Fluoride-Catalyzed Reduction of Palladium(II) to Palladium(0)−Phosphine Complexes

Patrick A. McLaughlin and John G. Verkade*

Department of Chemistry, Iowa State University, Ames, Iowa 50011-3111

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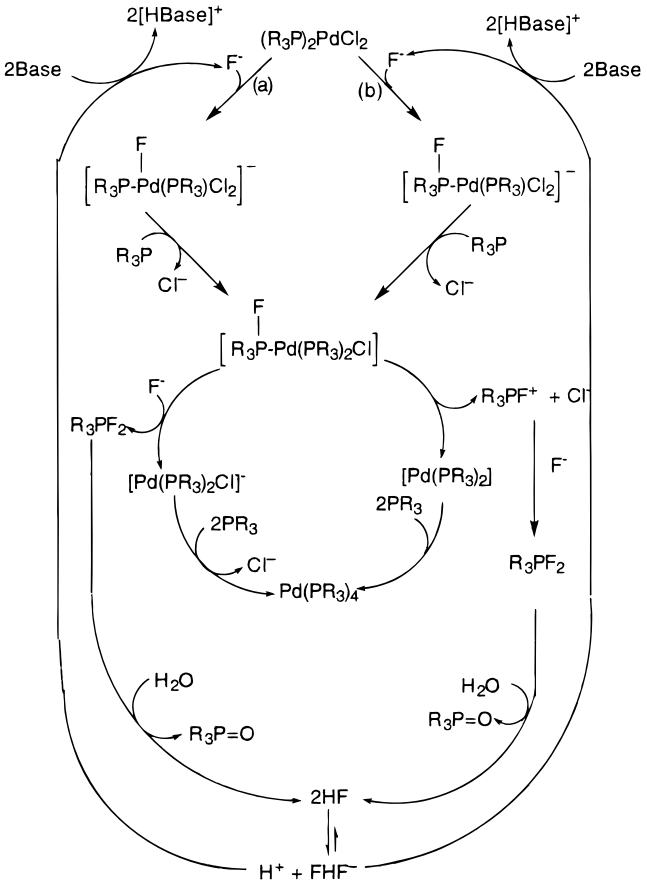
Summary: We demonstrate that in the presence of water and excess PPh_3, fluoride ion catalyzes the reduction of $(Ph_3P)_2PdCl_2$ under mild conditions to $Pd(PPh_3)_4$ in good yields. The inactivation of catalytic F^- by formation of highly stable HF_2^-, and other polyhydrogen fluorides that can form in the reaction, is prevented by adding a strong nonionic base such as $P(MeNCH_2CH_2)_3N$.

Introduction

Tetracoordinate Pd(0)−phosphine complexes are widely used as catalysts in organic synthesis. Interesting among the several routes to these compounds is the formation of a Pd(0) complex in quantitative conversion via a redox transmetalation involving Pd(II) and Pt(0).[1] In more traditional preparations, Pd(II)−halide complexes are reduced to the corresponding bis(diphosphine)Pd(0) or tetrakis(phosphine)Pd(0) analogues with $NaBH_4$ (11% to 68% yields)[2,3] in the presence of the phosphine or diphosphine, or to tetrakis(phosphine)Pd(0) complexes with (toxic) hydrazine in the presence of phosphines (90−95% isolated yields).[3,4] $(PPh_3)_2PdCl_2$ complexes can also be reduced efficiently to $(PPh_3)_4Pd$ by employing NaOH in the presence of a phase-transfer catalyst (84% yield),[5] with alkaline alkoxides (90% yield),[6] or with acetate ion in the presence of excess phosphine (quantitative conversion).[7] Displacement reactions of dba (dba = dibenzylideneacetone) and PPh_3 from $Pd(dba)_2$ and $Pd(PPh_3)_2$, respectively, by $P(CH_2OH)_3$ have been employed to synthesize the water-soluble complex $Pd[P(CH_2OH)_3]_4$ in good yields (89% and 77% yields, respectively).[8] The dicoordinate Pd(0) complex $Pd(PPh_3)_2$ is made by reduction of $Cl_2Pd(PPh_3)_2$ with RLi (quantitative conversion). The $Pd(PPh_3)_2$ can be further treated with PPh_3 to form $Pd(PPh_3)_4$.[9] In addition, the dimer $(Ph_3P)_2Pd_2$ has been synthesized by the treatment of $[Ph_3PPd(OAc)_2]_2$ with H_2 or Na/Hg (95% yields).[10] Finally, $PdCl_2$ has been reduced to $(PEt_3)_4Pd$ by potassium metal in the presence of excess PEt_3 (91% yield).[11]

