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Palladium Chemistry Related to Benzyl Bromide Carbonylation: Mechanistic Studies

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Summary. Palladium(II) complexes of the general formula $PdCl_2(PR_3)_2$ with $PR_3 = P(OPh)_3$, P(O-4-$MeC_6H_4)_3$, P(O-2-$MeC_6H_4)_3$, and $PPh_2(OBu)$ were reduced by NEt_3 in chloroform or benzene to Pd(0) complexes $Pd(PR_3)_4$ and $Pd(PR_3)_x(NEt_3)_{4-x}$. The same reaction performed in the presence of air gave CH_3CHO or CH_3CH_2CHO when NPr_3 was used instead of NEt_3. $Pd(P(OPh)_3)_4$ reacted with benzyl bromide affording the oxidative addition product *cis*-$PdBr(CH_2Ph)(P(OPh)_3)_2$. The reaction of $PdCl_2(P(OPh)_3)_2$ with benzyl bromide was observed only in the presence of NEt_3, and a dimeric complex of $[PdBr(CH_2Ph)(P(OPh)_3)]_2$ was identified as the reaction product. Both benzyl complexes reacted fast with CO (1 atm) to form acyl complexes exhibiting ν(CO) bands at 1709 and 1650 cm^{-1}.

Keywords. Palladium complexes; Palladium reduction; Carbonylation; Benzyl bromide.

Introduction

The carbonylation of aryl halides catalyzed by palladium complexes is an important and convenient method for the synthesis of carboxylic acids and their derivatives [1–3]. The accepted mechanism of carbonylation is based on the reactivity of palladium(0) complexes which activate the substrate, aryl halide, in oxidative addition reactions. Consequently, the key forms of the catalyst participating in aryl halide carbonylation are: a Pd(0) complex, an aryl complex, the product of the oxidative addition of the substrate to the palladium(0) precursor, and an acyl complex formed by CO insertion into the Pd–C bond (Eq. (1)) [4–7].

$$Pd^{(0)}L_n + PhX \longrightarrow Pd^{(II)}(Ph)(X)L \xrightarrow{CO} Pd^{(II)}(PhCO)(X)L_n \qquad (1)$$

The formation of these intermediates has been confirmed in many catalytic systems. However, triphenylphosphine palladium complexes are the most frequently ones to be used [6–8]. Pd(0) complexes in most of the known catalytic systems are formed *in situ* from a Pd(II) precursor and an appropriate reducing agent [5, 8, 9]. Alternatively, a separately synthesized stable Pd(0) complex, Pd(*dba*) (*dba* = dibenzylideneacetone), together with an excess of phosphine has been applied [10–13]. In the synthesis of Pd(0) complexes, different reducing agents have been applied, *e.g.* hydrazine [14], amines [15, 16], hydroxides [17], alkoxides [18], or F^- [19]. $PdCl_2$ has also been reduced by CO in the presence of water, even without any

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base added [20, 21]. In the absence of stabilizing ligands (*e.g.* phosphines), the black palladium metal is usually formed in few minutes. The excess of phosphine prevents the precipitation of palladium metal aggregates, and a soluble Pd(0) complex is formed instead [22].

The importance of the palladium reduction step in the carbonylation reaction has been pointed out and discussed by *Grushin* and *Alper* [18] who demonstrated the fundamental role of OH^- in the formation of Pd(0) complexes. According to their results, OH^- is the promotor of intramolecular palladium reduction by coordinated PPh_3 with the simultaneous formation of $OPPh_3$. The key steps of the palladium reduction mechanism starting from $PdCl_2L_2$ are as follows: a) substitution of Cl^- by OH^- in the coordination sphere of the palladium-phosphine complex, b) oxidation of phosphine, elimination of OPR_3, and palladium-hydrido complex formation, and c) reductive elimination of HCl with the formation of a coordinatively unsaturated Pd(0) complex ready for the oxidative addition of substrate (Eq. (2)).

$$PdCl_2(PR_3)_2 \xrightarrow{OH^-} PdCl(OH)(PR_3)_2 \xrightarrow[OPR_3]{} \left[Pd(H)(Cl)(PR_3)\right] \xrightarrow[HCl]{PR_3} \left[Pd(PR_3)_4\right] \quad (2)$$

That concept has also been used to explain the carbonylation reaction mechanism with a palladium complex modified with water-soluble sulfonated triphenylphosphine (*TPPTS*), and a $PdCl(OH)(TPPTS)_2$ complex has been postulated as an intermediate [9].

We have found that a $PdCl_2(PNS)_2$ complex ($PNS = Ph_2PCH_2CH_2C(O)NHC(CH_3)_2CH_2SO_3Li$) is easily reduced to a Pd(0) complex in methanolic solution in the presence of NEt_3 (Eq. (3)) [23].

$$PdCl_2(PNS)_2 \xrightarrow[PNS,\ MeOH]{NEt_3} Pd(PNS)_4 \quad (3)$$

However, because of the hygroscopic properties of *PNS* and the alkaline reaction medium we cannot definitely exclude the participation of OH^- in the process of the reduction of Pd(II) to Pd(0) according to the mechanism shown in Eq. (2).

