



Article The Role of Non-Covalent Interactions in the Reactions between Palladium Hydrido Complex with Amidoarylphosphine Pincer Ligand and Brønsted Acids

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Abstract: The interaction between (PNP)PdH (1); PNP = bis(2-diisopropylphosphino-4-methylphenyl)amide and different acids (CF₃SO₃H, HBF₄·Et₂O, fluorinated alcohols and formic acid) was studied in benzene or toluene as well as in neat alcohols by IR and NMR spectroscopies. The structures of hydrogen-bonded complexes were also optimized at the DFT/ ω B97-XD/def2-TZVP level. The nitrogen atom of the amidophosphine pincer ligand readily accepts proton not only from strong Brønsted acids but from relatively weak fluorinated alcohols. That suggests that binding to palladium(II) increases the diarylamine basicity, making it a strong base. Nevertheless, H⁺ can be taken from [(PN(H)P)PdH]⁺ (2) by pyridine or hexamethylphosphoramide (HMPA). These observations confirm the need for a shuttle base to form [(PN(H)P)PdH]⁺ (2) as the result of the heterolytic splitting of H₂ by [(PNP)Pd]⁺. At that, a stoichiometric amount of formic acid protonates a hydride ligand yielding an unstable η^2 -H₂ complex that rapidly converts into formate (PNP)Pd(OCHO), which loses CO₂ to restore (PNP)PdH, whereas the relatively high acid excess hampers this reaction through competitive protonation at nitrogen atom.

Keywords: palladium hydride; pincer ligand; hydrogen bonding; non-covalent interactions; reaction mechanism; proton transfer; formic acid dehydrogenation

1. Introduction

Homogeneous catalysis allows the implementation of many practically important and fundamentally interesting processes under relatively mild conditions. Many systems developed through the years rely on transition metal complexes, and in recent years, a lot of attention has been devoted to complexes based on pincer-type ligands [1–3]. Pincer ligands are defined as chelating ligands that bind through three adjacent donor sites in a meridional geometry. Featuring structural and electronic variability and a versatile fine-tuning of chemical properties, they give high thermal stability to transition metal complexes and well-defined reactivity to the available coordination sites. A plethora of complexes described operate using metal–ligand cooperation when the electrophilic metal center and the nucleophilic ligand site allow for the heterolytic splitting of polar (e.g., O–H, N–H) and nonpolar (e.g., H₂) bonds [4]. These steps are important for (de)hydrogenative transformations which span from a reduction in multiple bonds to a controlled release and fixation of dihydrogen for sustainable chemical energy storage [5,6].



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). The title palladium hydride complex with a diarylamido bis(phosphine) pincer ligand—(PNP)PdH, where PNP is bis(2-diisopropylphosphino-4-methylphenyl)amide—has been originally described by Ozerov and coworkers [7]. Its cationic [(PNP)Pd]⁺ fragment bearing p-lone pair at nitrogen (although delocalized over the diarylamide π -system) and an empty σ -orbital at Pd has been considered as related to the frustrated Lewis pairs [8]. Being interested in transition metal hydrides' chemistry and transition-metal-based FLPs, we explored the interaction of (PNP)PdH (1) with different acids to gain a deeper understanding of its basicity and its potential as a bifunctional catalyst.

2. Results and Discussion

2.1. (PNP)PdH Interaction with Strong Brønsted Acids TfOH and HBF₄, Chemical Properties of [(PN(H)P)PdH]⁺

It has been shown that (PNP)Pd-OTf is able to heterolytically split various X-H bonds including H₂, yielding in the latter case [(PN(H)P)PdH]⁺ species (**2**, Scheme 1) [8]. According to the accompanying DFT studies, the proton transfer from a coordinated H₂ (or another HX) to the amido-nitrogen of the PNP ligand should proceed with the assistance of an exogenous Brønsted base.



Scheme 1. Dihydrogen addition to cationic palladium complex 3. A = OTf.

