

Periodic Trends in Metal Hydride Donor Thermodynamics: Measurement and Comparison of the Hydride Donor Abilities of the Series $\text{HM}(\text{PNP})_2^+$ ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$; $\text{PNP} = \text{Et}_2\text{PCH}_2\text{N}(\text{Me})\text{CH}_2\text{PEt}_2$)

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Received November 5, 2003

The complexes $\text{M}(\text{PNP})_2^{2+}$ ($\text{M} = \text{Pd}, \text{Pt}$, $\text{PNP} = \text{Et}_2\text{PCH}_2\text{N}(\text{Me})\text{CH}_2\text{PEt}_2$) were synthesized by addition of PNP to $\text{Pd}(\text{CH}_3\text{CN})_4(\text{BF}_4)_2$ and $(\text{COD})\text{PtCl}_2$, respectively. $\text{Pd}(\text{PNP})_2$ was synthesized by reaction of $\text{Pd}(\text{PNP})_2^{2+}$ with H_2 and tetramethylguanidine (TMG) in CH_3CN . The thermodynamic hydride donor ability, $\Delta G_{\text{H}^-}^\circ$, for $\text{HPt}(\text{PNP})_2^+$ (54.7 kcal/mol) was measured by heterolytic cleavage of hydrogen in the presence of NET_3 in CH_3CN . The hydride donor ability of $\text{HPd}(\text{PNP})_2^+$ (51.1 kcal/mol) was determined by measuring the equilibrium constant for direct hydride transfer to $\text{Pt}(\text{PNP})_2^{2+}$. The $\text{M}(\text{II})$ complexes undergo reversible, two-electron reductions in benzonitrile. The measured reduction potentials were used in a thermodynamic cycle to estimate $\text{p}K_{\text{a}}$ values of 22.1 and 27.6 for deprotonation of $\text{HPd}(\text{PNP})_2^+$ and $\text{HPt}(\text{PNP})_2^+$, respectively. The palladium hydride has an acidity equal to that of the nickel hydride and is a better hydride donor than both the nickel and platinum analogues. This shows that it is possible for transition metal hydrides to act simultaneously as both acids and hydride donors.

Introduction

Thermodynamic hydride donor ability^{1–5} (reaction 1) and metal hydride acidity⁶ (reaction 2) are fundamental aspects of metal hydride reactivity that are relevant to a variety of catalytic processes including ionic hydrogenations^{7–11} and the function of hydrogenase enzymes.¹² As



good methods for measuring metal hydride acidities and

hydricities have been developed, periodic trends have begun to emerge. Norton and co-workers⁶ have found that metal hydride acidities generally decrease going down a column in the periodic table, with 3d transition metal hydrides more acidic than analogous 4d hydrides, which are in turn more acidic than their 5d congeners. Angelici and co-workers found the same trend in the heats of protonation of basic metal complexes to form hydrides.¹³ Much less is known about the quantitative hydricity of transition metal hydrides. Kinetic measurements on hydride transfer from anionic group 6 hydrides to BuBr made by Darensbourg and co-workers indicate that tungsten hydrides are more hydridic than analogous chromium hydrides.¹⁴ Bullock and co-workers have studied the kinetic hydricities of $\text{Cp}^*(\text{CO})_n\text{MH}$ complexes ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$, $n = 3$; $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$, $n = 2$) by measuring the rates of hydride transfer from these complexes to $\text{Ph}_3\text{C}^+\text{BF}_4^-$.^{15,16} They found that the kinetic hydricity increases in the order $\text{Cr} < \text{W} < \text{Mo}$ for the group 6 complexes and $\text{Os} < \text{Fe} < \text{Ru}$ for the group 8 complexes. Our recent data on group 9 and 10 metal hydrides indicate that rhodium hydrides are more hydridic than cobalt hydrides by 15 kcal/mol^{4,17} and Pt hydrides are better hydride donors than analogous Ni hydrides by 10 kcal/mol.^{1,2,18} Data on Pd hydrides to

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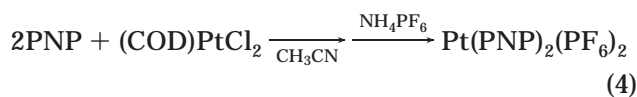
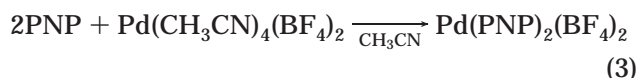
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compare to the Ni and Pt results have been difficult to obtain because many Pd hydrides have proven to be unstable with respect to loss of H₂. Trends in hydride donor ability with chelate ring size for HNi(diphosphine)₂⁺ and HPt(diphosphine)₂⁺ complexes¹ suggest that HPd(diphosphine)₂⁺ complexes with six-membered chelate rings should be more stable than those with five-membered rings. We report here the synthesis of a complete series of M(PNP)₂²⁺ complexes (M = Ni, Pd, Pt, PNP = Et₂PCH₂N(Me)CH₂PEt₂) and the measurement of the hydride donor abilities of the conjugate hydrides, HM(PNP)₂⁺, using three different methods. This represents the first opportunity to compare the acidities and hydricities of a complete periodic group of transition metal hydride complexes coordinated with the same ligands.

