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P Csp^3 P and P Csp^2 P Palladium(II) Hydride Pincer Complexes: Small Structural Difference—Large Effect on Reactivity

Roman Gerber, Thomas Fox, and Christian M. Frech*[a]

Late-transition-metal hydroxides and alkoxides are considered as important intermediates in various catalytic processes and much attention has been devoted to the study of their structures and reactivities.[1] Their hydrogenolysis, for example, leads to the elimination of water and alcohols, respectively, and concomitant formation of a metal hydride, an elementary step that is considered to be of high relevance for the product release and catalyst regeneration within a catalytic cycle. However, this process has rarely been documented and only very few model complexes show this reactivity.[2–5] Recent examples include the aromatic pincer complexes [{C_6H_3-2,6-(CH_2P*t*Bu_2)$_2$}Pd(OR)] (R = H or Me), which undergo hydrogenolysis when treated with dihydrogen (7 atm) at room temperature to generate water and methanol, respectively, and the corresponding palladium(II) hydride complex over a period of 60 h. The reverse reaction, the generation of dihydrogen and concomitant formation of a palladium(II) hydroxide complex, however, did not occur and is generally unknown for palladium(II) hydride complexes.[6]

We report herein the syntheses (from the chloro pincer complex **1**) of the palladium hydride and hydroxide pincer complexes [{$C_{10}H_{13}$-1,3-(CH_2PCy_2)$_2$}Pd(H)] (**2**) and [{$C_{10}H_{13}$-1,3-(CH_2PCy_2)$_2$}Pd(OH)] (**3**) with an adamantylic core. The stronger *trans*-influence of the aliphatic pincer core when compared to systems in which the metal center is σ-bound to an aromatic unit was expected to lengthen (and weaken) the Pd–H and Pd–OH bonds to enhance their reactivities or possibly even change their reactivity modes towards water and dihydrogen for example. A recently reported literature example, in which an iridium complex with an aliphatic core oxidatively adds the N–H bond in ammonia, while another one with a central aryl C does not, supports this assumption.[7] We demonstrate that the stronger *trans*-influence of the aliphatic pincer core causes a dramatic change in the reactivity pattern of **2** when compared to [{C_6H_3-2,6-(CH_2P*t*Bu_2)$_2$}Pd(H)]. Thus, whereas the generation of dihydrogen and concomitant formation of the stable palladium(II) hydroxide pincer complex [{$C_{10}H_{13}$-1,3-(CH_2PCy_2)$_2$}Pd(OH)] (**3**) was observed when water was added to solutions of the palladium hydride pincer complex **2** in THF, no reaction (but a H/D exchange when D_2O was added) was noticed for [{C_6H_3-2,6-(CH_2P*t*Bu)$_2$}$_2$Pd(H)] (even though the overall electron density on the metal center of the latter is higher). Moreover, the formation of **3** is reversible and undergoes fast hydrogenolysis to regenerate the palladium(II) hydride pincer complex **2** (and H_2O) under an atmosphere of dihydrogen, demonstrating that small structural differences can indeed change the reactivity pattern of seemingly very similar compounds.

When the aliphatic, phosphine based pincer complex [{$C_{10}H_{13}$-1,3-(CH_2PCy_2)$_2$}Pd(Cl)] (**1**) was treated with an excess (≈50 equiv) of sodium hydride and stirred in THF for 12 h at 100 °C,[8] the pentane soluble hydride complex [($C_{10}H_{13}$-1,3-(CH_2PCy_2)$_2$)Pd(H)] (**2**) was almost quantitatively formed (Scheme 1). The reaction progress was monitored by NMR spectroscopy; in the $^{31}P\{^1H\}$ NMR spectrum, the gradual disappearance of the singlet for **1** at $\delta = 52.6$ ppm was noted along with the appearance of another singlet for **2** at $\delta = 66.8$ ppm. Complex **2** was isolated as an off-white solid in 95 % yield. It's ^{1}H NMR spectrum exhibits a sharp triplet centered at $\delta = -3.39$ ppm with coupling constants of $^3J_{PH} = 20.8$ Hz, confirming the formation of a Pd–H bond. The hydride pincer complex **2** undergoes smooth deuterium scrambling with D_2 at room temperature to yield the deuteride complex **2′** (and HD) within few minutes, as indicated by ^{1}H and ^{2}H NMR spectroscopy. By analogy, treatment of **2′** with H_2 yielded the hydride pincer complex **2**. These processes most probably involve four-center transition states in which a proton is transferred intramolecularly from a coordinated deuterium (or dihydrogen) molecule to the hydride (or deuteride) ligand rather than the oxidative addition of

