J|A|C|S
ARTICLES

Measurement of the Hydride Donor Abilities of $[HM(diphosphine)_2]^+$ Complexes (M = Ni, Pt) by Heterolytic Activation of Hydrogen

Calvin J. Curtis, Alex Miedaner, William W. Ellis, and Daniel L. DuBois*

Contribution from the National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, Colorado 80401

Received July 10, 2001

Abstract: $[M(diphosphine)_2]^{2+}$ complexes (where M = Ni and Pt) react with hydrogen in the presence of bases to form the corresponding hydrides, $[HM(diphosphine)_2]^+$. In seven cases, equilibria have been observed from which the hydride donor ability ($\Delta G^\circ_{H^-}$) of the hydrides can be calculated. For six of these complexes, the $\Delta G^\circ_{H^-}$ values calculated using heterolytic activation of hydrogen are compared with those based on thermodynamic cycles using pK_a measurements and electrochemical half-wave potentials. The agreement between these two methods is good (within 1 kcal/mol). The reactivity of the various $[M(diphosphine)_2]^{2+}$ complexes toward hydrogen parallels their measured hydride acceptor abilities.

Introduction

The thermodynamic properties of transition-metal hydride bonds are of fundamental importance in understanding their stability, reactivity, and catalytic properties. The metal hydride bond, like any bond, can be cleaved in three different ways as shown in Scheme 1. If both electrons of the bond remain associated with the metal, then the reaction is a simple deprotonation reaction. The free energy of this reaction in solution is generally determined by measuring the equilibrium constant for the proton-transfer reaction between the metal hydride being studied and a base whose pK_a value is known.[1] A second method is to determine the heat of protonation using calorimetric measurements and correcting for the entropic term.[2−4] In the past 20 years, our knowledge of the acidity of metal−hydride bonds has increased significantly.[5−24] This knowledge is useful in understanding the regiospecificity of reactions and the exact nature of catalytically active species.[25−28] Recent studies of certain classes of metal hydrides have shown linear correlations between the pK_a values of the hydrides (or enthalpies of protonation of their conjugate bases) and the oxidation potentials of the conjugate bases.[29,30] These studies indicate that pK_a values of at least some classes of hydrides can be predicted from electrochemical data of the corresponding conjugate bases.

Scheme 1

$$MH^+ \longrightarrow M + H^+$$

$$MH^+ \longrightarrow M^+ + H^\bullet$$

$$MH^+ \longrightarrow M^{2+} + H^-$$

Similar progress has been made in the measurement of homolytic bond dissociation energies in solution. A commonly used method for determining homolytic bond dissociation free

---

(1) Kristjansdottir, S. S.; Norton, J. R. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, 1991; pp 309−359.
(2) Angelici, R. J. *Acc. Chem. Res.* **1995**, *28*, 51−60.
(3) Sowa, J. R., Jr.; Zanotti, V.; Facchin, G.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 9185−9192.
(4) Busch, R. C.; Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 681−686.
(5) Jordan, R. F.; Norton, J. R. *ACS Symp. Ser.* **1982**, *198*, 403−423.
(6) Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257−2263.
(7) Edidin, R. T.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 3945−3953.
(8) Kristjansdottir, S. S.; Moody, A. E.; Weberg, R. T.; Norton, J. R. *Organometallics* **1988**, *7*, 1983−1987.
(9) Kristjansdottir, S. S.; Loendorf, A. J.; Norton, J. R. *Inorg. Chem.* **1991**, *30*, 4470−4471.
(10) Song, J. S.; Szalda, D. J.; Bullock, R. M.; Lawrie, C. J. C.; Rodkin, M. A.; Norton, J. R. *Angew. Chem.* **1992**, *104*, 1280−1282 (See also *Angew. Chem., Int. Ed. Engl.* **1992**, *1231*(1289), 1233−1285).
(11) Gusev, D. G.; Huebener, R.; Burger, P.; Orama, O.; Berke, H. *J. Am. Chem. Soc.* **1997**, *119*, 3716−3731.
(12) Peterson, T. H.; Golden, J. T.; Bergman, R. G. *Organometallics* **1999**, *18*, 2005−2020.
(13) Chin, B.;. Lough, A. J.; Morris, R. H.; Schweitzer, C. T.; D'Agostino, C. *Inorg. Chem.* **1994**, *33*, 6278−6288.
(14) Cappellani, E. P.; Drouin, S. D.; Jia, G.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T. *J. Am. Chem. Soc.* **1994**, *116*, 3375−3388.
(15) Bullock, R. M.; Song, J.-S.; Szalda, D. J. *Organometallics* **1996**, *15*, 2504−2516.
(16) Jia, G.; Morris, R. H. *Inorg. Chem.* **1990**, *29*, 581−582.
(17) Jia, G.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 875−883.
(18) Jia, G.; Lau, C. P. *Coord. Chem. Rev.* **1999**, *190−192*, 83−108.
(19) Ontko, A. C.; Houlis, J. F.; Schnabel, R. C.; Roddick, D. M.; Fong, T. P.; Lough, A. J.; Morris, R. H. *Organometallics* **1998**, *17*, 5467−5476.
(20) Schunn, R. A. In *Transition Metal Hydrides*; Muetterties, E. L., Ed.; M. Dekker: New York, 1971; pp 203−269.
(21) Miller, A. E. S.; Miller, T. M. *NATOASISer., Ser. C* **1992**, *367*, 253−267.
(22) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155.
(23) Davies, S. C.; Henderson, R. A.; Hughes, D. L.; Oglieve, K. E. *J. Chem. Soc., Dalton Trans.* **1998**, 425−431.
(24) Abdur-Rashid, K.; Fong, T. P.; Greaves, B.; Gusev, D. G.; Hinman, J. G.; Landau, S. E.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 9155−9171.
(25) Bullock, R. M.; Song, J.-S. *J. Am. Chem. Soc.* **1994**, *116*, 8602−8612.
(26) Kollar, K.; Sandor, P.; Szalontai, G.; Heil, B. J. *Organomet. Chem.* **1990**, *393*, 153.
(27) Takahashi, H.; Achiwa, K. *Chem. Lett.* **1987**, 1921−1922.
(28) Chao, T.-H.; Espenson, J. H. *J. Am. Chem. Soc.* **1978**, *100*, 129−133.
(29) Wang, D.; Angelici, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 935−942.
(30) Bering, D. E.; Miedaner, A.; Curtis, C. J.; Noll, B. C.; DuBois, M. C. R.; DuBois, D. L. *Organometallics* **2001**, *20*, 1832−1839.

