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# Synthesis of Palladium Benzyl Complexes from the Reaction of $PdCl_2[P(OPh)_3]_2$ with Benzyl Bromide and Triethylamine: Important Intermediates in Catalytic Carbonylation

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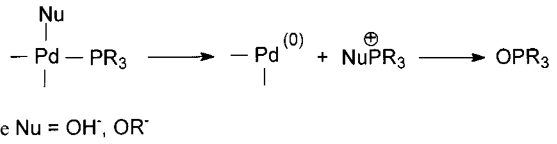
The palladium complex $PdCl_2(P(OPh)_3)_2$ is reduced to $Pd(P(OPh)_3)_4$ by tertiary amines ($NEt_3$, $NPr_3$, $NBu_3$) in the presence of water. The formation of aldehydes and corresponding secondary amines in this reaction has confirmed the role of amines as reducing agents. The new palladium benzyl complexes, *cis*-$[PdBr_2(CH_2Ph)(P(OPh)_3)][PhCH_2NEt_3]$ (**1**) and $[PdBr(CH_2Ph)(P(O\text{-}o\text{-}MeC_6H_4)_3)]_2$ (**2a**), were obtained in one-step syntheses from $PdCl_2(P(OPh)_3)_2$ or $PdCl_2[P(O\text{-}o\text{-}MeC_6H_4)_3)]_2$, $NEt_3$, and benzyl bromide and X-ray characterized. The air oxidation of complex **1** led to $[PdBr_3(P(OPh)_3)][PhCH_2NEt_3]$ (**4**) with the abstraction of benzaldehyde.

## Introduction

The results reported in this paper are relevant to the carbonylation of aryl halides, an important process in the production of carboxylic acids and their derivatives.[1] It has recently been demonstrated that the $PdCl_2(P(OPh)_3)_2$ complex is a highly efficient catalyst of carbonylation performed in supercritical $CO_2$.[2] We have also found that the $PdCl_2(P(OPh)_3)_2$ complex in methanol exhibits very high activity in the carbonylation of benzyl bromide to phenylacetic acid methyl ester, and the total conversion of substrate is achieved in just 15 min at 40 °C and 1 atm of CO.[3] These facts prompted us to study the elementary interactions of $PdCl_2(P(OPh)_3)_2$ with $NEt_3$ and benzyl bromide with the aim of isolating and characterizing palladium benzyl complexes, the most important intermediates in the carbonylation reaction.

In the first step of the well-established carbonylation reaction mechanism, a Pd(II) complex is reduced to a Pd(0) complex.[4] This step, very important also in the Heck reaction,[5] has been studied in detail by many authors.[5−7] The general scheme of Pd(II) reduction to Pd(0) assisted by hard nucleophiles, such as $OH^-$, $F^-$, or $OR^-$, has been presented:[5]



The studies on palladium reduction assisted by the hydroxide ion have shown the importance of $OH^-$ attack on coordinated $PPh_3$, followed by oxygen transfer and $OPPh_3$ formation.[6] Similarly, the mechanism proposed for reduction assisted by $F^-$ has been supported by the finding of $PPh_3F_2$ in the reaction medium.[7]

In this paper we present new data related to palladium reduction by $NEt_3$ (or other tertiary amines such as $NPr_3$, $NBu_3$) in the presence of water. The reaction of $NEt_3$ with $PdCl_2(PPh_3)_2$ was reported as far back as 1973,[8] and since then it has been known that, in contrast to secondary amines, tertiary amines do not reduce palladium in the $PdCl_2(PPh_3)_2$ complex. The formation of palladium metal has, however, been reported for a system containing $PdCl_2(PPh_3)_2$, $NEt_3$, and water.[6] The reduction of $PdCl_2{\cdot}2PhCN$ by tertiary amines was also reported.[9] We have found that some palladium complexes with phoshites and phosphinites undergo reduction to palladium(0) complexes in the presence of $NEt_3$.[3a,10]

## Results and Discussion

The $PdCl_2(P(OPh)_3)_2$ complex reacts with $NEt_3$ as well as with $NPr_3$ and $NBu_3$ forming the $Pd(P(OPh)_3)_4$ complex identified by a singlet at 138 ppm in the $^{31}P$

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[1] (a) Applied Homogeneous Catalysis with Organometallic Compounds. In *A Comprehensive Handbook in Two Volumes*; Cornils, B., Herrmann, W. A., Eds.; VCH: Weinheim, New York, 1996. (b) Beller, M.; Cornils, B.; Frohning, C. D.; Kohlpaintner, C. W. *J. Mol. Catal. A: Chem*. **1995**, *104*, 17. (c) Grushin, V. V.; Alper, H. *Chem. Rev.* **1994**, *94*, 1047.

