

Hydride Donor Abilities of Cationic Transition Metal Hydrides from DFT-PCM Calculations

Gábor Kovács^{†,‡} and Imre Pápai^{*,§}

Institute of Physical Chemistry, University of Debrecen, P.O. Box 7, 4010 Debrecen, Hungary, Research Group of Homogeneous Catalysis, Hungarian Academy of Sciences, University of Debrecen, P.O. Box 7, 4010 Debrecen, Hungary, and Chemical Research Centre of the Hungarian Academy of Sciences, Pusztaszeri út 59-67, H-1025 Budapest, Hungary

Received August 22, 2005

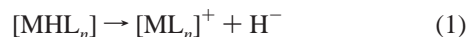
Density functional theory and the polarizable continuum solvation model have been applied to compute thermodynamic hydride donor abilities of cationic $[\text{MH}(\text{diphosphine})_2]^+$ complexes ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$). The accuracy of the applied computational methods has been assessed by comparison of calculated Gibbs free energies of reactions involving the hydrides as products with available experimental data. The mean absolute deviation of the calculated results from experiment varies between 2 and 5 kcal/mol depending on the choice of the solute cavity model. The PCM-UA0 method, which was found to provide the most reliable predictions for the investigated reactions, was applied to estimate the hydricity of $[\text{MH}(\text{diphosphine})_2]^+$ complexes. The recently synthesized $[\text{PdH}(\text{dppe})_2]^+$ cation is predicted to be an effective hydride donor.

Introduction

Transition metal hydride complexes are usually very reactive species, which may undergo a variety of chemical transformations including protonation and deprotonation, hydride transfer, insertion reactions with unsaturated compounds, or H-transfer via homolytic M–H bond dissociation.¹ A wide range of homogeneous catalytic reactions are also thought to involve metal hydrides either as reaction intermediates or as the active forms of the catalysts.^{2,3} The reactivity of metal hydrides is often associated with their abilities to function as H^+ , H^- , or H atom donors; therefore, it is of great interest to identify the factors that govern the acidity and hydricity of the M–H bonds. These properties can be quantitatively assessed either by kinetic measurements⁴ or by thermodynamic data obtained usually from equilibrium studies.⁵

Thermodynamic hydricities, defined as the standard Gibbs free energy ($\Delta G_{\text{H}}^\circ$) of reaction 1, have shown to be particularly sensitive to the nature of the metal atom (M) and the

electronic properties of the coordinating ligands (L).⁶ For example, recent thermodynamic studies on $[\text{MH}(\text{diphosphine})_2]^+$ complexes (where $\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$) reported by DuBois et al.^{6c,e,f} indicated that the hydride donor abilities vary in the range 42–70 kcal/mol following the order $\text{Pd} \geq \text{Pt} > \text{Ni}$ for a given chelating ligand. Correlation has also been established between the natural bite angle of various diphosphines and the hydricities of $[\text{PdH}(\text{diphosphine})_2]^+$ complexes.^{6f}



In principle, quantum chemical calculations may provide an alternative way to determine the relative hydricities by calculating the Gibbs free energies of the species involved in reaction 1. However, the computation of vibrational frequencies required to estimate the zero-point energy component of the thermodynamical state functions render the quantum chemical calculations rather time-consuming, for larger L ligands even computationally prohibitive. Another limiting factor in these calculations is that a reliable model is needed to account for solvent effects, since the energy balance of reaction 1, which involves charged species, is fairly sensitive to the reaction medium. Quantum chemical continuum solvation models⁷ have long been used in theoretical studies of chemical reactivity in solutions, and recent

* Corresponding author. E-mail: papai@chemres.hu.

[†] Institute of Physical Chemistry, University of Debrecen.

[‡] Research Group of Homogeneous Catalysis, University of Debrecen.

[§] Chemical Research Centre of the Hungarian Academy of Sciences.

(1) Crabtree, R. H. *The Organometallic Chemistry of the Metals*; Wiley: New York, 2001.

(2) Peruzzini, M.; Poli, R., Eds. *Recent Advances in Hydride Chemistry*; Elsevier: Amsterdam, 2001.

(3) Dedieu A., Ed. *Metal Hydrides*; VCH: Weinheim, 1992.

