

The main subject of this paper is the account of studies on the application of a water-soluble phosphine PNS (PNS = $Ph_2PCH_2CH_2C(O)\text{-}NHC(CH_3)_2CH_2SO_3Li$) as a modifying ligand to a palladium homogeneous catalyst for the carbonylation of benzyl bromide to benzeneacetic acid and its esters. Earlier studies of rhodium complexes with PNS have shown their high catalytic activity and selectivity in olefin hydroformylation and hydrogenation in biphasic systems [17,18]. It was expected that the studies of the carbonylation of benzyl bromide as a model reaction would enable the identification
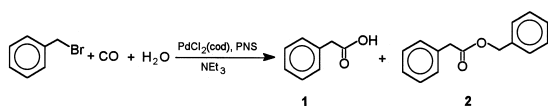
Scheme 2.
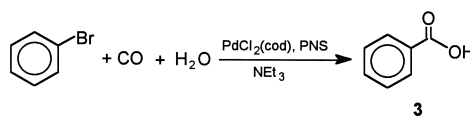
Scheme 3.

of new catalytically active palladium species as well as the description of their transformations under reaction conditions. The recognition of these processes is fundamental for the design of effective catalytic processes.

3. Results and discussion

3.1. Carbonylation of benzyl bromide to benzeneacetic acid

The carbonylation reaction of benzyl bromide in water/toluene medium proceeds according to Scheme 2.

Benzeneacetic acid (**1**) is the main product and benzeneacetic acid benzyl ester (**2**) appears as a side product (Table 1). It was proved in separate experiment that the ester (**2**) is formed in a noncatalytic reaction during the thermal reaction of benzyl bromide with the acid (**1**) in the absence of a palladium complex. Therefore the total yields of (**1**) in catalytic reactions under study are about 13–16% higher than those presented in Table 1.

The experimentally determined optimal parameters of the carbonylation reaction guaran-

teeing high yield of acid are as follows: temperature 130°C, time 5 h, [PNS]:[Pd] = 14.4, [Pd] complex concentration 1.5×10^{-3} to 3.8×10^{-3} M, [CO] pressure 5–10 atm.

The same catalytic system was also applied for the carbonylation of bromobenzene and ca. 90% of benzoic acid (**3**) was obtained after 5 h (Scheme 3).

3.2. Carbonylation of benzyl bromide to benzeneacetic acid esters

The synthesis of benzeneacetic acid esters with the catalytic system under study attains a 100% yield within 2 h when water is replaced by alcohol (e.g., ethanol) (Scheme 4).

The data collected in Table 2 demonstrate the effect of ethanol addition in comparison to the system containing only water as a solvent. To obtain ca. 80% yield of the ester, already ca. 13% of ethanol added to water is sufficient. The composition of reaction products is practically independent of ethanol concentration. It was experimentally found that a higher concentration of ethanol causes catalytic system deactivation, particularly when, prior to the addition of the substrate, the catalytic system was heated for 2 h under 10 atm pressure of CO. In such experiments, the yield of the ester decreased as ethanol concentration increased (Table 2). The catalytic activity loss may be explained as due to the reduction of Pd(II) to Pd(0), since some

Table 1

Benzyl bromide carbonylation to benzeneacetic acid with palladium/PNS system in toluene–water medium

Reaction conditions: 2 cm^3 toluene, 2 cm^3 water, 1.5 cm^3 (0.01 mol) NEt$_3$, [PdCl$_2$(cod)] 2.5×10^{-5} mol, [C$_6$H$_5$CH$_2$Br] 4.2×10^{-3} mol, 10 atm CO, 12 h.

[PNS]:[Pd]	Temperature [°C]	Products [% mol]	
		1	**2**
14.4	140	74	26
14.4	130	87	13
14.4	120	64	36
7.2	130	72	28
4.8	130	63	37
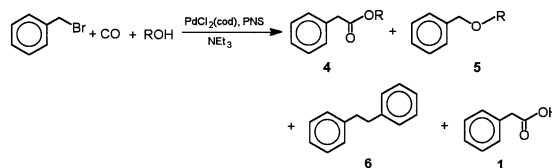
Scheme 4.