Results

Synthesis and Characterization of Complexes.

We have reported the syntheses of Ni(PNP)₂²⁺ and HNi(PNP)₂⁺ and the measurement of the p*K*_a and hydride donor ability of HNi(PNP)₂⁺ previously.¹² The Pd and Pt analogues were synthesized by addition of 2 equiv of the PNP ligand to Pd(CH₃CN)₄(BF₄)₂ and (COD)-PtCl₂, respectively, as shown in reactions 3 and 4.



The light yellow Pd complex is characterized by a single resonance in the ³¹P NMR spectrum at -0.18 ppm due to the four equivalent phosphorus atoms of the two PNP ligands. The ¹H NMR spectrum shows resonances characteristic of the PNP ligand at 3.15 ppm (backbone CH₂) and 2.51 ppm (N-CH₃) in the expected 4:3 ratio, along with resonances due to the ethyl groups on phosphorus. The white Pt complex exhibits a singlet in the ³¹P NMR spectrum at -8.56 ppm with satellites due to coupling to ¹⁹⁵Pt (¹J_{PtP} = 2086 Hz). The ¹H NMR spectrum shows resonances at 3.20 ppm for the backbone CH₂ protons (³J_{PtH} = 25 Hz) and 2.46 ppm for the protons from the methyl group on nitrogen, in addition to resonances due to the ethyl groups on phosphorus.

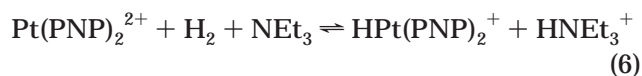
Pd(PNP)₂ was synthesized by the reaction of Pd(PNP)₂²⁺ with H₂ and tetramethylguanidine (TMG, p*K*_a(BH⁺) = 23.3) in acetonitrile according to reaction 5.



The Pd(0) complex is nearly insoluble in acetonitrile, and the colorless crystalline product precipitates from the reaction mixture. It is characterized by a single resonance in the ³¹P NMR spectrum at -2.85 ppm and resonances in the ¹H NMR spectrum at 2.48 ppm (backbone CH₂) and 2.22 ppm (N-CH₃) that are characteristic of the PNP ligand. In NMR tube reactions, this complex reacts cleanly and quantitatively with HNET₃⁺ in benzonitrile or acetonitrile solution to form

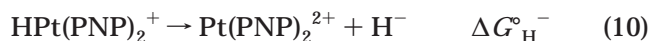
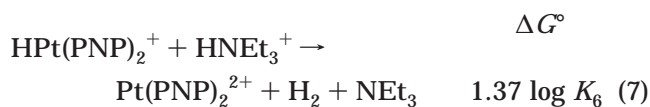
HPd(PNP)₂⁺. However, preparative scale reactions produced significant amounts of Pd(PNP)₂²⁺ when the reaction mixture was concentrated to isolate the product. This may be due to disproportionation of the hydride or its reaction with excess acid to produce H₂ in concentrated solution. The ³¹P NMR spectrum of the hydride shows two resonances at -3.02 and -3.31 ppm due to two sets of inequivalent phosphorus nuclei in this complex. This inequivalence is thought to arise from conformational differences in the two ligands because inequivalence is also observed in the spectrum of HPd(depp)₂⁺ (where depp is 1,3-bis(diethylphosphino)propane) and has been structurally confirmed for a number of analogous Pd and Pt complexes containing bidentate phosphine ligands with large bite angles.¹⁹

Heterolytic Cleavage of Hydrogen Using Pt-(PNP)₂²⁺. The hydride donor ability, Δ*G*_{H⁻}, of HPT-(PNP)₂⁺ was obtained from equilibrium studies of the heterolytic cleavage of H₂ using Pt(PNP)₂²⁺ in the presence of NEt₃, as shown in reaction 6.²



The equilibrium was studied in both acetonitrile and benzonitrile solvents. Equilibrium constants for reaction 6 were determined by combining weighed amounts of Pt(PNP)₂²⁺, NEt₃, and HNET₃BF₄ with the desired solvent in NMR tubes saturated with H₂ at 1 atm and following the concentrations of the metal species by ³¹P NMR. Pt(PNP)₂²⁺ is a good hydride acceptor in combination with NEt₃, and excesses of NEt₃ were found to drive reaction 6 to completion. The equilibrium reactions were therefore carried out using a large excess of HNET₃BF₄ and slightly more than a stoichiometric amount of NEt₃ in this case. The amounts of Pt(PNP)₂²⁺ and HPT-(PNP)₂⁺ present at equilibrium were determined by integration of the ³¹P NMR spectrum, and the concentrations of NEt₃ and HNET₃⁺ were calculated using the amounts added and the stoichiometry of the reaction. The results from five measurements in each solvent gave an equilibrium constant for reaction 6 of 790 atm⁻¹ in acetonitrile and 760 atm⁻¹ in benzonitrile.