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[a] R. Gerber, Dr. T. Fox, Dr. C. M. Frech
Department of Inorganic Chemistry
University of Zürich, 8057 Zürich (Switzerland)
Fax: (+41) 44-635-46-92
E-mail: chfrech@aci.uzh.ch

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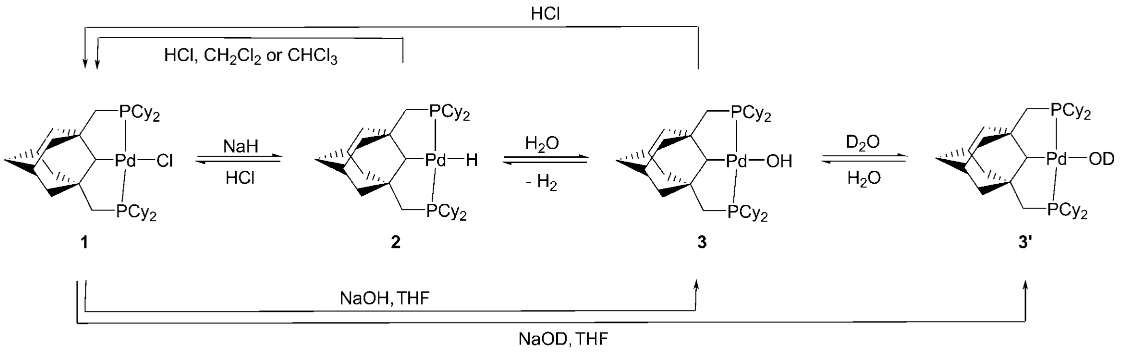


Scheme 1. Reactivity pattern of **2** and **3** towards water and H_2, and related reactions.

D_2 (or H_2) on the palladium(II) hydride/deuteride pincer complexes **2** and **2′**, respectively.[6] However, the hydride pincer complex **2** also undergoes smooth H/Cl exchange with chlorinated solvents. For example, when dichloromethane or chloroform ($\approx$50 equiv) was added to solutions of **2** in THF at room temperature, complex **1** and a corresponding amount of CH_3Cl and CH_2Cl_2, respectively, were cleanly, instantly formed. Their formation was confirmed by ^1H NMR spectroscopy and by GC/MS. $CDHCl_2$ was detectable by ^1H and ^2H NMR spectroscopy when **2** was allowed to react with $CDCl_3$. Similarly, treatment of **2** or **2′** with a slight excess ($\approx$5 equiv) of hydrochloric acid ($\approx$1.0 M in diethyl ether or 32 % aqueous HCl) instantly and quantitatively yielded the chloro pincer complex **1** and a corresponding amount of H_2 and HD, respectively (as indicated by ^1H and ^2H NMR spectroscopy and GC equipped with a TCD detector).