Table 2

Benzyl bromide carbonylation to benzeneacetic acid with palladium/PNS system in water–ethanol medium

Reaction conditions: 1.5 cm^3 (0.01 mol) NEt$_3$, [PdCl$_2$(cod)] 2.5×10^{-5} mol, [PNS] 1.8×10^{-4} mol, [C$_6$H$_5$CH$_2$Br] (8.4×10^{-3} mol), 10 atm CO, 120°C, 4 h.

[H$_2$O]/cm^3	[EtOH]/cm^3	Products [% mol]		
		1	**4**	**2**
2.3	–	59	–	30
2	0.3	–	83	12
1.3	1	–	79	10
2[a]	0.4	38	27	20
0.4[a]	2	–	10	–

[a] Before C$_6$H$_5$CH$_2$Br (8.4×10^{-3} mol) was added the reaction mixture was heated at 120°C under 10 atm CO during 2 h. After substrate (C$_6$H$_5$CH$_2$Br) addition the reaction was carried out 3 h and than reaction products were analysed.
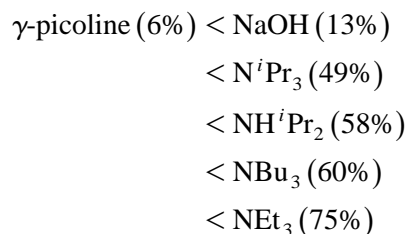
precipitation of palladium black was observed in the reaction mixture. It must be noted, however, that most of the palladium catalyst remained in a soluble form. The catalytic activity loss may also be caused by a reaction of PNS with alcohol, which may lead to the formation of an acidic form of the initial lithium salt of PNS. Such a reaction has recently been observed during the hydroformylation of unsaturated alcohols with a rhodium catalysts [19] modified with PNS. As a consequence of the formation of an acidic form of PNS, its coordination properties are changed and a pH decrease may lead to catalyst deactivation. In carbonylation reaction conditions, the formation of phosphonic cations is also possible as a product of a reaction of PNS with PhCH$_2$Br.

The occurrence of the above-mentioned reaction may significantly decrease the coordination ability of PNS to form complexes with palladium [20].

The highest yield (ca. 80%) of esters was obtained in reactions with the participation of ethanol or methanol. Pressure and temperature changes in the range 5–10 atm and 100–130°C, respectively, have no significant effect on the yield (ca. 75–81%) and the composition of the esters formed. The reaction yield of esters was much lower when higher alcohols (^{i}PrOH,

BuOH) were used (Table 3). The methyl ester synthesis at 50–100°C and 5–10 atm with different catalyst concentrations revealed TOF of ca. 300 h^{-1}. A relatively high TOF factor points to a rather high activity of the catalytic system under study.

The kind of base used has considerable influence on the reaction course. Among the bases tested, triethylamine (NEt$_3$) was found the best. Using as a parameter the yield (% in parenthesis) of benzeneacetic methyl ester (**4**) at 10 atm and 80°C, the following order of bases can be proposed:

$$\gamma\text{-picoline}\,(6\%) < \text{NaOH}\,(13\%)$$
$$< \text{N}^i\text{Pr}_3\,(49\%)$$
$$< \text{NH}^i\text{Pr}_2\,(58\%)$$
$$< \text{NBu}_3\,(60\%)$$
$$< \text{NEt}_3\,(75\%)$$

This order is almost consistent with the increase of basicity, and the amine structure does not play any important role. Generally, ester yield is higher when amines are applied, but not hydroxides.

In carbonylation reactions carried out in a water/methanol mixture, partial reduction of the catalyst to black palladium metal was observed, much higher than in water/ethanol solution. These black agglomerates are catalytically inactive, which is in agreement with the earlier

Table 3

Benzyl bromide carbonylation to benzeneacetic acid esters with palladium/PNS system in water–ROH medium

Reaction conditions: 3 cm^3 ROH, 1 cm^3 water, 1.5 cm^3 (0.01 mol) NEt$_3$, [PdCl$_2$(cod)] 2.5×10^{-5} mol, [C$_6$H$_5$CH$_2$Br] 4.2×10^{-3} mol, 10 atm CO, 2 h, 130°C.