The hydride donor ability, Δ*G*_{H⁻}, of HPt(PNP)₂⁺ can be calculated using the thermodynamic cycle shown in reactions 7–10.



$$\Delta G_{\text{H}^-}^\circ = 1.37 \log K_6 - 1.37\text{p}K_a(\text{HNET}_3^+) + 76.0 \text{ kcal/mol} \quad (11)$$

Equation 11 then expresses Δ*G*_{H⁻} as the sum of the free energies of reactions 7–9, which depend on the

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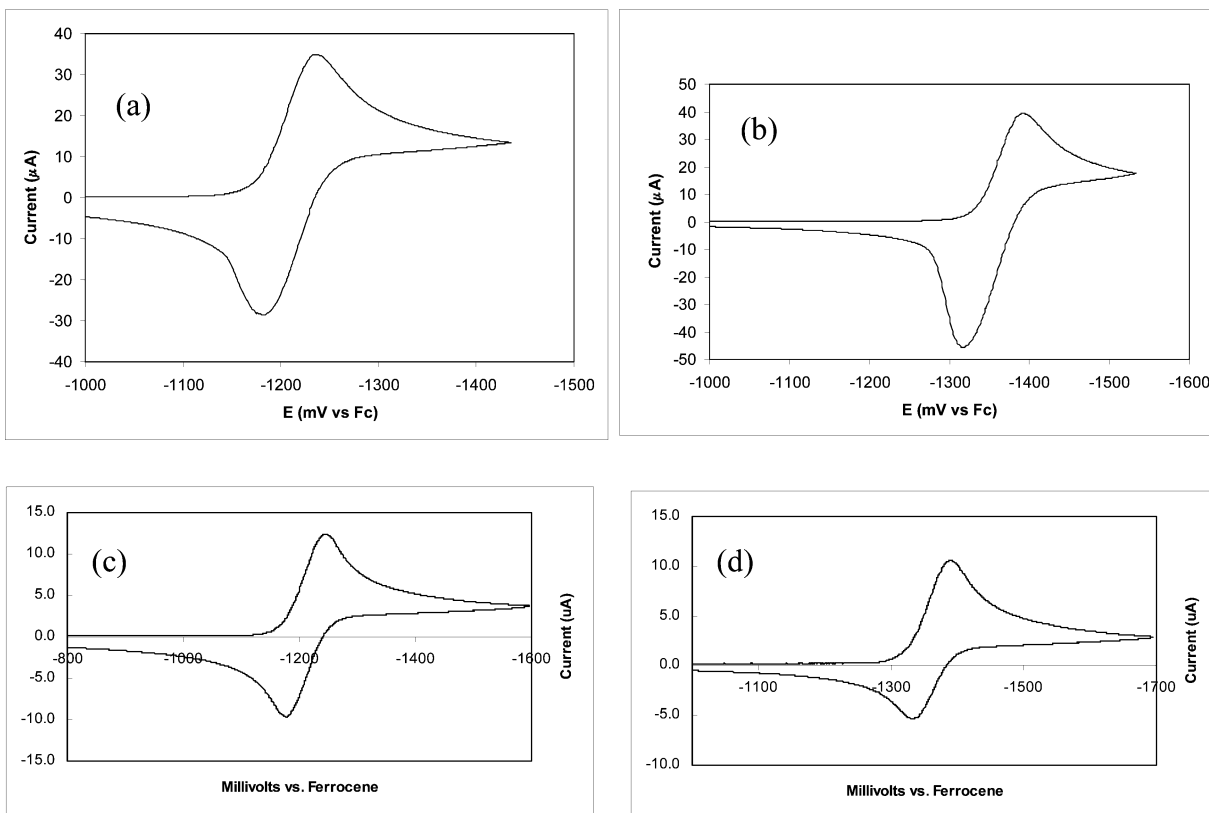
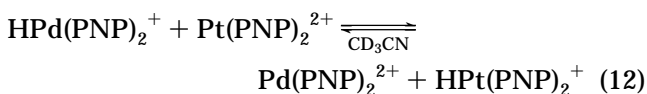


Figure 1. (a) Cyclic voltammogram of a 1.3 mM solution of $\text{Pd}(\text{PNP})_2(\text{BF}_4)_2$ in acetonitrile/0.2 M tetraethylammonium tetrafluoroborate at a scan rate of 0.050 V/s. (b) Cyclic voltammogram of a 1.0 mM solution of $\text{Pt}(\text{PNP})_2(\text{PF}_6)_2$ in acetonitrile/0.2 M tetraethylammonium tetrafluoroborate at a scan rate of 0.050 V/s. (c) Cyclic voltammogram of a 2.1 mM solution of $\text{Pd}(\text{PNP})_2(\text{BF}_4)_2$ in benzonitrile/0.2 M tetrabutylammonium tetrafluoroborate at a scan rate of 0.100 V/s. (d) Cyclic voltammogram of a 2.2 mM solution of $\text{Pt}(\text{PNP})_2(\text{PF}_6)_2$ in benzonitrile/0.2 M tetrabutylammonium tetrafluoroborate at a scan rate of 0.100 V/s. The potential scales are referenced to the ferrocene/ferrocenium couple.