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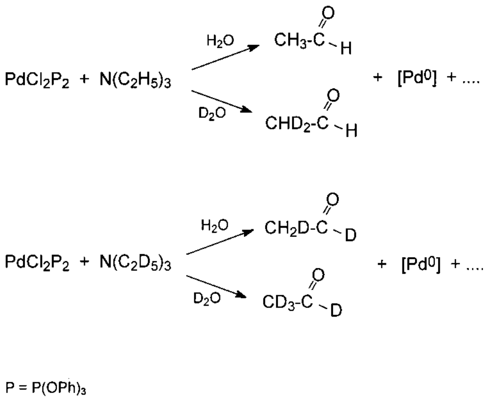
10.1021/om010541c CCC: $22.00

NMR spectrum. The palladium reduction is accompanied by the decomposition of each amine used in the experiment to the appropriate aldehyde and corresponding secondary amine, the products identified by GC−MS. The formation of acetaldehyde was also observed by other authors in reaction of $PdCl_2 \cdot 2PhCN$ with *N*,*N*-diethylaniline.[9] We have confirmed the formation of $CH_3CHO$, $CH_3CH_2CHO$, and $CH_3CH_2CH_2CHO$ when $PdCl_2(P(OPh)_3)_2$ reacted with a 10-fold excess of $NEt_3$, $NPr_3$, or $NBu_3$, respectively. Similarly acetaldehyde was found as a product of $NEt_3$ reaction with $PdCl_2(P(O\text{-}o\text{-}MeC_6H_4)_3)_2$, $PdCl_2(P(O\text{-}p\text{-}MeC_6H_4)_3)_2$, and $PdCl_2[PPh_2(OBu)]_2$. Under the same conditions no reaction products were obtained in reaction of $PdCl_2(PPh_3)_2$ with $NEt_3$.

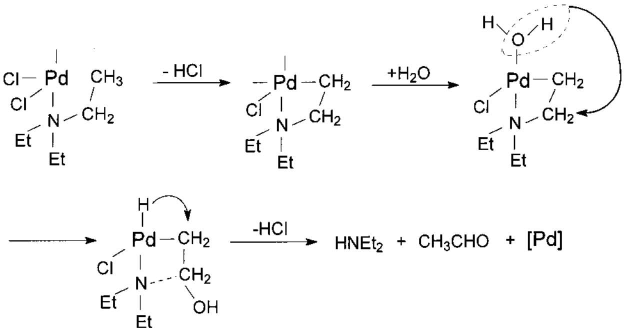
The $^{31}P$ NMR monitoring of the mixture of $PdCl_2(P(OPh)_3)_2$ and a 10-fold excess of $NEt_3$ in $CDCl_3$ showed that the reaction stopped at ca. 30% conversion of palladium to $Pd(P(OPh)_3)_4$. However, the addition of traces of water facilitated the immediate conversion of the starting palladium complex, partially to a Pd(0) complex and partially to another product with the proposed composition of $[Pd(P(OPh)_3)_2(NEt_3)Cl]OH$. This complex was characterized by a $^{31}P$ NMR spectrum containing two doublets with parameters depending on the kind of amine.[11] The new intermediate complex, $[Pd(P(OPh)_3)_2(NEt_3)Cl]OH$, contained two strongly inequivalent $P(OPh)_3$ ligands in the *cis* position and one labile ligand, $NEt_3$, which can be easily replaced by $P(OPh)_3$. By analogy to the recently reported cationic palladium complexes,[12] we propose the formula $[Pd(P(OPh)_3)_2(NEt_3)Cl]OH$ or $[Pd(P(OPh)_3)_2(NEt_3)(OH)]Cl$ for the new product. The first formula, with the $OH^-$ ligand not directly coordinated to the palladium, is preferred because in the $^{31}P$ NMR spectra no couplings to a proton or deuterium from the OH or OD ligand respectively were observed. Furthermore, the parameters of $^{31}P$ NMR spectra are the same for complexes containing OH and OD ligands, respectively. When $P(OPh)_3$ was added to the solution containing $[Pd(P(OPh)_3)_2(NEt_3)Cl]OH$, formed in situ from $PdCl_2(P(OPh)_3)_2$ and $NEt_3$, the two doublets in the $^{31}P$ NMR were changed to a doublet and a triplet[13] characteristic of three $P(OPh)_3$ ligands coordinated to palladium in the $[Pd(P(OPh)_3)_3Cl]OH$ complex.

The reaction of the palladium complex $PdCl_2(P(OPh)_3)_2$ with $NEt_3$ carried out in the presence of added water and excess $P(OPh)_3$ led to the formation of the $Pd(P(OPh)_3)_4$ complex, isolated with a yield of 53%. This synthesis can be completed in ca. 1 h. Attempts to synthesize $Pd(P(OPh)_3)_4$ under anhydrous conditions (using freshly dried and distilled $NEt_3$) led to a yield of ca. 30% of the palladium(0) complex, and unreacted $PdCl_2(P(OPh)_3)_2$ was present in the reaction mixture even after 4 h. We believe that the observed conversion of Pd(II) to Pd(0) is caused by small amounts of water, still present in the hygroscopic reagents. Further, experiments performed in the presence of $D_2O$ showed that both the amine as well as the water molecules reacted with palladium. This was evidenced by the incorporation of deuterium into aldehydes formed from amines during the reaction (Scheme 1). The MS spectra confirmed the presence of at least two deuterium atoms in the aldehyde hydrocarbon chain, but never in the CHO group (Scheme 1). In the MS spectra of all the aldehydes ($CH_3CHO$, $CH_3CH_2CHO$, and $CH_3CH_2CH_2CHO$) formed from $NEt_3$, $NPr_3$, and $NBu_3$ in the presence of $H_2O$ or $D_2O$, a peak at *m*/*e* 29, due to the CHO group, was found. However, when $N(C_2D_5)_3$ reacted with $PdCl_2(P(OPh)_3)_2$, a peak at *m*/*e* 30 (CDO) was present instead. The introduction of $H_2O$ into the reaction mixture containing $PdCl_2(P(OPh)_3)_2$ and $N(C_2D_5)_3$ led to the formation of the mixture of aldehydes, $CD_3CDO$ (*m*/*e* 48), $CD_2HCDO$ (*m*/*e* 47), and $CDH_2CDO$ (*m*/*e* 46), and again up to two deuterium atoms in the methyl group were exchanged for protons.