The reactivity of the $PdCl_2(PNS)_2$ complex is quite different from that of $PdCl_2(PPh_3)_2$. As has been reported, a $PdCl_2(PPh_3)_2$ complex does not react with NEt_3 in the absence of water, but its reaction with CO in methanol in the presence of NEt_3 leads to the formation of the stable carbomethoxy Pd(II) complex $PdCl(COOMe)(PPh_3)_2$ (Eq. (4)) [16].

$$PdCl_2(PPh_3)_2 \xrightarrow[MeOH,\ CO]{NEt_3} Pd(COOMe)(Cl)(PPh_3)_2 \quad (4)$$

These facts indicate that the ability of $PhCl_2(PR_3)_2$ complexes to undergo reduction in the presence of amines is strongly influenced by the kind of phosphorus ligand PR_3.

Our studies of the reactivity of $PdCl_2(PR_3)_2$ complexes with different phosphorus ligands PR_3 allowed us to specify the group of compounds undergoing reduction to Pd(0) complexes in the presence of NEt_3 in aprotic solvents. We have found that NEt_3 reduces palladium in $PdCl_2(PR_3)_2$ complexes where $PR_3 =$ $P(OPh)_3$, $P(O\text{-}4\text{-}MeC_6H_4)_3$, $P(O\text{-}2\text{-}MeC_6H_4)_3$, and $PPh_2(OBu)$ in the absence of

methanol, water, or CO. In this paper we confirm the pathway of $PdCl_2(P(OPh)_3)_2$ reduction to a $Pd(P(OPh)_3)_4$ complex with only NEt_3 as a reducing agent. The characteristics of benzyl complexes, $PdBr(CH_2Ph)(P(OPh)_3)_2$ and/or $[PdBr(CH_2Ph)(P(OPh)_3)_2]_2$, formed in reactions of $Pd(P(OPh)_3)_4$ and $PdCl_2(P(OPh)_3)_2$ with benzyl bromide as well as their reactivity towards CO are also reported.

Results and Discussion

Reactions of $PdCl_2(PR_3)_2$ complexes with tertiary amines

$PdCl_2(PR_3)_2$ complexes with $PR_3 = P(OPh)_3$, (**1a**), $P(O\text{-}4\text{-}MeC_6H_4)_3$, (**1b**), $P(O\text{-}2\text{-}MeC_6H_4)_3$ (**1c**), and $PPh_2(OBu)$ (**1d**) reacted with NEt_3 at room temperature in aprotic solvents, such as chloroform or benzene, forming Pd(0) complexes. The reactions were monitored by $^{31}P\{^1H\}$ NMR spectroscopy in solutions containing $PdCl_2(PR_3)_2$ and different amounts of NEt_3 with NEt_3: Pd ratios of 1–20.

$$\underset{\mathbf{1}}{PdCl_2(P(OR)_3)_2} + n\ NEt_3 \rightarrow \underset{\mathbf{2}}{Pd(P(OR)_3)_4} + \underset{\mathbf{3}}{Pd(P(OR)_3)_x(NEt_3)_{4-x}} \qquad (5)$$

1a, **2a**, **3a**: $R = Ph$
1b, **2b**, **3b**: $R = 4\text{-}MeC_6H_4$
1c, **2c**, **3c**: $R = 2\text{-}MeC_6H_4$

In the reaction of **1a** with NEt_3 in $CDCl_3$, a new intensive ^{31}P NMR signal was observed at 137.3 ppm which was assigned to $Pd(P(OPh)_3)_4$ (**2a**) by comparison with the spectrum of the original **2a** obtained by reduction of $PdCl_2(P(OPh)_3)_2$ with $NaBH_4$ in the presence of and excess of $P(OPh)_3$ (Eq. (6)).

$$\underset{\mathbf{1}}{PdCl_2(P(OR)_3)_2} \xrightarrow[P(OR)_3]{NaBH_4} \underset{\mathbf{2}}{Pd(P(OR)_3)_4} \quad (R = Ph,\ 2\text{-}MeC_6H_4) \qquad (6)$$

Similarly, the main product of the reaction of **1c** with NEt_3 exhibited a singlet at 134.2 ppm in its $^{31}P\{^1H\}$ NMR spectrum, identical with that observed for $Pd(P(O\text{-}2\text{-}MeC_6H_4)_3)_4$ (**2c**) prepared according to Eq. (6). The second product of Eq. (5), **3c**, was characterized by a ^{31}P resonance at 75.4 ppm. **1b** reacted with NEt_3 in C_6D_6 in the NMR tube (Eq. (5)) forming two new products characterized by new $^{31}P\{^1H\}$ signals at 138.6 and 77.1 ppm (Table 1).

