In Situ Preparation of Palladium Diphosphane Catalysts

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The efficiency of a superficially simple preparation procedure for palladium-diphosphane catalysts has been examined. Preparation of Pd(dppe)X_2 in situ by mixing equimolar amounts of $Pd(OAc)_2$ and 1,2-bis(diphenylphosphanyl)ethane (dppe) in methanol in the first step unexpectedly affords the bischelate $[Pd(dppe)_2](OAc)_2$ as the (main) kinetic product. Subsequently, the slow reaction of $[Pd(dppe)_2](OAc)_2$ and unreacted $Pd(OAc)_2$ forms the thermodynamically favored monochelate $[Pd(dppe)(OAc)_2]$ (following first-order kinetics). Conversion of the bischelate into the monochelate stops after addition of strong acid (HX) in the second step, thus affording a mixture of active — Pd(dppe)X_2 — virtually inactive — $[Pd(dppe)_2]X_2$ — and unstable — PdX_2 — species. This procedure was also evaluated for some other diphosphane ligands and methods are given to overcome the encountered problem.

The potential of homogeneous catalysis in the selective preparation of chemicals has been widely recognized, and the number of applications, both on a laboratory scale and on an industrial scale, is growing steadily.[1] In situ preparation of homogeneous catalysts from readily available precursors is a useful method, in particular when testing larger numbers of catalysts as in parallel screening. A convenient and frequently explored method to prepare cationic palladium diphosphane catalysts in situ involves two steps.[2] First, a suitable palladium source, such as $Pd(OAc)_2$, and the ligand of choice are mixed in a selected solvent [Equation (1)]. Next, a strong acid is added to exchange the anions [Equation (2)].

$$Pd(OAc)_2 + P\text{-}P \rightarrow [Pd(P\text{-}P)(OAc)_2] \qquad (1)$$

$$[Pd(P\text{-}P)(OAc)_2] + 2\,HX \rightarrow [Pd(P\text{-}P)X_2] + 2\,HOAc \qquad (2)$$

Although this method is often used, little attention has been given to the efficiency of catalyst preparation when using this procedure.

In the mid-eighties it was discovered that palladium(II)-based catalysts modified with the combination of a chelating diphosphane ligand and weakly or non-coordinating anions are highly active for the synthesis of perfectly alternating CO/ethene-based copolymer (PK-E). The most efficient system was based on 1,3-bis(diphenylphosphanyl)propane, which produces snow white PK-E with high rates (of 6 kg PK-E/g Pd·h and higher).[2,3] The activity of the catalyst based on its C_2-bridged counterpart, 1,2-bis(diphenylphosphanyl)ethane (dppe), was considerably lower.[2a] Moreover, the grey color of the PK-E product obtained during CO/ethene copolymerization employing the Pd(dppe)-based catalyst prepared in situ in methanol [Equations (1) and (2)] indicated significant catalyst decomposition to solid palladium(0) ("plating"). This prompted us to examine the in situ catalyst preparation procedure in methanol.

To this end, an equimolar mixture of $Pd(OAc)_2$ and dppe (32 μmol) was prepared in [D$_4$]methanol (0.8 mL). It was found that instead of the expected monochelate $[Pd(dppe)(OAc)_2]$ (**1**), the bischelate derivative $[Pd(dppe)_2](OAc)_2$ (**2**), characterized by a single ^{31}P NMR resonance at $\delta = 58.7$ ppm, was formed initially. Upon standing, slow conversion of **2** into **1** ($\delta = 63.4$ ppm) was observed (Scheme 1), which was virtually completed only after about 24 h, and accompanied by plating.

Mimicking the full in situ catalyst preparation procedure, six equivalents of a strong acid (CF_3CO_2H) were added well before the conversion of **2** into **1** was completed. Besides the expected exchange of the anions of the various palladium species [**1**, **2**, and unreacted $Pd(OAc)_2$], conversion of the catalytically inactive bischelate $[Pd(dppe)_2](CF_3CO_2)_2$ (**4**, $\delta = 58.6$ ppm) into the active monochelate species $[Pd(dppe)(CF_3CO_2)_2]$ (**3**, $\delta = 69.2$ ppm) also stopped (Scheme 1). This indicates that conversion of **2** into **1** is acetate-assisted. Moreover, a significant amount of palladium black was formed within a few hours due to decomposition of the co-formed palladium trifluoroacetate, a labile species in alcoholic media.