Our study showed that cationic complex **2** can be also obtained via the protonation of (PNP)PdH (**1**) [9] with trifluoromethanesulfonic acid (TfOH; $pK_a = 0.7$ in MeCN [10]) or HBF₄·Et₂O ($pK_a = 3.4$ in DMF [11]). The NMR signals of the protonation products **2**[**OTf**] ($\delta_{PdH} = -12.04$, $\delta_{NH} = 10.41$, $\delta_P = 56.7$ in C₆D₆) and **2**[**BF**₄] ($\delta_{PdH} = -12.12$, $\delta_{NH} = 9.53$, $\delta_P = 56.9$ in toluene- d_8 ; Tables S1 and S2) are in agreement with that previously reported [8]. In IR, spectra protonation leads to the high-frequency shift of Pd-H stretching vibration from $v_{PdH}(1) = 1923$ cm⁻¹ to 1992 (**2**[**BF**₄]) or 1991 cm⁻¹ (**2**[**OTf**]). For **2**[**OTf**], the N-H stretching vibration band v_{NH} was also identified at 2811 cm⁻¹ (Figure S1). In the absence of a hydrogen atmosphere, **2**[**OTf**] and **2**[**BF**₄] appear moderately stable in solution, slowly evolving H₂. According to ³¹P NMR monitoring, ca. 40% of **2**[**OTf**] converts into (PNP)Pd-OTf ($\delta_P = 53.1$) in 7 days, whereas **2**[**BF**₄] decomposes slower, losing only 20% in six days. As dihydrogen evolution is only possible through the backward shuttling of the proton from nitrogen to hydride and the formation of the η^2 -H₂ complex, these observations evidence the participation of the triflate anion as a proton shuttle [12] in H₂ heterolytic splitting and backward transfer from NH to the hydride ligand (Scheme 2).

Cationic complex **2** can be deprotonated not only by a strong base such as Et₃N [8] $(pK_a(Et_3N-H^+) = 18.83 \text{ in MeCN [13]})$ but by moderately basic ones: the addition of the equimolar amount of pyridine (Py, $pK_a(Py-H^+) = 12.53$ in MeCN [13], Figure S2) or 10-fold excess hexamethylphosphoramide (HMPA ($pK_a(HMPA-H^+) = 6.1$ in MeNO₂ [14]) in toluene completely shifts the equilibrium toward (PNP)PdH (1). Much weaker base acetonitrile is not able to deprotonate **2**; the reaction stops at the first step—the formation of the hydrogen-bonded complex with the N-H group of **2** (**2**···B, Scheme 2), evident from a small higher frequency shift of Δv_{PdH} (**2**) vibration (v_{PdH} (NH···B) = 1996 cm⁻¹; $\Delta v_{PdH} = 4 \text{ cm}^{-1}$; Figure S3). The high-frequency shift of v_{PdH} upon the formation of a hydrogen bond with a base was confirmed by DFT calculations (*vide infra*).



Scheme 2. (PNP)PdH (1) interaction with Brønsted acids. Molecular structure of 1 is shown with the thermal ellipsoids at 30% probability. Hydrogen atoms except the hydride ligand are omitted for clarity. Selected bond lengths (in Å) and angles (in deg.): Pd(1)-H, 1.84(3), Pd(1)-P(1) 2.2589(6), Pd(1)-P(2) 2.2604(7), Pd(1)-N(1) 2.0855(9), P(1)-Pd(1)-P(2) 164.88(2), N(1)-Pd(1)-H 177.5(8). B = base.

2.2. Interaction with Fluorinated Alcohols

To study the proton transfer equilibria involving **1** in more detail, we used moderately strong acids—fluorinated alcohols (CF₃)_nCH_{3-n}OH (n = 1–3). The most acidic of them, perfluorinated *tert*-butanol (CF₃)₃COH (PFTB, pK_a = 20.5 in CH₃CN [10]), protonates the nitrogen atom of **1**. Taken in a slight excess (5 equiv.) at 190 K in toluene, it creates changes in the IR spectra similar to those observed with TfOH: new hydride (ν_{PdH} = 1994 cm⁻¹) and N-H (ν_{NH} = 2806 cm⁻¹) stretching vibration bands appear (Figures 1 and S4). Under these conditions, only half of the hydride complex **1** is protonated, and the equilibrium shifts back to the starting compounds upon warming to 250 K, restoring the intensity of the ν_{PdH} (**1**) band (Figure S5). These spectral changes allow the estimation of the equilibrium constant and the calculation of thermodynamic parameters for the proton transfer to the nitrogen atom of the PNP ligand (Figure S6): $\Delta H^{\circ} = -2.6 \text{ kcal} \cdot \text{mol}^{-1}$, $\Delta S^{\circ} = -9.8 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$.



Figure 1. IR spectra in the PdH stretching vibrations region of (PNP)PdH at 190 K (c = 0.032 M in toluene- d_8 ; blue, normalized intensity*), with 5 equiv. PFTB in toluene- d_8 at 190 K (purple), and in neat PFTB at 295 K (c = 0.032 M; green). Green dashed lines show the result of the band deconvolution. *—multiplied to make the intensity of $\nu_{PdH}(1)$ band equal to the intensity in the maximum point (1928 cm⁻¹) for ν_{PdH} in 1/PFTB mixture.

Interestingly, in neat PFTB, we observed a composite band (Figure 1) built by overlapping the $v_{PdH}(2[OC(CF_3)_3])$ band at 1994 cm⁻¹ and a new band at even higher frequencies $v_{PdH} = 2013 \text{ cm}^{-1}$. The corresponding v_{OH} band at 3268 cm⁻¹ (Figure S4) is shifted to a lower frequency relative to the band of free alcohol $v_{OH}(PFTB) = 3470 \text{ cm}^{-1}$ which suggests its involvement in a hydrogen bond [15].