equilibrium constant for reaction 6, K_6 , the $\text{p}K_a$ of HNET_3^+ , and the free energy of reaction 9^{2,20} in acetonitrile. Using this equation and the values for K_6 determined above, the hydride donor ability of $\text{HPt}(\text{PNP})_2^+$ was found to be 54.7 kcal/mol in acetonitrile and 54.6 kcal/mol in benzonitrile.

Hydride Transfer from $\text{HPd}(\text{PNP})_2^+$ to $\text{Pt}(\text{PNP})_2^{2+}$. Hydrogen cleavage using $\text{Pd}(\text{PNP})_2^{2+}$ in the presence of large excesses of NET_3 gave little or no reaction. Another method was needed to measure the hydride donor ability of $\text{HPd}(\text{PNP})_2^+$. The lack of hydrogen cleavage using $\text{Pd}(\text{PNP})_2^{2+}$ and NET_3 indicates that $\text{HPd}(\text{PNP})_2^+$ is a much better hydride donor than $\text{HPt}(\text{PNP})_2^+$ and suggests that direct hydride transfer from $\text{HPd}(\text{PNP})_2^+$ to $\text{Pt}(\text{PNP})_2^{2+}$ would be possible. The hydride donor ability of $\text{HPd}(\text{PNP})_2^+$ was determined using the equilibrium constant for the hydride transfer reaction shown in reaction 12.



A mixture of $\text{HPd}(\text{PNP})_2^+$, which was generated in situ by protonation of $\text{Pd}(\text{PNP})_2$ with HNET_3^+ , and $\text{Pt}(\text{PNP})_2^{2+}$ was prepared in CD_3CN , and the reaction was followed using ^{31}P NMR. The presence of NET_3 and traces of HNET_3^+ in this reaction mixture are not

expected to have any affect on reaction 12; no interaction between NET_3 and the complexes present in reaction 12 was observed in independent experiments. The equilibrium shown in reaction 12 was established very slowly, requiring 42 days to reach equilibrium. At that time, the concentrations of all species in reaction 12 were determined by integration of their respective resonances in the ^{31}P NMR spectrum, and the equilibrium constant K_{12} was evaluated. The value of K_{12} in acetonitrile was found to be 450, which corresponds to a free energy change for reaction 12 ($\Delta G_{12}^\circ = -1.37 \log K_{12}$) of -3.6 kcal/mol. A simple thermodynamic cycle can be used to derive the relationship between the known hydride donor ability of $\text{HPt}(\text{PNP})_2^+$, $\Delta G_{\text{H}^-}^\circ[\text{HPt}(\text{PNP})_2^+]$, the unknown hydride donor ability of $\text{HPd}(\text{PNP})_2^+$, $\Delta G_{\text{H}^-}^\circ[\text{HPd}(\text{PNP})_2^+]$, and the free energy of reaction 12, ΔG_{12}° , which is shown in eq 13.

$$\Delta G_{\text{H}^-}^\circ[\text{HPd}(\text{PNP})_2^+] = \Delta G_{\text{H}^-}^\circ[\text{HPt}(\text{PNP})_2^+] + \Delta G_{12}^\circ \quad (13)$$

Substituting the values found above gives a hydride donor ability for $\text{HPd}(\text{PNP})_2^+$ of 51.1 kcal/mol.

Electrochemical Studies. Cyclic voltammograms of $\text{Pd}(\text{PNP})_2(\text{BF}_4)_2$ and $\text{Pt}(\text{PNP})_2(\text{PF}_6)_2$ in acetonitrile and benzonitrile solutions are shown in Figure 1. Both complexes exhibit quasireversible two-electron reduction waves in acetonitrile. However, on closer inspection, the anodic waves have higher peak currents than the cathodic waves and also appear to be more symmetrical,

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indicating that a surface-confined species is being oxidized rather than a species in solution being oxidized under diffusion control. This behavior has been observed previously for similar compounds.^{1,2} The M(0) species produced by reduction are not very soluble in acetonitrile and precipitate on the electrode during the reduction. When this material is reoxidized, a surface-confined stripping wave is observed.

