

Hydrogenolysis of Palladium(II) Hydroxide and Methoxide Pincer Complexes

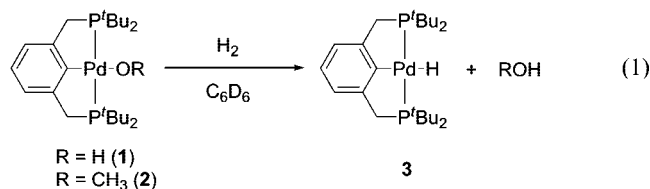
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Hydrogenolysis of late transition metal hydroxides or alkoxides is a seldom documented reaction.^{1,2} Yet this chemical process, resulting in release of water or alcohol and production of a metal hydride, could be a highly valuable combination step of product release and catalyst regeneration within a catalytic cycle.^{1,3} Remarkably, there are few model systems to allow direct investigation of this potentially powerful reaction step.^{3,4} In this contribution, the hydrogenolysis of mononuclear palladium(II) hydroxide and methoxide complexes to generate water and methanol, respectively, and the corresponding palladium(II) hydride is reported. The reactions of the Pd(II) hydroxide and methoxide complexes (^tBuPCP)PdOR (^tBuPCP = 2,6-bis(CH₂P^tBu₂)C₆H₃, R = H (**1**),⁵ R = CH₃ (**2**)) with molecular hydrogen are presented along with the results of experimental and computational mechanistic investigations of the reactions.

The addition of hydrogen (7.0 atm) to a benzene-*d*₆ solution of the palladium hydroxide complex **1** at room temperature resulted in quantitative conversion (>95%) to the palladium(II) hydride (^tBuPCP)-PdH (**3**) and water (eq 1) over a period of 60 h. The reaction progress was easily monitored by NMR spectroscopy; in the ³¹P{¹H} NMR spectrum, the gradual disappearance of the singlet for **1** at 70.8 ppm was noted along with the appearance of another singlet for **3** at 94.5 ppm. Hydride complex **3** has been previously reported, and NMR data for the reaction product matched those of **3**, including a diagnostic virtual triplet in the ¹H NMR spectrum at -3.7 ppm (²J_{HP} = 13.8 Hz).⁶



The kinetic progress of the reaction of **1** with H₂ was followed by integration of the ¹H NMR signals against a hexamethylbenzene internal standard. Each individual reaction of **1** with H₂ was found to obey half-order kinetics with respect to [**1**] (Figure 1). Initially, the observed rate constants at a given pressure of H₂ were not consistent among different kinetic experiments. It was then discovered that when excess water (9 equiv)⁷ was deliberately added to the reaction solutions, the rate constants were highly reproducible, albeit the reactions were slower than without added water. A first-order dependence of the rate on [H₂]⁸ was determined. As shown in Figure 1, at ambient temperature with excess H₂O, doubling the pressure of H₂ from 3.5 to 7.0 atm effected a doubling of the observed rate constant (2.0(1) × 10⁻⁷ M^{-1/2} s⁻¹ to 4.3(3) × 10⁻⁷ M^{-1/2} s⁻¹, respectively).

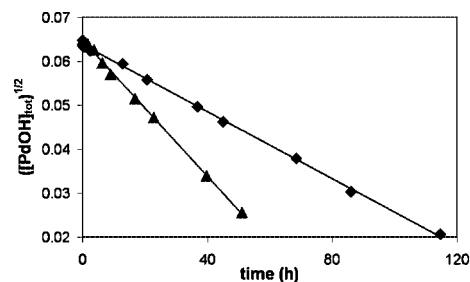


Figure 1. Linear relationship between ([PdOH]_{tot})^{1/2} and time. Kinetic plots for reactions of **1** with 3.5 atm (◆) and 7.0 atm (▲) H₂ are shown.