The alcohol of the lowest acidity in the series—2,2,2-trifluoroethanol (TFE; $pK_a = 35.3$ in MeCN [16])—binds to a hydride ligand forming the dihydrogen-bonded complex (PNP)PdH···HOCH₂CF₃. The addition of the 30-fold excess TFE to the solution of **1** in toluene at 190 K leads to a low-frequency shift of its v_{PdH} band from 1928 cm⁻¹ to 1924 cm⁻¹ (Figure 2). Under similar conditions, ¹H NMR spectra reveal a broadening and high-field shift of hydride resonance from δ_H –10.42 to –10.66 ppm at 295 K typical for dihydrogen bond formation [15]. The use of very large TFE excess (465 equiv., taken as 2/1 v/v mixture with benzene) not only makes these changes more pronounced but also allows us to observe the N-protonated species characterized by the v_{PdH} band at 2009 cm⁻¹ (Figure 2). The latter frequency is again higher than that of the v_{PdH} (**2[OTf]**) band.



Figure 2. IR spectra (normalized intensities) in the v_{PdH} stretching vibrations region of (PNP)PdH (c = 0.04 M; blue) * and (PNP)PdH in the presence of 30 equiv. TFE (purple) at 190 K; (PNP)PdH (c = 0.04 M; sky blue) ** and (PNP)PdH in the presence of 465 equiv. TFE (green) *** at 295 K. Toluene- d_8 , l = 0.1 cm. *—multiplied to make the intensity of the $v_{PdH}(1)$ band at 190 K (blue line) equal to that in the mixture with 30 equiv. TFE. **—multiplied by the same coefficient as applied to blue line. ***—multiplied to make the intensity in the maximum point (1923 cm⁻¹) equal to that of the $v_{PdH}(1)$ band at 295 K (sky blue line).

The use of (CF₃)₂CHOH (HFIP; pK_a = 29.9 in MeCN [16]), the acidity of which is intermediate between PFTB and TFE, allows us to observe a whole variety of hydrogenbonded and protonated species. At four-fold excess HFIP at 190 K, we observe in the IR spectra the lower frequency shoulder for the $v_{PdH}(1)$ band due to dihydrogen bonding (PNP)PdH···HOCH(CF₃)₂ and a band of the protonated complex $v_{PdH}(2[OCH(CF_3)_2])$ at 1998 cm⁻¹ (Figure 3). The formation of a dihydrogen-bonded complex under these conditions is confirmed by NMR spectra. The hydride resonance in ¹H NMR spectra broadens and shifts high-field by 0.28 ppm ($\delta_{PdH}(1) = -10.18$, $\delta_{PdH}^{H···H} = -10.46$ in toluene- d_8 at 190 K; Figure 4) while its longitudinal spin-lattice relaxation time T₁ decreases from 784.0 ms to 605.4 ms. At the same time, the singlet in the ³¹P NMR spectrum shifts to a stronger field by -0.26 ppm ($\delta_P(1) = 58.25$, $\delta_P^{H···H} = 57.99$; Figure 4). NMR and IR spectra also confirm the presence of a protonated complex 2[OCH(CF₃)₂], the resonances of which ($\delta_{PdH} - 12.33$, $\delta_P 54.29$) disappear at 220 K (Figures 4 and S7).



Figure 3. IR spectra (normalized intensities) in the v_{PdH} stretching vibrations region of (PNP)PdH at 190 K (c = 0.025 M; blue) *, in the presence of 4 (red) * and 8 (purple) equiv. HFIP at 190 K in toluene- d_8 , and in neat HFIP at 295 K (c = 0.025 M; green). Dashed lines are the result of band deconvolution; grey dashed line is for the HFIP band. * —multiplied to make the intensity of v_{PdH} (1) band equal to that in the mixture with 8 equiv. HFIP.



Figure 4. ¹H (300 MHz, left) and ³¹P{¹H} (121.5 MHz, right) NMR spectra of (PNP)PdH (1) at 190 K (bottom line) and 290 K (top line) and in the presence of 4 equiv. HFIP in 190–290 K temperature range. c(1) = 0.04 M, toluene- d_8 .

The increase in the HFIP excess shifts the equilibrium toward species **2** protonated at nitrogen atom: in the presence of 8 equiv. HFIP, the new high-frequency band appears in the IR spectra at 190 K composed of two bands (Figure 3) — $v_{PdH} = 1998 \text{ cm}^{-1}$ belonging to [(PN(H)P)PdH]⁺[OCH(CF₃)₂]⁻ (**2[OCH(CF₃)**₂]) and a second band at 2015 cm⁻¹. The latter species become dominant when **1** is dissolved in the neat HFIP (Figure 3).