10.1021/ja0116829 CCC: $22.00

Scheme 2

$$\begin{array}{lll} L_nMH^+ \longrightarrow L_nM + H^+ & & \Delta G° = 1.37(pK_a) \\ L_nM \longrightarrow L_nM^+ + e^- & & \Delta G° = 23.06E°(I/0) \\ H^+ + e^- \longrightarrow H^\bullet & & \Delta G° = -23.06E°(H^+/H^\bullet) \\ \hline L_nMH^+ \longrightarrow L_nM^+ + H^\bullet & & \end{array}$$

Scheme 3

$$\begin{array}{lll} L_nMH^+ \longrightarrow L_nM + H^+ & & \Delta G° = 1.37(pK_a) \\ L_nM \longrightarrow L_nM^{2+} + 2e^- & & \Delta G° = 46.1E°(II/0) \\ H^+ + 2e^- \longrightarrow H^- & & \Delta G° = -46.1E°(H^+/H^-) \\ \hline L_nMH^+ \longrightarrow L_nM^{2+} + H^- & & \end{array}$$

energies is to measure equilibrium reactions between the metal complexes and H_2 as shown in eq 1.[31−33] Another powerful method for determining homolytic bond dissociation energies involves measurement of the pK_a of a metal hydride and the potential for the one-electron oxidation of its conjugate base. These values can be used to calculate the homolytic bond dissociation free energy using eq 2, which is derived from the thermodynamic cycle shown in Scheme 2.[34] These data are useful for determining the hydrogen pressure under which the transition-metal hydride of interest will be present, and the stability of the hydride complex with respect to hydrogen loss. This reaction can involve either one or two metal centers. If two metal centers are involved, it provides information on the energy required for cleaving individual M−H bonds.[31,33,35] This can be useful in assessing the feasibility of M−H bond cleavage in certain proposed reaction mechanisms.

$$2M^\bullet + H_2 \rightarrow 2MH \tag{1}$$

$$\Delta G°_{H\bullet} = 1.37(pK_a) + 23.06E°(I/0) + 53.6 \text{ kcal/mol} \tag{2}$$

Free energy measurements of the heterolytic cleavage of the M−H bond in solution to form the hydride ion (as shown in the final reactions of Schemes 1 and 3 with free energy $\Delta G°_{H^-}$) have only been reported recently,[36] although kinetic measurements that are related to this quantity were made earlier.[37−48]

Two methods for measuring $\Delta G°_{H^-}$ have been described. One method measures equilibria between transition metal hydrides and acceptor molecules such as triarylcarbonium ions whose hydride acceptor abilities have been determined by a thermochemical cycle using estimated bond enthalpies and measured redox potentials.[49,50] A second method uses the thermochemical cycle shown in Scheme 3. This method requires the measurement of the pK_a value of the hydride and the potential associated with a two-electron oxidation of its conjugate base.[36] Equation 3 is then used to calculate $\Delta G°_{H^-}$ using the pK_a of the metal hydride determined in CH_3CN and the potential of the II/0 couple measured in CH_3CN and referenced to the ferrocene/ferrocenium couple. Quantitative values of $\Delta G°_{H^-}$ for transition-metal hydride complexes are useful for predicting the following: (1) the stability of hydride complexes to acids of different strengths, (2) the ability of these compounds to act as hydride donors toward organic substrates and other metal complexes, and (3) the conditions required for heterolytic cleavage of H_2 by the conjugate hydride acceptor of the transition metal hydride.

$$\Delta G°_{H^-} = 1.37(pK_a) + 46.1E°(II/0) + 79.6 \text{ kcal/mol} \tag{3}$$

In this paper, we describe a third method for measuring the hydride donor abilities of transition-metal hydrides. It is based on equilibrium measurements for the heterolytic cleavage of hydrogen by transition metal complexes in the presence of bases for which the conjugate acid pK_a values are known. This method provides an independent check of the two methods used previously, and it requires only one equilibrium measurement. This method is particularly useful for systems where reversible electrochemistry is not observed for the conjugate base of the hydride, because it does not require any electrochemical measurements. It is also useful for systems in which the conjugate base of the hydride is unstable. As described below, this approach results in values of $\Delta G°_{H^-}$ that are typically within 1 kcal/mol of those determined by measuring the pK_a of the metal hydride and the potential of the two-electron oxidation of the conjugate base.

Results

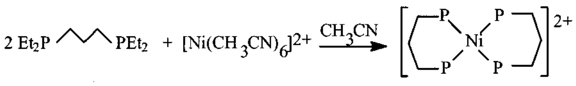
Synthesis. Bis(diethylphosphino)propane (depp) is a clear, colorless, air-sensitive liquid. It can be prepared by the reaction of $LiPEt_2$ with 1,3-dibromopropane, reaction 4. A single resonance is observed in the ^{31}P NMR spectrum of this compound at −23.3 ppm compared to a value of −22 ppm calculated using an empirical group additivity relationship.[51] The ^{1}H NMR and ^{13}C NMR spectra are consistent with three different methylene resonances, two from the 3-carbon chain connecting the phosphorus atoms and one from the ethyl groups on phosphorus, and one methyl resonance arising from the four ethyl groups. The $^3J_{PH}$ coupling of the methyl protons with phosphorus is larger than the $^2J_{PH}$ coupling of the methylene

---

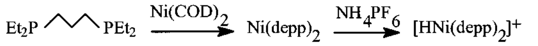
[31] Kiss, G.; Zhang, K.; Mukerjee, S. L.; Hoff, C. D.; Roper, G. C. *J. Am. Chem. Soc.* **1990**, *112*, 5657−5658.
[32] Wei, M.; Wayland, B. B. *Organometallics* **1996**, *15*, 4681−4683.
[33] Wayland, B. B. *Polyhedron* **1988**, *7*, 1545−1555.
[34] Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 6711−6717.
[35] Kiss, G.; Nolan, S. P.; Hoff, C. D. *Inorg. Chim. Acta* **1994**, *227*, 285−292.
[36] Berning, D. E.; Noll, B. C.; DuBois, D. L. *J. Am. Chem. Soc.* **1999**, *121*, 11432−11447.
[37] Darensbourg, M. Y.; Ash, C. E.; Arndt, L. W.; Janzen, C. P.; Youngdahl, K. A.; Park, Y. K. *J. Organomet. Chem.* **1990**, *383*, 191−199.
[38] Silva, R. M.; Darensbourg, M. Y. *J. Braz. Chem. Soc.* **1992**, *3*, 55−60.
[39] Labinger, J. A. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, 1991; pp 361−379.
[40] Labinger, J. A.; Komadina, K. H. *J. Organomet. Chem.* **1978**, *155*, C25−C28.
[41] Kao, S. C.; Spillett, C. T.; Ash, C.; Lusk, R.; Park, Y. K.; Darensbourg, M. Y. *Organometallics* **1985**, *4*, 83−91.
[42] Gaus, P. L.; Kao, S. C.; Youngdahl, K.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1985**, *107*, 2428−2434.
[43] Kao, S. C.; Darensbourg, M. Y. *Organometallics* **1984**, *3*, 646−647.
[44] Kinney, R. J.; Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 7902−7915.
[45] Martin, B. D.; Warner, K. E.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 33−39.
[46] Hembre, R. T.; McQueen, J. S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 65−67.
[47] Hembre, R. T.; McQueen, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 2141−2142.
[48] Cheng, T.-Y.; Brunschwig, B. S.; Bullock, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 13121−13137.
[49] Zhang, X.-M.; Bruno, J. W.; Enyinnaya, E. *J. Org. Chem.* **1998**, *63*, 4671−4678.
[50] Sarker, N.; Bruno, J. W. *J. Am. Chem. Soc.* **1999**, *121*, 2174−2180.
[51] Fluck, E.; Heckmann, G. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH Publishers: Deerfield Beach, Florida, 1987; Vol. 8, pp 88−92.

