PAPER

NJC

www.rsc.org/njc

The role of Pd colloids as catalysts in the phosphane-free methoxycarbonylation of iodobenzene

Anna M. Trzeciak,*[a] Wojciech Wojtków,[a] Józef J. Ziółkowski,[a] Józef Wrzyszcz[b] and Mirosław Zawadzki[b]

[a] *Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie, 50-383, Wrocław, Poland E-mail: ania@wchuwr.chem.uni.wroc.pl; Fax: +48 71 3757356; Tel: +48 71 3757356*

[b] *Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 937, 50-950, Wrocław, Poland. E-mail: zawadzki@int.pan.wroc.pl Tel: +48 71 3435021*

Received* (*in Montpellier, France*) *7th February 2004, Accepted 18th March 2004
First published as an Advance Article on the web 15th June 2004

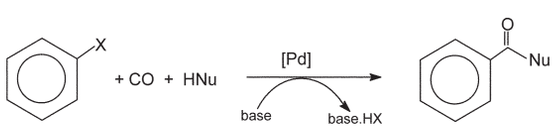
The catalytic activity of $PdCl_2$(cod) (**1**) in the methoxycarbonylation of iodobenzene (at 40–70 °C, 1–5 atm of CO, in methanol solution) increased remarkably when tetra-*n*-butylammonium salts [$^nBu_4N$]X (X = Br, Cl, I, BF_4, PF_6) were added to the system. XRD analyses confirmed that under methoxycarbonylation reaction conditions palladium was reduced to a Pd colloid of nanometer size, 2.0–5.6 nm, which was responsible for the catalytic activity. In the absence of ammonium salts fast deactivation of the colloid was observed, even when PVP (polyvinylpyrrolidone) was added as a stabilizer. Catalytic tests performed with isolated Pd colloid demonstrated its high catalytic activity in methoxycarbonylation when used together with [$^nBu_4N$]X salts. A mechanism of palladium reduction to Pd nanoparticles is proposed.

Introduction

Organic reactions catalyzed by palladium compounds are known as a universal tool in organic synthesis, especially when carbon–carbon bond formation or the introduction of a functional group into the substrate molecules is the main purpose of the synthesis.[1–4] Such reactions include palladium-catalyzed carbonylation of aryl halides, which makes it possible to synthesize carboxylic acids, esters or amides, depending on the reaction conditions, in a one-step process. The kind of product depends on the nature of the nucleophile reactant used, that is water, alcohol or secondary amine, respectively (Scheme 1).[5]

Palladium compounds, usually palladium complexes with phosphane ligands,[1,2,6] are the most effective carbonylation catalyst precursors. Such complexes are often formed *in situ* from a palladium precursor and the selected phosphane ligand. Phosphanes play the role of stabilizers of *in situ* formed Pd(0) complexes, generally considered the catalytically active forms.[3,7,8]

In contrast, catalytic systems based on palladium precursors without phosphorus ligands, so called "ligand-free systems", are very attractive and have recently generated great interest not only because of the lower cost of the process but also because of the minimization of wastes and environmental problems.[9] However, a major disadvantage of such catalytic systems is their low stability due to the formation of catalytically inactive "palladium black". It is worth noting that the carbonylation reaction medium is favorable for the reduction of Pd(II) to Pd(0) ("palladium black") because of the presence of potential reducing agents like carbon monoxide and bases (particularly amines). We have recently found that the palladium(II) complex $PdCl_2[P(OPh)_3]_2$ is reduced to Pd(0) by Et_3N in the presence of water and forms $Pd[P(OPh)_3]_4$, even in the absence of carbon monoxide.[10] Our earlier studies on the carbonylation of iodobenzene with $PdCl_2$(cod) as the catalyst precursor have shown its high activity (93% of the carbonylation product) in the absence of phosphane ligands when the reaction was performed in the presence of the ammonium salt [$^nBu_4N$]Cl.[11] Palladium(II) reduction to "palladium black" was easily detected after just a few minutes of reaction; however, the system remained catalytically active. This suggested that the carbonylation reaction is in fact catalyzed by a palladium colloid stabilized by the ammonium salt. In this paper we present studies performed to prove the catalytic role of *in situ* formed Pd colloid.