Scheme 1



In 1992 the novel redox reaction 1 was reported from our laboratories.[12] Here Pd(II) bis−phosphine complexes are reduced to tetrakis(phosphine)Pd(0) complexes while part of the excess phosphine is oxidized to $R_3P{=}O$. The formation of an R_3PF_2 phosphorane intermediate in the reduction and its subsequent reaction with water present in the reaction mixture to give $R_3P{=}O$ (Scheme 1) was demonstrated by NMR spectroscopy.

$$(R_3P)_2PdCl_2 + 2F^- + H_2O + 3PR_3 \rightarrow (R_3P)_4Pd + 2Cl^- + 2HF + R_3P{=}O \quad (1)$$

Although reaction 1 could be taken to imply that fluoride is acting as a catalyst, HF readily forms very robust HF_2^- as well as other stable polyhydrogen fluorides.[13] Evidence for the robustness of these anionic

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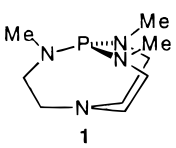
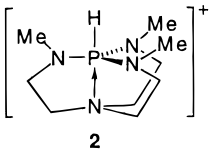
species was the failure to produce any significant product in reaction 1 when an attempt was made to generate fluoride from KHF_2 in the presence of the very strong nonionic base 2-(dimethylamino)pyridine[12] (DMAP, pK_a = 13 in acetonitrile).[14] It was of interest, therefore, to seek a nonionic base of sufficient strength to deprotonate the hydrogen fluoride species in reaction 1, to determine whether fluoride plays a catalytic role.

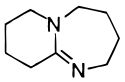
Recently we have been exploring the application of pro-azaphosphatrane **1**, first reported from our laboratories,[15−18] as a superior nonionic base in the synthesis of acylated alcohols,[19] porphyrins,[20] α-C-acylamino acids,[20] trans olefins,[21,22] chiral auxiliary-bearing isocyanides,[23] mono-alkylated *β*-dicarbonyls,[24] and as an efficient catalyst for the trimerization of isocyanates[25] and the protective silylation of alcohols.[26] The very stable conjugate acid **2** of commercially available **1** has a pK_a (41 in MeCN[17]) which is about 17 units larger than the conjugate acid of DBU,[17] a strong nonnucleophilic base widely used in synthetic applications. We show here that reaction 1 is catalytic in fluoride in the presence of the very strong nonionic bases **1**, DBU, and P_4-*t*-Bu; the latter possessing a base strength very comparable to that of **1**.[17] We also report that the tetracoordinated palladium(0) product of reaction 1 is contaminated with ca. 6% of an uncharacterized impurity that can be removed by column chromatography.



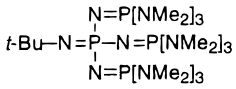
1



2



DBU



P_4-*t*-Bu

Experimental Section

Reagent grade $PdCl_2$ (Aldrich), PPh_3 (Aldrich), the phosphazene base P_4-*t*-Bu (Fluka), and *n*-$Bu_4NCl{\cdot}3H_2O$ (Aldrich) were used as received. DBU (Aldrich) was distilled under reduced pressure (0.07 Torr, 48 °C) prior to use. Pro-azaphosphatrane **1** was synthesized and purified according to literature methods.[16,17] ^{31}P NMR spectra were acquired on a Bruker AC 200 Mz instrument. All organic solvents were distilled under nitrogen. In addition, chloroform was degassed using the freeze−pump−thaw method. All experiments were carried out under an inert atmosphere.

Synthesis of $Pd(PPh_3)_4$ Using Catalytic Fluoride and 1. Method A. $PdCl_2$ (0.100 g, 0.563 mmol) and PPh_3 (0.817 g, 3.11 mmol) were dissolved in 15 mL of DMSO, and the reaction mixture was heated in an oil bath at 140 °C. Heating was discontinued after 15 min (the time required to dissolve all reactants), and a solution of *n*-$Bu_4NF{\cdot}3\ H_2O$ (0.029 g, 0.11 mmol) in 5 mL of DMSO was added via syringe. The remaining water (3.5 μL, 0.19 mmol) was added via a microliter syringe, followed by the addition of **1** (0.25 g, 1.2 mmol) in 5 mL of DMSO. The yellow solution was allowed to cool to room temperature during which time a yellow solid precipitated. Ethanol (30 mL) was added to the vessel, and the reaction mixture was stirred overnight to effect complete precipitation. The product was isolated by filtration and rinsed with two 10-mL portions of cold ethanol (5 °C) and 10 mL of diethyl ether. The product was dried in vacuo (395 mg, 94% crude). This crude mixture was purified using a silica gel column employing degassed chloroform as the eluent (81% yield). ^{31}P NMR ($CDCl_3$) δ 19 (lit.[12] 19), mp: 190−194 °C (lit.[12] 190−194 °C).