The conversion of **2** into **1** in [D$_4$]methanol at 20 °C was monitored by ^{31}P NMR spectroscopy and found to nicely follow first-order kinetics ($k = 0.145\ h^{-1}$; see Figure 1). At a higher degree of conversion (>80%), however, this conversion proceeded somewhat slower, which might be due to partial decomposition (plating) of $Pd(OAc)_2$ and **1**. Extrapolation of the kinetic curve to $t = 0$ h showed that, ini-

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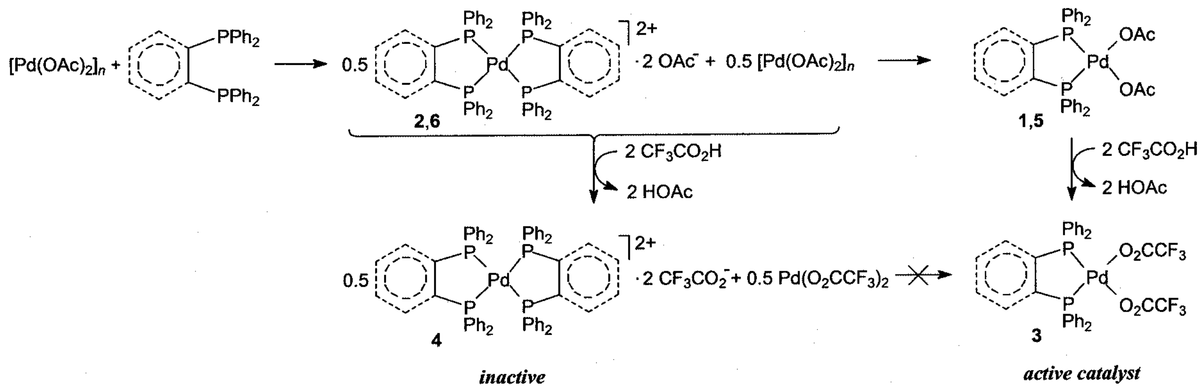

Scheme 1. Reactions observed during preparation of some palladium diphosphane catalysts in situ; P-P = dppe (**1**−**4**) or dppbz (**5**,**6**)

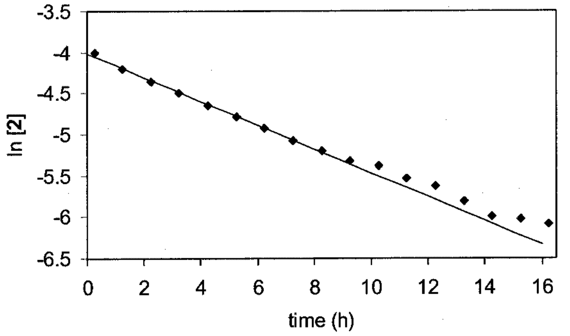

Figure 1. Conversion of **2** + $Pd(OAc)_2$ into **1** in [D$_4$]methanol at 20 °C

tially, **2** had formed almost quantitatively (approx. 90%). In a separate experiment equimolar amounts of isolated, pure **2** and $Pd(OAc)_2$ were dissolved in [D$_4$]methanol and the conversion into **1** was found to exhibit identical kinetics.

These observations clearly indicate that **2** is the kinetic product of the reaction of $Pd(OAc)_2$ and dppe, but **1** is thermodynamically favored. Further, it indicates that **1** and **2**, in contrast to Bianchini's recent conclusion,[4] are not involved in an autoionization equilibrium (2 [Pd(dppe)(OAc)$_2$] (**1**) $\rightleftharpoons$ [Pd(dppe)$_2$](OAc)$_2$ (**2**) + $Pd(OAc)_2$ in methanol, otherwise conversion of **2** into **1** would not have proceeded to completeness.[5] This was confirmed in a separate experiment using isolated, pure **1**: upon dissolution in [D$_4$]methanol, no conversion of **1** into **2** was observed (over 24 h).