The electrochemistry is better behaved in benzonitrile, where both M(II) and M(0) species are soluble. Reversible two-electron reductions were observed for both complexes with the $E_{1/2}$ for Pd(PNP)₂(BF₄)₂ at -1.21 V vs ferrocene/ferrocenium and that for Pt(PNP)₂(PF₆)₂ at -1.36 V. The peak-to-peak separations observed were 0.066 and 0.059 V, respectively. A linear dependence of the peak current on the square root of the scan rate indicates that these reductions are diffusion controlled. For Pd(PNP)₂(BF₄)₂, the ratio of the peak current for the anodic wave to the peak current of the cathodic wave (i_{pa}/i_{pc}) is 0.95 ± 0.1 , also supporting a reversible process. For Pt(PNP)₂(PF₆)₂, i_{pa}/i_{pc} varies as a function of the scan rate. At higher scan rates this ratio approaches unity, but at lower scan rates it is considerably smaller (0.63 ± 0.1 at 0.1 V/s). This behavior is consistent with a fast reaction to form a new product upon reduction of the Pt(II) complex to Pt(0). This may be due to the presence of water in the benzonitrile solvent, which is known to react rapidly with Pt(PNP)₂ to form HPt(PNP)₂⁺. This behavior was not observed in acetonitrile.

Discussion

We have reported the syntheses of Ni(PNP)₂(BF₄)₂, HNi(PNP)₂(PF₆), and Ni(PNP)₂ previously.¹² In that study, the hydride donor ability of HNi(PNP)₂⁺ was determined to be 66 kcal/mol using the measured pK_a of the complex (22.2) and the electrochemical potentials for the (II/I) and (I/0) couples of Ni(PNP)₂²⁺.¹ The new complexes Pd(PNP)₂(BF₄)₂ and Pt(PNP)₂(PF₆)₂ were synthesized as described above. The ¹H and ³¹P spectra of these complexes support their formulation as nominally square-planar metal complexes containing two equivalent bidentate phosphine ligands. There is no evidence to support any involvement of the backbone N atom in coordination to the metals.

Different methods were used to measure the hydride donor abilities of the hydrides HM(PNP)₂⁺ (M = Pd, Pt). Pt(PNP)₂²⁺ reacts with H₂ in acetonitrile or benzonitrile solvents in the presence of triethylamine to yield an equilibrium mixture containing HPt(PNP)₂⁺. The formation of this hydride is accompanied by the appearance of new resonances in the ³¹P NMR spectrum (-27.37, -27.52 ppm (¹J_{Pt-P} = 2288 Hz)) and a high-field quintet in the ¹H NMR spectrum (-12.84 ppm (²J_{P-H} = 33 Hz, ¹J_{Pt-H} = 607 Hz)) that are characteristic of HM(diphosphine)₂⁺ complexes.^{1,21,22}

Equilibrium constants for the heterolytic cleavage of H₂ (reaction 6) were used to calculate the hydride donor ability, $\Delta G_{H^-}^\circ$, of the Pt hydride, as described above. The values obtained were 54.7 kcal/mol in acetonitrile and 54.6 kcal/mol in benzonitrile. As we have observed

before,^{1,17} the values of $\Delta G_{H^-}^\circ$ obtained in acetonitrile and benzonitrile are the same within experimental error.

No H₂ cleavage was observed when Pd(PNP)₂²⁺ was used in conjunction with NEt₃, indicating that HPd(PNP)₂⁺ is a much better hydride donor than HPt(PNP)₂⁺. Hydrogen cleavage was observed using Pd(PNP)₂²⁺ in the presence of the stronger base TMG. But in that case, TMG is also basic enough to deprotonate the HPd(PNP)₂⁺ initially formed and the final product is Pd(PNP)₂. Direct hydride transfer from HPd(PNP)₂⁺ to Pt(PNP)₂²⁺, reaction 12 above, was used to measure the hydride donor ability of HPd(PNP)₂⁺. This reaction is slow, but it is not complicated by ligand exchange reactions that are observed when hydrides that contain different phosphine ligands react.¹ The equilibrium constant for reaction 12 was found to be 450, giving a free energy change of -3.6 kcal/mol for this reaction. This means that HPd(PNP)₂⁺ is a better hydride donor by 3.6 kcal/mol than HPt(PNP)₂⁺. The hydride donor ability, $\Delta G_{H^-}^\circ$, for the Pt hydride is 54.7 kcal/mol, so $\Delta G_{H^-}^\circ$ for the Pd hydride is 51.1 kcal/mol.

With the hydride donor abilities of the hydrides and the reduction potentials of the M(PNP)₂²⁺ complexes in hand, eq 14 can be used to calculate the pK_a values of the hydrides.¹

$$\Delta G_{H^-}^\circ = 1.37pK_a(MH^+) + 46.1[E^\circ(II/0)] + 79.6 \text{ kcal/mol} \quad (14)$$

Substitution of the $\Delta G_{H^-}^\circ$ and $E^\circ(II/0)$ values obtained above gives pK_a values of 22.1 and 27.6 for HPd(PNP)₂⁺ and HPt(PNP)₂⁺, respectively. It should be noted that measurements made in acetonitrile and measurements made in benzonitrile were mixed in this thermodynamic cycle to obtain these pK_a values. To determine the effect of using these two solvents, the hydrogen cleavage equilibria using Pt(PNP)₂²⁺ were measured in both solvents and the electrochemistry was examined in both solvents. In each of these cases, the results obtained in acetonitrile and benzonitrile were the same within experimental error. Therefore, the pK_a values obtained above are also expected to be the same in acetonitrile and benzonitrile.