Table 1. $^{31}P\{^1H\}$ NMR data (δ in ppm) of $PdCl_2(P(OR)_3)_2$ (**1**), $Pd(P(OR)_3)_4$ (**2**), and $Pd(P(OR)_3)_x(NEt_3)_{4-x}$ (**3**) complexes

	1	**2**	**3**
$R = Ph$ (**a**)	83.7	137.3	75[c]
		137.8[b]	
$R = 4\text{-}MeC_6H_4$ (**b**)	83.7	137.8	75.0
	86.6[a]	136.6[a]	77.1[a]
$R = 2\text{-}MeC_6H_4$ (**c**)	81.1	134.2	75.4
		134.3[b]	

[a] In C_6D_6; [b] Eq. (6); [c] Eqs. (7) and (8)

The signals observed at *ca*. 75 ppm were assigned to Pd(0) complexes of the type $Pd(P(OR)_3)_x(NEt_3)_{4-x}$ (**3**) on the basic of an additional experiment of ligand exchange between **2a** and $PdCl_2(NEt_3)_2$ (**4**), in which the signal at 75 ppm appeared together with a second one at 83.7 ppm, attributable to **1a** (Eq. (7)). The mixed complexes of the type **3** were observed only in solution and were not isolated in analytically pure form, which is reflected by the tentative formula.

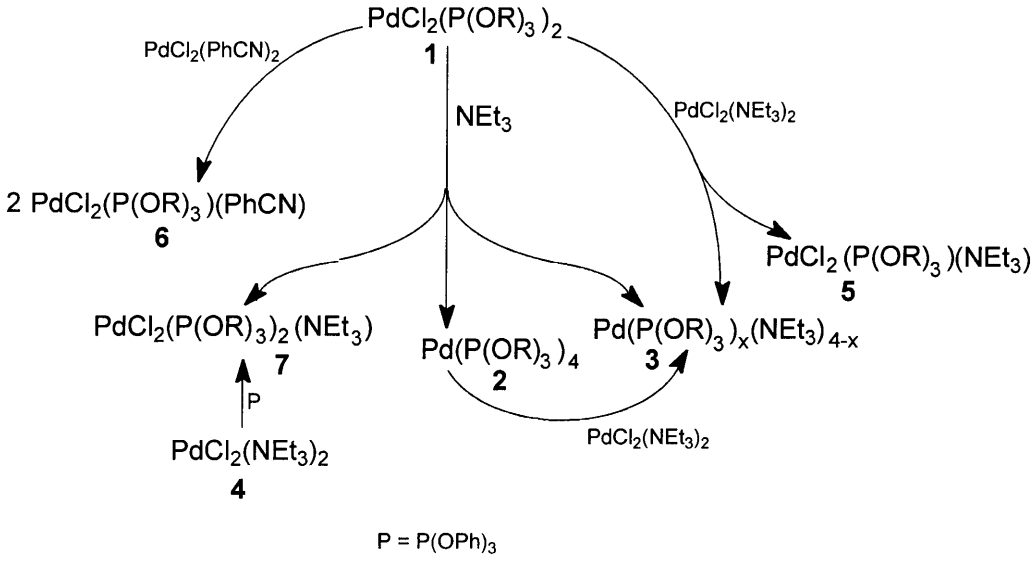
$$\underset{\mathbf{2a}}{Pd(P(OPh)_3)_4} + PdCl_2(NEt_3)_2 \longrightarrow \underset{\mathbf{3a}}{Pd(P(OPh)_3)_x(NEt_3)_{4-x}} + \underset{\mathbf{1a}}{PdCl_2(P(OPh)_3)_2} \quad (7)$$

Unexpectedly, $Pd(P(OPh)_3)_x(NEt_3)_{4-x}$ (**3a**) was also identified in a solution containing **1a** and **4** (Eq. (8)).

$$\underset{\mathbf{1a}}{PdCl_2(P(OPh)_3)_2} + \underset{\mathbf{4}}{PdCl_2(NEt_3)_2} \longrightarrow \underset{\mathbf{3a}}{Pd(P(OPh)_3)_x(NEt_3)_{4-x}} + \underset{\mathbf{5}}{PdCl_2(P(OPh)_3)(NEt_3)} \quad (8)$$

This reaction is an example of palladium reduction in the absence of free amine, but with the participation of an amine coordinated in complex **4**. The mixed complex $PdCl_2(P(OPh)_3)(NEt_3)$ (**5**), the second product of Eq. (8), was characterized by a signal at 69.8 ppm in the $^{31}P\{^1H\}$ NMR. An analogous mixed complex, $PdCl_2(P(OPh)_3)(PhCN)$ (**6**), was found in a solution containing **1a** and $PdCl_2(PhCN)_2$ as the only product of that reaction in which palladium reduction was not observed. This fact is in agreement with the observation that NEt_3 easily substitutes of PhCN in the $PdCl_2(PhCN)_2$ complex forming the complex **4**. The coordination of NEt_3 after its addition to the solution of $PdCl_2(PhCN)_2$ was clearly monitored in its ^1H NMR spectrum, in which-besides the signals of the free amine-new downfield-shifted resonances appeared at 1.35 (CH_3) and 2.8 (CH_2) ppm. The same signals were also observed in the spectrum of the isolated complex **4**. The analogous $PdCl_2(HNEt_2)_2$ complex, very poorly soluble, was obtained by treating $PdCl_2(PhCN)_2$ with an excess of $HNEt_2$. The reactions of palladium-triphenylphosphito complexes are summarized in Scheme 1.