Remarkably, the hydride pincer complex **2** exhibits a strikingly different reactivity towards water when compared to the phenyl-based pincer hydride complex $[\{C_6H_3\text{-}2,6\text{-}(CH_2P\mathit{t}Bu)_2\}_2Pd(H)]$.[9] Whereas deuterium scrambling was observed over a period of four days at 60 °C when D_2O was added to solutions of $[\{C_6H_3\text{-}2,6\text{-}(CH_2P\mathit{t}Bu)_2\}_2Pd(H)]$ in benzene,[6] slow H_2 evolution and concomitant quantitative formation of the hydroxide pincer complex $[\{C_{10}H_{13}\text{-}1,3\text{-}(CH_2PCy_2)_2\}Pd(OH)]$ (**3**) was observed within 36 h when water was added to solutions of **2** in benzene. The formation of **3** was indicated by $^{31}P\{^1H\}$ NMR spectroscopy, in which a gradual disappearance of the singlet for **2** at $\delta = 66.8$ ppm was noted along with the appearance of another singlet for **3** at $\delta = 49.3$ ppm. However, full conversion of **2** into **3** and H_2 was observed within only few minutes when the reaction was performed in THF at room temperature. The liberation of dihydrogen was verified by ^1H NMR spectroscopy and GC (equipped with a TCD detector) and by the reaction of a sample of the gas phase with $[(PEt_3)_3Ir(Cl)]$ to form *mer-cis*-$[(PEt_3)_3Ir(H)_2(Cl)]$.[10] The identity of **3** was confirmed by a weak signal due to the hydroxide proton at −2.25 ppm in the ^1H NMR spectrum and by treatment of **2** with D_2O, which cleanly yielded the deuteroxide complex $[\{C_{10}H_{13}\text{-}1,3\text{-}(CH_2PCy_2)_2\}Pd(OD)]$ (**3′**) and a corresponding amount of HD. The deuteroxide complex **3′** displayed a signal at $\delta = -2.25$ ppm in the ^2H NMR spectrum and verifies its identity.[11] The formation of HD was confirmed by a sharp triplet ($^1J_{HD} = 41.9$ Hz) centered at $\delta = 4.41$ ppm in the ^1H NMR spectrum and by a doublet ($^1J_{HD} = 41.9$ Hz) in the ^2H NMR spectrum. When a drop of D_2O was added to solutions of the hydroxide pincer complex **3** (and H_2O to [D8]THF solutions of **3′**) in THF, a complete H/D exchange occurred, leading to the formation of **3′** (and **3**) within only few minutes—another indication for the identity of **3**. Indeed, treatment of **3** with a slight excess ($\approx$5 equiv) of hydrochloric acid ($\approx$1.0 M in diethyl ether) instantly and quantitatively yielded the chloro pincer complex **1** and a corresponding amount of water. The independent syntheses of **3** and **3′** by reactions of **1** with sodium hydroxide and sodium deuteroxide, respectively, in THF confirmed their formation further (Scheme 1).

The conversion of the hydride pincer complex **2** into the hydroxide pincer complex **3** and H_2 is reversible: when solutions of **3** in THF were stirred in an atmosphere of dihydrogen gas (1 atm) complete hydrogenolysis occurred, to exclusively yield the hydride complex $[\{C_{10}H_{13}\text{-}1,3\text{-}(CH_2PCy_2)_2\}Pd(H)]$ (**2**) and H_2O within $\approx$15 min at 35 °C in the presence of a large excess (50 to 100 equiv) of water.[12] By analogy, reactions of **3** with deuterium gas cleanly yielded the palladium deuteride complex **2′** (and HDO). Accordingly, reactions of **3′** with H_2 or deuterium gas yielded the hydride pincer complex **2** and **2′**, respectively.

Even though proton transfers from a protic substrate to a hydride complex with subsequent dissociation of dihydrogen is a well-established phenomenon,[13] complex **2** is the first palladium(II) hydride complex reported that leads to generation of dihydrogen and concomitant formation of a stable palladium(II) hydroxide complex by reaction with water. The striking difference in reactivity with respect to its aromatic analogue $[\{C_6H_3\text{-}2,6\text{-}(CH_2P\mathit{t}Bu_2)_2\}Pd(H)]$ was attributed to the stronger *trans*-influence of the aliphatic pincer core, which lengthens and thus, weakens the Pd−H bond.[14] This effect is measurable by IR spectroscopy: the IR spectrum of **2** exhibits an absorption band at $\nu_{Pd-H} = 1610\ cm^{-1}$, which is significantly shifted to lower wavenumbers ($\Delta\nu_{Pd-H} = 120\ cm^{-1}$) when compared to the Pd−H stretching frequency of its aromatic analogue $[\{C_6H_3\text{-}2,6\text{-}$