protons, as observed previously for ethyl groups attached to phosphorus.[30] Reaction of this ligand with $[Ni(CH_3CN)_6](BF_4)_2$ produces $[Ni(depp)_2](BF_4)_2$ as a yellow solid, after isolation, that is moderately air-sensitive in solution, reaction 5. A single resonance is observed in the ^{31}P NMR spectrum at 3.22 ppm, 26 ppm downfield of the free ligand. The reaction of 2 equiv of depp with $Ni(COD)_2$ (where COD is 1,5-cyclooctadiene) gives $Ni(depp)_2$ as an orange, air-sensitive solid, step 1 of reaction 6. Again the ^{31}P NMR spectrum exhibits a single resonance at 3.82 ppm. Reaction of the latter complex with NH_4PF_6 produces $[HNi(depp)_2](PF_6)$, step 2 of reaction 6. The ^{31}P NMR spectrum of $[HNi(depp)_2]^+$ is a singlet (3.28 ppm) at room temperature and remains unchanged on cooling to −90 °C. The ^1H NMR spectrum shows resonances expected for the diphosphine ligand and a quintet at −15.69 ppm assigned to the hydride ligand coupling to the four phosphorus atoms. The equivalence of the four phosphorus atoms is attributed to a rapid fluxional process. $[Pt(depp)_2](PF_6)_2$, a yellow air-stable solid, was prepared by the reaction of 2 equiv of depp with $Pt(COD)Cl_2$ followed by metathesis with NH_4PF_6. The ^{31}P NMR spectrum of $[Pt(depp)_2](PF_6)_2$ shows a singlet at 5.72 ppm, with satellites due to the presence of ^{195}Pt, and a septet resonance for PF_6^-.

(4)



(5)



(6)

Electrochemical Studies. Cyclic voltammograms of $[Ni(depp)_2](BF_4)_2$ and $[Pt(depp)_2](PF_6)_2$ in benzonitrile solutions are shown in Figure 1. For $[Ni(depp)_2](BF_4)_2$, two reversible one-electron waves are observed at −0.58 and −1.34 V vs the ferrocene/ferrocenium couple. These waves are assigned to the Ni(II/I) couple and the Ni(I/0) couple, respectively. The peak-to-peak separations of 0.067 and 0.071 V at a scan rate of 0.050 V/s and the ratio of the peak heights ($ip_a/ip_c = 1.0 \pm 0.1$ for both couples) are consistent with reversible one-electron processes. Under the same conditions, the peak-to-peak separation observed for ferrocene was 0.071 V. A linear dependence of the peak current on the square root of the scan rate indicates that these reductions are diffusion controlled. Similar cyclic voltammograms are obtained for $Ni(depp)_2$ in benzonitrile. In acetonitrile, the Ni(II/I) wave of $[Ni(depp)_2]^{2+}$ ($E_{1/2} = -0.60$ V) is reversible, but the behavior of the Ni(I/0) (−1.35 V) couple is variable due to precipitation of $Ni(depp)_2$ in this solvent.

For $[Pt(depp)_2](PF_6)_2$, a quasireversible two-electron reduction wave is observed at −1.40 V in benzonitrile. The peak current for the cathodic wave is 2.8 ± 0.1 times that observed for the analogous Ni complex when the concentrations are normalized. A ratio of 2.83 is expected for a comparison of a reversible two-electron reduction to a reversible one-electron reduction with the same diffusion coefficient. The peak-to-peak separation is 0.045 V compared to an expected value of 0.030 V for a fully reversible two-electron reduction. Under the same conditions, ferrocene had a peak-to-peak separation of 0.071 V compared to the expected 0.060 V separation. For $[Pt(depp)_2](PF_6)_2$, the ratio of the peak current for the anodic wave to the peak current for the cathodic wave (ip_a/ip_c) varies as a function of the scan rate. At higher scan rates, this ratio approaches unity (0.8 ± 0.1 at 0.5 V/s), but at lower scan rates this ratio is considerably smaller (0.25 ± 0.1 at 0.050 V/s). An anodic wave at −0.08 V is also associated with the cathodic wave. This behavior is consistent with a reversible two-electron reduction followed by a fast chemical reaction to form a new product, which is observed at −0.08 V. These results indicate that monomeric $Pt(depp)_2$ is unstable, and therefore no attempts were made to prepare this complex. In acetonitrile, the reduction of $Pt(depp)_2^{2+}$ causes precipitation of a Pt(0) species on the electrode and a large cathodic stripping wave (not diffusion controlled) associated with reoxidation of this material is observed.

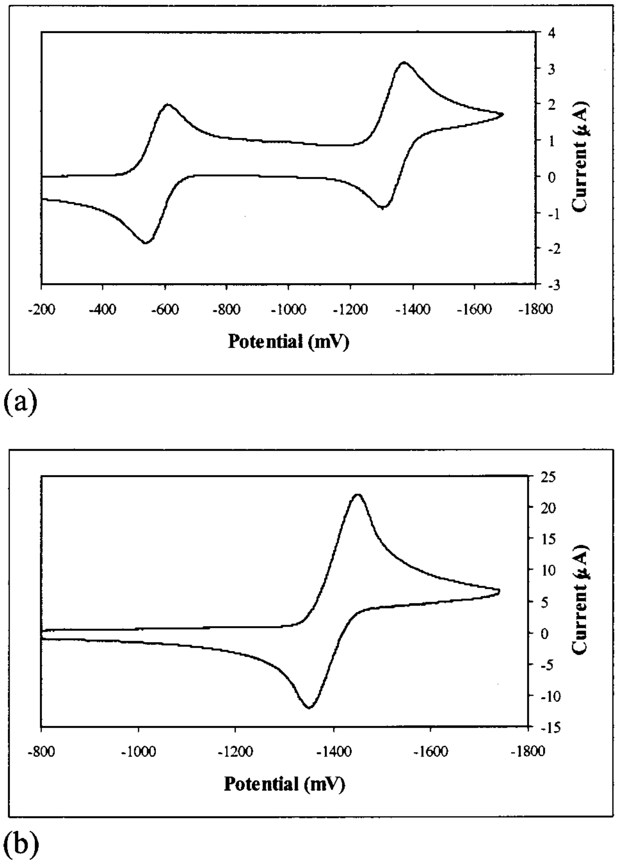


Figure 1. (a) Cyclic voltamogram of a 2.7 mM solution of $[Ni(depp)_2](BF_4)_2$ in benzonitrile/0.2 M tetrabutylammonium tetrafluoroborate at a scan rate of 0.050 V/s. (b) Cyclic voltamogram of a 1.9 mM solution of $[Pt(depp)_2](PF_6)_2$ in benzonitrile/0.15 M tetrabutylammonium tetrafluoroborate at a scan rate of 0.5 V/s. The potential scales are referenced to the ferrocene/ferrocenium couple.