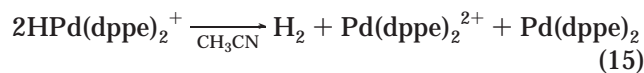
The trend in $\Delta G_{H^-}^\circ$ observed for the HM(PNP)₂⁺ complexes is Pd (51.1) > Pt (54.7) > Ni (66.0) (smaller values of $\Delta G_{H^-}^\circ$ indicate better hydride donors). The palladium hydride is a better hydride donor than the platinum hydride by 3.6 kcal/mol, and the platinum hydride is better than the nickel hydride by 11 kcal/mol. The observed trend in acidity for the HM(PNP)₂⁺ complexes is Pd (22.1) ~ Ni (22.2) > Pt (27.6). The palladium and nickel hydrides have comparable acidities, while the platinum hydride is much less acidic. The palladium hydride is both very acidic and more hydridic than either of the platinum or nickel analogues. This clearly indicates that increased acidity does not necessarily imply decreased hydricity for metal hydride complexes. This property of being simultaneously a good hydride and a good proton donor may be related to the higher reactivity and catalytic activity that is often observed for second-row transition metal complexes.

These thermodynamic data on the palladium hydride also have interesting implications on the stability of palladium hydrides in general. Aresta has recently

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reported the synthesis of HPd(dppe)₂⁺ (dppe = 1,2-bis-(diphenylphosphino)ethane) by protonation of Pd(dppe)₂ with triflic acid in THF, where the product hydride immediately precipitates.²³ When this hydride is dissolved in CH₃CN, it reacts to form H₂ according to reaction 15.



In this case, the hydride acts as both a hydride donor and a proton donor to form H₂ along with Pd(dppe)₂²⁺, the product of hydride donation, and Pd(dppe)₂, the product of proton donation.

Knowing the value of ΔG^o_{H⁻}, eq 11 can be used to calculate the pK_a of an acid that will react with the metal hydride to produce hydrogen, the reverse of reaction 6. Substituting the value of ΔG^o_{H⁻} for HPd-(PNP)₂⁺ (51.1 kcal/mol) and solving for pK_a(BH⁺), we find that acids with pK_a less than 18.2 will react with the hydride to generate H₂. Also, the pK_a of the hydride is 22.1, so conjugate bases of acids with pK_a's greater than 22.1 will deprotonate the hydride. The hydride is stable to acids and bases only over the narrow range of 4 pK units.

This illustrates the reason that palladium hydrides of this type have been difficult to isolate. They are good hydride donors and react readily with acid to produce H₂. They are stable in acid only over a narrow pH range. They are also good acids and react with hydrides such as AlH₄⁻ or BH₄⁻ to give H₂ and Pd(0) species. In some cases, such as HPd(dppe)₂⁺, these hydrides are also unstable with respect to disproportionation to produce H₂.

Conclusion

The hydride donor abilities of the series of complexes HM(PNP)₂⁺ (M = Ni, Pd, Pt) have been determined using three different methods. In this series, the Pd hydride was found to be the best hydride donor of the three, while also being a good acid, with an acidity comparable to that of the Ni hydride. This shows that metal hydride acidity and hydricity are not necessarily coupled. The ability of Pd hydrides to be simultaneously good hydride donors and good proton donors explains the instability of Pd hydrides with respect to H₂ loss under a variety of conditions.

Experimental Section

Spectral and Electrochemical Measurements. ¹H and ³¹P NMR spectra were recorded using Varian Unity 300 and Inova 400 spectrometers. ¹H chemical shifts are reported relative to tetramethylsilane using the residual resonances of solvent protons as a secondary reference. ³¹P NMR spectra were proton decoupled and referenced to external phosphoric acid. ¹H NMR spectra in benzonitrile were recorded on the Varian Inova 400 spectrometer with solvent suppression using the Varian WET1D pulse sequence. In experiments where accurate integrations of ³¹P resonances were required, the relaxation times (T₁) were measured for the compounds of interest using the inversion–recovery method. Quantitative

spectra were then collected using gated proton decoupling, a 70° pulse, and a repetition rate set to 5 times the longest T₁.

All electrochemical experiments were carried out under an atmosphere of N₂ in 0.2 M Et₄NBF₄ acetonitrile solutions or 0.2 M Bu₄NBF₄ benzonitrile solutions. Cyclic voltammetry studies were done on a Cypress Systems computer-aided electrolysis system. The working electrode was a glassy carbon disk, the counter electrode was a glassy carbon rod, and the reference electrode was a silver wire immersed in a permethylferrocene/permethylferrocenium solution. Ferrocene was used as an internal standard, and all potentials are referenced to the ferrocene/ferrocenium couple.