Thus, (PNP)PdH (1) can form a dihydrogen bond (PNP)PdH···HA with relatively weak proton donors, which should precede the proton transfer to a hydride and the formation of an η^2 -H₂ species and dihydrogen evolution [15,17]. However, this reaction does not occur in the case of fluorinated alcohols, and the proton goes instead to the nitrogen atom

of the amidophosphine pincer ligand (Scheme 3). The complexes **2**[**A**] are characterized by a separate hydride resonance at ca. -12 ppm for all HA used, but the signal of their NH proton is clearly visible at ca. 10 ppm only for weakly binding anions—OTf⁻ and BF₄⁻. Interestingly, the corresponding v_{PdH} band changes its position depending on the acid used shifting from 1991 cm⁻¹ for OTf⁻ to 1998 cm⁻¹ for OCH(CF₃)₂⁻ (Table S1). Such a shift can be explained by hydrogen bonding NH⁺…A⁻ within the ion pair if we recall that the hydrogen bonding of **2**[**OTf**] with acetonitrile, NH⁺…NCMe, also leads to a small high-frequency shift of v_{PdH}(**2**[**OTf**]) (*vide supra*).



Scheme 3. The mechanism of (PNP)PdH (1) interaction with acids.

Another puzzling question is the nature of the complexes observed at high alcohol content, in which v_{PdH} bands are observed above 2000 cm⁻¹. We thought this effect could be caused by the hydrogen bonding of NH⁺ with the oxygen atoms of alcohols. To verify this hypothesis, we studied the interaction of HFIP with [(PN(H)P)PdH]⁺ (2) obtained by the reaction with HBF₄·Et₂O. An addition of 10 equiv. HFIP causes a high-frequency shift of v_{PdH} by 5 cm⁻¹ ($v_{PdH}(2\cdots AH) = 1997 \text{ cm}^{-1}$) (Figure 5), whereas the progressive increase in HFIP excess shifts the v_{PdH} band further to 2003 cm⁻¹ (Figure 5). Based on DFT calculations on the example of 2TFE·[(PN(H)P)PdH]⁺ (*vide infra*), we assign this band to a hydrogen-bonded complex of **2** with two molecules of HFIP, in which an oxygen atom of one alcohol molecule interacts with a NH proton and the second one bridges it with Pd-H (Figure 6).



Figure 5. IR spectra in the v_{PdH} stretching vibrations region of $[(PN(H)P)PdH]^+[BF_4]^-$ (**2**[**B**F₄], c = 0.02 M) (red), with 10 (sky blue), 20 (purple), 30 (yellow), and 50 (orange) equivalents of HFIP in benzene-d₆ and in neat HFIP (green), 295 K, l = 0.1 cm.



Figure 6. Hydrogen bonding cycle in trimolecular complex $2R^{F}OH \cdot [(PN(H)P)PdH]^{+}$ and DFT optimized structure of $2 \cdots (TFE)_{2}$. Key distances (in Å) are given. Aryl and *i*-propyl groups of the pincer ligand are shown as a wireframe.

2.3. DFT Calculations

To rationalize the observed spectral behavior, we performed the DFT calculations on possible intermolecular adducts formed by **1** and **2** with acids and bases in toluene. Neutral hydride **1** readily forms hydrogen bonds with alcohols (exemplified by TFE) binding to the N atom as well as the hydride ligand (Figure 7) with nearly the same energy (ca. -9 kcal/mol on the ΔE scale; Table S3). The formation of an OH…N complex entails a high-frequency shift of v_{PdH} ($\Delta v_{PdH} = 18 \text{ cm}^{-1}$) in contrast to the low-frequency shift found for dihydrogen-bonded PdH…HO ($\Delta v_{PdH} = -34 \text{ cm}^{-1}$; Table S3). It is worth noting that in the dihydrogen-bonded complex, the alcohol molecule approaches the hydride ligand in the direction orthogonal to the PNPPdH plane as reflected by the PdHH angle close to 90° while the OHH moiety is almost linear (Figure 7). Such geometry is not typical for group 10 metal hydrides [18] and was found for the platinum hydrido complexes featuring the significant impact of alcohol binding to the core metal [19].



Figure 7. DFT-optimized structures of hydrogen-bonded complexes between 1 and TFE. Key distances (in Å) and angles (in deg.) are given. Aryl and *i*-propyl groups of the pincer ligand are shown as a wireframe.