A half-order rate dependence on a substrate is often associated with dissociation of a dimer and a subsequent reaction step involving the monomer.⁹ An X-ray structural determination of **1** from crystals grown under rigorously anhydrous conditions indicated that **1** is a monomer.¹⁰ Notably, other PCP-type palladium(II) hydroxides were observed to dimerize through bridging water molecules in the solid state.^{5,11} In fact, a crystallographically characterized water-bridged dimeric structure for **1** was recently reported.¹¹ As water is a stoichiometric product in the hydrogenolysis of **1** and reproducible rates were only determined in the presence of water, we also examined crystals of **1** grown in the presence of H₂O.¹⁰ A water-bridged dimeric species [(^tBuPCP)PdOH]₂·4H₂O was found, consistent with the literature.¹¹

The presence of a dimeric species under the hydrogenolysis reaction conditions is consistent with the observed half-order dependence on the total hydroxide concentration [PdOH]_{tot} (eq 2–3). The participation of water in forming this dimer is also consistent with the irreproducibility observed in the initial kinetic studies as the adventitious water concentration should vary in different experiments. The qualitative inhibition of the reaction observed in the presence of added water is expected as water shifts the pre-equilibrium toward the unreactive dimer. A full quantitative study of the concentration dependence on water was not pursued due to the limited solubility of water in benzene.⁷ Thus, our observations are consistent with the mechanism shown in eq 2–3.



The ¹H NMR signals for **1** shift upfield when in the presence of water.¹⁰ Integration of these signals against an internal standard provides a measurement of the total palladium(II) hydroxide concentration, [PdOH]_{tot} (Supporting Information, eq S3). A rate equation in terms of [PdOH]_{tot} was derived¹⁰ (eq 4) where the composite constants $k = k_2/4K'_{\text{eq}}$ and $K'_{\text{eq}} = k_1[\text{H}_2\text{O}]^n/k_{-1}$.

$$\text{rate} = k[\text{H}_2] \left(\sqrt{1 + 8K'_{\text{eq}}[\text{PdOH}]_{\text{tot}}} - 1 \right) \quad (4)$$

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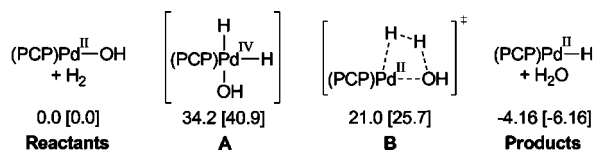


Figure 2. Energies (ΔH [ΔG]) are in kcal/mol for gas phase species. **A** corresponds to the Pd^{IV} intermediate for the oxidative addition/reductive elimination pathway and **B** to the transition state for the four-center intramolecular proton transfer. PCP = $^{\text{Me}}\text{PCP}$ (2,6-bis($\text{CH}_2\text{P}(\text{CH}_3)_2$) C_6H_3).

Since eq 4 does not have an easily handled analytical solution, the kinetic data were fitted by numerical integration using the Runge–Kutta fourth-order method.¹⁰ Best-fit rate constants were obtained for the overall process given in eq 2–3, where $K_{\text{eq}}^{\text{r}} = 1.0 (\pm 0.1) \times 10^3 \text{ M}^{-1}$ and $k_2 = 1.5 (\pm 0.3) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$.

Several mechanisms for the hydrogenolysis of the palladium complex **1** to form **3** and H_2O can be considered. One mechanism is oxidative addition of H_2 to the $\text{Pd}^{\text{II}}\text{-OH}$ complex to form an octahedral Pd^{IV} intermediate, followed by reductive elimination of H_2O to form **3**. Notably, Pd^{IV} complexes have been reported and significant evidence provided for their involvement as intermediates in Pd^{II} -mediated reactions.¹² The second proposed mechanism involves a four-center transition state wherein a proton is transferred intramolecularly from a coordinated dihydrogen to the oxygen.^{13,14} Both of these pathways could proceed via the initial coordination of H_2 to the 16 electron palladium center. Notably, as a cationic dihydrogen complex of the $^{\text{tBu}}\text{PCP}$ platinum system is known,¹⁵ a third mechanism would be the dissociation of the OH^- ligand, H_2 coordination, and deprotonation by the resulting OH^- to form water and the $\text{Pd}^{\text{II}}\text{-H}$. However, if hydroxide dissociation were involved as a preliminary step, the addition of excess water to the reaction would be expected to increase,¹⁶ rather than decrease the rate of reaction as was confirmed experimentally.