Syntheses and Materials. All reactions were performed using standard Schlenk techniques in an N₂ atmosphere. Dichloro(1,5-cyclooctadiene)platinum(II) was purchased from Strem Chemical Co. and used without further purification. Anhydrous benzonitrile, anhydrous acetonitrile, TMG, ammonium hexafluorophosphate, and triethylamine were purchased from Aldrich Chemical Co. and used as received. CD₃CN was purchased from Aldrich Chemical Co., vacuum transferred from CaH₂, and stored in the glovebox. Diethyl ether was purchased from Aldrich Chemical Co. and distilled over Na/benzophenone prior to use. The PNP ligand¹² and [Pd(CH₃CN)₄](BF₄)₂²⁴ were prepared by literature routes. HNEt₃BF₄ was synthesized by addition of HBF₄ diethyl ether complex to NEt₃ in diethyl ether and recrystallized from acetonitrile/diethyl ether.

[Pd(PNP)₂](BF₄)₂. To a Schlenk flask containing a solution of PNP (0.47 g, 2.0 mmol) in acetonitrile (50 mL) was added solid [Pd(CH₃CN)₄](BF₄)₂ (0.44 g, 1.0 mmol). The resulting red solution was stirred at room temperature for 1 h. Removal of the solvent under vacuum resulted in a yellow powder, which was dried under vacuum and analyzed correctly without further purification (0.54 g, 85% yield). Anal. Calcd for C₂₂H₅₄N₂P₄B₂F₈Pd: C, 35.20; H, 7.25; N, 3.73. Found: C, 35.32; H, 7.42; N, 3.96. ¹H NMR (CD₃CN): δ 3.15 (s, 4.1 H, PCH₂N), 2.51 (s, 3.0 H, NCH₃), 2.07 (q, ³J_{H-H} = 7.8 Hz, PCH₂CH₃), 1.20 (m, PCH₂CH₃). ³¹P NMR (CD₃CN): δ -0.18 (s). T₁ = 4.14 ± 0.02 s.

[Pd(PNP)₂]. A 50 mL centrifuge tube was charged with [Pd-(CH₃CN)₄](BF₄)₂ (0.45 g, 1.01 mmol), PNP (0.48 g, 2.04 mmol), and acetonitrile (10 mL) and capped with a rubber septum. The resulting dark yellow solution was stirred for 1 h, and TMG (0.42 mL, 0.39 g, 3.4 mmol) was added to give a dark green solution. The solution was then saturated with H₂ by bubbling gas through a needle into the solution for 10 min. A white crystalline solid precipitated from the solution overnight. The solvent was then decanted via cannula, and the solid was washed with acetonitrile (3 × 2 mL) and dried under vacuum to yield 0.103 g. Two additional crops of product were obtained by combining the reaction solvent and the washes, saturating with H₂, and collecting the product in a similar manner. The combined yield was 0.34 g (58%). Anal. Calcd for C₂₂H₅₄N₂P₄Pd: C, 45.79; H, 9.43; N, 4.86. Found: C, 45.86; H, 9.30; N, 4.95. ¹H NMR (toluene-*d*₆): δ 2.48 (s, 4.0 H, PCH₂N), 2.22 (s, 3.0 H, NCH₃), 1.51 (m, 4.1 H, PCH₂CH₃), 1.33 (m, 4.2 H, PCH₂CH₃), 1.13 (m, 11.9 H, PCH₂CH₃). ³¹P NMR (toluene-*d*₆): δ -2.85 (s). T₁ = 6.54 ± 0.07 s.

[Pt(PNP)₂](PF₆)₂. To a Schlenk flask containing a solution of PNP (0.47 g, 2.0 mmol) in acetonitrile (50 mL) was added solid Pt(COD)Cl₂ (0.37 g, 1.0 mmol). The resulting clear solution was stirred at room temperature for 1 h. The volume of solvent was reduced under vacuum to 5 mL, and a solution of NH₄PF₆ (0.33 g, 2.0 mmol) in ethanol (5 mL) was added. The white precipitate that formed immediately was collected by filtration, washed with diethyl ether (10 mL), and dried under vacuum. It was recrystallized from acetonitrile (~2 mL) by addition of diethyl ether to yield a microcrystalline powder (0.48 g, 50% yield). Anal. Calcd for C₂₂H₅₄N₂P₆F₁₂Pt: C, 27.65;

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H, 5.70; N, 2.93. Found: C, 27.44; H, 5.74; N, 2.99. ^1H NMR (CD_3CN): δ 3.20 (s, 3.9 H, $^3J_{\text{Pt-H}} = 25$ Hz, PCH_2N), 2.46 (s, 3.0 H, N-CH_3), 2.15 (m, PCH_2CH_3), 1.20 (m, PCH_2CH_3). ^{31}P NMR (CD_3CN): δ -8.56 (s, $^1J_{\text{Pt-P}} = 2086$ Hz). $T_1 = 4.5 \pm 0.1$ s.