The only new product, $Pd(PPh_2(OBu))_4$, showing a $^{31}P\{^1H\}$ NMr signal at 122 ppm, was found in the reaction of $PdCl_2(PPh_2(OBu))_2$ (**1d**) with NEt_3. $^{31}P\{^1H\}$ NMR spectra of solutions containing the complex **1a** and NEt_3 allowed us to find evidence of NEt_3 coordination to palladium(II) before its reduction. The new palladium(II) complexes were identified by two pairs of doublets of quite different chemical shifts (95 and 48 ppm), typical for two slightly different complexes each containing two nonequivalent $P(OPh)_3$ ligands in *cis* position. Two doublets of the first product, formulated as $PdCl_2(P(OPh)_3)_2(NEt_3)$ (**7**), are observed at 96.8 and 47.7 ppm with $^2J(P\text{-}P) = 76$ Hz. The second product, $[PdCl(P(OPh)_3)_2(NEt_3)]Cl$ (**7a**), exhibited two doublets at 89.9 and 49.5 ppm with $^2J(P\text{-}P) = 107$ Hz. The same products were formed when **4** reacted with $P(OPh)_3$. As long as a solution contained an excess of amine, the spectra were badly resolved, probably because of dynamic effects and ligand exchange. Much better spectra were obtained when the sample was evaporated to dryness and dissolved in $CDCl_3$.



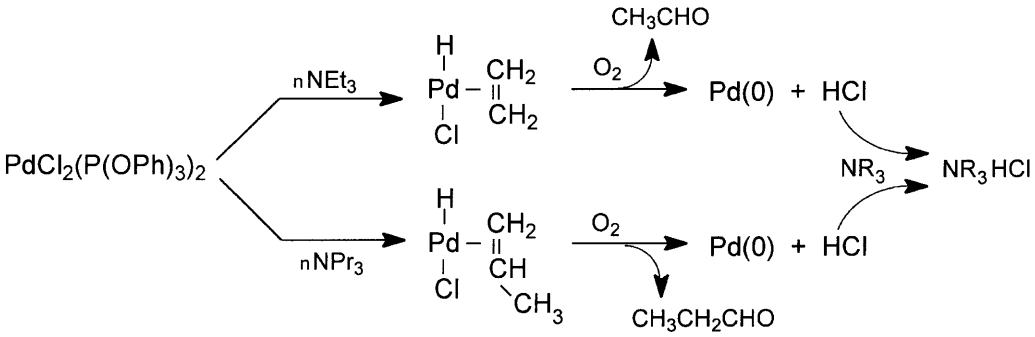
Scheme 1

The analysis of the IR and ^{1}H NMR spectra of all reaction mixtures in which Pd(0) complexes were formed allowed us to find the ammonium salt by-product, NEt_3HCl, identical to that obtained in the reaction of NEt_3 with HCl. The formation of NEt_3HCl was confirmed in all experiments in which Pd(II) was reduced to Pd(0) and explains the manner in which Cl^- ligands are removed from the coordination sphere in the first step of the reduction. It seems worth noting that NEt_3HCl was also found in the product of the reaction of **1a** with **4** in which a Pd(0) complex was formed without free amine added (Eq. (8)).

The Cl^- abstraction from the palladium coordination sphere, rather fast in triphenylphosphito complexes $PdCl_2(P(OR)_3)_2$, was not observed under the same conditions for a similar $PdCl_2(PPh_3)_2$ complex or for $(PdCl_2(PhCN)_2)$. Pure $PdCl_2(NEt_3)_2$ (**4**) and $PdCl_2(NHEt_2)_2$ (**4a**) complexes were obtained by substitution of PhCN in $PdCl_2(PhCN)_2$ with an excess of NEt_3 or $NHEt_2$.

The GC-MS analysis of a xylene solution containing **1a** and an excess of NEt_3 left in contact with air for 3 h showed the presence of acetaldehyde. The same result was obtained for the reaction of **1b** with NEt_3. When NPr_3 was used instead of NEt_3, the reaction mixture contained propanal. In all of the above cases, the formation of aldehydes can be explained by air-oxidation of olefin evolved during amine decomposition. A control experiment in which the $PdCl_2(PPh_3)_2$ complex was allowed to react with NEt_3 or NPr_3 under the same conditions revealed no organic product, as expected, because $PdCl_2(PPh_3)_2$ was not reduced by tertiary amines [16].

The most probable mechanism of palladium reduction is based on the decomposition of the coordinated amine with the splitting of the N–C bond and the formation of a hydrido-olefin-palladium complex (Scheme 2). The elimination of HCl from the coordination sphere of palladium causes its reduction to Pd(0), and subsequently HCl reacts with NEt_3 forming the salt NEt_3HCl identified in the post-reaction mixture.