[PNS]:[Pd]	ROH	Products [% mol]			
		4	**1**	**6**	**5**
14.4	EtOH	78	18		5
5.9	EtOH	75	15	5	6
14.4	MeOH	78	6	4	–
6.3	MeOH	85	–	8	7
14.4	^{i}PrOH	62	11	–	5
14.4	BuOH	24	–	–	–

observation of other authors [10]. Two experiments, illustrating the catalyst deactivation, were performed. In the first experiment, a reaction mixture (without benzyl bromide) containing the catalyst in 3 cm^3 of methanol and 1 cm^3 of water was heated in 100°C under 5 atm of CO for 2 h; next, the benzyl bromide was added and the reaction continued for 3 h under 5 atm of CO. In the second experiment, pre-treatment of the reaction mixture was prolonged for 3 h before introduction of benzyl bromide. The yield of the ester (**4**) in the two experiments was, respectively, 38% and 18%. The catalytic activity decrease may be explained by the elimination of the catalyst (palladium complex) as a result of palladium reduction to metal, found as a black precipitate. An important practical conclusion to draw from these experiments — one which may ensure a high yield of carbonylation — is that all reagents must be carefully introduced simultaneously at the beginning of the process. A similar conclusion has been drawn earlier for the Pd/TPPTS system [11].

3.3. Role of palladium complexes in catalytic processes

Transformations of palladium precursors during the carbonylation reaction were investigated by careful studies of different transient species isolated from reaction and post-reaction mixtures. However, for studies of carbonylation elementary steps it was reasonable to use as catalyst precursors specially synthesised complexes of Pd(II) and/or Pd(0). The reactions of the palladium complexes under study are presented on Scheme 5.

The catalyst precursor, PdCl$_2$(cod), reacts easily with PNS, forming PdCl$_2$(PNS)$_2$ species as a result of cyclooctadiene replacement by the phosphine. The substitution takes place both in CH$_2$Cl$_2$ (although PNS is insoluble in CH$_2$Cl$_2$) and in MeOH with the same result. However the substitution reaction in MeOH proceeds differently in the presence of the amine (NEt$_3$). In such reaction conditions, palladium reduction

Scheme 5.
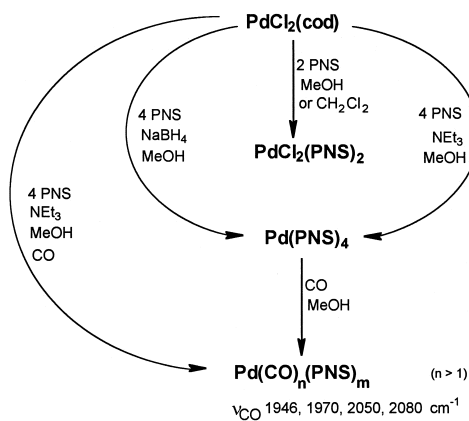
occurs, and a palladium(0) complex represented by the formula Pd(PNS)$_4$ was isolated with spectroscopic characteristics (^{31}P{^{1}H}NMR) identical to those of the complex obtained with NaBH$_4$ used as a reducing agent. The Pd(PNS)$_4$ complex was isolated with a different content of water, which makes it impossible to obtain reproducible analytical data, and ^{31}P{^{1}H}NMR was found to be the best method to determine its composition. The position of a signal at 16.7 ppm is closer to that observed in PdL$_4$ than that in PdL$_3$ complexes. For comparison, the signals in Pd(TPPTS)$_3$ and Pd(PPh$_3$)$_3$ spectra were found at ca. 22.6 ppm, whereas for Pd(PPh$_3$)$_4$ at 18.4 ppm [21–23]. In the presence of the free phosphine (PNS), the complex Pd(PNS)$_4$ shows dynamic behaviour in solution, demonstrated by the ^{31}P{^{1}H} NMR line broadening with a shift towards higher fields.