where X = Cl, Br, I; Nu = OH^-, OR^-, NR_2^-; base: *e.g.* Et_3N

Scheme 1

Reetz and Westermann have shown that under Heck reaction conditions palladium nanoparticles are formed from $PdCl_2(C_6H_5CN)_2$ on reduction with acetate ions.[12] They also demonstrated the high catalytic activity of those nanoparticles. Recently, palladium colloids have been frequently used as catalysts of Heck[12,13] and Suzuki[14] reactions, as well as for the hydrogenation of hydrocarbons[15] and the hydroxycarbonylation of olefins,[16] but not the carbonylation of aryl halides.

In this paper the results of iodobenzene carbonylation with $PdCl_2$(cod) as the catalyst precursor are presented. The aim of the studies was to confirm the formation and catalytic function of palladium nanoparticles formed *in situ* from a palladium precursor in the carbonylation reaction medium. The mechanism of Pd colloid formation was also investigated.

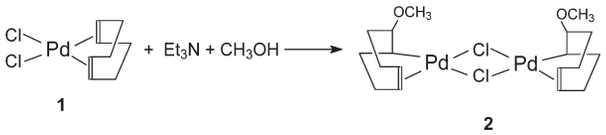
Results and discussion

Identification of palladium nanoparticles produced in the reaction of $PdCl_2$(cod) with Et_3N and CO in methanol

$PdCl_2$(cod) (**1**) reacts with methanol in the presence of Et_3N to form di-μ-chlorobis(2-methoxycyclooct-5-ene)dipalladium(II)

DOI: 10.1039/b401912a

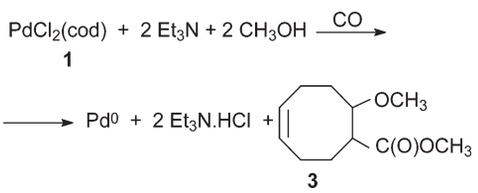
(**2**) as a result of nucleophilic attack of the –OCH_3 group on the olefinic carbon atom of cyclooctadiene, as shown in eqn. (1):



(1)

Complex **2** was previously obtained in the reaction of $PdCl_2$(cod) with methanol in the presence of $Na_2(CO_3)$,[17] but its reactivity was not extensively studied. The product of reaction (1) was isolated with 65% yield and characterized with ^{1}H and ^{13}C NMR. Particularly characteristic are two signals of the non-equivalent vinyl protons at 5.46 and 5.90 ppm in ^{1}H NMR and two signals of the carbon atoms forming a double bond at 101.9 and 106.4 ppm in the ^{13}C NMR spectrum. Besides, signals of six non-equivalent enyl-ligand carbons and a signal at 56.6 ppm originating from the methoxy (OCH_3) group were observed. The last signal was assigned by comparison with ^{13}C NMR spectra of complexes with OCH_3 and OCD_3 groups bonded to carbon C-2 of the enyl ligand. Both spectra were identical except for the signal at 56.6 ppm, which was shifted to 45.9 ppm after deuteration.

The reaction of **1** with Et_3N in methanol under CO (1 atm) does not stop at the stage of complex **2** but proceeds further and after a few minutes one may observe precipitation of "palladium black" as given in eqn. (2):



(2)