**Scheme 1**



**Scheme 2**



The proposed mechanism of palladium reduction by $NEt_3$ in the presence of water is presented in Scheme 2. The reaction starts with the activation of the C−H bonds of the amine coordinated to palladium and formation of the Pd−C bond. The next step consists of the nucleophilic attack of $OH^-$ (from water) on the α-carbon of the intermediate complex followed by the rearrangement to aldehyde and secondary amine. A similar transformation, leading to aldehyde and Pd(0), can be also postulated for the $[Pd(P(OPh)_3)_2(NEt_3)Cl]OH$ intermediate. The proposed reaction pathway is close to the mechanism of the Wacker process, and summing up, the final equation is proposed:

$$PdCl_2P_2 + N(C_2H_5)_3 + H_2O \rightarrow [Pd^0] + 2\,HCl + CH_3CHO + HN(C_2H_5)_2 + 2\,P$$

$$P = P(OPh)_3$$

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(11) $^{31}P$ NMR ($CDCl_3$, 297 K) data ($\delta$, $J(P-P)$) for $[Pd(P(OPh)_3)_2(NR_3)Cl]OH$ or $[Pd(P(OPh)_3)_2(NR_3)OH]Cl$ complexes: R = Et 90.5 d, 49.8 d, (107.0); R = Pr 90.1 d, 49.7 d (107.7); R = Bu 89.9 d, 49.8 d (108.3).

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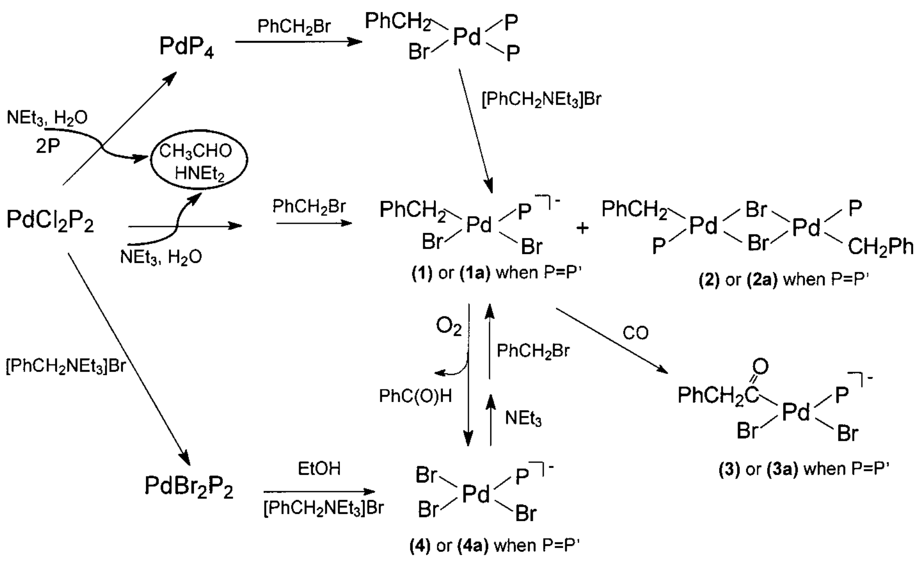
(13) $^{31}P$ NMR ($CDCl_3$, 297 K): $\delta$ 92.7 d, 44.4 t, (51.2).

**Scheme 3**



P = P(OPh)$_3$, P' = P(O-o-MeC$_6$H$_4$)$_3$

Complexes **2** and **4** crystallized with cation [PhCH$_2$NEt$_3$]$^+$

The presence of two deuteriums in the alkyl fragment of the aldehydes formed in the experiments with D$_2$O can be explained by the H/D exchange in an intermediate palladium hydride.

The formation of the enamine palladium(II) complex as an intermediate during amine conversion cannot be excluded; however in our reaction conditions, quite different from those in ref 9, we did not observe any product of this type.

The competing process of the palladium reduction can be the transfer of oxygen from the coordinated OH$^-$ to phosphite and the formation of OP(OPh)$_3$, similarly as reported earlier for the PdCl$_2$(PPh$_3$)$_2$ complex.[5,6] In fact, some amounts of OP(OPh)$_3$ were observed in the reaction mixtures by $^{31}$P NMR ($\delta$: $-17$ ppm).

As an alternative explanation of the aldehyde formation and palladium reduction, we considered the conversion of the amine used to olefin, initiated by palladium, which next could be transformed into aldehyde according to the Wacker process mechanism. In accordance with the original Wacker process mechanism, we should, however, obtain ketones in reactions with NPr$_3$ (acetone) and NBu$_3$ (methyl ethyl ketone), which however were not found in the reaction mixtures.

During the formation of a palladium(0) complex, chloride ligands are removed from the palladium coordination sphere in the form of amine hydrochloride, NR$_3$·HCl, easily identified by IR spectra.[14] A completely deuterated salt, N(C$_2$D$_5$)$_3$·DCl, was formed in the reaction of PdCl$_2$(P(OPh)$_3$)$_2$ with N(C$_2$D$_5$)$_3$ in the presence of D$_2$O, and N(C$_2$D$_5$)$_3$·HCl was found when H$_2$O was used, respectively.