For cationic complex **2**, the computed frequency of Pd-H stretching vibration is 35 cm⁻¹ higher than that for neutral **1** (Table S4). This difference is smaller than observed experimentally, probably because the calculations are performed for the "naked" cation and do

not take into account solvation and counter-ion influence. Complex **2** can interact both with acids and bases, the reactivity toward the base being more pronounced. The model base—pyridine—effectively binds the NH⁺ proton ($\Delta E = -12 \text{ kcal/mol}$) leading to the high-frequency shift of v_{dH} by 9 cm⁻¹ relative to the naked cation **2**. Alcohol (TFE was considered as a model) interacts with **2** either as a base forming a NH⁺…O(H)R hydrogen bond or as an acid forming a hydrogen bond between the OH group and the PdH moiety, with the geometry resembling that of the dihydrogen-bonded complex of **1** with a slight inclination to the hydride ligand (Figure 8). Notably, both the OH…HPd and NH⁺…O(H)R interactions have nearly the same energy ($\Delta E \approx -7 \text{ kcal/mol}$) and lead to high-frequency shifts of v_{PdH} band (+36 and +9, respectively; Table S4). As we observed additional high-frequency shifts of v_{PdH} (**2**) in the presence of excess alcohol in the experimental IR spectra (), we considered also a cyclic complex with two TFE molecules (**2**…(TFE)₂, Figure 6), which appeared much more energetically favorable ($\Delta E = -18.5 \text{ kcal/mol}$) than the OH…HPd and NH⁺…O(H)R bonds of **2** and also give a high-frequency shift of v_{PdH} (**2**).



Figure 8. DFT optimized structures of hydrogen-bonded complexes between **2** and TFE. Key distances (in Å) and angles (in deg.) are given. Aryl and *i*-propyl groups of the pincer ligand are shown as a wireframe.

2.4. Interaction with Formic Acid

The acidity of formic acid (p $K_a = 20.9$ in CH₃CN [20]) is comparable to that of PFTB. Surprisingly HCOOH exhibits a very peculiar reactivity in respect of 1 that depends on the acid excess. Taken closely to the stoichiometric amount (0.5–2.0 equiv. HCOOH to 1), it undergoes dehydrogenation to give CO₂ and H₂ (Equation (1)). The reaction can be followed by IR spectroscopy which shows the accumulation of CO₂ (the v_{CO2} band is visible in toluene- d_8 ; Figures S10 and S11) and the consumption of formic acid (FA, Figure S12). Analysis of the v_{CO} (FA^{monomer}) band intensity changes shows the increase in the reaction rate and the increase in the FA excess up to two equivalents. However, a further increase in the acid content leads to a slower reaction and a very long time to reach a full conversion (more than 72 h for a 10/1 ratio FA/1). The absorbance of FA bands can be converted into concentration, and its dependence on time is linear in the zero-order coordinates [FA^{monomer}] vs. *t* (Figures S13 and S14) yielding reaction rate constants of ca. 10^{-7} M⁻¹·s⁻¹ (Table 1).

$$\begin{array}{ccc} \text{HCOOH} & \stackrel{1}{\rightarrow} & \text{CO}_2 + \text{H}_2 \\ & \text{benzene} \\ & \text{or toluene} \end{array} \tag{1}$$

FA Amount, Equiv.	$k_{e\!f\!f},{ m M}^{-1}{\cdot}{ m s}^{-1}$	t of Full FA Conversion
0.5	$3.5 \cdot 10^{-7}$	40 min
1	$3.5 \cdot 10^{-7}$	40 min
2	$4.1 \cdot 10^{-7}$	2.5 h
5	$9.1 \cdot 10^{-8}$	more than 24 h
10		Ca. 10% conversion after 3 days

Table 1. Kinetic data for formic acid dehydrogenation in presence of (PNP)PdH.

Both IR and NMR spectra show different forms of palladium complexes depending on the FA amount added. In the presence of 1–2 equiv. FA, the palladium hydride partially transforms into formate (PNP)Pd(OCHO) (3; Figure S15). Its NMR signals change their position in the course of the reaction shifting upon the FA consumption: $\delta_{\rm H}$ (Pd-OCHO) = 8.24 (in the beginning, 7 min after mixing), 8.21 (in the end, 160 min), $\delta_P = 49.1$ (12 min) and 48.0 (160 min) (Figure S16). That can be due to hydrogen bonding (PNP)Pd-OCHO···HOOCH that assists the formic acid dehydrogenation [21]. A further increase in the acid content initiates the proton transfer to the nitrogen atom of (PNP)PdH. At a 10-fold FA excess, the palladium complex exists in two forms: protonated [(PN(H)P)PdH]⁺[OCHO]⁻ (2[OCHO], v_{PdH} = 1993 cm⁻¹, δ_{PdH} –11.94, δ_{NH} 10.70, δ_{P} 56.5) and (PNP)Pd-OCHO (Figure S17). The latter is hydrogen-bonded to the acid excess as suggested by the shift in its signals: δ_H (Pd-OCHO = 8.27 and δ_P = 49.9–50.2 relative to non-bonded **3** (8.21 and 48.0 ppm, respectively; Figures S16 and S17). At the very beginning of the reaction, the low-frequency shifted v_{PdH} at 1917 cm⁻¹ (Figure S15) and δ_{PdH} -11.8 (Figure S17) are visible in the spectra which could be due to the formation of hydrogen-bonded species featuring Pd-H···HOOCH, N…HOOCH, and NH⁺…OCHO⁻ bonds.