This "palladium black" was isolated in two different ways: by evaporation of the reaction solution to dryness or by centrifugation. Both obtained materials were XRD analyzed to investigate the crystal structure of the palladium. A typical XRD pattern is shown in Fig. 1. The peaks at $2\Theta \sim 40.1$ and 46.6 deg correspond to the (111) and (200) reflections, respectively, for the fcc structure of Pd with space group *Fm3m* (JCPDS card no. 5-681). The nanometer size of the Pd crystallites was evidenced by the broad X-ray reflections and the nanoparticle size was determined from the X-ray (111) line broadening using the Debye–Scherrer equation. The remaining diffraction lines observed in the XRD pattern were attributed to Et_3N. HCl. Based on the analytical data presented in Table 1 it can be concluded that Pd(II) is reduced to colloidal nanoparticles of size from 2 to 5.6 nm. No effect of the reaction conditions (temperature change from 40 to 70 °C and time change from 0.5 to 3 h) on the size of Pd nanoparticles was observed. Also the presence of the ammonium salt [^{n}Bu$_4$N]Cl had no significant influence on the reaction course and the average Pd nanoparticle size was 4.6 nm, the same as in the absence of the ammonium salt.

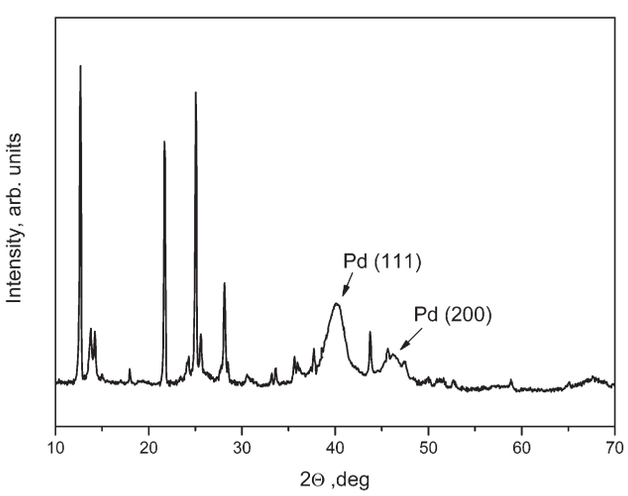
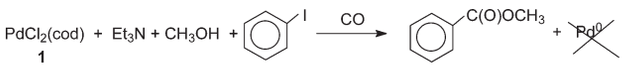


Fig. 1 The XRD pattern of the product obtained according to eqn. (2).

However, the above-described Pd reduction course changed completely when iodobenzene was introduced into the system, in which case Pd colloid was not identified in the reaction products although carbonylation of iodobenzene occurred (Table 2) *via* eqn. (3):



(3)

This may suggest that the *in situ* formed, catalytically active Pd colloid immediately reacted with iodobenzene according to an oxidative addition reaction scheme, giving a Pd(II) species containing an I–Pd^{II}–Ph fragment, not identified by the XRD method. Alternatively, it may be assumed that Pd nanoparticles formed in the presence of PhI are smaller than 1.5 nm in diameter and are not detected by XRD.

Reduction of **1** in methanol solution in the presence of Et_3N and CO [eqn. (2)] was found to be a convenient method of palladium colloid preparation. When the reaction was carried out in methanol in the presence of PVP (PVP = polyvinylpyrrolidone), a black solution of Pd colloid stabilized by the polymer (PVP) was obtained, whereas "black palladium" was precipitated in the absence of PVP. Replacement of methanol with benzene in the reduction of **1** in the presence of PVP also led to a similar black Pd colloid solution instead of "palladium black", which was precipitated when PVP was not added. XRD analysis of both Pd colloids (obtained in methanol and in benzene) showed similar sizes of Pd nanoparticles, *ca.* 2.5 nm (Table 1).

UV-vis measurements were used to check the completeness of palladium(II) reduction to Pd colloid. When palladium(II) reduction was performed without the addition of PVP, the solution obtained after separation of the palladium precipitate was analyzed. No bands characteristic for $PdCl_2$(cod) were found in the UV-vis spectra at 268 (sh), 302, 332 (sh) nm. These bands were also absent from the spectrum of the black

Table 1 $PdCl_2$(cod) (**1**) reduction conditions and XRD analysis of obtained Pd colloids.