Determination of the pK_a Values for $[HM(diphosphine)_2]^+$ Complexes. The pK_a value of $[HNi(depp)_2]^+$ was determined using tetramethylguanidine (TMG) as a base and proved to be much more difficult to measure than expected. The measurement was complicated by the slow reaction of the hydride with TMG, by the complete insolubility of $Ni(depp)_2$ in CD_3CN, and by the fact that the ^{31}P resonances for the hydride and $Ni(depp)_2$ could not be resolved in benzonitrile. The measurement was accomplished by dissolving the hydride in benzonitrile-d_5 and adding a measured amount of TMG. After 2 days, equilibration was complete and the 500 MHz ^1H NMR spectrum of the sample was recorded. Considerable overlap of the resonances

Table 1. Results of Reactions of [M(diphosphine)$_2$]$^{2+}$ Complexes with H_2 and Base According to Reaction 8 and Associated $\Delta G^\circ_{H^-}$ Values

M	L	B (pK_a of BH$^+$)	reaction obsd?	$\Delta G^\circ_{H^-}$ (3)[a]	$\Delta G^\circ_{H^-}$ (17)[b]
Ni	dmpp	NEt_3 (18.5)	yes	61.2	60.4
		proton sponge((18.2)	yes		
		p-bromoaniline (9.6)	$K_8 = 0.016 \pm 0.005$		
	depp	NEt_3	yes	67.2	66.2
		2,4-dichloroaniline (8.0)	$K_8 = 7.7 \pm 4$		
	depe	NEt_3	yes	56.0	56.0
		anisidine (11.3)	$K_8 = 0.00052 \pm 0.00015$		
	dmpe	NEt_3	$K_8 = 0.49$ (0.06	50.9	50.8
		proton sponge	no		
Pt	dmpp	NEt_3	$K_8 = 1.7 \pm 0.3$	50.7	51.0
	depp	NEt_3	yes		53.8
		pyridine (12.3)	$K_8 = 0.00014 \pm 0.00004$		53.9
		morpholine (16.6)	$K_8 = 2.9 \pm 0.5$		
	dmpe	NEt_3	no	42.5	42.0
		KOPh (26.6)	yes		
		TMG (23.3)	$K_8 = 0.0089 \pm 0.0012$		

[a] $\Delta G^\circ_{H^-}$ values determined using the cycle in Scheme 3 and calculated using eq 3.[36] [b] $\Delta G^\circ_{H^-}$ values determined by heterolytic cleavage of H_2 and calculated using eq 17.

of the two complexes was still observed, even at 500 MHz, but the peak heights of the methyl resonances of the hydride (1.03 ppm) and the Ni(0) complex (1.62 ppm) were used to calculate the concentrations of these species. The concentrations of TMG and TMGH$^+$ were then calculated using the stoichiometry of the reaction and the amount of TMG added. These concentrations were then used to evaluate the equilibrium constant, K_{eq}, for reaction 7. This value was then combined with the known

$$\mathrm{HNi(depp)_2}^+ + \mathrm{TMG} \rightleftharpoons \mathrm{Ni(depp)_2} + \mathrm{TMGH}^+ \qquad (7)$$

pK_a value for TMGH$^+$ in acetonitrile (23.3)[52] to obtain the pK_a value for [HNi(depp)$_2$]$^+$, as described previously.[6,36] The value of K_{eq} was found to be 0.93, leading to a pK_a value for the hydride of 23.3.

The pK_a value of [HPt(depe)$_2$]$^+$ (where depe is bis(diethylphosphino)ethane) was originally determined by equilibration with a large excess of TMG.[36] However, a comparison of the $\Delta G^\circ_{H^-}$ value calculated using this pK_a with the value obtained by hydrogen cleavage (see below) led us to suspect that the original pK_a value was incorrect. The pK_a value was therefore redetermined in acetonitrile using potassium phenoxide (KOPh) as the base. The results from six experiments using different concentrations of hydride and phenoxide gave a pK_a value of 29.7 ± 0.1 for [HPt(depe)$_2$]$^+$. This is significantly larger than the original value of 27.1 and has led to adjustment of the pK_a values for [HPt(dmpp)$_2$]$^+$ (30.4) and [HPt(dmpe)$_2$]$^+$ (31.1) as well, since those were determined by equilibration with [HPt(depe)$_2$]$^+$. The new pK_a values give $\Delta G^\circ_{H^-}$ values calculated using eq 3 of 50.7 kcal/mol for [HPt(dmpp)$_2$]$^+$, 44.2 kcal/mol for [HPt(depe)$_2$]$^+$, and 42.5 kcal/mol for [HPt(dmpe)$_2$]$^+$.

Heterolytic Cleavage of Hydrogen. The results of the reaction of a number of [M(diphosphine)$_2$]$^{2+}$ complexes with hydrogen and base in acetonitrile according to reaction 8 are summarized in Table 1. In seven cases, equilibria are observed. Reaction 8 proceeds in both directions, as expected for true equilibria. This was confirmed for four of the cases. For example, [Ni(dmpe)$_2$]$^{2+}$ (where dmpe is bis(dimethylphosphino)ethane) reacts with H_2 in the presence of NEt_3 or NEt_3/$HNEt_3^+$ mixtures to form an equilibrium mixture containing [HNi(dmpe)$_2$]$^+$. The reaction can be performed in the other direction by adding NEt_3/$HNEt_3^+$ to [HNi(dmpe)$_2$]$^+$ under H_2. This reaction is very slow in both directions, but after 3 weeks, both reactions reach equilibrium and give the same value for the equilibrium constant. For [Ni(dmpe)$_2$]$^{2+}$, [Ni(dmpp)$_2$]$^{2+}$, [Pt(dmpe)$_2$]$^{2+}$, [Pt(dmpp)$_2$]$^{2+}$, and [Pt(depp)$_2$]$^{2+}$ (where dmpp is bis(dimethylphosphino)propane) the equilibrium constants shown were calculated for at least three independent experiments using ratios for the metal complexes that were determined by integration of the ^{31}P NMR signals on spectra collected using a repetition rate long enough to ensure adequate relaxation of the phosphorus nuclei. For [Ni(depp)$_2$]$^{2+}$ and [HNi(depp)$_2$]$^+$, integration of the ^{1}H signal from the methyl resonance of the ethyl group on the diphosphine ligand was used to determine the ratios of these two species because the ^{31}P resonances for these two complexes could not be resolved. In three cases ([Pt(dmpp)$_2$]$^{2+}$, [Ni(dmpp)$_2$]$^{2+}$, and [Ni(dmpe)$_2$]$^{2+}$), the concentrations of the base and protonated base added were determined by using a large excess (~10-fold) of both so that changes due to reaction 8 could be neglected. In the other cases, the concentrations of base and protonated base at equilibrium were calculated using the amount of base added, the measured concentrations of the metal complexes, and the stoichiometry of reaction 8. All equilibria were measured at room temperature (21 °C) using 1.0 atm of hydrogen as a standard condition. This is also the standard condition of the standard hydrogen electrode. The units for the equilibrium constants for reaction 8 are atm^{-1}.

$$[\mathrm{ML_2}]^{2+} + \mathrm{H_2} + \mathrm{B} \rightleftharpoons [\mathrm{HML_2}]^+ + \mathrm{BH}^+ \qquad (8)$$

[Pt(dmpp)$_2$]$^{2+}$, [Pt(depp)$_2$]$^{2+}$, [Ni(depp)$_2$]$^{2+}$, [Ni(dmpp)$_2$]$^{2+}$, [Ni(depe)$_2$]$^{2+}$, and [Ni(dmpe)$_2$]$^{2+}$ (where depe is bis(diethylphosphino)ethane) all heterolytically cleave hydrogen at room temperature in the presence of triethylamine over a period of several hours to two weeks. [Pt(dmpe)$_2$]$^{2+}$ does not react with H_2 in the presence of triethylamine, but it does react in the presence of KOPh or TMG. [Ni(dmpp)$_2$]$^{2+}$ reacts with hydrogen in the presence of either triethylamine (pK_a($HNEt_3^+$) = 18.5) or proton sponge((1,8-bis(dimethylamino)naphthalene, pK_a(BH$^+$) ~ 18)[53,54] to form [HNi(dmpp)$_2$]$^+$ at approximately the