$(CH_2PtBu_2)_2\}Pd(H)]$ ($\nu_{Pd-H} = 1730\ cm^{-1}$).[8,15] Lengthened Pd–H bonds have an enhanced hydridic character provided that the polarization of this bond leads to accumulation of negative charge at the H atom. This in turn leads to stronger Pd–H···H–OR interactions (dihydrogen bonding) with protic substrates, such as water and alcohols and promotes the formation of dihydrogen complexes—proposed intermediates of proton transfer processes—and consequently the liberation of H_2 (Scheme 2).[16–18] Indeed, the formation of intermediates of type **A** were detected by ^1H NOE spectra for **2**/MeOH (0.014/0.116 $mol\,L^{-1}$) as well as for $[\{C_6H_3\text{-}2,6\text{-}(CH_2PtBu_2)_2\}Pd(H)]$/MeOH (0.014/0.116 $mol\,L^{-1}$) in $[D_8]$toluene at −30 °C.[19,20] Irradiation of the Pd–H resonances led in both systems to the enhancement of the OH protons—a clear indication for Pd–H···H–OMe interactions. To better understand the reactivity difference of **2** and $[\{C_6H_3\text{-}2,6\text{-}(CH_2PtBu_2)_2\}Pd(H)]$, the Pd–H···H–OR hydrogen–hydrogen interactions of **2**/MeOH and $[\{C_6H_3\text{-}2,6\text{-}(CH_2PtBu_2)_2\}Pd(H)]$/MeOH were investigated in more detail.

Analysis of the Pd–H···H–OR hydrogen–hydrogen bonds: The main characteristic of Pd-H···H-OMe interactions (see intermediate **A** in Scheme 2) is of electrostatic nature and thus, its strength is directly related to the basicity or hydridicity of the Pd–H bond. Since bond ionicities represent the hydridic character of $L_nM\text{–}H$ bonds, they were deduced from the ^2H-spin-lattice relaxation times ($T_{1\,min}$) in **2′** and $[\{C_6H_3\text{-}2,6\text{-}(CH_2PtBu_2)_2\}Pd(D)]$ by using the calculated deuterium quadrupole coupling constants (DQCC).[21–23] The estimated ionicities of the Pd–D bonds in **2′** and $[\{C_6H_3\text{-}2,6\text{-}(CH_2PtBu_2)_2\}Pd(D)]$ are 69 and 67 %, respectively, and show the expected trend with respect to the observed reactivity difference.[24] It is important to note, that comparisons with any other transition-metal hydride couples are not possible, since **2** and $[\{C_6H_3\text{-}2,6\text{-}(CH_2PtBu_2)_2\}Pd(H)]$ are the only (structural strongly related) hydride complexes reported with a strikingly different reactivity pattern, for which the reactivity difference can directly be correlated to the metal hydride bond ionicity.

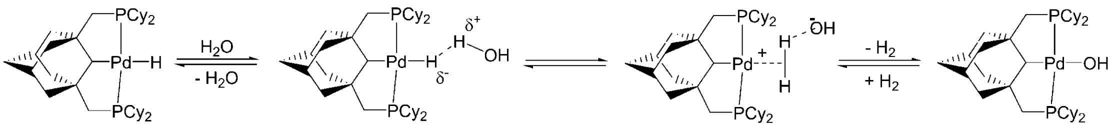
Another proof for dihydrogen bonding is the decrease of the hydride-^1H longitudinal relaxation time ($T_{1\,min}$) in the presence of proton donors.[25] The strength of dipolar M–H···HX interactions and, therefore, the longitudinal T_1 relaxation behavior, are strongly distance dependent ($\propto r^{-6}$-(H···H)). In fact, the hydride T_1 minimum of pure **2** strongly decreases from 1249 to 399 ms after the addition of MeOH ([**2**]/[MeOH] = 0.014/0.116 $mol\,L^{-1}$) in $[D_8]$toluene,[20,26] which leads to the assignment of the hydride in **2** as the proton accepting site. Indeed, a (short) Pd–H···H–OMe distance of 1.89 Å, clearly less than the sum of the van der Waals radii (2.4 Å), was determined. This distance is in the range of values (1.7–1.9 Å) reported for intramolecular NH···HIr and OH···HIr dihydrogen bonds.[27] In contrast, for $[\{C_6H_3\text{-}2,6\text{-}(CH_2PtBu_2)_2\}Pd(H)]$ the hydride T_1 minima without and with MeOH differ only slightly ([Pd-H]/[MeOH] = 0.014/0.116 $mol\,L^{-1}$), indicating a much weaker Pd–H···H–OR interaction. Indeed, a very long Pd–H···H–OMe distance of about 2.3 Å was estimated.[23,28]