Scheme 2

Palladium-triphenylphosphito complexes as catalyst precursors in carbonylation reactions

The complex **2a** reacts with benzyl bromide, forming the oxidative addition product *cis*-$PdBr(CH_2Ph)(P(OPh)_3)_2$ (**8**) in few minutes (Eq. (9)).

$$\underset{\mathbf{2a}}{Pd(P(OPh)_3)_4} + PhCH_2Br \rightarrow \underset{\mathbf{8}}{\textit{cis}\text{-}PdBr(CH_2Ph)(P(OPh)_3)_2} + 2\ P(OPh)_3 \quad (9)$$

The reaction was first performed in the NMR tube, and in the $^{31}P\{^1H\}$ NMR spectrum the appearance of two doublets at 105.0 and 113.5 ppm with $^2J(P\text{-}P) = 139$ Hz was registered immediately after $PhCH_2Br$ addition. The same spectrum was observed for the dissolved isolated product and confirmed the *cis*-position of both $P(OPh)_3$ ligands in **8**. An additional proof of the *cis*-structure was provided by the presence of two doublets of the CH_2 signal at 4.5 ppm (^1H NMR), split by two nonequivalent phosphorus atoms. It is worth noting that in most examples known from literature *trans* or dimeric structures have been reported for products of aryl halide oxidative addition to Pd(0) [6, 24–29].

The benzyl complex **8** reacts with CO (1 atm) producing the acyl complex $PdBr(C(O)CH_2Ph)(P(OPh)_3)_2$ (**9**) with a characteristic $\nu(CO)$ band at 1709 cm^{-1} (Eq. (10)). A terminal CO was not observed, suggesting a rather quick insertion of CO into the Pd–C bond. The acyl complex exhibits one ^{31}P NMR signal of two equivalent $P(OPh)_3$ ligands at 102.6 ppm, thus corroborating its *trans* geometry.

$$\underset{\mathbf{8}}{\textit{cis}\text{-}PdBr(CH_2Ph)(P(OPh)_3)_2} + CO \rightarrow [PdBr(CH_2Ph)(P(OPh)_3)_2(CO)]]^{\#} \rightarrow$$

$$\underset{\mathbf{9}}{\textit{trans}\text{-}PdBr(C(O)CH_2Ph)(P(OPh)_3)_2} \quad (10)$$

On the basis of the above results showing the formation of Pd(0) complexes in the reaction of **1** with NEt_3 it was expected that the benzyl complex could also be prepared by a reaction of **1a** with $PhCH_2Br$ in the presence of NEt_3. The analysis of the ^1H and $^{31}P\{^1H\}$ NMR spectra of a $CDCl_3$ solution containing **1a** and benzyl bromide clearly showed no reaction. However, immediately after NEt_3 was added to the reaction mixture, a new broad multiplet appeared at 102 ppm in the $^{31}P\{^1H\}$

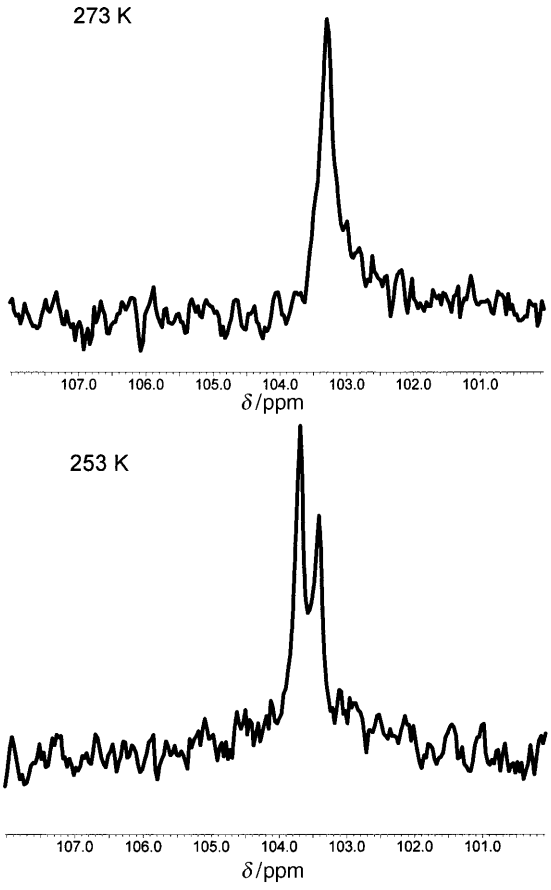


Fig. 1. $^{31}P\{^{1}H\}$ NMR spectra of $[PdBr(CH_2Ph)(P(OPh)_3)]_2$ (**10**) in $CDCl_3$ at different temperatures

NMR spectrum. Cooling of the solution to −20°C made it possible to measure two separate signals of *cis*- and *trans*-isomers (Fig. 1). A similar interconversion of isomers involving the cleavage of bridges was also observed in other complexes. The isolated complex had the same spectroscopic characteristics, and its ^{1}H NMR spectrum showed a CH_2 signal at 4.48 ppm confirming the coordination of the $PhCH_2$ ligand to palladium (Eq. (11)).

$$\underset{\mathbf{1a}}{PdCl_2(P(OPh)_3)_2} + PhCH_2Br \xrightarrow{NEt_3} 1/2\ \underset{\mathbf{10}}{[PdBr(CH_2Ph)(P(OPh)_3)]_2} \quad (11)$$

The dimeric complex $[PdBr(CH_2Ph)(P(OPh)_3)]_2$ (**10**) reacts with CO (1 atm), producing, in few seconds the acyl complex **11** with a characteristic ν(CO) band at 1650 cm^{-1} (r. 12).