Method B. $PdCl_2$ (0.050 g, 0.28 mmol) and PPh_3 (0.370 g, 1.43 mmol) were dissolved in 15 mL of DMSO. The reaction mixture was heated in an oil bath at 80 °C for 15 min (the time required to dissolve all reactants), and then a solution of *n*-$Bu_4NF{\cdot}3\ H_2O$ (0.014 g, 0.054 mmol) in 5 mL of DMSO was added via syringe. The remaining water (2.0 μL, 0.11 mmol) was added via syringe, and this was followed by the addition of **1** (0.12 g, 0.56 mmol) in 5 mL of DMSO. The yellow solution was allowed to cool to room temperature during which time a yellow solid precipitated. Ethanol (30 mL) was added to the vessel, and the reaction mixture was stirred overnight to complete precipitation. The product was isolated by filtration and rinsed with two 10-mL portions of cold ethanol (5 °C) and 10 mL of diethyl ether. The product was dried in vacuo (314 mg, 96% crude and purified as in method A above (82% yield). ^{31}P NMR ($CDCl_3$) δ 19 (lit.[12] 19), mp: 190−194 °C (lit.[12] 190−194 °C).

Synthesis of $Pd(PPh_3)_4$ Using Catalytic Fluoride and P_4-*t*-Bu. This reaction was identical to that in method B, except that P_4-*t*-Bu (0.564 mL of a 1.0 M solution in hexane, 0.56 mmol) was used as a base instead of **1**. The product was isolated as described above, dried in vacuo (294 mg, 90% crude), and purified as in method A above (77% yield). ^{31}P NMR ($CDCl_3$) δ 19 (lit.[12] 19).

Synthesis of $Pd(PPh_3)_4$ Using Catalytic Fluoride and DBU. This reaction was identical to that in method B, except that DBU (0.085 mL, 0.56 mmol) was used as a base instead of **1**. The product was isolated as described above, dried in vacuo (237 mg, 73% crude), and purified as in method A above (62% yield). ^{31}P NMR ($CDCl_3$) δ 19 (lit.[12] 19).

Synthesis of $Pd(dppb)_2$ Using Catalytic Fluoride and 1. Method A. This reaction was the same as that

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which gave $Pd(PPh_3)_4$ in method A above, except that the phosphine used was dppb (0.364 g, 0.854 mmol), and half the molar amounts of $PdCl_2$, **1**, and fluoride were employed. No chromatography was required to give ^{31}P NMR-spectroscopically pure $Pd(dppb)_2$ (187 mg, 69%). ^{31}P NMR (C_6D_6): δ 12 (br) (lit.[12] 12).

Method B. This reaction was identical to that which gave $Pd(PPh_3)_4$ in method B above, except that the phosphine used was dppb (0.364 g, 0.854 mmol), and half the molar amounts of $PdCl_2$, **1**, and fluoride were employed. No chromatography was required to give ^{31}P NMR-spectroscopically pure $Pd(dppb)_2$ (211 mg, 78%). ^{31}P NMR (C_6D_6): δ 12 (br) (lit.[12] 12).

Synthesis of $Pd_2(dppm)_3$ Using Catalytic Fluoride and 1. This reaction was identical to that which gave $Pd(PPh_3)_4$ in method B above, except that the phosphine used was dppm (0.328 g, 0.854 mmol), and no chromatography was required to give ^{31}P NMR-spectroscopically pure $Pd_2(dppm)_3$ (164 mg, 85%). ^{31}P NMR (C_6D_6): δ 14 (br) (lit.[12] 14).

Results and Discussion

Previously, it was demonstrated that stoichiometric F^- in reaction 1 afforded an 80% yield of crude $Pd(PPh_3)_4$ in DMSO as the solvent.[12] In the presence of the strong nonionic bases **1**, P$_4$-*t*-Bu, and DBU, fluoride is observed in the present work to behave catalytically, effecting the transformation of $PdCl_2$ to $Pd(PPh_3)_4$ in DMSO in improved yields of crude product (96%, 90%, and 73%, respectively). The observation of comparable yields of product using **1** ($pK_a = 41$ in acetonitrile[18]) and P$_4$-*t*-Bu ($pK_a = 42$ in acetonitrile[18]) is in accord with the similar strengths of these bases,[17] while the lower yield observed with DBU ($pK_a = 24$ in acetonitrile[18]) can be attributed to its considerable weaker basicity.[18] It may be noted here that unlike P$_4$-*t*-Bu, in which protonation occurs on the imino nitrogen, **1** is protonated on the phosphorus giving **2** (which was observed in the ^{31}P NMR spectrum of the filtrate).