---

(52) Kolthoff, I. M.; Chantooni, M. K., Jr.; Bhowmik, S. *J. Am. Chem. Soc.* **1968**, *90*, 23.

same rate (half-life of ~2 days). The more sterically hindered proton sponge is not slower than triethylamine in this case. For $[Ni(dmpe)_2]^{2+}$, the reaction with hydrogen is slow, requiring 3 weeks to reach equilibrium in the presence of triethylamine, while no reaction at all is observed using proton sponge. The reaction of $[Ni(depe)_2]^{2+}$ with hydrogen in the presence of triethylamine is also extremely slow and requires approximately 9 days to reach 50% completion. Using anisidine as base, the reaction requires 2 weeks to reach equilibrium.

As expected, the position of equilibrium varies with H_2 pressure. When $[Ni(dmpp)_2]^{2+}$ and 4-bromoaniline are equilibrated with 2.5 mL of H_2 added to the NMR tube (~2 atm of H_2), more hydride is produced compared to samples equilibrated at 1 atm of H_2. When the pressure is released, the equilibrium shifts back to give the amount of hydride expected at 1 atm.

The solvent also plays a major role in the rate of reaction 8. For example, $[Ni(dmpp)_2]^{2+}$ is 50% converted to the corresponding hydride in dimethylformamide (DMF) in approximately 30 min with no added base. The heterolytic cleavage of H_2 in DMF is expected to be inherently much easier than that in acetonitrile because of the stronger solvating power of DMF toward protons.[55]

Discussion

The heterolytic cleavage of hydrogen by transition metal complexes can be used to determine the hydride donor ability of the resulting hydride complexes. The free energy for the heterolytic cleavage of hydrogen in acetonitrile can be calculated using the thermodynamic cycle shown by eqs 9−12 and free energy values from the literature.[55] The 76.0 kcal/mol value calculated for reaction 12 is 2.2 kcal/mol larger than the 73.8 kcal/mol calculated by Sarker and Bruno[50] and slightly smaller than the 76.6 kcal/mol calculated from the data provided by Wayner and Parker.[55] These differences reflect the lack of agreement in the literature values for reactions 9−11 or their equivalent. The origin and nature of these uncertainties have been discussed elsewhere.[1,55,56] For internal self-consistency, the free energy values associated with reactions 10 and 11 are the same as those used by us in previous measurements of free energies for hydride transfer and hydrogen atom transfer reactions.[36] These measurements were based on the thermodynamic cycle shown in Scheme 3.

$$\begin{array}{lrr}
H_2(g) \longrightarrow 2H^{\bullet}(sol) & 103.6 & (9) \\
H^{\bullet}(sol) \longrightarrow H^{+}(sol) + e^{-} & -53.6 & (10) \\
H^{\bullet}(sol) + e^{-} \longrightarrow H^{-}(sol) & 26.0 & (11) \\
\hline
H_2(g) \longrightarrow H^{+}(sol) + H^{-}(sol) & 76.0 & (12)
\end{array}$$

Once the free energy of reaction 12 has been established, a thermodynamic cycle can be constructed that allows the hydride donor ability ($\Delta G^\circ_{H^-}$) of a metal hydride to be calculated using a measured equilibrium constant for reaction 8 and the pK_a for the protonated base used. Reactions 13−16 constitute such a cycle.

$$\begin{array}{lrr}
 & \Delta G^\circ & \\
[HML_2]^{+} + BH^{+} \longrightarrow [ML_2]^{2+} + H_2 + B & 1.37\log K_8 & (13) \\
B + H^{+} \longrightarrow BH^{+} & -1.37pK_a(BH^{+}) & (14) \\
H_2 \longrightarrow H^{+} + H^{-} & 76.0 & (15) \\
\hline
[HML_2]^{+} \longrightarrow [ML_2]^{2+} + H^{-} & \Delta G^\circ_{H^-} & (16)
\end{array}$$

Reaction 13 is just the reverse of reaction 8 and its free energy is given by $-RT \ln K_{13}$, but since $K_{13} = 1/K_8$, it can also be expressed as $RT \ln K_8$ (=$2.303RT \log K_8$ or $1.37 \log K_8$). The sum of reactions 13−15 is the hydride donation reaction for $[HML_2]^+$ and the hydride donor ability of this hydride is the sum of the free energies of reactions 13−15, as shown in eq 17.

$$\Delta G^\circ_{H^-} = 1.37 \log K_8 - 1.37pK_a(BH^+) + 76.0 \text{ kcal/mol} \quad (17)$$

Equilibria are observed when $[Ni(dmpe)_2]^{2+}$, $[Ni(dmpp)_2]^{2+}$, $[Ni(depe)_2]^{2+}$, $[Ni(depp)_2]^{2+}$, $[Pt(dmpe)_2]^{2+}$, $[Pt(dmpp)_2]^{2+}$, and $[Pt(depp)_2]^{2+}$ react with hydrogen in the presence of different bases to form the corresponding hydrides, as shown in Table 1. Equation 17 was used to calculate the $\Delta G^\circ_{H^-}$ values for the corresponding hydride complexes and the results are also shown in Table 1. $\Delta G^\circ_{H^-}$ values of 51.0, 66.2, and 53.9 kcal/mol can be calculated for $[HPt(dmpp)_2]^+$, $[HNi(depp)_2]^+$, and $[HPt(depp)_2]^+$, respectively, using eq 17 and the equilibrium constants shown for reaction 8. The value of 66.2 kcal/mol for $[HNi(depp)_2]^+$ compares favorably with the value of 67.2 kcal/mol derived from eq 3 using the measured pK_a value of 23.3 and the $E_{1/2}$(II/0) value of −0.96 V. However, for $[HPt(dmpp)_2]^+$ the $\Delta G^\circ_{H^-}$ value calculated from eq 3 (47.2 kcal/mol) using data from previous work[36] and the $\Delta G^\circ_{H^-}$ value calculated from eq 17 (51.0 kcal/mol) are significantly different. This led us to reinvestigate the values determined in our previous work. First the electrochemical experiments were repeated, but the new values obtained agreed well with the previously reported values. The pK_a value of $[HPt(dmpp)_2]^+$ was determined in the previous work by equilibration with $Pt(depe)_2$ and relies on the pK_a of $[HPt(depe)_2]^+$, which was determined by equilibration with a large excess of TMG. When the pK_a of $[HPt(depe)_2]^+$ was remeasured using potassium phenoxide ($pK_a = 26.6$) as the base instead of TMG ($pK_a = 23.3$), the value found was 29.7, compared to the value of 27.1 measured previously. This resulted in significantly higher pK_a values for both $[HPt(dmpp)_2]^+$ (30.4 vs 27.8) and $[HPt(dmpe)_2]^+$ (31.1 vs 28.5) compared to those measured previously. The new pK_a values give $\Delta G^\circ_{H^-}$ values calculated from eq 3 of 50.7 kcal/mol for $[HPt(dmpp)_2]^+$ and 42.5 kcal/mol for $[HPt(dmpe)_2]^+$. These are now in good agreement with the values of 51.0 and 42.0 kcal/mol found for these complexes using eq 17. Presumably the source of error in our previous measurement was related to the use of large quantities of a base whose pK_a value did not closely match the pK_a of the metal complex.