A mixture of palladium carbonyl–phosphine complexes represented by the formula Pd(CO)$_n$(PNS)$_m$ ($n + m = 4$), identified by IR (four ν_{CO} bands at 2080, 2050, 1970 and 1946 cm^{-1}), was isolated as the product of a reaction of Pd(PNS)$_4$ with CO (Scheme 5). The formation of Pd(CO)$_n$(PNS)$_m$ complexes have been monitored by IR spectroscopy. It was found that already after 5 min saturation with CO of Pd(PNS)$_4$ solution in CH$_3$OH the bands at 2050 and 2080 cm^{-1} appeared. In the next few minutes the bands at 1946 and 1970 cm^{-1} are

formed. Finally, all four ν_{CO} bands are observed with that one at 1946 cm^{-1} of the highest intensity. The same carbonyl–phosphine species were found and identified in the post-reaction mixture. The presence of ν_{CO} frequencies around 2000 cm^{-1} may suggest the formation of palladium complexes containing more than one CO ligand per palladium atom, as has been found earlier for Pd(CO)$_2$(PPh$_3$)$_2$ (ν_{CO} 1985 and 2023 cm^{-1}) [24].

In typical carbonylation reaction conditions (PdCl$_2$(cod)/4 PNS, 80°C, 10 atm CO), the mixture of ''palladium carbonyls'' is formed relatively fast (after 1 h), which may be proved by IR and/or NMR measurements. An analysis of carbonylation products obtained in reactions catalysed by the Pd(PNS)$_4$ or PdCl$_2$(cod)/PNS systems (Table 4) showed that the formation of Pd(CO)$_n$(PNS)$_m$ species is tantamount to the appearance of catalytic activity. In both reactions, after only 15 min, similar yields of esters were obtained at relatively mild reaction conditions (5 atm CO, 70°C) and without an induction period.

We also studied reactions of PdCl$_2$(PNS)$_2$ with CO in the presence of NEt$_3$ as well as NH^{i}Pr$_2$. According to literature data, in the system PdCl$_2$(PPh$_3$)$_2$/CO/MeOH/amine, a mixture of Pd(CO)(PPh$_3$)$_3$ and Pd$_3$(CO)$_3$-(PPh$_3$)$_3$ has been obtained in analogous conditions in a reaction with NH^{i}Pr$_2$ added, whereas only a carbomethoxy complex described by the formula PdCl(PPh$_3$)$_2$(COOMe) has been obtained in the presence of NEt$_3$ [25]. In similar
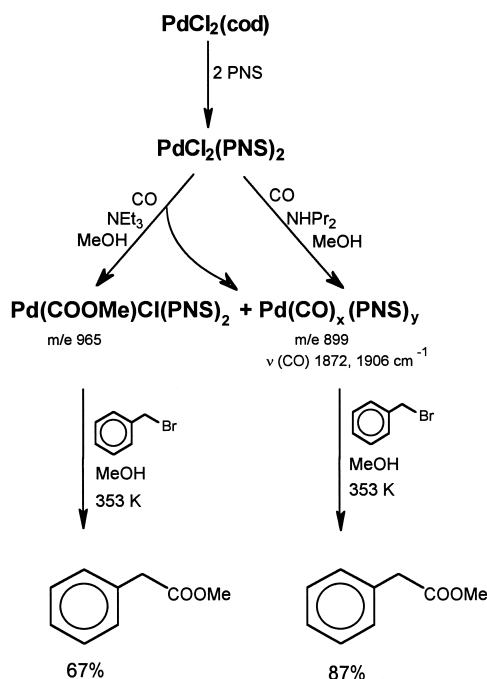

Scheme 6.