The Pd–H···H–OMe hydrogen–hydrogen bond strengths were determined by NMR spectroscopy for **2**/MeOH and $[\{C_6H_3\text{-}2,6\text{-}(CH_2PtBu_2)_2\}Pd(H)]$/MeOH and were consistent with the dihydrogen bond distances established.[25,29] The adduct formation equilibrium constants K were obtained from the temperature-dependent chemical shifts of the hydride signals (δ_{Pd-H}) at different concentrations of MeOH. The averaged equilibrium chemical shift δ_{Pd-H} is related to the chemical shifts of the free and hydrogen-bonded complexes, δ_1 and δ_2, through the equilibrium constant (K) and the initial concentrations of [Pd–H] (w) and [MeOH] (x) [Eq. (1)],[25] in which $a = Kw - Kx + 1K$ and δ_2 were determined by non-linear fit of the experimental data to the above equation using the Levenberg-Marquardt algorithm.[30]

$$\delta_{Pd-H} = [\delta_1 + 0.5\,\delta_2\{(a^2 + 4Kx)^{1/2} - a\}] / [1 + 0.5\{(a^2 + 4Kx)^{1/2} - a\}] \quad (1)$$

The ΔH and ΔS values for the adduct formation were obtained from van't Hoff plots.[23] Whereas a ΔH value of -5.6 ± 0.1 kcal mol^{-1} and hence, a relatively strong dihydrogen bonding was calculated for **2**/MeOH in toluene,[31] a much weaker Pd–H···H–OMe interaction ($\Delta H = -2.0 \pm 0.1$ kcal mol^{-1}) was estimated for $[\{C_6H_3\text{-}2,6\text{-}(CH_2PtBu_2)_2\}Pd(H)]$,[32,33] which is in full agreement with the reactivity difference observed for **2** and $[\{C_6H_3\text{-}2,6\text{-}(CH_2PtBu_2)_2\}Pd(H)]$. Another empirical correlation, the "factor of basicity" (E_j)[34] further characterizes the Pd–H bond in hydrogen bond formation. The E_j values determined for **2** and $[\{C_6H_3\text{-}2,6\text{-}(CH_2PtBu_2)_2\}Pd(H)]$ are 1.56 and 0.56, respectively, which correspond to the basicity of the hydrides (the proton accepting site) of pyridine and nitromethane, respectively,[23] further illustrating that these palladium(II) pincer hydride complexes must be different in their reactivity towards protonation by weak acids, such as alcohols or water.[35]

Even though the overall electron density on the metal center of the aromatic, PCsp^{2}P-based palladium(II) hydride



2 **A** **B** **3**

Scheme 2. Proposed mechanism for the generation of dihydrogen and concomitant formation of **3** by treatment of **2** with water.[18]

pincer complex [{C_6H_3-2,6-(CH_2PtBu_2)$_2$}Pd(H)] is higher when compared to the metal center of the aliphatic, PCsp^{3}P-based pincer complex **2**,[14] the hydride of the latter is (due to the stronger *trans*-influence of the aliphatic pincer core) significantly more hydridic.