Heterolytic Cleavage of H_2 Using $[\text{Pt}(\text{PNP})_2](\text{PF}_6)_2$. The reaction was carried out in NMR tubes in the presence of $\text{NEt}_3/\text{HNEt}_3^+$ in both CD_3CN and benzonitrile solvents. Five separate reactions were carried out in each solvent. The reactions in CD_3CN are described here; the reactions in benzonitrile were done in essentially the same way. An initial reaction using $\text{Pt}(\text{PNP})_2(\text{PF}_6)_2$ (19 mg, 0.020 mmol) and NEt_3 (20.2 mg, 0.20 mmol) in CD_3CN (0.7 mL) under ~ 2 atm H_2 was carried out to observe the spectra of $\text{HPt}(\text{PNP})_2^+$. After 3 days, complete conversion to the hydride was observed, and the following spectral data for $\text{HPt}(\text{PNP})_2^+$ were noted. ^1H NMR (CD_3CN): δ 2.83 (s, $^3J_{\text{Pt-H}} = 17$ Hz, PCH_2N), 2.33 (s, NCH_3), 1.82 and 1.67 (m, PCH_2CH_3), 1.01 (m, PCH_2CH_3), -12.85 (quintet, $^2J_{\text{P-H}} = 33$ Hz, $^1J_{\text{Pt-H}} = 607$ Hz, Pt-H). ^{31}P NMR (CD_3CN): δ -27.37 (s, $^1J_{\text{Pt-P}} = 2288$ Hz), -27.52 (s, $^1J_{\text{Pt-P}} = 2288$ Hz). $T_1 = 5.9 \pm 0.1$ s. For the equilibrium studies, $\text{Pt}(\text{PNP})_2(\text{PF}_6)_2$ (20–25 mg, 0.021–0.026 mmol) and HNEt_3BF_4 (59–85 mg, 0.31–0.45 mmol) were weighed into each of five NMR tubes, CD_3CN (0.8 mL) was added to each, and the tubes were capped with rubber septa. NEt_3 (2.2–2.7 mg, 0.022–0.027 mmol) was then added by syringe, and the exact amount added was determined by weighing. The solutions were then saturated with H_2 at 1 atm (620 mmHg) by bubbling gas slowly through a needle into each solution for 10 min. The solutions were re-saturated with H_2 daily. The reactions were monitored by ^{31}P and ^1H NMR spectroscopy until equilibrium was reached (8 days in this case). The concentrations of $\text{Pt}(\text{PNP})_2^{2+}$ and $\text{HPt}(\text{PNP})_2^+$ present at equilibrium were then determined by integration of their ^{31}P resonances. The amount of NEt_3

consumed by the reaction was then assumed to be equal to the amount of $\text{HPt}(\text{PNP})_2^+$ produced, and the concentrations of NEt_3 and HNEt_3^+ present at equilibrium were calculated. The equilibrium constant K_6 was then calculated using these concentrations. The values obtained from five experiments were 1086, 662, 620, 858, and 720 atm^{-1} in CD_3CN and 710, 770, 790, 860, and 650 atm^{-1} in benzonitrile. The average values and standard deviations are 790 ± 170 and 760 ± 70 atm^{-1} , respectively.

Hydride Transfer from $\text{HPd}(\text{PNP})_2^+$ to $\text{Pt}(\text{PNP})_2^{2+}$. In an NMR tube, $\text{Pd}(\text{PNP})_2$ (15 mg, 0.026 mmol) and HNEt_3BF_4 (5 mg, 0.026 mmol) were combined with CD_3CN (0.7 mL) to form a yellow solution of $\text{HPd}(\text{PNP})_2^+$, and the following spectral data were noted. ^1H NMR (CD_3CN): δ 2.80 (s, 7.8 H, PCH_2N), 2.40 (s, 6.0 H, NCH_3), 1.71 and 1.63 (m, 16.2 H, PCH_2CH_3), 1.06 (m, 23.4 H, PCH_2CH_3), -9.35 (quintet, $^2J_{\text{P-H}} = 54$ Hz, Pd-H). ^{31}P NMR (CD_3CN): δ -3.02 (t, $^2J_{\text{P-P}} = 17$ Hz), -3.31 (t, $^2J_{\text{P-P}} = 17$ Hz). $T_1 = 6.72 \pm 0.10$ s. $\text{Pt}(\text{PNP})_2(\text{PF}_6)_2$ (24 mg, 0.025 mmol) was then added to the tube, and the reaction was monitored by recording ^{31}P NMR spectra at 4 day intervals. The NMR tube was stored in the glovebox, except for the time required to collect spectra, to protect the sample from oxygen. After 42 days, the reaction reached equilibrium and the concentrations of all four complexes present were determined by integration of their respective resonances in the ^{31}P NMR spectrum. The equilibrium constant for reaction 12 was calculated to be 450 using these concentrations.

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Science, Chemical and Biological Sciences Division, under contract No. DE-AC36-99G010337.

OM0342816