reactions with PNS instead of PPh$_3$, the effect of the amine used is not so distinct. Mixtures of red in colour carbonyls with ν_{CO} at 1872 and 1906 cm^{-1} were obtained in reactions with both amines. The only difference was a slightly lower intensity of the ν_{CO} band in the IR spectrum of the product obtained in the reaction with NEt$_3$, which may suggest the presence of another compound, not containing CO in the coordination sphere. The presence of MS signal at m/e 965, corresponding to the Pd(COOMe)(PNS)$_2^+$ fragment, may suggest the formation of some amounts of carbomethoxy species. In the MS spectrum of the sample obtained with NH^{i}Pr$_2$, such a signal was not observed. The composition of carbonyls formed in both systems is not easy to determine; however, the fragment at m/e 899 described for Pd(PNS)$_2^+$ was found in both cases. The products of both reactions were tested in benzyl bromide carbonylation without free CO at 80°C. At the same concentration of palladium species, after 2 h, respectively 67% and 87% of benzeneacetic acid methyl ester (**4**) were obtained (Scheme 6).

Table 4
The yield of benzeneacetic methyl ester in carbonylation of benzyl bromide catalysed by Pd(PNS)$_4$ and PdCl$_2$(cod)/4 PNS catalytic systems
Reaction conditions: 3 cm^3 MeOH, 1 cm^3 water, 1.5 cm^3 (0.01 mol) NEt$_3$, [PdCl$_2$(cod)] 1×10^{-5} mol, [C$_6$H$_5$CH$_2$Br] 8.4×10^{-3} mol, 5 atm CO, 70°C.

| Time [min]	Pd(PNS)$_4$	PdCl$_2$(cod)/4 PNS
15	15	19
60	62	68
75	66	70

On the basis of those results, one may conclude that complexes containing a carbomethoxy ligand show lower catalytic activity (67%) as compared with carbonyl-only complexes (87%). This is consistent with the statement that PdCl(COOMe)(PPh$_3$)$_2$ [27] is not an active form in the carbonylation of bromobenzene, although its contribution in the carbonylation of other substrates cannot be excluded [26].

From the results discussed above, it may be deduced that Pd(0) complex formed from the catalyst precursor PdCl$_2$(cod), PNS and CO, in the presence of an amine, is responsible for the catalytic activity of the system (Scheme 5). According to the generally accepted carbonylation mechanism [27], this complex activates the substrate (benzyl bromide) via oxidative addition. As was proved by ^{31}P{^{1}H} NMR, immediately after the addition of benzyl bromide to the solution of Pd(PNS)$_4$ in CD$_3$OD, a new intensive signal at 29.4 ppm appears, which may be assigned to a Pd(II) complex.

$$Pd(PNS)_4 + PhCH_2Br$$

$$\rightarrow Pd(PNS)_2(PhCH_2)(Br)$$
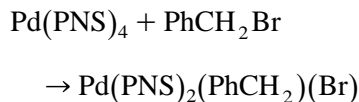
A similar chemical shift (27.9 ppm) was detected for the Pd(Ph)Br(TPPTS)$_2$ complex, isolated as a product of oxidative addition of bromobenzene to Pd(TPTS)$_3$ [10].

We did not succeed in directly detecting CO-insertion into the Pd–C bond in a solution of Pd(PNS)$_4$ and C$_6$H$_5$CH$_2$Br saturated with CO. Instead, the ^{31}P{^{1}H} NMR spectrum showed a decrease of the line at 29.4 ppm and the appearance of two new signals at 15.6 and 16.4 ppm. The GC-MS analysis of the solution showed the presence of a PhCH$_2$C(O)OCD$_3$ ester, in which the methoxy group originates from the solvent (CD$_3$OD) used in the reaction (Scheme 7). This may suggest that both steps — CO-coordination and CO-insertion into the Pd–C bond — proceed too fast to be detected using the ^{31}P{^{1}H} NMR method. Moreover, the
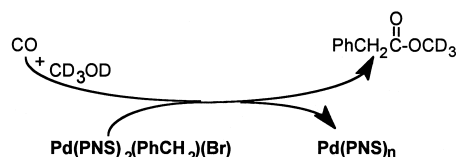
Scheme 7.

presence of the ester is yet another proof that a Pd(0) complex with coordinated PNS ligands is a catalytically active form in the carbonylation reaction.