$$\underset{\mathbf{10}}{[PdBr(CH_2Ph)(P(OPh)_3)]_2} + CO \rightarrow \underset{\mathbf{11}}{[PdBr(C(O)CH_2Ph)(P(OPh)_3)]_2} \quad (12)$$

Conclusions

The reduction of Pd(II) to Pd(0) in the presence of secondary amines is well documented in the literature [16] and was used for the preparation of Pd(0) complexes with PPh_3 [16] and $P(OEt)_3$ [30]. To our knowledge, there are no reported examples of the successful application of a tertiary amine in a similar synthesis. We have shown that tertiary amines, like NEt_3 or NPr_3, react with $PdCl_2(PR_3)_2$ complexes ($PR_3 = P(OPh)_3$, $P(O\text{-}4\text{-}MeC_6H_4)_3$, $P(O\text{-}2\text{-}MeC_6H_4)_3$, $PPh_2(OBu)$) forming Pd(0) complexes. The reaction of $PdCl_2(PR_3)_2$ complexes with NEt_3 facilitates the activation of $PhCH_2Br$ by forming a benzyl complex, which is a very important step in the carbonylation reaction.

Experimental

All operations were performed under N_2 using the *Schlenk* technique. Solvents were purified according to standard methods [31]. $PdCl_2(cod)$ [32] and $PdCl_2(PhCN)_2$ [33] were obtained according to literature methods. Elemental analyses agreed favourably with the calculated values (C, H). NMR spectra were recorded with a Bruker ARX 300 NMR spectrometer and chemical shifts are given relative to internal *TMS* (^1H) and relative to external 85% H_3PO_4 (^{31}P). IR spectra were measured with a FT-IR Nicolet Impact 400 instrument, UV/Vis spectra with an HP 4852 Diode Array spectrophotometer. GC-MS analyses were carried out with HP 5890 II setup linked to an HP 5971 A mass detector.

Dichloro-bis-(triphenylphosphite) palladium(II) (**1a**; $C_{36}H_{30}O_6P_2Cl_2Pd$)

To a stirred suspension of 0.1 g $PdCl_2(cod)$ in 2 cm^3 benzene, 0.25 g $P(OPh)_3$ were added slowly. In a few minutes the colour of the mixture changed from yellow to very pale yellow, and a white precipitate was formed. The stirring was continued for 5 min, and the precipitate was filtered off, washed with ethyl ether, and dried *in vacuo*.

Yield: 86%; $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, 121.5 MHz): 83.7 ppm; ^1H NMR ($CDCl_3$, δ, 300 MHz): 7.07 (m, Ph), 7.19 (m, Ph) ppm; IR (KBr): $\nu = 1585$ s, 1492 vs, 1184 vs, 1158 vs, 1027 m, 944 vs, 767 s, 690 s, 596 m cm^{-1}; UV/Vis (CH_2Cl_2): $\lambda = 320$ nm.

Dichloro-bis-(p-totylphosphite) palladium(II) (**1b**; $C_{42}H_{42}O_6P_2Cl_2Pd$)

The complex was obtained according to the procedure given for **1a** in ethyl ether instead of benzene.

Yield: 85%; $^{31}P\{^1H\}$ NMR (C_6D_6, δ, 121.5 MHz): 86.6 ppm; ^1H NMR (C_6D_6, δ, 300 MHz): 2.1 (s, CH_3), 6.85 (d, Ph), 7.45 (d, Ph) ppm; IR (KBr): $\nu = 1508$ vs, 1191 vs, 1164 s, 947 vs, 934 vs, 814 m cm^{-1}; UV/Vis (CH_2Cl_2): $\lambda = 268$, 316 nm.

Dichloro-bis-(o-totylphosphite) palladium(II) (**1c**; $C_{42}H_{42}O_6P_2Cl_2Pd$)

The complex was obtained according to the procedure given for **1b**; however, because of slower reaction stirring of the mixture was continued for 30 min.

Yield: 60%; $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, 121.5 MHz): 81.1 ppm; ^1H NMR ($CDCl_3$, δ, 300 MHz): 2.03 (s, CH_3), 7.04 (m, Ph), 7.19 (m, Ph) ppm; IR (KBr): $\nu = 1590$ s, 1488 vs, 1465 m, 1225 vs, 1171 vs, 1111 vs, 1051 m, 951 vs, 924 vs, 807 s, 764 s, 607 m cm^{-1}; UV/Vis (CH_2Cl_2): $\lambda = 266$ sh, 324 nm.

Dichloro-bis-(butyldiphenylphosphinite) palladium(II) (**1d**; $C_{32}H_{38}O_2P_2Cl_2Pd$)

To a stirred suspension of 0.11 g $PdCl_2(cod)$ in 2 cm^3 CH_2Cl_2, 0.3 cm^3 of $PPh_2(OBu)$ were added forming a colorless solution which was evaporated after 10 min. The residue was washed with ethyl ether to give 88% of a white product.