Run No	T/°C	Time/h	X in [^{n}Bu$_4$N]X	PhI	Particle size/nm
1[a]	40	1	Cl	–	4.6
2[a]	70	0.5	–	–	5.6
3[a]	40	0.5	–	–	3.8
4[b]	40	3	–	–	3.0
5[b c]	40	3	–	–	2.5
6[b d]	40	3	–	–	2.6
7[a e]	40	2	Cl	+	Not found
8[a f]	40	2	Cl	+	Not found
9[a]	40	2	Br	+	Not found
10[a]	40	2	I	+	Not found

[a] [Pd] = 1.3×10^{-4} mol, [NEt_3] = 1.3×10^{-2} mol, [CH_3OH] = 0.28 mol, [^{n}Bu$_4$N]X = 6×10^{-3} mol, [PhI] = 1.3×10^{-2} mol. [b] [Pd] = 1.75×10^{-4} mol, [NEt_3] = 7.2×10^{-4} mol, [CH_3OH] = 2.5×10^{-2} mol. [c] Reduction performed in CH_3OH in the presence of PVP. [d] Reduction performed in C_6H_6 in the presence of PVP. [e] Iodobenzene was added after 10 min. [f] Iodobenzene was added at the beginning of the reaction.

Table 2 Results of iodobenzene carbonylation with $PdCl_2$(cod) (**1**) in CH_3OH under 1 atm of CO[a]

Run No	X in [^{n}Bu$_4$N]X	Time/h	T/°C	Yield of ester/mol %	TON[b]
11	–	2	40	14	31
12	–	3	40	21	47
13	I	3	40	22	50
14	I	4	70	43	97
15	Br	3	70	44	99
16	Br	4	70	64	144
17[c]	Br	4	70	25	56
18[d]	Br	4	70	36	81
19[e]	Br	5	70	72	110

[a] [Pd] = 2×10^{-5} mol, [NEt_3] = 1×10^{-2} mol, [CH_3OH] = 3.7×10^{-2} mol, [PhI] = 4.5×10^{-3} mol, [^{n}Bu$_4$N]X = 4.9×10^{-3} mol. [b] TON = (mol of ester)/(mol of Pd). [c] [^{n}Bu$_4$N]X = 2.2×10^{-3} mol. [d] [^{n}Bu$_4$N]X = 8.9×10^{-3} mol. [e] [Pd] = 2.9×10^{-5} mol.

solution obtained when reduction was performed in the presence of PVP.

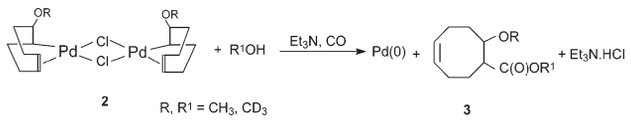
IR spectra measured during the reduction process presented a ν(CO) band at 1742 cm^{-1} attributed to ester **3**. However, it can not be excluded that ν(CO) originated from an intermediate Pd complex formed according to Scheme 2. The terminal ν(CO) bands were not observed.

Our attempts to identify the eventual product of oxidative addition of iodobenzene to Pd colloids using ^{1}H and ^{13}C NMR in $CDCl_3$ were unsuccessful, although a similar experiment was described by Reetz and Westermann[12] We only observed signals due to PVP and unchanged iodobenzene when mixtures of Pd colloid and iodobenzene ([PhI]:[Pd] = 1–5) were analyzed.