On the basis of the experiment described above, it may be expected that a Pd/PNS catalytic system may also be used in very mild conditions, even at 1 atm of CO what requires further studies.

4. Experimental

The PdCl$_2$(cod) complex (cod = 1,5-cyclooctadiene) [28] and the PNS phosphine [29] were prepared according to relevant literature methods.

All solvents: toluene, water, methanol and ethanol were purified using standard procedures [30].

All syntheses of palladium compounds were carried out in N$_2$ atmosphere using the standard Schlenk technique.

4.1. PdCl$_2$(PNS)$_2$

A suspension of 0.05 g PdCl$_2$(cod) and 0.14 g PNS in 3 cm^3 of CH$_2$Cl$_2$ was stirred for 3 h and the yellow product was filtered off and dried in vacuo.

^{31}P{^{1}H} NMR (CD$_3$OD) 35.3 ppm, UV–VIS λ 358 nm, MS (m/e) 939 (PdCl(PNS)$_2^+$).

4.2. Pd(PNS)$_4$

0.2 g PdCl$_2$(cod) and 1.66 g PNS in 5 cm^3 of MeOH were stirred until all components were

dissolved. Then, 0.13 g $NaBH_4$ in ca. 4 cm^3 of MeOH was added drop by drop, stirred for ca. 2 h, filtered, and the filtrate was evaporated to dryness.

$^{31}P\{^1H\}$ NMR (CD_3OD) 16.7 ppm

4.2.1. Reactions of $PdCl_2(cod)$ with PNS and NEt_3 (or NH^1Pr_2) in MeOH solution

0.025 g $PdCl_2(cod)$, 0.17 g PNS and 1 cm^3 of amine in 2 cm^3 of MeOH were stirred for ca. 20 h at room temperature. The solution was filtered and the red filtrate was evaporated to dryness yielding a red powder.

4.2.2. Stoichiometric carbonylation

0.05 g of the palladium complex obtained in the above reaction, 0.02 cm^3 $C_6H_5CH_2Br$, 0.05 cm^3 NEt_3 in 1 cm^3 MeOH in N_2 atmosphere were placed in an autoclave at 80°C for 2 h. The reaction products were extracted with diethyl ether and GC-analysed.

4.2.3. Carbonylation reaction procedure

The carbonylation reaction was carried out in a 150-cm^3 steel autoclave. Proper volumes of liquid reagents were introduced into the autoclave in N_2 atmosphere. The palladium complex and the phosphine were weighted in small teflon vessels and placed in the autoclave. After closing, the autoclave was twice purged with CO, and then the appropriate CO pressure and temperature were fixed. After the reaction, the autoclave was cooled down, the CO excess was removed, the reaction products extracted with diethyl ether and analysed using the GC-MS method.

The MS (m/e) data of carbonylation reaction products

Benzeneacetic acid (**1**), $PhCH_2COOH$: 136(37, M^+), 91(100, $PhCH_2^+$), 65(20);
Benzyl methyl ether (**5**), $PhCH_2OMe$: 122(60, M^+), 121(57), 91(100, $PhCH_2^+$), 77(25, Ph^+), 65(16);

Benzeneacetic acid methyl ester (**4**), $PhCH_2COOMe$: 150(26, M^+), 91(100, $PhCH_2^+$),65(28), 59(15);
Benzeneacetic acid ethyl ester (**4a**), $PhCH_2COOEt$: 164(18, M^+), 91(100, $PhCH_2^+$),65(15);
Dibenzyl (**6**), $Ph(CH_2)_2Ph$: 182(20), 91(100), 65(11);
Benzeneacetic acid benzyl ester (**2**), $PhCH_2COOCH_2Ph$, 226(8, M^+), 108(5, $PhCH_2CO^+$), 91(100, $PhCH_2^+$), 65(18).

4.3. Instruments

IR spectra were measured with FT-IR Nicolet Impact 400. UV–VIS spectra were measured with an HP 4852 Diode Array spectrophotometer. ^1H and ^{31}P NMR spectra were recorded with Bruker 300. Chemical shifts are given vs. TMS for ^1H and vs. 85% H_3PO_4, respectively. GC-MS analyses were carried out with HP 5890 II linked to an HP 5971 A mass detector.