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, δ, 121.5 MHz): 108.9 ppm; ^{1}H NMR ($CDCl_3$, δ, 300 MHz): 0.74 (t, J(H-H) = 7 Hz, CH_3), 1.09 (ps-qui, CH_2–CH_3), 1.23 (ps-qui, CH_2–CH_2–CH_3), 3.63 (m, O–CH_2), 7.4 (m, Ph), 7.5 (m, Ph), 7.8 (m, Ph) ppm; IR (KBr): ν = 2970 m, 1439 s, 1108 s, 974 s, 975 s, 757 m, 694 m cm^{-1}; UV/Vis (CH_2Cl_2): λ = 266, 328 nm.

Tetra-(triphenylphosphite) palladium(0) (**2a**; $C_{72}H_{60}O_{12}P_4Pd$)

A suspension of 0.075 g of $PdCl_2$(*cod*) and 0.4 cm^3 of $P(OPh)_3$ was stirred in 2 cm^3 of benzene until a white precipitate of **1a** was formed (*ca*. 5 min). Then, 0.015 g of $NaBH_4$ dissolved in 1 cm^3 of EtOH were added drop by drop during 5 min. The mixture was stirred for 1 h, concentrated *in vacuo*, and the white precipitate was filtrated off and dried *in vacuo*.

Yield: 70%; decomposes to dark non-identified products on air; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, δ, 121.5 MHz): 137.3 ppm; IR (KBr): ν = 1592 s, 1495 vs, 1208 vs, 1188 vs, 1027 m, 914 vs, 874 vs, 767 s, 730 m, 694 s, 600 m cm^{-1}.

Benzylbromo-bis-(triphenylphosphite) palladium(II) (**8**; $C_{43}H_{37}O_6P_2BrPd$)

A solution containing 0.055 g of $Pd(P(OPh)_3)_4$ and 0.08 cm^3 of $PhCH_2Br$ in 2 cm^3 of benzene was stirred for 1 h during which time the colourless solution became yellow. The solvent was removed under reduced pressure, and the yellow residue was washed with EtOH and dried.

Yield: 75%; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, δ, 121.5 MHz): 105.0, 113.5 (d,d; ^{2}J(P-P) = 139 Hz) ppm; ^{1}H NMR ($CDCl_3$, δ, 300 MHz): 4.50, 4.67 (d,d, ^{3}J(H-P) = 14.8 Hz, CH_2) ppm; IR (KBr): ν = 1592 s, 1488 vs, 1181 vs, 1161 vs, 1030 m, 920 vs, 773 m, 695 m cm^{-1}; UV/Vis (CH_2Cl_2): λ = 290, 356 nm.

Bromophenylacetyl-bis-(triphenylphosphite) palladium(II) (**9**; $C_{44}H_{37}O_7P_2BrPd$)

A solution of 0.03 g $PdBr(CH_2Ph)(P(OPh)_3)_2$ in 1 cm^3 of $CHCl_3$ was stirred in a CO atmosphere (1 atm) for 30 min. The solvent was removed, and the yellow residue was washed with ethanol and dried.

$^{31}P\{^{1}H\}$ NMR (C_6D_6, δ, 121.5 MHz): 102.6 ppm; ^{1}H NMR (C_6D_6, δ, 300 MHz): 4.15 (s, CH_2) ppm; IR (KBr): ν = 1709 m, 1592 s, 1495 vs, 1188 vs, 1164 s, 917 vs, 767 m, 693 m cm^{-1}; UV/Vis (CH_2Cl_2): λ = 288, 366 nm.

Bis-(bromobenzyltriphenylphosphite palladium(II)) (**10**; $C_{50}H_{44}O_6P_2Br_2Pd_2$)

To a suspension of 0.06 g of $PdCl_2(P(OPh)_3)_2$ in 2 cm^3 of benzene, 0.01 cm^3 of NEt_3 and 0.01 cm^3 of $PhCH_2Br$ were added, and the mixture was stirred until a yellow solution was formed. The yellow product precipitated after addition of EtOH.

Yield: 85%; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, δ, 121.5 MHz): 102.0 ppm; ^{1}H NMR ($CDCl_3$, δ, 300 MHz): 4.48 (CH_2) ppm; IR (KBr): ν = 1589 s, 1488 vs, 1181 vs, 1158 s, 941 vs, 777 m, 761 m, 693 m cm^{-1}; UV/Vis (CH_2Cl_2): δ = 258, 328 nm.

Bis-(bromophenylacetyltriphenylphosphite palladium(II)) (**11**; $C_{26}H_{22}O_4PBrPd$)

A solution of 0.25 g $[PdBr(CH_2Ph)(P(OPh)_3)]_2$ in 1 cm^3 $CHCl_3$ was stirred in a CO atmosphere (1 atm) for 30 min. The solvent was removed and the yellow residue was washed with ethanol and dried.

$^{31}P\{^{1}H\}$ NMR (C_6D_6, δ, 121.5 MHz): 102.6 ppm; ^{1}H NMR (C_6D_6, δ, 300 MHz): 0.74 (t, J(H-H) = 7 Hz, CH_3), 1.09 (ps-qui, CH_2–CH_3), 1.23 (ps-q, CH_2–CH_2–CH_3), 3.63 (m, O–CH_2), 7.4 (m,

Ph), 7.5 (m, Ph), 7.8 (m, Ph) ppm; IR (Kbr): $\nu = 1650$ m, 1580 m, 1470 s, 1182 s, 942 vs, 750 m, 672 m cm^{-1}.