The easy and relatively fast reduction of palladium(II) to palladium(0) by tertiary amines enabled the preparation of benzyl palladium complexes in a direct reaction starting from PdCl$_2$(P(OPh)$_3$)$_2$; the reactions under study are summarized in Scheme 3. The PdCl$_2$(P(OPh)$_3$)$_2$ complex reacted first with NEt$_3$ for ca. 15 min, to form a Pd$^0$ species, and next an excess of benzyl bromide was added. The crystals formed in this reaction were studied by X-ray methods and found to consist of an anionic palladium benzyl complex, *cis*-[PdBr$_2$(CH$_2$Ph)(P(OPh)$_3$)][PhCH$_2$NEt$_3$] (**1**), with two bromide ligands occupying the *cis* position (Figure 1). Surprisingly, both the Pd–Br bonds were of the same length, and the *trans* influence of the benzyl group was not evidenced. For comparison, in *cis*-PdBr(CH$_2$Ph)(P(OPh)$_3$)$_2$, the two Pd–P bonds are strongly inequivalent, the one *trans* to benzyl being ca. 0.13 Å longer.[3b] Complex **1** was also obtained when *cis*-PdBr(CH$_2$Ph)(P(OPh)$_3$)$_2$[9] was treated with [PhCH$_2$NEt$_3$]Br, and this reaction was studied in situ by $^{31}$P NMR. Immediately after the addition of [PhCH$_2$NEt$_3$]Br to the solution of *cis*-PdBr(CH$_2$Ph)(P(OPh)$_3$)$_2$ in CDCl$_3$, the intensity of the sharp doublet at 103 ppm from the starting complex decreased and a broad line appeared instead. The isolated complex **1** also showed a broad signal in the $^{31}$P NMR at 103 ppm. A similar spectrum was also registered for the analogous complex [PdBr$_2$(CH$_2$Ph)(P(O-o-MeC$_6$H$_4$)$_3$)][PhCH$_2$NEt$_3$] (**1a**), prepared in the reaction of PdCl$_2$(P(O-o-MeC$_6$H$_4$)$_3$)$_2$ with NEt$_3$ and benzyl bromide. The $^{31}$P NMR spectrum of the noncrystalline product obtained in the reaction of PdCl$_2$(P(OPh)$_3$)$_2$ with NEt$_3$ and PhCH$_2$Br, measured at a lower temperature (243 K), exhibited two narrow lines of nonequal intensity (at 104.1 and 103.7 ppm), suggesting the presence of another complex, **2**, in the mixture with **1**. We were not able to separate the complexes **1** and **2** in the reaction of PdCl$_2$(P(OPh)$_3$)$_2$ with NEt$_3$ and PhCH$_2$Br; however, when PdCl$_2$(P(OPh)$_3$)$_2$ was replaced by PdCl$_2$(P(O-o-MeC$_6$H$_4$)$_3$)$_2$, the crystalline dimeric complex of the formula [PdBr(CH$_2$Ph)(P(O-o-MeC$_6$H$_4$)$_3$)]$_2$ (**2a**) was obtained (Figure 2). Complex **2a** crystallizes in two structurally independent molecules, shown in Figure 2. Both the palladium atoms in square planar coordination are connected by two asymmetrical

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(14) IR data (KBr), cm$^{-1}$: N(C$_2$D$_5$)$_3$·DCl 2684 vs, 2918 s; N(C$_2$D$_5$)$_3$·HCl 2604 s, 2638 s, 2684 s, 2911 s; N(C$_2$H$_5$)$_3$·HCl 2500 s, 2607 s, 2620 s, 2677 sh, 2945 m, 2985 m.

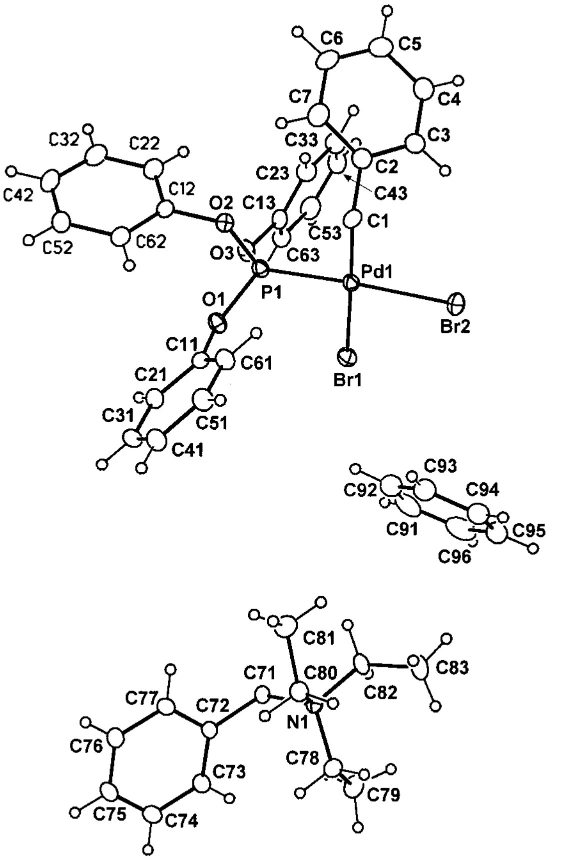

**Figure 1.** Molecular structure of **1** with atom numbering. The benzene molecule present in the lattice is also shown. Selected bond distances (Å) and angles (deg): Pd(1)−C(1) 2.116(4), Pd(1)−P(1) 2.1811(11), Pd(1)−Br(2) 2.4967(6), Pd(1)−Br(1) 2.5022(6), C(1)−Pd(1)−P(1) 93.62(11), C(1)−Pd(1)−Br(2) 90.32(10), P(1)−Pd(1)−Br(2) 176.05(3), C(1)−Pd(1)−Br(1) 177.09(11), P(1)−Pd(1)−Br(1) 85.62(3), Br(2)−Pd(1)−Br(1) 90.43(2).

bridging bromides in the Pd($\mu$-Br)$_2$Pd core, and benzyl groups are located on opposite sides of the core. Complexes **1a** and **2a** cannot be distinguished in solution since they exhibit the same broad resonance at 103 ppm in the $^{31}$P NMR spectra and practically the same UV−vis spectra.