It was considered that the initial formation of [Pd(dppe)$_2$](OAc)$_2$ might be due to a relatively slow dissolution of $Pd(OAc)_2$ in methanol in comparison with dppe, causing an initial deficiency of accessible (dissolved) $Pd(OAc)_2$. To check this hypothesis, an experiment was done in which $Pd(OAc)_2$ was first dissolved in a mixture of methanol/dichloromethane (9:1) before dppe was added. Immediate formation of **2** and some **1** was observed by ^{31}P NMR spectroscopy, followed by slow conversion of **2** into **1**. Extrapolation of the kinetic curve for the conversion of **2** into **1** back to t = 0 h indicated initial formation of **2** and **1** in a ratio of about 80:20. The hypothesis of slow dissolution of $Pd(OAc)_2$ being the prime cause for the initial formation of **2** instead of **1** could therefore be discarded. The origin of the anomalous course of the reaction is possibly related to the nature of $Pd(OAc)_2$ dissolved in methanol. It is well-known that in solution $Pd(OAc)_2$ may occur in various forms. For example, in benzene and toluene $Pd(OAc)_2$ exists as a linear trimer at 39 °C, and as a monomer at 80 °C, while an acetate-bridged cyclic trimer with D_{3h} symmetry is obtained when $Pd(OAc)_2$ is crystallized from benzene.[6] The ^{1}H NMR spectrum of $Pd(OAc)_2$ in methanol shows a large number of signals around δ = 2 ppm for the acetate anion, the relative intensities of the signals being dependent on the concentration and on the water content of the methanol, amongst other factors. This is indicative of the presence of $Pd(OAc)_2$ in a variety of aggregates, $[Pd(OAc)_2]_n$, with n = 1, 2, 3, etc., while even the occurrence of ionic species like $[Pd_n(OAc)_{2n-1}]^+(OAc)^-$ cannot be excluded. Apparently, the kinetically preferred pathways along which these clusters break up give rise to the preferential formation of **2**.

Subsequent conversion of **2** into **1** occurs with first-order kinetics and is acetate-assisted, suggesting the involvement of a single species in the rate-determining step. Taking the involvement of acetate into account, a possible option for this species is the adduct of **2** and acetate, five-coordinated, mono-cationic $[Pd(dppe)_2(OAc)]^+$. However, the difference in the ^{31}P chemical shift between **2** (δ = 58.7 ppm) and [Pd(dppe)$_2$](CF$_3$CO$_2$)$_2$ (**4**, δ = 58.6 ppm) is negligible and does not point to association of an acetate anion in the former. Hence, step-wise dissociation of one of the dppe ligands starting from $[Pd(dppe)_2]^{2+}$ (**2**) seems a more likely pathway. The first, rate-determining step could well be the generation of $[Pd(\sigma,\sigma\text{-dppe})(\sigma\text{-dppe})(S)]^{2+}$, which is rapidly transferred into the more stable $[Pd(\sigma,\sigma\text{-dppe})(\sigma\text{-dppe})(OAc)]^+$, from which the dppe ligand can fully dissociate, possibly via a dppe-bridged dimer of type $[(OAc)Pd(\sigma,\sigma\text{-dppe})(\mu\text{-dppe})Pd(OAc)_2]^+$.

Next, the influence of the preparation procedure on the performance of [Pd(dppe)(CF$_3$CO$_2$)$_2$] (**3**) as a catalyst for CO/ethene copolymerization was investigated. The catalyst was either prepared in situ in methanol, by mixing dppe and $Pd(OAc)_2$, followed by addition of six equivalents of trifluoroacetic acid after about 10 min (run A) or by anion exchange starting from isolated, pure **1** (run B). The CO/ethene copolymerizations were performed under standard catalyst screening conditions (90 °C, 5 MPa) for 2.5 h, in a solvent mixture consisting of methanol and water (98:2). In run A a grey copolymer product was obtained at a productivity of 390 g/g Pd·h, while in run B an almost white product was obtained at much higher productivity (910 g/g Pd·h). This clearly shows that preparation of catalyst **3** in methanol in situ from $Pd(OAc)_2$, ligand and acid is inferior to preparation from pure **1**, which is fully in line with the NMR studies. Interestingly, the ester to ketone end-group ratio in the copolymer products (ca. 45:55) deviated from the theoretical value of 1.[7,8] Formation of an excess of ketone end-groups is probably caused by increased partial initiation via a Pd-H species instead of via $Pd\text{-}OCH_3$. This can occur if initiation via the reactions given in Equations (7) to (10) efficiently competes with those given in Equation (5) and (6).