These results show that it is possible to obtain good agreement between the three different methods that we have used to determine the hydricity of transition metal hydrides: (1)

---

(53) Pozharskii, A. F.; Chikina, N. L.; Vistorobskii, N. V.; Ozeryanskii, V. A. *Russ. J. Org. Chem.* **1997**, *33*, 1727−1730.
(54) Kurasov, L. A.; Pozharskii, A. F.; Kuz'menko, V. V.; Klyuev, N. A.; Chemyshev, A. I. *J. Org. Chem. USSR* **1983**, *19*, 520−525.
(55) Wayner, D. D. M.; Parker, V. D. *Acc. Chem. Res.* **1993**, *26*, 287−294.
(56) Parker, V. D.; Handoo, K. L.; Roness, F.; Tilset, M. *J. Am. Chem. Soc.* **1991**, *113*, 7493−7498.

equilibrium measurements of hydride transfer from complexes with known hydride donor abilities to complexes with unknown acceptor abilities, (2) calculations based on Scheme 3 using eq 3 and measured pK_a values and half-wave potentials, and (3) calculations using eq 17 and pK_a values of reference bases with the observed equilibrium constants for heterolytic cleavage of hydrogen.

It is worth noting that the hydride donor ability of [HPt(depp)$_2$]$^+$ could not be measured using the thermodynamic cycle based on the pK_a value of the hydride and the potential of the Pt(II/0) couple, because the monomeric Pt(0) complex is not stable. However, the hydride donor ability of this complex is readily measured from the heterolytic cleavage of hydrogen using either pyridine or morpholine as the base. This illustrates the value of having several different methods for determining the hydride donor ability of metal hydrides, in addition to providing an internal check for consistency.

If the hydride donor ability of a complex is known, then the strength of the base required to drive the heterolytic cleavage of hydrogen using the conjugate hydride acceptor of that complex can be calculated. Equation 17 can be used to find the strength of the base required to observe heterolytic cleavage according to reaction 8, when the hydride donor ability of the metal complex is known, by setting $K_8 = 1$, substituting the known value of $\Delta G°_{H^-}$, and solving for pK_a(BH$^+$). Alternatively, eq 17 can be used to predict the reaction of a metal hydride with an acid to form H$_2$ (reaction 13).

For example, the hydride donor ability of [HNi(dmpp)$_2$]$^+$ has been calculated in a previous study to be 62.1 kcal/mol using eq 3.[36] Using this value in eq 17, we find that the pK_a of the protonated base must be near 10.1 to drive the heterolytic cleavage of H$_2$ using [Ni(dmpp)$_2$]$^{2+}$. Stronger bases, that is bases whose conjugate acids have pK_a's larger than 10.1, will drive reaction 8 farther to the right, while for weaker bases the equilibrium in eq 8 will lie farther to the left. Protonated *p*-bromoaniline has a pK_a of 9.6,[8] and therefore [Ni(dmpp)$_2$]$^{2+}$ should be thermodynamically capable of reacting with 1 atm of hydrogen in the presence of *p*-bromoaniline to form [HNi(dmpp)$_2$]$^+$. As shown in Table 1, *p*-bromoaniline does react with [Ni(dmpp)$_2$]$^{2+}$ and H$_2$ to form an equilibrium mixture ($K_8 = 0.016$) with [HNi(dmpp)$_2$]$^+$ and protonated *p*-bromoaniline. In this example, the known hydride donor ability of [HNi(dmpp)$_2$]$^+$ was used to predict the strength of the base required to obtain an equilibrium.

The quantitative measurement of the hydride donor ability of metal hydrides is useful in understanding the reactivity patterns observed for heterolytic activation of hydrogen by the [M(diphosphine)$_2$]$^{2+}$ complexes studied. For example, from Table 1 it can be seen that hydrogen does not react with [Pt(dmpe)$_2$]$^{2+}$ in the presence of triethylamine while [Pt(dmpp)$_2$]$^{2+}$ proceeds to an equilibrium. These complexes with similar ligands show very different reactivity. However, this difference can be understood in terms of the hydride acceptor abilities of these two compounds, which indicate that [Pt(dmpe)$_2$]$^{2+}$ is a poorer hydride acceptor by 9 kcal/mol. This would be a rather unexpected result in the absence of any thermodynamic data and using only structural similarities to assess reactivity. A similar comparison holds true for [Ni(dmpe)$_2$]$^{2+}$ ($\Delta G°_{H^-} = 50.9$ kcal/mol) and [Ni(dmpp)$_2$]$^{2+}$ ($\Delta G°_{H^-} = 61.2$ kcal/mol). The similarity of the ligands might lead one to predict similar reactivity with H$_2$, but the difference in hydride acceptor ability of 10 kcal/mol readily explains why [Ni(dmpp)$_2$]$^{2+}$ goes completely to [HNi(dmpp)$_2$]$^+$ in the presence of hydrogen and triethylamine, while [Ni(dmpe)$_2$]$^{2+}$ gives an equilibrium mixture ($K_8 = 0.49$) under the same conditions. In some cases, differences in reaction rate also correlate qualitatively with differences in $\Delta G°_{H^-}$. For example, [Ni(depp)$_2$]$^{2+}$ and [Pt(depp)$_2$]$^{2+}$ react faster with H$_2$ in the presence of triethylamine than do [Ni(dmpp)$_2$]$^{2+}$ and [Pt(dmpp)$_2$]$^{2+}$, respectively. The reaction of [Ni(depp)$_2$]$^{2+}$ with hydrogen is nearly complete in 3 h, while the same reaction with [Ni(dmpp)$_2$]$^{2+}$ requires two weeks to reach completion. [Ni(depp)$_2$]$^{2+}$ reacts faster with hydrogen than any of the other complexes examined in this study and it also is the best hydride acceptor ($\Delta G°_{H^-} = 67.2$ kcal/mol). In short, the differences in reactivity observed for the complexes in Table 1 can be qualitatively understood in terms of their relative hydride acceptor abilities.

Summary and Conclusions

Two methods have been used to determine the hydride donor abilities of six [HM(diphosphine)$_2$]$^+$ complexes (where M = Pt and Ni). The first method involves the use of a thermochemical cycle (Scheme 3) that requires measurement of pK_a values of the metal hydrides and the half-wave potentials of the M(II/0) couples of the conjugate bases of the hydrides, eq 3. The second method is based on the cycle shown in reactions 13−16 and relies on measurement of the equilibrium constant for the heterolytic cleavage of hydrogen in the presence of a base for which the conjugate acid pK_a is known. In this case, eq 17 is used to calculate the hydride donor ability of the hydride. In the six cases where we have been able to obtain both types of measurements, the results obtained by the two methods agree to within 1 kcal/mol, which is well within estimated experimental errors.