Dihydrogen bonding (PNP)PdH···HOOCH ($\delta_{PdH} = -10.26$, $\delta_P = 57.9$) precedes the proton transfer to a hydride ligand and formation of an unstable η^2 -H₂ complex that immediately loses H₂ to yield palladium formate. The latter loses CO₂, restoring the starting (PNP)PdH (**1**) (Scheme 4). This FA dehydrogenation reaction is the only one that occurs with **1** at close to a stoichiometric amount of formic acid (1–2 equiv.). A very fast formation of formate **3** and zero-order reaction kinetics suggest the β -hydride migration and CO₂ elimination is a rate-determining step (**rds**, Scheme 4).



Scheme 4. The mechanism of (PNP)PdH (1) interaction with formic acid.

At higher FA excess, the competing protonation of the ligand's nitrogen takes place, withdrawing the hydride 1 from the dehydrogenation reaction. Based on the data described herein, we can argue that involvement of the formic acid excess in various hydrogen bonds, such as NH⁺···O=CHOH, N···HOOCH, PdH···HOOCH, Pd-OCHO···HOOCH, and their combination, hampers the dehydrogenation reaction. The experiments with the portioned addition of HCOOH (by 2 equiv.) to 1 show that avoiding the presence of high FA excess allows running at least three cycles before the reaction slows down.

3. Materials and Methods

All reactions were performed using standard Schlenk procedures under a dry argon atmosphere. Dry and oxygen-free organic solvents (toluene, heptane, pentane, THF, CH₂Cl₂, ethanol) were obtained using a solvent purification system from M. Braun (Garching, Germany). Deuterated solvents (toluene-d₈, benzene-d₆) for NMR and IR were degassed before use by three freeze–pump–thaw cycles and kept over 3 Å molecular sieves. A liquid nitrogen/isopropanol slush bath was used to maintain samples at the desired low temperature.

Variable-temperature (VT) NMR spectra were recorded on Bruker Avance 300, Bruker Avance 400 (Bruker, Billerica, MA, USA), and Varian Inova 400 (Varian, Palo Alto, CA, USA) spectrometers operating at 300 and 400 MHz in the 180–300 K temperature range. ¹H chemical shifts are reported in parts per million (ppm) downfield of tetramethylsilane (TMS) and were calibrated against the residual resonance of the deuterated solvent, while ³¹P{¹H} chemical shifts were referenced to 85% H₃PO₄ with downfield shift taken as positive. The IR spectra were recorded at different temperatures (190–295 K) using a home-modified cryostat (Carl Zeiss Jena) with a Nicolet iS50 FTIR (Thermo Scientific, Waltham, MA, USA) spectrometer using 0.05–0.2 cm CaF₂ cells. The accuracy of the experimental temperature adjustment was ± 0.5 °C. The cryostat modification allowed the transfer of the reagents (premixed at either low or room temperature) under an inert atmosphere directly into the cells.

All reagent-grade chemicals purchased from commercial sources were used as received.

Complex (PNP)PdH (1) was prepared as described in the literature [7]. Complex 1 was crystalized from the toluene/hexane mixture at -35 °C. Crystals of 1 (C₃₃H₄₉NP₂Pd, M = 628.07) were monoclinic, space group P2₁/c, at 100 K: a = 12.1794(2), b = 9.6190(2), c = 27.9618(5) Å, β = 94.7130(10)°, V = 3264.75(10) Å³, Z = 4 (Z' = 1), d_{calc} = 1.278 gcm⁻³, μ (MoK α) = 6.87 cm⁻¹, F(000) = 1320. Intensities of 167,806 reflections were measured with a Bruker Quest D8 CMOS diffractometer [λ (MoK α) = 0.71073 Å, ω -scans, 2 θ < 90°], and 26,761 independent reflections were used in further refinement. Using Olex2 [22], the structures were solved with the ShelXT structure solution program [23] using Intrinsic Phasing and refined with the XL refinement package [24] using least-squares minimization. The hydrogen atom at the metal ion was located from the difference Fourier synthesis and refined in the isotropic approximation. The positions of other hydrogen atoms were calculated, and they were refined in the isotropic approximation within the riding model. The refinement converged to wR2 = 0.1038 and GOF = 1.070 for all the independent reflections with I > 2 σ (I)). CCDC 2257866 contains supplementary crystallographic information.