In agreement with spectroscopic data we postulate the equilibrium between complexes **1** and **2** (as well as between **1a** and **2a**) in solution:

$$[\mathrm{PdBr(PhCH_2)(P(OPh)_3)}]_2 + 2\,[\mathrm{PhCH_2NEt_3}]\mathrm{Br} \rightleftarrows [\mathrm{PdBr_2(PhCH_2)(P(OPh)_3)}][\mathrm{PhCH_2NEt_3}]$$

Complexes **1** and **2** were obtained only in consecutive reactions in which PdCl$_2$(P(OPh)$_3$)$_2$ was allowed first to react with NEt$_3$ and next with PhCH$_2$Br. When both reagents were introduced simultaneously, a bromide complex, PdBr$_2$(P(OPh)$_3$)$_2$,[15] identical with the complex prepared in the reaction of PdBr$_2$(cod) with P(OPh)$_3$, was formed instead, as a product of a reaction between PdCl$_2$(P(OPh)$_3$)$_2$ and [PhCH$_2$NEt$_3$]Br. Similarly, PdCl$_2$(P(OPh)$_3$)$_2$ reacted with $^n$Bu$_4$I producing PdI$_2$(P(OPh)$_3$)$_2$. In both the reactions reported above, the PdBr$_2$(P(OPh)$_3$)$_2$ or PdI$_2$(P(OPh)$_3$)$_2$ complexes, respectively, were the only products. No anionic complexes of the type PdX$_3$(P(OPh)$_3$)$^-$ (X = Br, I) were observed, even when an excess of the appropriate ammonium bromide or iodide was used. This is clearly different from the reactivity of PdCl$_2$(PPh$_3$)$_2$, which forms [PdI$_3$(PPh$_3$)]$^-$ in a reaction with $^n$Bu$_4$I.[16]

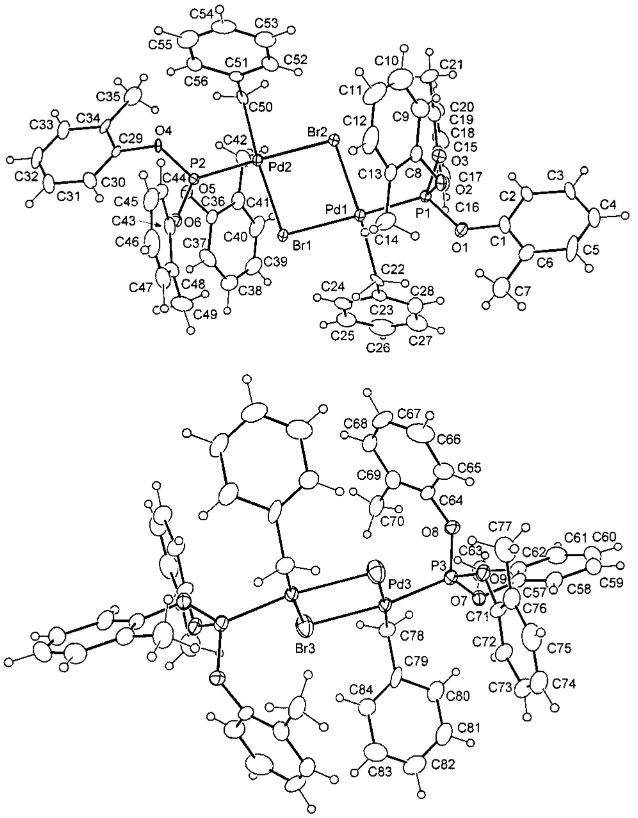

**Figure 2.** Molecular structure of **2a** (two symmetry-independent molecules). Selected bond distances (Å) and angles (deg): Pd(1)−C(22) 2.126(8); Pd(1)−P(1) 2.188(2); Pd(1)−Br(1) 2.5373(12); Pd(1)−Br(2) 2.5726(11); Pd(2)−C(50) 2.099(7); Pd(2)−P(2) 2.1950(19); Pd(2)−Br(2) 2.5354(11); Pd(2)−Br(1) 2.5631(11); Pd(3)−C(78) 2.029(9); Pd(3)−P(3) 2.193(2); Pd(3)−Br(3) 2.5299(15); Pd(3)−Br(3)#1 2.5747(14); Br(3)−Pd(3)#1 2.5747(15); C(22)−Pd(1)−P(1) 90.3(2); C(22)−Pd(1)−Br(1) 90.8(2); P(1)−Pd(1)−Br(1) 171.55(6); Pd(1)−Br(1)−Pd(2) 94.77(4); Pd(2)−Br(2)−Pd(1) 94.58(4); Pd(3)−Br(3)−Pd(3)#1 94.57(5).