Mechanism of palladium(II) reduction in $PdCl_2$(cod)

With a view to determining the palladium(II) reduction mechanism, we studied both the Pd colloid and the organic products of the reaction. GC-MS analysis of the methanol solution after reduction of **1** with Et_3N and CO gave evidence for 2-methoxy-5-cyclooctene carboxylic acid methyl ester (**3**). The formation of such a product had been observed earlier in the reaction of $PdCl_2$ with cyclooctadiene in the presence of CO in methanol.[18]

When the reduction of **1** was conducted in ethanol solution, 2-ethoxy-5-cyclooctene carboxylic acid ethoxy ester was obtained. Since both of the above-mentioned compounds were the only organic products found by GC-MS, we propose the mechanism shown in Scheme 2 for Pd(II) →Pd(0) reduction in the system under consideration. The essential steps of this mechanism are CO insertion into the Pd–C (cyclooctadiene) bond and nucleophilic attack of the OR^1 group on the carbonyl carbon atom. As a result the corresponding ester is formed whereas the hydrido complex with the H–Pd–X fragment undergoes reductive elimination to Pd(0). Hydrochloride molecules are bonded by NEt_3, forming $Et_3N{\cdot}HCl$, as was proved by IR spectra and XRD analysis. As the suggested mechanism is slightly different from that proposed for Pd(II) reduction with carbon monoxide in water solution,[17] we carried out additional studies of the reduction of enyl complexes (**2**) with OCH_3 or OCD_3 groups attached to the C-2 carbon [eqn. (4)]:



2 R, R^1 = CH_3, CD_3 **3**

(4)

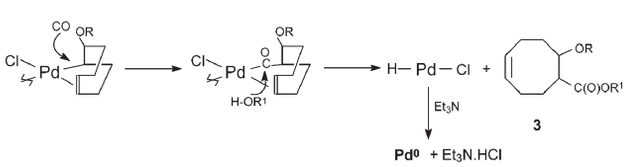
In all cases Pd(0) was precipitated and in the remaining solutions substituted esters were identified by GC-MS. The respective MS data are collected in Table 3.

From the presented results one may conclude that the OR group of the enyl ligand is not replaced by OR^1; therefore, in reactions in which $R \neq R^1$ (R, R^1 = CH_3 or CD_3) only one compound with the molecular ion M^+ at m/z = 201 containing three deuterium atoms was obtained. During fragmentation of **3**, the first to be eliminated are the OR groups, followed by the ester groups as m/z = 59 [$C(O)OCH_3$] or m/z = 62 [$C(O)OCD_3$], respectively. Identification of both ester groups strongly suggests CO insertion into the Pd–C bond rather than into the C–O bond.

Catalytic activity of Pd colloid

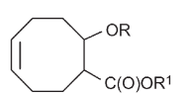
The results of iodobenzene carbonylation reactions carried out under rather mild conditions (comparable to those applied for palladium(II) reduction) are presented in Table 2. Complex **1** itself, used as a catalyst, produced *ca.* 20% of ester after 3 h and then the reaction stopped, probably because of agglomeration of the Pd^0 nanoparticles. The reaction yield can be improved by addition of tetra-*n*-butyl ammonium salt and, at the same time, better results were obtained with [^{n}Bu$_4$N]Br than with [^{n}Bu$_4$N]I. It is worth noting that the best result was obtained at almost equivalent concentrations of [^{n}Bu$_4$N]Br] and [PhI] (run 19). Lower (run 17) and higher (run 18) concentrations of ammonium salt are not advisable.

Much higher yields of benzoic acid methyl ester were obtained at 5 atm of CO and 70 °C (Table 4). Three different catalyst precursors were used under these conditions: complexes **1** and **2** and Pd colloid stabilized on PVP [the one obtained in the reaction according to eqn. (2)]. Complex **1** by itself produced only 17% of ester. When all components were mixed for 1 h in a CO atmosphere at 70 °C before the introduction of iodobenzene, the yield was even lower and only 3% of ester was obtained. This may be explained as an effect of agglomeration of Pd nanoparticles and formation of bigger, catalytically inactive crystallites. Agglomeration of nanoparticles is, however, retarded very effectively by ammonium salts, as was proved by the high yields of ester (98% and 91%)



Scheme 2

Table 3 MS data of 2-alkoxy-5-cyclooctene carboxylic acid esters (**3**) obtained according to Scheme 2