Dichloro-bis-(diethylamine) palladium(II) (**4a**; $C_8H_{22}N_2Cl_2Pd$)

To a stirred suspension of 0.03 g $PdCl_2(PhCN)_2$ in 2 cm^3 $CHCl_3$, 0.1 cm^3 $NHEt_2$ were added. After 5 min a yellow precipitate was formed which was filtered and dried *in vacuo*.

Yield: 90%; IR (KBr): $\nu = 3200$ s, 2960 s, 1480 s, 1360 m, 1050 m, 800 m cm^{-1}.

Dichloro-bis-(triethylamine) palladium(II) (**4**; $C_{12}H_{30}N_2Cl_2Pd$)

To a stirred suspension of 0.03 g $PdCl_2(PhCN)_2$ in 2 cm^3 $CHCl_3$, 0.1 cm^3 NEt_3 were added. After 10 min a dark red solution was formed which was evaporated to dryness. The residue was washed with hexane giving an orange product.

Yield: 50%; IR (KBr): $\nu = 2950$ s, 1470 s, 1380 s, 1000 m, 750 m, 800 m cm^{-1}; ^{1}H NMR ($CDCl_3$, δ, 300 MHz): 1.35 (t, CH_3), 2.8 (q, CH_2) ppm.

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References

[1] Cornils B, Herrmann WA (eds) (1996) Applied Homogeneous Catalysis with Organometallic Compounds. A Comprehensive Handbook in Two Volumes. VCH Weinheim, New York
[2] Beller M, Cornils B, Frohning CD, Kohlpaintner CW (1995) J Mol Catal A: Chemical **104**: 17
[3] Tkatchenko I (1982) In: Stone AGF, Abel WE (eds) Comprehensive Organometallic Chemistry, vol 8. Pergamon Press, Oxford, UK
[4] Moser WR, Wang AW, Kildahl NK (1988) J Am Chem Soc **110**: 2816
[5] Monteil F, Kalck P (1994) J Organomet Chem **482**: 45
[6] Garrou PE, Heck RF (1976) J Am Chem Soc **98**: 4115
[7] Milstein D (1988) Acc Chem Res **21**: 428
[8] Grushin VV, Alper H (1993) Organometallics **12**: 1890
[9] Kohlpaintner CW, Beller M (1997) J Mol Catal A: Chemical **116**: 259
[10] Amatore C, Jutand A (1998) Coord Chem Rev **178–180**: 511
[11] Bei X, Turner HW, Weinberg WH, Guram AS, Petersen JL (1999) J Org Chem **64**: 6797
[12] Widenhoefer RA, Zhong HA, Buchwald SL (1996) Organometallics **15**: 2745
[13] Kayaki Y, Noguchi Y, Iwasa S, Ikariya T, Noyori R (1999) J Chem Commun 1235
[14] Coulson DR (1972) Inorganic Synthesis **13**: 121
[15] Meier M, Basolo F, Pearson RG (1969) Inorganic Synthesis **8**: 795
[16] Hidai M, Kokura M, Uchida Y (1973) J Organometal Chem **52**: 431
[17] Ioele M, Ortaggi G, Scarsella M, Sleiter G (1991) Polyhedron **10**: 2475
[18] Roffia P, Gregorio G, Conti F, Preglalia GF (1977) J Mol Catal **2**: 191
[19] McLaughlin PA, Verkade JG (1998) Organometallics **17**: 5937
[20] Cavinato G, Pasualetto M, Ronchin L, Toniolo L (1997) J Mol Catal A: Chemical **125**: 15
[21] Cavinato G, Toniolo L (1999) J Mol Catal A: Chemical **143**: 325
[22] Bertoux F, Monflier E, Castanet Y, Mortreux A (1999) J Mol Catal A: Chemical **143**: 23
[23] Trzeciak AM, Ziółkowski JJ (2000) J Mol Catal A: Chemical **154**: 93
[24] Otsuka S, Nakamura A, Yoshida T, Naruto M, Ataka K (1973) J Am Chem Soc **95**: 3180

[25] Gretz E, Sen A (1986) J Am Chem Soc **108**: 6038
[26] Lin Yong-Shou, Yamamoto A (1998) Organometallics **17**: 3466
[27] Anderson GK (1983) Organometallics **2**: 665
[28] Kubota M, Boegeman SC, Keil RN, Webb CG (1989) Organometallics **8**: 1616
[29] Paul F, Patt J, Hartwig JF (1995) Organometallics **14**: 3030
[30] Meier M, Basolo F, Pearson RG (1969) Inorg Chem **8**: 795
[31] Perrin DD, Armarego WLF (1988) Purification of Laboratory Chemicals. Pergamon Press
[32] Drew D, Doyle JR (1990) Inorg Synthesis **28**: 348
[33] Anderson GA, Liu M (1990) Inorg Synthesis **28**: 61

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