The values obtained for $\Delta G°_{H^-}$ using either of these methods are quite useful for understanding the differences in the reactivity of the [M(diphosphine)$_2$]$^{2+}$ complexes studied in this paper with hydrogen. In most cases, these differences in reactivity would not likely have been anticipated in the absence of the thermodynamic data. Values of $\Delta G°_{H^-}$ can also be used to predict the stability of metal hydride complexes in acidic solution. In the following paper, the hydride donor abilities of these complexes are used to measure the hydride donor abilities of a series of metal formyl complexes and to predict hydride transfer reactions to cationic metal carbonyls to generate formyl complexes.[57]

Experimental Section

Physical Measurements and General Procedures. ^{1}H and ^{31}P NMR spectra were recorded on a Varian Unity 300 MHz spectrometer at 299.95 and 121.42 MHz, respectively. ^{1}H chemical shifts are reported relative to tetramethylsilane using residual solvent protons as a secondary reference. ^{31}P chemical shifts are reported relative to external phosphoric acid. In experiments where accurate integrations of ^{31}P resonances were required, spectra were collected using a 52° pulse and a repetition rate of 11.96 s. This is sufficient to allow complete relaxation of nuclei with $T_1 < 27$ s. Infrared spectra were recorded on a Nicolet 510P spectrometer as Nujol mulls. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. All syntheses

---

(57) Ellis, W. W.; Miedaner, A.; Curtis, C. J.; DuBois, D. L. *J. Am. Chem. Soc.* **2002**, *124*, 1926−1932.

and manipulations of air-sensitive compounds were carried out using Schlenk and drybox techniques.

Electrochemical Studies. All electrochemical experiments were carried out under an atmosphere of N_2 in 0.3 M Bu_4NBF_4 in benzonitrile or 0.3 M Et_4NBF_4 in acetonitrile. Cyclic voltammetry experiments were carried out on a Cypress Systems computer-aided electrolysis system. The working electrode was a glassy carbon disk (2 mm diameter), and the counter electrode was a glassy carbon rod. A platinum wire immersed in a permethylferrocene/permethylferrocenium solution was used as a pseudoreference electrode to fix the potential. Ferrocene was used as an internal standard, and all potentials are referenced to the ferrocene/ferrocenium couple.

Materials. Bis(1,5-cyclooctadiene)nickel(0), dichloro(1,5-cyclooctadiene)platinum(II), and diethylphosphine were purchased from Strem Chemical Co. and used without further purification. Anhydrous benzonitrile, anhydrous acetonitrile, 1,3-dibromopropane, benzonitrile-d_5, TMG, ammonium hexafluorophosphate, *p*-bromoaniline, pyridine, and triethylamine were purchased from Aldrich Chemical Co. and used as received. CD_3CN and toluene-d_8 purchased from Aldrich Chemical Co. were vacuum transferred from CaH_2 and stored in the glovebox. Anisidine was purchased from Aldrich Chemical Co. and sublimed. Tetrahydrofuran and diethyl ether were purchased from Aldrich Chemical Co. and distilled over Na/benzophenone prior to use. HPLC grade *N*,*N*-dimethylformamide was purchased from Burdick & Jackson, purged with nitrogen, and stored in the glovebox. $LiPEt_2$ was prepared by deprotonation of $HPEt_2$ with butyllithium in hexane. $[Ni(CH_3CN)_{6.5}](BF_4)_2$ was prepared by the published procedure.[58] $[Ni(diphosphine)_2](BF_4)_2$ and $[Pt(diphosphine)_2](PF_6)_2$ complexes used for hydrogen activation and electrochemical studies were prepared as described previously.[36,59] KOPh was prepared from KOH and phenol in absolute ethanol, recrystallized from CH_3CN, and stored in the glovebox.

$Et_2P(CH_2)_3PEt_2$, depp. A solution of Et_2PLi (2.40 g, 0.025 mol) in THF (100 mL) was cooled to −80 °C and 1,3-dibromopropane (2.52 g, 0.0125 mol) was added with a syringe. The color changed rapidly from yellow to colorless. The solution was then allowed to warm to room temperature and stirred for 60 min. Then the solvent was removed under vacuum and the residue extracted with diethyl ether (100 mL). The ether phase was washed with water (2 × 50 mL) and dried over $MgSO_4$. This was filtered and the solvent was removed from the filtrate under vacuum to yield 2.15 g (78%) of colorless liquid product. ^1H NMR (toluene-d_8): δ 1.00 (d of t, $^3J_{H-H} = 7.0$ Hz, $^3J_{P-H} = 15.0$ Hz, $PCH_2\mathit{CH_3}$); 1.23 (q, $^3J_{H-H} = 7.0$ Hz, $P\mathit{CH_2}CH_3$); 1.57 (m, $-CH_2\mathit{CH_2}P$); 1.36 (m, $-\mathit{CH_2}CH_2P$). ^{31}P NMR (toluene-d_8): δ −23.3 (s).

$Ni(depp)_2$. A solution of depp (0.88 g, 0.004 mol) in THF (30 mL) was cooled to − 80 °C, solid $Ni(COD)_2$ (0.55 g, 0.002 mol) was added, and the mixture was allowed to warm to room temperature. After stirring 30 min at room temperature, the solvent was removed from the yellow solution to give an oily white solid. This was washed with acetonitrile (30 mL) and filtered and the white solid collected was dried under vacuum (0.85 g, 85% yield). Crystalline material for analysis was obtained by deprotonating a sample of $[HNi(depp)_2](PF_6)$ in acetonitrile with a 5-fold excess of 1,1,3,3-tetramethylguanidine. This is a slow reaction and crystals form over 2 days. The crystals were collected, washed with acetonitrile, and dried under vacuum. Anal. Calcd for $C_{22}H_{52}P_4Ni$: C, 52.93; H, 10.50. Found: C, 51.70; H, 10.29. ^1H NMR (toluene-d_8): δ 1.01 (m, $PCH_2\mathit{CH_3}$); 1.34 (m, $P\mathit{CH_2}CH_3$); 1.5−1.9 (m, $P\mathit{CH_2CH_2CH_2}P$). ^{31}P NMR (toluene-d_8): δ 3.82 (s)

$[HNi(depp)_2](PF_6)$. To a stirred suspension of $Ni(depp)_2$ (0.35 g, 0.0007 mol) in acetonitrile (30 mL) was added solid NH_4PF_6 (0.12 g, 0.00075 mol). This was stirred for 1 h, during which time a clear, yellow solution formed. The solvent was removed under vacuum and the residue was dissolved in warm ethanol (25 mL) and filtered. When this solution was cooled to −20 °C, yellow crystals formed. The product was collected by filtration and dried under vacuum (0.28 g, 62% yield). Anal. Cald for $C_{22}H_{53}P_5F_6Ni$: C, 40.95; H, 8.28. Found: C, 40.55; H, 8.21. ^1H NMR (CD_3CN): δ 1.03 (m, $PCH_2\mathit{CH_3}$), 1.62 (seven line pattern, $J = 7.5$ Hz, $P\mathit{CH_2}CH_3$), 1.65−2.0 (m, $P\mathit{CH_2CH_2CH_2}P$), −15.69 (quintet, $^2J_{P-H} = 3.0$ Hz, $Ni-\mathit{H}$). ^{31}P NMR (CD_3CN): δ 3.28 (s).