3

R	R^1	MS m/z
CH_3	CH_3	198 (M^+), 166 ($M^+ - OCH_3$), 107 [$M^+ - OCH_3 - C(O)OCH_3$]
CH_3	CD_3	201 (M^+), 169 ($M^+ - OCH_3$), 107 [$M^+ - OCH_3 - C(O)OCD_3$]
CD_3	CH_3	201 (M^+), 166 ($M^+ - OCD_3$), 107 [$M^+ - OCH_3 - C(O)OCH_3$]
C_2H_5	C_2H_5	226 (M^+), 180 ($M^+ - OC_2H_5$), 107 [$M^+ - OC_2H_5 - C(O)OC_2H_5$]

Table 4 Results of iodobenzene carbonylation with **1**, **2** and Pd colloid on PVP[a]

	Catalyst					
	1		**2**		Pd colloid[b]	
X in [^{n}Bu$_4$N]X	% Yield	TON	% Yield	TON	% Yield	TON
–	17	31	9	17	4	16
–[c]	3	5	8	15	–	
Br[c]	93	171	93	171	–	
Br	98	180	91	167	73	292
I	87	160	89	163	39	156
Cl	83	152	95	174	72	288
BF_4	95	174	88	162	70	280
PF_6	77	141	74	136	60	240

[a] [Pd] = 4.9×10^{-5} mol, [NEt_3] = 2.2×10^{-2} mol, [CH_3OH] = 2.5×10^{-2} mol, [PhI] = 9×10^{-3} mol [^{n}Bu$_4$N]X = 9×10^{-3} mol; 2 h, 5 atm CO, 70 °C. [b] [Pd] = 2.25×10^{-5} mol. [c] Reaction mixture was stirred 1 h at 70 °C and under 5 atm CO before PhI introduction.

obtained for the catalytic system with addition of [^{n}Bu$_4$N]Br (Table 4). In the first reaction (98% yield of ester) all reaction components were simultaneously introduced into the autoclave, whereas in the second reaction (ester yield 91%) iodobenzene was introduced into the autoclave after prior heating of all other components for 1 h. Complex **2** used as a catalyst precursor demonstrated behavior similar to complex **1**. The addition of [^{n}Bu$_4$N]Br increased the reaction yield from 9% to 93% or 91%. The heating of all reactants for 1 h before iodobenzene introduction had very little influence on reaction yield, which was 93%. Both systems (based on precursors **1** and **2**) presented high catalytic activity in the carbonylation reaction with all the ammonium salts used (Table 4). It may be concluded that the [^{n}Bu$_4$N]$^+$ cation plays the most important role in stabilizing *in situ* formed Pd colloids, whereas the effect of the anion is insignificant.

The positive effect of ammonium salts was also evident in reactions catalyzed by Pd colloid stabilized on PVP. The presence of PVP is not sufficient to stabilize a catalytically active form of Pd colloid, as evidenced by the very low yield of ester (*ca.* 4%). However, the addition of ammonium salt increased the yield of ester to 73% for [^{n}Bu$_4$N]Br and 39% for [^{n}Bu$_4$N]I. The data collected in Table 4 allow us to assume that Pd colloid stabilized on PVP is slightly less active than that obtained *in situ* from precursors **1** or **2**. This may be explained as an effect of a decrease in the colloid active surface as a result of Pd nanoparticle interaction with a large excess of the polymer PVP ([PVP]:[Pd] > 10). A similar effect of PVP was also observed in the Suzuki reaction.[14]

Experimental

General

$PdCl_2$(cod) was obtained according to the literature method.[19] Methanol, Et_3N and diethyl ether were purified using standard procedures.[20] Iodobenzene and mesitylene were used without purification. Ammonium salts, [^{n}Bu$_4$N]X (X = Br, Cl, I, BF_4, PF_6, were purchased from Merck and PVP was purchased from Aldrich.