Acknowledgements

References

[1] Applied, Homogeneous Catalysis with Organometallic Compounds, in: B. Cornils, W.A. Herrmann (Eds.), A Comprehensive Handbook in Two Volumes V.C.H. Weinheim, New York, 1996.
[2] M. Beller, B. Cornils, C.D. Frohning, C.W. Kohlpaintner, J. Mol. Catal. A: Chem. 104 (1995) 17.
[3] C. Zucchi, G. Palyi, V. Galamb, E. Sampar-Szerencses, L. Marko, P. Li, H. Alper, Organometallics 15 (1996) 3222.
[4] V.V. Grushin, H. Alper, Organometallics 12 (1993) 1890.
[5] H. Urata, N.X. Hu, H. Mackawa, T. Fuchikami, Tetrahedron Lett. 32 (1991) 4733.
[6] J.B. Woell, S.B. Fergusson, H. Alper, J. Org. Chem. 50 (1985) 2134.
[7] R.A. Sawicki, J. Org. Chem. 48 (1983) 5382.

[8] F. Joo, A. Katho, J. Mol. Catal. A: Chem. 116 (1997) 3.

[9] T. Okano, I. Uchida, T. Nakagaki, H. Konishi, J. Kiji, J. Mol. Catal. 54 (1989) 65.

[10] F. Monteil, Ph. Kalck, J. Organomet. Chem. 482 (1994) 45.

[11] C.W. Kohlpaintner, M. Beller, J. Mol. Catal. A: Chem. 116 (1997) 259.

[12] C.W. Kohlpaintner, M. Beller, DE 4415681A1, 1994.

[13] G. Papadogianakis, L. Maat, R.A. Sheldon, J. Mol. Catal. A: Chem. 116 (1997) 179.

[14] S. Tilloy, E. Monflier, F. Bertoux, Y. Castanet, A. Mortreux, New J. Chem. 21 (1997) 529.

[15] G. Papadogianakis, L. Maat, R.A. Sheldon, J. Chem. Technol. Biotechnol. 70 (1) (1997) 83.

[16] G. Verspui, G. Papadogianakis, R.A. Sheldon, Catal. Today 42 (4) (1998) 449.

[17] G. Fremy, Y. Castanet, R. Grzybek, E. Monflier, A. Mortreux, A.M. Trzeciak, J.J. Ziółkowski, J. Organomet. Chem. 505 (1995) 11.

[18] E. Mieczyńska, A.M. Trzeciak, R. Grzybek, J.J. Ziółkowski, J. Mol. Catal. A: Chem. 132 (1998) 203.

[19] E. Mieczyńska, A.M. Trzeciak, J.J. Ziółkowski, J. Mol. Catal. A: Chem., in press.

[20] C.B. Ziegler Jr., R.F. Heck, J. Org. Chem. 43 (1978) 2942.

[21] E.G. Kuntz, O.M. Vittori, J. Mol. Catal. A: Chem. 129 (1998) 159.

[22] B.E. Mann, A. Musco, J. Chem. Soc., Dalton Trans. (1975) 1673.

[23] W.A. Herrmann, J. Kellner, H. Fiepl, J. Organomet. Chem. 389 (1990) 103.

[24] R. Whyman, J. Organomet. Chem. 63 (1973) 467.

[25] M. Hidai, M. Kokura, Y. Uchida, J. Organomet. Chem. 52 (1973) 431.

[26] J.K. Stille, P.K. Wong, J. Org. Chem. 40 (1975) 532.

[27] W.R. Moser, A.W. Wang, N.K. Kildahl, J. Am. Chem. Soc. 110 (1988) 2816.

[28] F.A. Cotton, Inorg. Synth. XIII (1972) 52.

[29] R. Grzybek, Polish Pat., 303912, 1994.

[30] D.D. Perrin, W.L.F. Armarego, D.R. Perrin, Purification of Laboratory Chemicals, Pergamon, Oxford, England, 1986.