$$[Pd(P\text{-}P)]^{2+} + MeOH \rightleftharpoons [Pd(P\text{-}P)(OMe)]^{+} + H^{+} \tag{5}$$

$$[Pd(P\text{-}P)(OMe)]^{+} + CO + CH_2{=}CH_2 \rightarrow\rightarrow [Pd(P\text{-}P)\{CH_2CH_2C(O)OMe\}]^{+} \tag{6}$$

$$[Pd(P\text{-}P)(OMe)]^{+} \rightarrow [Pd(P\text{-}P)H]^{+} + CH_2O \tag{7}$$

$$[Pd(P\text{-}P)]^{2+} + H_2O \rightleftharpoons [Pd(P\text{-}P)(OH)]^{+} + H^{+} \tag{8}$$

$$[Pd(P\text{-}P)(OH)]^{+} + CO \rightleftharpoons [Pd(P\text{-}P)\{C(O)OH\}]^{+} \rightarrow [Pd(P\text{-}P)H]^{+} + CO_2 \tag{9}$$

$$[Pd(P\text{-}P)H]^{+} + CO + 2\,CH_2{=}CH_2 \rightarrow\rightarrow [Pd(P\text{-}P)\{CH_2CH_2C(O)CH_2H_3\}]^{+} \tag{10}$$

We also examined the efficiency of in situ catalyst preparation in methanol for some other palladium diphosphane systems. It was found that mixing of equimolar amounts of $Pd(OAc)_2$ and dppbz in methanol at room temp. also initially affords a mixture of monochelate $[Pd(dppbz)(OAc)_2]$ (**5**; δ = 60.3 ppm) and bischelate $[Pd(dppbz)_2](OAc)_2$ (**6**; δ = 56.0 ppm) in a ratio of about 20:80. Subsequent conversion of **6** and unreacted $Pd(OAc)_2$ into **5** proceeded about four times slower ($k = 0.037\ h^{-1}$) than for the dppe counterpart and was inevitably accompanied by plating, as unprotected $Pd(OAc)_2$ is not stable in methanol. As a result, no complete conversion of **6** into **5** took place. As for **1**, the occurrence of autoionization of **5** in methanol was discarded in a separate experiment. No conversion was observed of **5** into **6** and $Pd(OAc)_2$ (h-scale).

Preparation of $[Pd(dppp)(CF_3CO_2)_2]$ in methanol via Equation (1) and (2) was found to proceed smoothly, and no species other than the desired one was observed by ^{31}P NMR spectroscopy. This does not necessarily imply that the bischelate $[Pd(dppp)_2](OAc)_2$ is not an intermediate in the first step. $[Pd(dppp)]_2(OAc)_2$ prepared in situ was found to convert instantaneously into the monochelate $[Pd(dppp)(OAc)_2]$ upon addition of an equimolar amount of $Pd(OAc)_2$, indicating its *kinetic stability* to be much lower than that of its C_2-bridged diphosphane counterparts **2** and **6**.

An anomalous feature was observed whilst monitoring in situ preparation of $[Pd(bdompp)(CF_3CO_2)_2]$ {bdompp = 1,3-bis[di-(*o*-methoxyphenyl)phosphanyl]propane}, the catalyst employed in the manufacture of polyketone on a commercial scale.[9] Mixing $Pd(OAc)_2$ and bdompp in methanol does not afford the monochelate $[Pd(bdompp)(OAc)_2]$ nor the bischelate $[Pd(bdompp)_2](OAc)_2$ as the kinetic product, but a complex mixture of palladium-diphosphane species. It is assumed that these species are oligomeric in nature, but all attempts to characterize these species unambiguously (by NMR spectroscopy and electrospray-MS) failed. Upon standing, the complex mixture slowly converted into monomeric $[Pd(bdompp)(OAc)_2]$. Almost complete conversion (>95%) took more than 16 h at ambient temperature and was accompanied by some plating.

In conclusion, it has been shown that in situ preparation of palladium diphosphane catalysts is not a trivial affair. Instead of the desired mononuclear monochelate catalyst, $Pd(P\text{-}P)X_2$, undesired formation of inactive bischelate (dppe, dppbz) or oligomeric species (bdompp) may occur. This problem may be overcome by rational selection of the solvent in which the catalyst is prepared, or by synthesis and isolation of the $[(P\text{-}P)Pd(OAc)_2]$ intermediate prior to anion exchange in methanol.