Structures of reactants and complexes were optimized at the ω B97-XD level [25] applying the def2-TZVP basis set [26] by Gaussian 09 [27]. Optimizations were performed without any restriction in the gas phase and then in toluene introduced by the SMD solvent model [28]. Vibrational frequencies were calculated for all optimized complexes at the same level of theory to confirm a character of local minima on the potential energy surface. Frequencies are reported without any scaling factors.

a. General procedure for the interaction of **1** with TfOH and HBF4 and of **2** with bases

The solution of (PNP)PdH (1, c = 0.02-0.06 M) was prepared at inert atmosphere at room temperature in toluene, toluene-d₈ or benzene-d₆. Then, it was placed into a cell (0.05-0.2 cm, for IR measurements) or into an NMR tube (for NMR measurements) under an inert atmosphere. After spectra of the initial complex were acquired, the necessary amount

of stock acid solution (1 M, to obtain 1 or 1.1 equivalents of TfOH or HBF₄) was added exactly to the cell or NMR tube. After spectra of $[(PN(H)P)PdH]^+[A]^-$ (2[A]), generated in situ, were acquired, the necessary amount of stock base solution (1 M) or neat base (Py, HMPA, MeCN) was added exactly to the cell or NMR tube.

b. General procedure for the interaction of **1** *with fluorinated alcohols*

For variable temperature IR studies.

The solution of (PNP)PdH (1, c = 0.02-0.06 M) was prepared at inert atmosphere at room temperature in toluene, toluene-d₈, or benzene-d₆. Then, it was placed into a cryostat (CaF₂ cell, l = 0.05-0.2 cm) and cooled to 190 K. After spectra of the initial complex were acquired at different temperatures in the range 190 to 290 K, the solution from the cryostat was put back in the Schlenk tube and mixed with stock solution (0.5-1 M) of corresponding fluorinated alcohol or neat alcohol (TFE, HFIP, PFTB; 1–30 eq., c = 0.02-1.2 M) kept at 190 K in a liquid nitrogen/*i*PrOH slush bath. The mixture obtained was quickly returned to the cryostat, and IR spectra were monitored in the 190–290 K temperature range.

For variable temperature NMR studies.

The solution of (PNP)PdH (1, c = 0.02-0.06 M) was prepared at inert atmosphere at room temperature in toluene-d₈ or benzene-d₆. Then, it was placed into an NMR tube and cooled to 190 K. After spectra of the initial complex were acquired at different temperatures in the range 190 to 290 K, the stock solution (0.5-1 M) of corresponding fluorinated alcohol (HFIP, PFTB; 1–8 eq., c = 0.02-0.2 M) was added exactly to the NMR tube kept at 190 K in a liquid nitrogen/*i*PrOH slush bath. NMR spectra were monitored in the 190–290 K temperature range.

For IR and NMR studies at room temperature.

The solution of (PNP)PdH (1, c = 0.02-0.08 M) was prepared in a Schlenk tube at inert atmosphere at room temperature in toluene, toluene-d₈, benzene-d₆ or neat alcohol (TFE, HFIP, PFTB). Then, the necessary amount neat alcohol or its stock solution (1 M) was added. The resulting solution was placed into a cell (0.05-0.2 cm, for IR measurements) or into an NMR tube (for NMR measurements) under an inert atmosphere. In some cases, the solution after IR measurements was put in an NMR tube to acquire NMR spectra.

c. General procedure for the studies of interaction of **1** with formic acid

Variable temperature IR and NMR studies of interaction between **1** and formic acid were carried out as described above for interactions between **1** and fluorinated alcohols.

For IR and NMR kinetic studies at room temperature. the solution of (PNP)PdH (1, c = 0.02 M) was prepared in a Schlenk tube at inert atmosphere at room temperature in toluene, toluene- d_8 or benzene- d_6 . Then, the necessary amount of formic acid stock solution (1 M; 0.5–10 eq., c = 0.01–0.2 M) was added. The resulting solution was quickly placed into a cell (0.1 cm, for IR measurements) or into a Young NMR tube (for NMR measurements) under an inert atmosphere.

d. Formic acid monomer concentration calculation.

The concentration of formic acid monomer, to obtain reaction rate constant of its dehydrogenation, was calculated using the Bouguer–Beer–Lambert law $D = \varepsilon \cdot l \cdot c$, taking ε (FA^{monomer}, 1746 cm⁻¹) = 1246 [21].