The palladium benzyl complex **1** reacted with CO (1 atm), producing an acyl complex [Pd(PhCH$_2$CO)Br$_2$(P(OPh)$_3$)$_2$][PhCH$_2$NEt$_3$] (**3**) within a few minutes, identified first in CDCl$_3$ solution by $^{31}$P NMR[17] and next isolated in solid form. The presence of PhCH$_2$C(O)$^-$ ligands was confirmed by the $\nu$(CO) bands at 1700 cm$^{-1}$. The attempt to obtain the acyl complex **3** in methanol failed due to the fast decomposition of the complex with the formation of quantitative amounts of phenylacetic acid methyl ester identified by GC−MS. Complex **3** left in methanol solution decomposed with the formation of the same ester.

In the reaction of PdCl$_2$(P(OPh)$_3$)$_2$ with PhCH$_2$Br and NEt$_3$ carried out in contact with air, the complex [PdBr$_3$(P(OPh)$_3$)][PhCH$_2$NEt$_3$] (**4**) was found and identified as the main product. It was isolated first from the filtrate

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[15] $^{31}$P NMR (CDCl$_3$, 297 K): $\delta$ 83.0. UV−vis (CHCl$_3$): 322. Anal. Calcd for C$_{36}$H$_{30}$P$_2$O$_6$Br$_2$Pd: C, 48.75; H, 3.41. Found: C, 49.5; H, 3.18.

[16] Amatore, C.; Jutand, A.; Mottier, L. *Eur. J. Inorg. Chem.* **1999**, 1081.

[17] $^{31}$P NMR (CDCl$_3$, 297 K): $\delta$ 101.2 s.

left in an open flask after the separation of **3**. Complex **4** was never obtained in an inert atmosphere. The role of dioxygen in the synthesis of **4** was clarified by an experiment in which $PdCl_2(P(O\text{-}o\text{-}MeC_6H_4)_3)_2$ reacted first with $NEt_3$ under dinitrogen for 15 min, and next $PhCH_2Br$ was added, and the reaction vessel was opened to the air. The solution was stirred in contact with air for 4 h. After the separation of the complex $[PdBr_3(P(O\text{-}o\text{-}MeC_6H_4)_3)][PhCH_2NEt_3]$ (**4a**),[18] the filtrate was analyzed by the GC−MS method, which showed the presence of benzaldehyde, formed by $PhCH_2^-$ oxidation.

The X-ray studies of **4** showed that the Pd−Br bond distances are significantly shorter in comparison to those in $[PdBr_3(P(OPh)_3)][NH_2Me_2]$[19] and the Pd−P bonds are of the same length in both complexes (2.199(3) Å in **4** and 2.193(4) Å in $[PdBr_3(P(OPh)_3)][NH_2Me_2]$). The elongation of Pd−Br bonding distances is well explained by the presence of N−H···Br hydrogen bondings in the complex with the $NH_2Me_2^+$ cation and the absence of these bondings in complex **4**.

From the catalysis point of view, it was very important to show how complex **4** can be transformed back to the benzyl complexes **1** or **2**, which are catalytically active intermediates. The conversion of **4** to **1** required the abstraction of one $Br^-$ ligand from the coordination sphere of palladium, and an excess of $NEt_3$ was used for this purpose. After a few minutes benzyl bromide was added to the resulting solution, which was next analyzed by means of the $^{31}P$ NMR spectrum. The appearance of the signal at 103 ppm (besides the one at 80.8 ppm from **4**) indicated the presence of the benzyl complex **1** or eventually **2**, confirming the reversibility of the **1** to **4** conversion (Scheme 3).

The presented new pathway of palladium complex reduction by tertiary amines can be important for the understanding of the formation of active carbonylation catalysts. We have also demonstrated that the reaction with amines is very useful in the synthesis of palladium−benzyl complexes.

## Experimental Part

All experiments were carried out under dinitrogen using standard Schlenk techniques, unless otherwise indicated. The solvents (benzene, toluene) were distilled from sodium/benzophenone, and methanol was distilled from magnesium wires prior to use. The amines ($NEt_3$, $NPr_3$, $NBu_3$) were distilled from KOH.

The NMR were recorded with a Bruker 300 spectrometer, and chemical shifts are given vs TMS ($^1H$) and vs 85% $H_3PO_4$ ($^{31}P$). Downfield chemical shifts are positive. IR spectra were measured with a FT-IR Nicolet Impact 400 instrument. UV−vis spectra were measured with an HP 4852 diode array spectrophotometer. GC−MS analyses were carried out with an HP 5890 II linked to an HP 5971 A mass detector.

**Synthesis of $Pd(P(OPh)_3)_4$.** A 0.1 g (0.35 mmol) sample of $PdCl_2(cod)$ was placed in a Schlenk tube under $N_2$, and 1 mL of benzene and 0.5 mL (ca. 1.6 mmol) of $P(OPh)_3$ were added. After a few minutes of stirring, the formation of a white precipitate of $PdCl_2(P(OPh)_3)_2$ was observed. $NEt_3$ (0.6 mL, 4.3 mmol) and water (0.2 mL, 10 mmol) were added, and the mixture became transparent in 10 min. The stirring was continued for 1 h, the solution was concentrated under vacuum to one-fourth of the initial volume, and EtOH (ca. 4 mL) was added to complete the precipitation of the white $Pd(P(OPh)_3)_4$ complex. The yield, after filtration and drying, was 53%.