In conclusion, palladium(II) hydride complexes have never been observed to undergo H_2 evolution and concomitant formation of a stable palladium(II) hydroxide complex in the presence of water. The reverse reaction, the hydrogenolysis of palladium(II) hydroxide complexes to regenerate the palladium(II) hydride complexes and release of a corresponding amount of water or alcohol has rarely been documented. Thus, the aliphatic palladium(II) hydride pincer complex **2** is the first palladium(II) hydride complex that leads to the evolution of dihydrogen under concomitant formation of the palladium(II) hydroxide complex **3** when reacted with an excess of water. This differs strikingly when compared to its aromatic analogue for which deuterium scrambling was observed. The reactivity difference could be attributed to the stronger *trans*-influence of the aliphatic, PCsp^{3}P-based pincer core, which apparently has a great impact on the hydridicity (and thus, reactivity) of an L_nM–H bond. Investigations by IR spectroscopy showed that the Pd–H bond in **2** is indeed significantly elongated and thus weaker when compared to its aromatic analogue. Moreover, even though the electron density on the metal center of the phenyl-based pincer hydride complex is higher when compared to the metal center of **2**, the Pd–D bond ionicity of the latter is higher (by ≈2%) and allows for the first time a direct correlation between the reactivity of structurally seemingly similar transition-metal hydride complexes and their M–H bond ionicity. As a direct consequence of the higher Pd–H bond ionicity, interactions of **2** with proton sources (MeOH) lead to significantly stronger and shorter Pd–H···H–OMe hydrogen–hydrogen bonds (dihydrogen bonding) when compared to those obtained for the aromatic, PCsp^{2}P-based system, providing a simple but powerful explanation for their striking reactivity difference. The conversion of **2** into **3** and H_2, however, is reversible. Moreover, the addition of an excess of water (50 to 100 equiv) considerably increased the rate of hydrogenolysis and thus, strongly supports a mechanism with initial dissociation of the hydroxide ligand and formation of a cationic dihydrogen complex, which is then deprotonated by the hydroxide anion to yield the hydride complex **2** (and water). Other experimental observations supported this mechanism further, which is different when compared to the aromatic pincer hydride complex [{C_6H_3-2,6-(CH_2PtBu_2)$_2$}Pd(H)], in which a four-center transition state was found to be traversed.

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Keywords: coordination modes · hydride ligands · hydrogenolysis · NMR spectroscopy · palladium · pincer ligands

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[14] Oxidative addition of water on **2** (to form the hexacoordinate dihydride pincer complex [{$C_{10}H_{13}$-1,3-(CH_2PCy_2)$_2$}Pd(H)$_2$(OH)]) and subsequent reductive elimination of dihydrogen and concomitant formation of **3** is unlike here, since the electron density at the metal center of **2** is lower when compared to [{C_6H_3-2,6-(CH_2PtBu_2)$_2$}Pd(H)], implying that the oxidative addition of water would preferentially occur on the metal center of the aromatic analogue. The CO stretching frequency of their cationic carbonyl derivatives is indicative for the lower electron density on the metal center of the adamantyl-based pincer complex [{$C_{10}H_{13}$-1,3-(CH_2PCy_2)$_2$}Pd(CO)][BF_4][8] ($\nu_{CO} = 2095\ cm^{-1}$) when compared to its aromatic analogue [{C_6H_3-2,6-(CH_2PtBu_2)$_2$}Pd(CO)][BF_4] ($\nu_{CO} = 2078\ cm^{-1}$).

[15] The assignment of the Pd–H stretching frequency was confirmed by comparing the IR spectrum of the Pd–D complex, in which the respective IR band was absent.