As mentioned above, it has been reported previously that hydroxide anion is capable of reducing Pd(II) in the presence of phosphines to give $Pd(PR_3)_4$.[5] Thus, we tested the possibility that hydroxide in equilibrium 2 is formed in sufficiently high concentration to achieve the reduction of Pd(II) by attempting a preparation of $Pd(PPh_3)_4$ in the presence of **1** but in the absence of

$$\mathbf{1} + H_2O \rightleftharpoons \mathbf{2} + OH^- \qquad (2)$$

fluoride anion (leaving all other conditions identical). However, the ^{31}P NMR spectrum of a solution of the precipitate showed no resonance indicative of the formation of $Pd(PPh_3)_4$. These results are consistent with the postulate we put forth earlier[12] that the catalytic fluoride ion concentration was reduced to ineffective values by HF_2^- and polyhydrogen fluoride formation in our original synthesis.

Whereas $Pd(dbbp)_2$ had previously been isolated in 65% yield using stoichiometric fluoride at 140 °C,[12] it was isolated here in 69% yield using **1** and catalytic fluoride at the same temperature. The yield was further increased to 78% by performing the reaction at lower temperature (80 °C) in the presence of **1** and catalytic fluoride. $Pd_2(dppm)_3$, which had previously been isolated in 86% yield using stoichiometric fluoride at 140 °C,[12] was herein isolated in 85% yield at 80 °C (although a longer reaction time was necessary) using **1** as the base.

An impurity in the $Pd(PPh_3)_4$ amounting to approximately 6% of the mixture was discovered by ^{31}P NMR spectroscopy (δ 33) in carrying out reaction 1 as originally described by us[12] as well as in all of our preparations described here. Column chromatography with degassed chloroform as the eluent permitted removal of this impurity. Thus the best yield of pure $Pd(PPh_3)_4$ obtained in the present work was 82%. Pyridine, acetonitrile, and NMP were investigated as alternative solvents to DMSO for reaction 1 wherein R_3P is Ph_3P, but product yields with both stoichiometric and catalytic fluoride were at most half of what was achieved in DMSO. The impurity in the $Pd(PPh_3)_4$ formed in our reactions may be dicoordinate $Pd(PPh_3)_2$ for which $\delta^{31}P = 31$ ppm has been reported.[27] Although it is conceivable that the impurity is $O_2Pd(PPh_3)_2$ formed by the reaction of the dicoordinate complex with adventitious oxygen, we were unable to find a $\delta^{31}P$ value for this complex in the literature for comparison. The lack of an analogous impurity detectable among the diphosphine tetracoordinate palladium complexes is made reasonable by the generally more robust nature of complexes of chelating versus monodentate ligands.

While the best yield of pure $Pd(PPh_3)_4$ in the present work is less than that obtained with some of the previously reported methods, our present results support our hypothesis that fluoride ion is a catalyst in reaction 1, and that this reaction offers an alternative route to Pd(0) phosphine complexes, at least for chelating phosphine ligands. A unique feature of reaction 1 is that fluoride donates sufficient electron density to the Pd(II) complex to reduce it as the oxidation product R_3PF_2 is formed. The latter subsequently reacts with the weak base H_2O giving $R_3P{=}O$ and liberated fluoride catalyst (Scheme 1). This contrasts similar reactions reported earlier with the more basic anions hydroxide,[5] alkoxide,[6] and acetate,[7] wherein the oxygen in these species serves both as electron donor and as oxygen source for the $R_3P{=}O$ product. The nucleophilic anions in redox reactions involving fluoride, hydroxide,[5] alkoxide,[6] and acetate[7] must attack phosphorus at some point. Whether they do so by migrating to the phosphorus after metal coordination or directly (see paths a and b in Scheme 1 for the present case of the fluoride ion) is not clear. It may be noted that in the reaction involving alkoxide, a second competing pathway involves hydrogen transfer rather than phosphine oxide formation.[6]

Pro-azaphosphatrane **1** appears to be of potentially wide use as a nonnucleophilic base in organometallic and transition metal chemistry owing to its solubility in a wide variety of polar and nonpolar solvents, the ease with which its protonation can be monitored by ^{31}P NMR spectroscopy, its facile recovery from product salts of **2** (which are generally insoluble in nonpolar solvents), and its rather poor metal ligating properties (especially

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when there is an opportunity for a deprotonation reaction to occur) and its commercial availability (Strem). Efforts to expand the utility of **1** and several of its even more basic analogues as deprotonating agents are underway.

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