**Synthesis of $[PdBr(CH_2Ph)(P(O\text{-}o\text{-}MeC_6H_4)_3]_2$, 2a.** A 0.06 mL (0.43 mmol) sample of $NEt_3$ was added to a solution of 0.066 g (0.075 mmol) of $PdCl_2[P(O\text{-}o\text{-}MeC_6H_4)_3]_2$[10] in methanol (1 mL), and the mixture was stirred under dinitrogen for 15 min until all of the solid was dissolved. Next, $PhCH_2Br$ (0.06 mL, 0.51 mmol) was added, and the solution was left to crystallize at room temperature. The pale yellow crystals were isolated with a yield of 65%, and one crystal suitable for X-ray examination was selected. $^1H$ NMR ($CDCl_3$, 297 K): $\delta$ 2.19 (s, $CH_3$), 3.15 (br, $CH_2$), 7.0−7.4 (m, Ph). $^{31}P$ NMR ($CDCl_3$, 297 K): $\delta$ 102.7 br. UV−vis ($CHCl_3$): 294, 368. Anal. Calcd for $C_{28}H_{28}PO_3BrPd$: C, 53.40; H, 4.48. Found: C, 53.5; H 4.73.

**Synthesis of $[PdBr_2(CH_2Ph)(P(OPh)_3][PhCH_2NEt_3]$, 1.** A 0.05 mL (0.36 mmol) sample of $NEt_3$ was added to a suspension of 0.068 g (0.085 mmol) of $PdCl_2(P(OPh)_3)_2$ in benzene (1 mL), and the mixture was stirred under dinitrogen for 10 min. Next, $PhCH_2Br$ (0.15 mL, 1.26 mmol) was added, and the solution was left to crystallize at room temperature. The yellow crystals of **2** were isolated the next day with 56% yield, and one crystal suitable for X-ray examination was selected. $^1H$ NMR ($CDCl_3$, 297 K): $\delta$ 1.35 (t, 2H, $CH_3$), 3.29 (q, $CH_2$), 3.50 (br, $CH_2$ benzyl), 4.61 ($CH_2$), 7−7.5 (m, Ph). $^{31}P$ NMR ($CDCl_3$, 297 K): 103.6, br. UV−vis ($CHCl_3$): 290, 368. Anal. Calcd for $C_{38}H_{44}PO_3NBr_2Pd$: C, 53.07; H, 5.16; N, 1.63. Found: C, 52.81; H, 5.10; N, 1.50.

**Synthesis of $[PdBr_3(P(OPh)_3)][PhCH_2NEt_3]$, 4.** The filtrate left after separation of complex **1** was condensed in vacuo, 1 mL of EtOH was added, and the orange solution was left for crystallization in an opened flask. After 3 days the orange needles of **4** were formed and one crystal was selected for X-ray examination. $^1H$ NMR ($CDCl_3$, 297 K): $\delta$ 1.31 (t, $CH_3$), 3.24 (q, $CH_2$), 4.45 ($CH_2$ benzyl), 7.0−7.4 (m, Ph). $^{31}P$ NMR ($CDCl_3$, 297 K): $\delta$ 80.8. UV−vis ($CHCl_3$): 252, 328. Anal. Calcd for $C_{31}H_{37}PO_3NBr_3Pd$: C, 43.87; H, 4.39; N, 1.65. Found: C, 43.92; H, 4.73; N, 1.60.

**Synthesis of $PdI_2(P(OPh)_3)_2$.** To the dark red solution containing 0.08 g (0.1 mmol) of $PdCl_2(P(OPh)_3)_2$ and 0.17 g (0.46 mmol) of $Bu_4NI$ in 2 mL of benzene was added 1 mL of ethanol. The solution was filtrated and concentrated in vacuo, giving an orange product with 70% yield. $^{31}P$ NMR ($CDCl_3$, 297 K): $\delta$ 94.4. UV−vis ($CHCl_3$): 370, 430. Anal. Calcd for $C_{36}H_{30}P_2O_6I_2Pd$: C, 44.09; H, 3.08. Found: C, 43.78; H, 3.32.

**Reactions of $PdCl_2(P(OPh)_3)_2$ with Amines and Water.** In a typical experiment to 0.04 g (0.05 mmol) of $PdCl_2(P(OPh)_3)_2$ in chloroform (0.5 mL) were added 0.01−0.02 mL (ca. 0.14−0.35 mmol) of amine ($NEt_3$, $NPr_3$, or $NBu_3$) and 0.001−0.002 mL (0.05−0.1 mmol) of water ($H_2O$ or $D_2O$). The mixture was allowed to react for 1 h, and the gas phase was analyzed by GC−MS. In some experiments the liquids were separated by vacuum transfer and analyzed by GC−MS. Below are given the representative MS data (*m/z*) of aldehydes obtained in the reactions of $PdCl_2(P(OPh)_3)_2$. $CD_3CDO$: 48(73, $M^+$), 47(16), 46(28), 31(15), 30(100), 29(13). $CH_3CH_2CH_2CHO + CH_3CH_2CD_2CHO$: 74(22, $M^+$), 73(27), 72(58, $M^+$), 59(5), 58(9), 57(28), 46(20), 45(67), 44(100), 43(65), 42(30), 41(55), 30(7), 29(49), 27(60).