All syntheses were performed under an N_2 atmosphere using Schlenk techniques.

The following instruments were used: BRUKER 300 MHz, GC-MS Hewlett Packard 8452A, DRON 3 powder diffractometer with CuKα radiation, Hewlett Packard 8452 Diode Array.

Synthesis of di-μ-chlorobis(2-methoxycyclooct-5-enyl)-dipalladium(II) (2)

Et_3N (0.1 g, 7.2×10^{-4} mol) was added to a suspension of 0.1 g ($3.5 \times \cdot 10^{-4}$ mol) **1** in 2 ml of methanol and stirring continued for 1 h. The color of the precipitate changed from yellow to white, whereas the solution became colorless. The white precipitate was filtered off and vacuum dried. Yield: 65%. Anal. calcd for $C_9H_{15}ClOPd$ (%): C 38.46, H 5.38; found: C 38.42, H 5.60. ^{1}H NMR ($CDCl_3$, δ): 1.40 m (1H), 1.94 m (2H), 2.18 m (3H), 2.59 m (2H), 3.22 s (3H, OCH_3), 3.55 m (2H), 5.46 m (1H, CH=CH), 5.88 m (1H, CH=CH). ^{13}C NMR ($CDCl_3$, δ): 26.5 (CH_2), 28.1 (CH_2), 30.8 (CH_2), 34.5 (CH_2), 52.2 (C2), 56.6 (OCH_3) 81.4 (C1), 101.9 (CH=), 106.4 (CH=). In the same way, using CD_3OD instead of CH_3OH, the analogous complex **2′**, with an attached OCD_3 group, was obtained. ^{1}H NMR ($CDCl_3$, δ): 1.38 m (1H), 1.93 m (2H), 2.18 m (3H), 2.60 m (2H), 3.58 m (2H), 5.46 m (1H, CH=), 5.87 m (1H, CH=). ^{13}C NMR ($CDCl_3$, δ): 26.5 (CH_2), 28.1 (CH_2), 30.8 (CH_2), 34.5 (CH_2), 46.0 (OCD_3), 51.9 (C2), 81.3 (C1), 101.8 (CH=), 106.3 (CH=)

Synthesis of Pd colloid/PVP

First **1** (0.078 g, 2.8×10^{-4} mol) and then 1 ml (7.2×10^{-3} mol) of Et_3N were added to 0.26 g PVP dissolved in 3 ml of benzene in a Schlenk tube. The color of the solution changed from yellow to orange and subsequently became turbid. When the Schlenk tube was filled up with CO, the solution immediately turned black. After mixing and heating at 40 °C for 3 h the solvent (benzene) was evaporated and the obtained Pd colloid was XRD analyzed and subsequently used as a catalyst in test reactions. XRD and IR analyses showed that the colloid contained Et_3N·HCl and the Pd content was *ca.* 8%.

Another Pd colloid was obtained in the same way using methanol instead of benzene.

Reduction of Pd(II) in the presence of Et_3N and CO

Reduction of complex 1. To a suspension of 0.05 g (1.75×10^{-4} mol) of **1** in 1 ml of methanol or ethanol in a Schlenk tube was added 0.1 ml (7.2×10^{-4} mol) of Et_3N in a CO atmosphere (1 atm) and stirring was continued for 0.5–3 h. A black precipitate was filtered off, vacuum dried and XRD analyzed. 2-Alkoxy-5-cyclooctene carboxylic acid esters were found in the filtrate by GC-MS. Some experiments were done at higher Et_3N concentrations—the reaction conditions are given in Table 1.

Reduction of complex 2. To a suspension of 0.024 g (9.1×10^{-5} mol) of **2** in 0.5 ml of CD_3OD in a Schlenk tube was added 0.05 ml (3.6×10^{-4} mol) of Et_3N and stirring was continued in a CO atmosphere (1 atm) for 3 h. A black precipitate of Pd colloid was separated and vacuum dried and the filtrate was GC-MS analyzed.