In the absence of observable intermediates, it is challenging to distinguish between the remaining two pathways. Insight into the mechanism of the reaction was thus sought via computational methods. B3LYP density functional theory was used to compare the energetics of the pathways.¹⁰ As illustrated in Figure 2 for the model PCP complex, the four-center transition state (**B**) was found to be significantly lower in energy than the oxidative addition intermediate (**A**). Notably the involvement of the oxygen lone pair distinguishes path **B** from a true σ -bond metathesis.¹⁴

When a solution of **3** was heated at 65 °C in C_6D_6 in the presence of a 40-molar excess of H_2O , no changes were detected by ^1H NMR spectroscopy, indicating that the hydrogenolysis reaction is thermodynamically favored. However, heating **3** at 60 °C in the presence of a 40-molar excess of D_2O for 4 days led to deuterium scrambling into **3** (>95%) to form the corresponding palladium deuteride (**3-d**₁). A possible mechanism for this H/D exchange involves the microscopic reverse of the IES pathway.¹⁴ Alternately, the protonation of **3** by D_2O to form a palladium H–D intermediate,¹⁷ followed by the rapid deprotonation by the resulting deuterioxide ion could lead to the $\text{Pd}\text{-D}$ product.

While we have not yet fully explored the generality of this hydrogenolysis reaction, the palladium(II) methoxide complex, ($^{\text{tBu}}\text{PCP}$)- PdOCH_3 (**2**), was found to react similarly with H_2 to produce methanol and **3**. Complex **2** was prepared in an analogous fashion to **1** and characterized by elemental analysis, NMR spectroscopy, and X-ray crystallography.¹⁰ Complex **2** is a rare example of a crystallographically characterized monomeric palladium alkoxide with the few other reported structures having fluorinated substituents on the alkoxide ligand.¹⁸ The reaction of H_2 (7.0 atm) with **2** in C_6D_6 yields complex **3** and methanol (eq 1) over a period of days at room temperature. Both products were observed in 96% yield by ^1H NMR spectroscopy. The use of D_2 gas resulted in the formation of **3-d**₁ confirming that

the H_2 (or D_2) is the source of the $\text{Pd}\text{-H}$ (or D). The observation of similar reactivity with $\text{Pd}\text{-OR}$ ($\text{R} = \text{H}$, $\text{R} = \text{Me}$) is promising for the development of this class of reactions.

In summary, the reaction of dihydrogen with a $\text{Pd}(\text{II})$ hydroxide to produce a $\text{Pd}(\text{II})$ hydride and water has been observed. Similar reactivity was also observed with the $\text{Pd}(\text{II})$ methoxide complex. Kinetic studies of the reaction of **1** reveal a half-order dependence on $[\text{PdOH}]_{\text{tot}}$ and a first-order dependence on $[\text{H}_2]$. The kinetics are consistent with the formation of a water-bridged hydroxide dimer which must dissociate to form the monomer prior to reaction with H_2 . DFT computational results suggest an intramolecular proton transfer as a lower energy pathway than an oxidative addition/reductive elimination mechanism for reaction of the monomer with H_2 . Hydrogenolysis of metal hydroxides or alkoxides allows regeneration of $\text{M}\text{-H}$ complexes from $\text{M}\text{-OR}$ complexes and thus may find significant utility in catalytic cycles.

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Supporting Information Available: Characterization data for **2** and **3-d**₁, experimental details, computational methodology, X-ray crystallographic data files in CIF format for **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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