Experimental Section

General: The ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra were recorded on Varian GEMINI-300 and Varian INOVA-400 spectrometers operating at 300.1 and 400.0 for ^{1}H, at 75.5 MHz and 100.6 MHz for ^{13}C, and at 121.5 MHz and 161.9 MHz for ^{31}P. Deuterated solvents were used as internal reference, and the ^{31}P data are given in δ units relative to triphenylphosphane (δ = −6 ppm). All chemicals were reagent grade and were used without further purification for synthetic and spectroscopic purposes. The diphosphanes 1,2-bis(diphenylphosphanyl)ethane (dppe), 1,3-bis(diphenylphosphanyl)propane (dppp) and 1,2-bis(diphenylphosphanyl)-benzene (dppbz) were purchased from Strem Chemicals. The diphosphane 1,3-bis[di-(*o*-methoxyphenyl)phosphanyl]propane (bdompp) was synthesized according to literature procedures.[10] The CO/ethene copolymerization reactions were carried out in a 250 mL, magnetically stirred AISI-316 steel batch autoclave.

Synthesis of $[Pd(dppe)(OAc)_2]$ (1): $Pd(OAc)_2$ (0.50 g; 2.23 mmol) was dissolved in 30 mL of dichloromethane and dppe (0.89 g, 2.23 mmol) was added to the filtered red solution, which turned yellow. After 10 min half of the solvent was removed under vacuum and a pale yellow solid precipitated upon addition of diethyl ether. This solid was isolated by filtration and washed twice with diethyl ether. Yield: 1.18 g (85%). $C_{30}H_{30}O_4P_2Pd$ (622.9): calcd. C 57.84, H 4.85; found C 57.89, H 4.91. ^{1}H NMR (CD_3OD): δ = 1.56 [s, 6 H, $CH_3C(O)O$], 2.58 (m, 4 H, CH_2P), 7.60 (m, 12 H), 7.89 (dd, 8 H) ppm. $^{31}P\{^{1}H\}$ NMR (CD_3OD, 20 °C): δ = 63.4 ppm.

Synthesis of $[Pd(dppe)_2](OAc)_2$ (2): dppe (0.32 g; 0.80 mmol) was added to a solution of the isolated complex **1** (0.50 g; 0.80 mmol) in 30 mL of methanol. After 10 min the solution was concentrated to half of the original volume and diethyl ether was added resulting in the precipitation of a yellow solid, which was isolated by filtration and washed twice with diethyl ether. Yield: 0.74 g (90%). $C_{56}H_{54}O_4P_4Pd$ (1021.3): calcd. C 65.85, H 5.33; found C 65.79, H 5.28. ^{1}H NMR (CD_3OD): δ = 1.78 [s, 6 H, $CH_3C(O)O$], 2.79 (m, 8 H, CH_2P), 7.26 (m, 16 H), 7.44 (t, 16 H), 7.61 (t, 8 H) ppm. $^{31}P\{^{1}H\}$ NMR (CD_3OD, 20 °C): δ = 58.7 ppm.

Copolymerization of Carbon Monoxide and Ethene: *Catalyst preparation*. The catalyst was either prepared in situ (run A) by mixing $Pd(OAc)_2$ (2.5 mg, 11 μmol) and dppe (5.6 mg, 12 μmol) in methanol (2 mL), followed by the addition of trifluoroacetic acid (7.8 mg, 68 μmol) after 15 min, or (run B) by mixing isolated $Pd(dppe)(OAc)_2$ (**1**, 7 mg, 11 μmol) and trifluoroacetic acid (7.8 mg, 68 μmol) in methanol (2 mL).

Copolymerization. The reactor was charged with catalyst solution and with 98 mL of a methanol/water mixture (98:2 v/v). After purging the reactor with nitrogen, it was charged with ethene (2.5 MPa) and carbon monoxide (2.5 MPa), and heated to 90 °C. After 2.5 h the reaction was stopped by cooling the reactor rapidly to room temperature and venting the remaining gases. The reaction product was collected by filtration and dried at 55 °C for one day under nitrogen. The isolated grey (run A) or slightly grey copolymer (run B) was weighed and characterized by ^{13}C NMR spectroscopy in C_6D_6/1,1,1,3,3,3-hexafluoro-isopropanol, using $Cr(acac)_3$ as a relaxation reagent, providing M_n, and the methyl ester (**E**) to ethyl ketone (**K**) end-group ratio.[2]

Yield (run A) = 1.08 g, rate = 390 g/g Pd·h, M_n = 6600 Da, **E**/**K** ratio = 42:58, bulk density = 210 g/L; Yield (run B) = 2.27 g, rate = 910 g/g Pd·h, M_n = 4100 Da, **E**/**K** ratio = 45:55, bulk density = 108 g/L.

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