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[18] The involvement of cationic dihydrogen complexes of type $[\{C_{10}H_{13}\text{-}1,3\text{-}(CH_2PCy_2)_2\}Pd(\eta^2\text{-}H_2)]^+$ (see intermediate B in Scheme 2) seems plausible, as such dihydrogen complexes are unstable (no reaction was noticed when $[\{C_{10}H_{13}\text{-}1,3\text{-}(CH_2PCy_2)_2\}Pd]^+$ was treated with dihydrogen at 25 °C) and thus, would instantly liberate dihydrogen as soon as formed (by analogy to the cationic carbonyl pincer complex, which is unstable as well).[8] However, as a consequence of the proposed mechanism (Scheme 2), the hydrogenolysis—its reverse reaction—would involve initial ion pair formation (instead of a four-center transition state).[6,14] The strong *trans*-influence, however, could indeed induce a change of mechanism when compared to $[\{C_6H_3\text{-}2,6\text{-}(CH_2P\mathit{t}Bu_2)_2\}Pd(OH)]$. Moreover, another (dissociative) reaction mechanism would additionally provide a simple explanation for the significantly higher reactivity of **3** towards dihydrogen when compared to $[\{C_6H_3\text{-}2,6\text{-}(CH_2P\mathit{t}Bu_2)_2\}Pd(OH)]$.[6] Following experimental observations support the proposed mechanism in Scheme 2: 1) The conversion of **3** into **2** (and H_2O) is significantly faster in THF than in benzene. 2) The hydrogenolysis is considerably accelerated in the presence of larger amounts of water.[6,19] 3) Conductivity measurements of **3** in THF (at 25 °C) clearly indicate (partial) ion pair formation. 4) Treatment of solutions of $[(C_{10}H_{13}\text{-}1,3\text{-}(CH_2PCy_2)_2)Pd][BF_4]$ in benzene or THF with H_2 instantly yielded the hydride complex **2** (and another, not identified complex) in the presence of tetramethylpiperidine.

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[22] The DQCCs depend on the electrical field gradient, which is zero for isotropic conditions as for isolated deuteride, and which is at maximum (227 kHz) for the ideally covalent D_2 molecule. These two extreme cases define 100 and 0 % bond ionicity, and the value for any intermediate case might be obtained by linear interpolation. If the ^2H nucleus is replaced by the ^1H nucleus, it is expected that the ionicities remain similar, and that the derived general trends are completely transferable.

[23] See the Supporting Information.

[24] Although the Pd−D bond ionicity between **2′** and $[\{C_6H_3\text{-}2,6\text{-}(CH_2P\mathit{t}Bu_2)_2\}Pd(D)]$ amounts just to ≈2 %, this difference is not negligible. For example the M−D bond ionicities of structurally identical rhenium hydride complexes of type $[Re(D)(CO)(NO)(PR_3)_2]$ with $PR_3 = PMe_3$, $P\mathit{i}Pr_3$, $P(O\mathit{i}Pr)_3$ or PCy_3 are the same for the trimethylphosphine, triisopropylphosphine, and tricyclohexylphosphine derivatives and differ only for the triisopropylphosphite derivative by 1 % (the T_1 minima vary between 0.2 and 1.4 ms). Similarly, no difference in the W−D bond ionicity was measured for $[W(D)(CO)_2(NO)(PR_3)_2]$ with $PR_3 = PMe_3$ and PPh_3. On the other hand, a Re−D bond ionicity difference of 4 % was measured for *cis*-$[Re(D)(CO)(PMe_3)_4]$ and *trans*-$[Re(D)(CO)(PMe_3)_4]$, which demonstrates that the effect of the *trans* ligand on the polarization of the M−H bond and hence, their ionicity (and thus, reactivity) is far stronger than the overall electron density on the metal center.[21a]

[25] E. S. Shubina, N. V. Belkova, A. N. Krylov, E. V. Vorontsov, L. M. Epstein, D. G. Gusev, M. Niedermann, H. Berke, *J. Am. Chem. Soc.* **1996**, *118*, 1105.

[26] The H···H distance (in Å) was calculated from following equation: $r(H\cdots H) = 5.817(\nu\Delta R_{1\,\text{min}})^{-1/6}$, in which ν is the NMR frequency in MHz and $\Delta R_{1\text{min}}$ is the difference between $1/T_{1\,\text{min}}$ of the hydride signal in the presence and absence of proton donors. For further details see: L. H. Desrosiers, Z. R. Cai, R. Lin, R. Richards, J. Halpern, *J. Am. Chem. Soc.* **1991**, *113*, 4173.