$[Ni(depp)_2](BF_4)_2$. To a suspension of depp (0.88 g, 0.004 mol) in acetonitrile (30 mL) at room temperature was added solid $[Ni(CH_3CN)_{6.5}](BF_4)_2$ (1.0 g, 0.002 mol) and the resulting dark red solution was stirred overnight. The solvent was then removed under vacuum and the dark red powder that remained was used without further purification (1.23 g, 91%). Anal. Calcd for $C_{22}H_{52}P_4B_2F_8Ni$: C, 39.27; H, 7.79. Found: C, 39.67; H, 7.81. ^1H NMR (CD_3CN): δ 1.28 (m, $PCH_2\mathit{CH_3}$), 1.94 (m, $P\mathit{CH_2}CH_3$), 2.0−2.2 (m, $P\mathit{CH_2CH_2CH_2}P$). ^{31}P NMR (CD_3CN): δ 3.22 (s).

$[Pt(depp)_2](PF_6)_2$. To a suspension of depp (1.10 g, 0.005 mol) in acetonitrile (50 mL) was added solid $Pt(COD)Cl_2$ (0.93 g. 0.0025 mol). The solution was stirred overnight and the solvent was removed under vacuum to give a yellow solid. This was dissolved in H_2O (50 mL) and solid NH_4PF_6 (1.50 g, 0.009 mol) was added, precipitating the product as a white powder. This was collected by filtration, washed with water (20 mL) and diethyl ether (20 mL), and then dried under vacuum to give 2.40 g (96%) of product. Anal. Calcd for $C_{22}H_{52}P_6F_{12}Pt$: C, 28.55; H, 5.66. Found: C, 27.97; H, 5.38. ^1H NMR (CD_3CN): δ 1.19 (m, $PCH_2\mathit{CH_3}$), 2.1 (m, $P\mathit{CH_2}CH_3$), 2.1−2.4 (m, $P\mathit{CH_2CH_2CH_2}P$). ^{31}P NMR (CD_3CN): δ 5.72 (s, $^1J_{Pt-P} = 2087$ Hz).

pK_a of $[HNi(depp)_2]PF_6$ in Benzonitrile. $[HNi(depp)_2]PF_6$ (0.024 g, 0.037 mmol) was placed in a 5 mm NMR tube, benzonitrile-d_5 (0.7 mL) was added, and the tube was capped with a rubber septum. TMG (2.0 μL) was then added via syringe. The ^1H NMR spectrum of the sample was monitored for 3 days, during which time resonances for $Ni(depp)_2$ grew and those of the starting hydride diminished. After 3 d the reaction had stopped and the concentrations of $Ni(depp)_2$ and $[HNi(depp)_2]^+$ were estimated using the peak heights of the respective methyl resonances at 1.62 and 1.03 ppm in the 500 MHz spectrum. Once these concentrations were known, $[TMGH^+]$ was assumed to be equal to $[Ni(depp)_2]$, $[TMG]$ was found by subtracting $[TMGH^+]$ from the amount initially added, and the equilibrium constant for reaction 7 was evaluated. Equation 18 and the known pK_a of $TMGH^+$ (23.3) were then used to calculate the pK_a of the nickel hydride.

$$\mathrm{p}K_a(\mathrm{MH}) = \mathrm{p}K_a(\mathrm{BH}^+) + \mathrm{p}K_{eq} \tag{18}$$

pK_a of $[HPt(depe)_2]PF_6$ in Acetonitrile. $[HPt(depe)_2](PF_6)$ (21−29 mg, 0.028−0.038 mmol) was weighed into five NMR tubes. The tubes were then treated with aliquots of 0.051 M KOPh solution in CH_3CN (0.30, 0.40, 0.50, 0.60, 0.70 mL, 0.0153−0.0357 mmol) and CH_3CN was added to bring the volume in each tube to 0.7 mL. As a check of the KOPh solution, another tube was prepared using 25 mg (0.033 mmol) of $[HPt(depe)_2](PF_6)$ and 0.30 mL of 0.100 M KOPh solution (0.030 mmol). Equilibrium was established within 30 min, and the ^{31}P spectra were recorded. The concentrations of the hydride and Pt(0) complexes were then determined by integration of the appropriate resonances. The phenol and phenoxide concentrations were then calculated from the amount of phenoxide added and the reaction stoichiometry, and corrected for the association of phenol with phenoxide using the method described by Norton.[6] The equilibrium constant for the deprotonation reaction was then calculated and eq 18 was used to determine the pK_a value for the hydride complex.

Hydrogen Activation with $[Ni(dmpp)_2](BF_4)_2$. The reaction was carried out five times with different ratios of 4-bromoaniline/4-bromoanilinium in each run. $[Ni(dmpp)_2](BF_4)_2$ (22−24 mg, 0.039−0.043 mmol), $4\text{-}BrC_6H_4NH_2$ (34−87 mg, 0.20−0.51 mmol), and $[4\text{-}BrC_6H_4NH_3](BF_4)$ (6−48 mg, 0.02−0.18 mmol) were weighed into five NMR tubes and 0.7 mL of CD_3CN was added to each. The tubes were capped with septa and H_2 was bubbled slowly through a needle into each solution for 10 min to produce a saturated solution at 1 atm (620

---

(58) Hathaway, B. J.; Holah, D. G.; Underhill, A. E. *J. Chem. Soc.* **1962**, 2444.

(59) Miedaner, A.; Haltiwanger, R. C.; DuBois, D. L. *Inorg. Chem.* **1991**, *30*, 417−427.

mmHg). The solutions were re-saturated with H_2 daily. The reactions were monitored by ^{31}P and ^{1}H NMR spectroscopy until equilibrium was reached (3 days in this case). The concentrations of Ni(dmpp)$_2^{2+}$ and HNi(dmpp)$_2^+$ were determined by integrating the ^{31}P resonances of these complexes. When the reaction did not significantly alter the 4-BrC$_6$H$_4$NH$_3^+$/4-BrC$_6$H$_4$NH$_2$ ratio, the equilibrium constant was calculated using these concentrations and the known 4-BrC$_6$H$_4$NH$_3^+$/4-BrC$_6$H$_4$NH$_2$ ratio. When the reaction did significantly alter the 4-BrC$_6$H$_4$NH$_3^+$/4-BrC$_6$H$_4$NH$_2$ ratio, the amounts of 4-BrC$_6$H$_4$NH$_3^+$ and 4-BrC$_6$H$_4$NH$_2$ were corrected using the stoichiometry of the reaction and the corrected values were used to calculate the equilibrium constant. The reaction was also carried out in the reverse direction with [HNi(dmpp)$_2$](PF$_6$) (22 mg, 0.041 mmol), [4-BrC$_6$H$_4$NH$_3$](BF$_4$) (20 mg, 0.077 mmol), and 4-BrC$_6$H$_4$NH$_2$ (55 mg, 0.32 mmol) in 0.7 mL of CD$_3$CN under 1 atm of H_2. Similar experiments were performed for the other [Ni(diphosphine)$_2$]$^{2+}$ and [Pt(diphosphine)$_2$]$^{2+}$ complexes shown in Table 1.

Acknowledgment. The help of Rebecca Ciancanelli in obtaining 500 MHz ^{1}H NMR spectra is gratefully acknowledged. This work was supported by the U.S. Department of Energy, Office of Science, Chemical Sciences Division.

JA0116829