Carbonylation reaction procedure

The carbonylation reactions were carried out in 50 cm^3 glass thermostatted vessel (reactions under 1 atm of CO) or in a 130 cm^3 steel autoclave. Proper volumes of liquid reagents were introduced under an N_2 atmosphere. The palladium catalyst was weighted in a small teflon vessel and placed in the autoclave. After closing 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 (3×3 cm^3) and analyzed using the GC-MS method with mesitylene as internal standard.

Acknowledgements

Financial support by the State Committee for Scientific Research KBN (Poland) with the Grant 4T09A 080 25 is gratefully acknowledged. The authors are indebted to Nicolas Courtisse (Univ. Clermont Ferrand) for his technical assistance.

References

1 *Applied Homogeneous Catalysis with Organometallic Compounds*, eds. B. Cornils and W. A. Herrmann V. C. H., Weinheim, New York, 1996.
2 M. Beller and A. F. Indolese, *Chimia*, 2001, **55**, 684.
3 R. Skoda-Foldes and L. Kollar, *Curr. Org. Chem.*, 2002, **6**, 1097.
4 M. Beller, B. Cornils, C. D. Frohning and C. W. Kohlpaintner, *J. Mol. Catal. A: Chem.*, 1995, **104**, 17.
5 W. Mägerlein, M. Beller and A. F. Indolese, *J. Mol. Catal. A: Chem.*, 2000, **156**, 213.
6 A. M. Trzeciak, H. Bartosz-Bechowski, K. Niesyty, Z. Ciunik and J. J. Ziółkowski, *Can. J. Chem.*, 2001, **79**, 752.
7 W. R. Moser, A. W. Wang and N. K. Kildahl, *J. Am. Chem. Soc.*, 1988, **110**, 2816.
8 F. Monteil and P. Kalck, *J. Organomet. Chem.*, 1994, **482**, 45.
9 J. Yang, A. Haynes and P. M. Maitlis, *Chem. Commun.*, 1999, 179.
10 A. M. Trzeciak, Z. Ciunik and J. J. Ziółkowski, *Organomet.*, 2002, **21**, 132.
11 A. M. Trzeciak, W. Wojtków and J. J. Ziółkowski, *Inorg. Chem. Commun.*, 2003, **6**, 823.
12 M. T. Reetz and E. Westermann, *Angew. Chem., Int. Ed.*, 2000, **39**, 165.
13 (*a*) M. Beller, H. Fischer, K. Kuhlein, C.-P. Reisinger and W. A. Herrmann, *J. Organomet. Chem.*, 1996, **520**, 257; (*b*) V. Calo, A. Nacci, A. Monopoli, S. Laeva and N. Cioffi, *J. Org. Chem.*, 2003, **68**, 2929; (*c*) M. T. Reetz and G. Lohmer, *Chem. Commun.*, 1996, 1921.
14 R. Narayanan and M. A. El-Sayed, *J. Am. Chem. Soc.*, 2003, **125**, 8340.
15 (*a*) J. D. Aiken III and R. G. Finke, *J. Mol. Catal. A: Chem.*, 1999, **145**; (*b*) B. Yoon, H. Kim and C. M. Wai, *Chem. Commun.*, 2003, 1040.
16 J.-L. Pellegatta, C. Blandy, R. Choukroun, C. Lorber, B. Chaudret, P. Lecante and E. Snoeck, *New J. Chem.*, 2003, **27**, 1528.
17 R. G. Schultz, *J. Organomet. Chem.*, 1966, **6**, 435.
18 J. K. Stille and D. E. James, *J. Organomet. Chem.*, 1976, **108**, 401.
19 F. A. Cotton, *Inorg. Synth.*, 1972, **Coll. Vol. XIII**, 52.
20 D. D. Perrin, W. L. F. Armarego, D. R. Perrin, *Purification of Laboratory Chemicals*, Pergamon, , Oxford, UK, 1986.