[27] a) A. J. Lough, S. Park, R. Ramachandran, R. H. Morris, *J. Am. Chem. Soc.* **1994**, *116*, 8356; b) S. Park, R. Ramachandran, A. J. Lough, R. H. Morris, *J. Chem. Soc. Chem. Commun.* **1994**, 2201; c) J. C. Lee, A. L. Rheingold, B. Muller, P. S. Pregosin, R. H. Crabtree, *J. Chem. Soc. Chem. Commun.* **1994**, 1021; d) J. C. Lee, E. Peris, A. L. Rheingold, R. H. Crabtree, *J. Am. Chem. Soc.* **1994**, *116*, 11014; e) R. C. Stevens, R. Bau, D. Milstein, O. Blum, T. F. Koetzle, *J. Chem. Soc. Dalton Trans.* **1990**, 1429; f) E. Peris, J. C. Lee, J. R. Rambo, O. Eisenstein, R. H. Crabtree, *J. Am. Chem. Soc.* **1995**, *117*, 3485.

[28] The hydride T_1 minimum decreases from 984 ms in $[\{C_6H_3\text{-}2,6\text{-}(CH_2P\mathit{t}Bu_2)_2\}Pd(H)]$ to 767 ms after the addition of MeOH ([Pd−H]/[MeOH] = 0.014:0.116 mol L^{-1}) in [D$_8$]toluene.

[29] A. Messmer, H. Jacobsen, H. Berke, *Chem. Eur. J.* **1999**, *5*, 3341.

[30] W. H. Press, B. P. Flannery, S. A. Teukolsky, W. T. Vetterling *Nummerical Recipes*, Cambridge University Press, Cambridge, **1986**, Chapter 14.4.

[31] Notably, the strength of the hydrogen bonding is even higher to the estimated energy of *intramolecular* Ir−H···H−N hydrogen bonds (3–5 kcal mol^{-1}).[21d,f]

[32] Whereas in the most concentrated sample a relatively large difference in the chemical shift was obtained for **2**/MeOH ($\Delta\delta = -0.25$ ppm) at −60 °C only a slight shift change ($\Delta\delta = -0.07$ ppm) was noticed for its aromatic analogue $[\{C_6H_3\text{-}2,6\text{-}(CH_2P\mathit{t}Bu_2)_2\}Pd(H)]$. Only at temperatures below −60 °C and/or higher MeOH concentrations a considerable drift of the δ values was measured—a strong indication that the strength of the Pd−H···H−OMe hydrogen bond is significantly higher in the case of **2**/MeOH.

[33] The $\Delta S°$ value for **2** is -5.5 ± 0.2 eu and hence, lies in the expected range.[22] The $\Delta S°$ value for $[\{C_6H_3\text{-}2,6\text{-}(CH_2P\mathit{t}Bu_2)_2\}Pd(H)]$ is -1.8 ± 0.3 eu and rather small—another indication for weak Pd−H···H−OMe hydrogen-bond formation.

[34] A. V. Iogansen, *Theor. Exp. Chem.* **1971**, *7*, 302.

[35] Note, that proton transfers by weak acids (such as fluorinated alcohols) to hydrides having E_j values less than 0.8 does not occur, even in the presence of a large excess of the acid. On the other hand, if the E_j value is greater than 0.8, proton transfers were found to take place also by rather weak acids, which is in full agreement with our results obtained. See, for example, a) E. S. Shubina, N. V. Belkova, E. V. Bakhmutova, E. V. Vorontsov, V. I. Bakhmutov, A. V. Ionidis, C. Bianchini, L. Marvelli, M. Peruzzini, L. M. Epstein, *Inorg. Chim. Acta* **1998**, *280*, 302; b) V. I. Bakhmutov, E. V. Bakhmutova, N. V. Belkova, C. Bianchini, L. M. Epstein, M. Peruzzini, E. S. Shubina, E. V. Vorontsov, F. Zanobini, *Can. J. Chem.* **1998**, *76*, 302.

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