4. Conclusions

Thus, the results of the IR and NMR spectroscopic study of the interaction between (PNP)PdH (1) and different acids show that the nitrogen atom of the amidophosphine pincer ligand readily interacts not only with strong Brønsted acids such as CF₃SO₃H but with relatively weak fluorinated alcohols. This is the result of the nitrogen binding to palladium(II) which increases the diarylamine basicity (for comparison, $pK_a(Ph_2NH_2^+) = 5.98$ and $pK_a(Ph_2MeNH^+) = 6.52$ in MeCN [13]) making it a strong base probably due to the better delocalization of the acquired positive charge in the presence of a transition metal. Nevertheless, H⁺ can be taken from [(PN(H)P)PdH]⁺ (2) by pyridine (pK_a (PyH⁺) = 12.53

in MeCN) or HMPA (pK_a (HMPA-H⁺) = 6.1 in MeNO₂). These observations confirm the need for a shuttle base for the heterolytic splitting of H₂ by [(PNP)Pd]⁺ to form [(PN(H)P)PdH]⁺ (**2**).

Still, formic acid ($pK_a = 20.9$ in CH₃CN) appears to be able to protonate a hydride ligand yielding an unstable η^2 -H₂ complex that rapidly converts into a formate complex (PNP)Pd(OCHO). The CO₂ elimination from the latter is the rate-determining step for formic acid dehydrogenation in the presence of (PNP)PdH. However, the relatively high acid excess hampers this reaction through competitive protonation at nitrogen atom yielding [(PN(H)P)PdH]⁺ and the formation of a variety of hydrogen bonds with **1** or **2**.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/inorganics11050212/s1: IR and NMR spectroscopic characterization of different Pd(II) complexes; details of kinetic parameters determination, computed frequencies, and energies. Table S1: Key spectral parameters of (PNP)PdH (1) in toluene- d_8 ; Table S2: Key spectral parameters of palladium complexes formed by the interaction of 1 with acids; Table S3: DFT calculated frequencies of PdH stretching vibrations and formation energies of 1 and its bimolecular complexes with TFE in toluene; Table S4: DFT calculated frequencies of PdH stretching vibrations and formation energies of 2 and its non-covalent adducts with pyridine and TFE; Figure S1: IR spectra of (PNP)PdH, TfOH and their mixture in toluene-d₈ at 295 K; Figure S2: IR spectra of (PNP)PdH, with 1 equivalent of $H[BF_4]$ ·Et₂O and their mixture with pyridine in benzene-d₆ at 295 K; Figure S3: IR spectra in v_{PdH} stretching vibrations region of [(PN(H)P)PdH]⁺[BF₄]⁻, with 5, 20, 50 and 100 equivalents of MeCN in benzene-d₆, 295 K; Figure S4: IR spectra in the PdH stretching vibrations region of (PNP)PdH, with 5 equiv. PFTB in toluene-d₈ and in neat PFTB; Figure S5: IR spectra of v_{CO} stretching vibrations region of (PNP)PdH with 5 equiv. PFTB in toluene-d₈ at 190–295 K; Figure S6: The temperature dependence of equilibrium constant for $1 + PFTB \leftrightarrow 2[OC(CF_3)_3]$ in toluene-d₈; Figure S7: IR spectra of v_{PdH} stretching vibrations region of (PNP)PdH and with 4 equiv. HFIP in toluene-d₈ at 190–295 K; Figure S8: IR spectra of ν_{CO} stretching vibrations region of HCOOH with 0.5 equiv. (PNP)PdH in toluene at 190–290 K; Figure S9: IR spectra of v_{CO} stretching vibrations region of HCOOH and with 0.5 equiv. (PNP)PdH in toluene at 190 K; Figure S10: IR spectra of v_{CO} stretching vibrations region of CO₂ evolved from HCOOH with 0.5 equiv. (PNP)PdH in toluene-d₈ at 295 K, t = 80-10,000 s; Figure S11: Kinetics of CO₂ evolution from formic acid, monitored by change of v_{CO2} band intensity for the mixture of (PNP)PdH with 0.5, 1, 2, 5 and 10 equiv. HCOOH; Figure S12: IR spectra of v_{PdH} of (PNP)PdH and v_{CO} of HCOOH stretching vibrations regions in toluene-d₈ at 295 K, t = 80–10,000 s; Figure S13: Kinetics of formic acid decomposition, monitored by change of $\nu_{CO}(FA^{monomer})$ band intensity for the mixture of (PNP)PdH with 0.5, 1 and 2 equiv. HCOOH; Figure S14: Kinetics of formic acid decomposition, monitored by change of $v_{CO}(FA^{monomer})$ band intensity for the mixture of (PNP)PdH with 5 equiv. HCOOH; Figure S15: IR spectra in the vPdH stretching vibrations region of (PNP)PdH in the presence of 0.5, 1, 2, 5 and 10 equiv. HCOOH measured in 150 s after mixing; Figure S16: ³¹P{¹H} and ¹H NMR monitoring of (PNP)PdH with 2 equiv. HCOOH; Figure S17: ³¹P{¹H} and ¹H NMR monitoring of (PNP)PdH with 10 equiv. HCOOH in benzene-d₆, 295 K.

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