**X-ray Structure Determination of 1, 2a, and 4.** Suitable crystals of **1**, **2a**, and **4** were glued on top of a glass fiber and transferred into the cold nitrogen stream on a Kuma KM4CCD $\kappa$-axis diffractometer (graphite-monochromated Mo K$\alpha$ radiation, $\lambda = 0.71073$ Å). Crystals were positioned at 65 mm from the CCD camera; 612 frames were measured at 0.75° intervals with a counting time of 20 s. Accurate cell parameters were determined and refined by least-squares fit of 6000−7000 of

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[18] $^1H$ NMR ($CDCl_3$, 297 K): $\delta$ 1.24 (t, $CH_3$), 1.46 (s, $CH_3$), 3.00 (q, $CH_2$), 4.3 ($CH_2$ benzyl), 6.9−7.4 (m, Ph). $^{31}P$ NMR ($CDCl_3$, 297 K): $\delta$ 81.4. Anal. Calcd for $C_{34}H_{43}PO_3NBr_3Pd$: C, 45.84; H, 4.87; N, 1.57. Found: C, 45.25; H, 5.10; N, 1.48.

[19] Nyrkova, A. N.; Kuzmina, L. G.; Struchkov, Yu. T.; Temkin, O. N. *Koord. Khim.* **1982**, *8* (1), 82.

**Table 1. Crystallographic Data**

| | **1** | **2a** | **4** |
|---|---|---|---|
| formula | $C_{44}H_{46}Br_2NO_3PPd$ | $C_{84}H_{84}Br_3O_9P_3Pd_3$ | $C_{31}H_{35}Br_3NO_3PPd$ |
| $M_r$ | 934.01 | 1889.35 | 846.70 |
| cryst syst | triclinic | triclinic | orthorhombic |
| color, habit | yellow needles | pale yellow plates | orange needles |
| size (mm) | 0.20 × 0.20 × 0.10 | 0.10 × 0.10 × 0.08 | 0.15 × 0.10 × 0.10 |
| space group | $P\bar{1}$ | $P\bar{1}$ | *Pbca* |
| $a$ (Å) | 9.5730(10) | 10.005(2) | 20.482(4) |
| $b$ (Å) | 11.5620(10) | 12.810(3) | 9.485(2) |
| $c$ (Å) | 19.0280(10) | 31.070(6) | 33.630(7) |
| $\alpha$ (deg) | 77.340(10) | 88.44(3) | |
| $\beta$ (deg) | 87.670(10) | 89.21(3) | |
| $\gamma$ (deg) | 84.720(10) | 77.10(3) | |
| $V$ (Å$^3$) | 2045.7(3) | 3880.0(13) | 6533(2) |
| $Z$ | 2 | 2 | 8 |
| $D_c$/Mg·m$^{-3}$ | 1.516 | 1.617 | 1.722 |
| $\mu$(Mo K$\alpha$) (cm$^{-1}$) | 24.85 | 23.52 | 43.18 |
| $F$(000) | 944 | 1896 | 3344 |
| data collection temp (K) | 100(2) | 100(2) | 100(2) |
| $\theta$ range (deg) | 3.44−28.76 | 3.26−28.81 | 3.17−25.00 |
| ranges of $h,k,l$ | −12→12,−9→15,−24→24 | −13→12,−16→16,−30→41 | −24→24,−11→7,−39→39 |
| no. of rflns collected | 14524 | 28011 | 35206 |
| no. of ind rflns | 9282 | 17 645 | 5734 |
| no. of obsd rflns | 6444 | 8117 | 4268 |
| no. of params refined | 469 | 928 | 364 |
| weighting $a$, $b^a$ | 0.0736, 0 | 0.0423, 22.4582 | 0.0922, 26.9469 |
| gof | 1.024 | 1.076 | 1.205 |
| R1 ($I>2\sigma_I$) | 0.0460 | 0.0752 | 0.0920 |
| wR2($F^2$) (all data) | 0.1194 | 0.1456 | 0.1976 |
| residual density (e·Å$^{-3}$) | −0.912 to 1.813 | −1.254 to 0.779 | −1.967 to 1.948 |

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\mathrm{Max}(F_o^2,0) + 2F_c^2]/c$.

the strongest reflections. Data were corrected for Lorentz and polarization effects. Absorption corrections based on least-squares fitted to $|F_c| - |F_o|$ differences were also applied.[20] Data reduction and analysis were carried out with the Oxford Diffraction (Poland) (formerly Kuma Diffraction Wrocław, Poland) programs. The structures were solved by the heavy method (program SHELXS97[21]) and refined by the full-matrix least-squares method on all $F^2$ data using the SHELXL97 programs.[22] Non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included from geometry of molecules but were not refined. Neutral atom scattering factors were taken from Cromer and Waber.[23] Final refinement details are collected in Table 1, and the numbering schemes employed are shown in Figures 1 and 2, which were drawn with ORTEP as 30% probability ellipsoids.

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**Supporting Information Available:** Complete tables of atomic coordinates, anisotropic displacement parameters, hydrogen coordinates, bond distances, bond angles, and torsion angles for **1**, **2a**, and **4**. This material is also available free of charge via the Internet at http://pubs.acs.org

OM010541C

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[21] Sheldrick, G. M. *SHELXS97*: Program for Solution of Crystal Structures; University of Göttingen, 1997.

[22] Sheldrick, G. M. *SHELXL97*: Program for Crystal Structure Refinement; University of Göttingen, 1997.

[23] Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography;* Kynoch Press: Brimingham, U.K., 1974; Vol. 4.