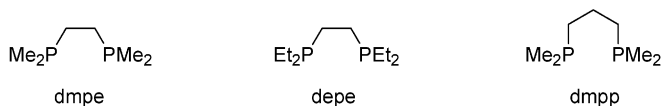
(4) For selected kinetic studies see: (a) Gaus, P. L.; Kao, S. C.; Youngdahl, K.; Darenbourg, M. Y. *J. Am. Chem. Soc.* **1985**, *107*, 2528. (b) Hembre, R. T.; McQueen, J. S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 65. (c) Cheng, T. Y.; Brunschwig, B. S.; Bullock, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 13121. (d) Cheng, T. Y.; Bullock, R. M. *Organometallics* **2002**, *21*, 2325. (e) Guan, H.; Imura, M.; Magee, M. P.; Norton, J. R.; Janak, K. E. *Organometallics* **2003**, *22*, 4084.

(5) For selected thermodynamic studies see: (a) Angelici, R. J. *Acc. Chem. Res.* **1995**, *28*, 51. (b) Sarker, N.; Bruno, J. W. *J. Am. Chem. Soc.* **1999**, *121*, 2174. (c) Kiss, G.; Zhang, K.; Mukerjee, S. L.; Hoff, C. D.; Roper, G. C. *J. Am. Chem. Soc.* **1990**, *112*, 5657. (d) Wei, M.; Wayland, B. B. *Organometallics* **1996**, *15*, 4681. (e) Berning, D. E.; Noll, B. C.; DuBois, D. L. *J. Am. Chem. Soc.* **1999**, *121*, 11432.

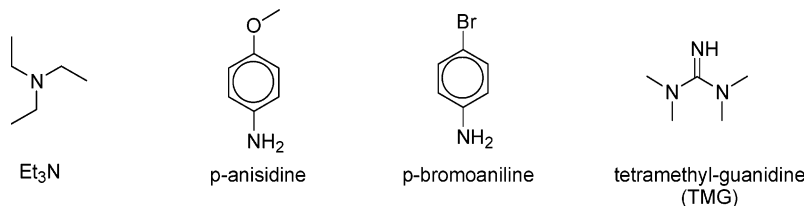
(6) (a) Berning, D. E.; Miedaner, A.; Curtis, C. J.; Noll, B. C.; DuBois, M. R.; DuBois, D. L. *Organometallics* **2001**, *20*, 1832. (b) Price, A. J.; Ciancanelli, R.; Noll, B. C.; Curtis, C. J.; DuBois, D. L.; DuBois, M. R. *Organometallics* **2002**, *21*, 4833. (c) Curtis, C. J.; Miedaner, A.; Ellis, W. W.; DuBois, D. L. *J. Am. Chem. Soc.* **2002**, *124*, 1918. (d) Ciancanelli, R.; Noll, B. C.; DuBois, D. L. *J. Am. Chem. Soc.* **2002**, *124*, 2984. (e) Curtis, C. J.; Miedaner, A.; Raebiger, J. W.; DuBois, D. L. *Organometallics* **2004**, *23*, 511. (f) Raebiger, J. W.; Miedaner, A.; Curtis, C. J.; Miller, S. M.; Anderson, O. P.; DuBois, D. L. *J. Am. Chem. Soc.* **2004**, *126*, 5502. (g) Raebiger, J. W.; DuBois, D. L. *Organometallics* **2005**, *24*, 110.

(7) (a) Tomasi, J.; Persico, M. *Chem. Rev.* **1994**, *94*, 2027. (b) Cramer, C. J.; Truhlar, D. G. *Chem. Rev.* **1999**, *99*, 2161. (c) Luque, F. J.; Curutchet, C.; Muñoz-Muriedas, J.; Bidon-Chanal, A.; Soteras, I.; Morreale, A.; Gelpí, J. L.; Orozco, M. *Phys. Chem. Chem. Phys.* **2003**, *5*, 3827.

Chart 1
Chelating phosphines (L)



Bases (B)



developments introduced in the family of PCM (polarizable continuum model)⁸ and CPCM (conductor-like polarizable continuum model)⁹ methods offer an efficient methodology for larger solute molecules as well.

Several recent theoretical investigations indicate that continuum solvation models can be successfully applied to compute solvation free energies of neutral and ionic organic molecules.¹⁰ These models have also gained wide acceptance in mechanistic studies of organometallic reactions;¹¹ however, the applicability for charged metal systems, such as those involved in hydride transfer reactions, is quite unexplored.

In the present work, we focus on a series of reactions that have been studied experimentally to determine the hydride donor ability of $[\text{MHL}_2]^+$ type complexes,^{6c} where M = Ni or Pt, and L is one of the following diphosphine ligands: 1,2-bis-(dimethylphosphino)ethane (dmpe), 1,2-bis(diethylphosphino)ethane (depe), and 1,3-bis(dimethylphosphino)propane (dmpp). The method proposed by DuBois et al. is based on equilibrium measurements for the heterolytic cleavage of H_2 by $[\text{ML}_2]^{2+}$ complexes in the presence of appropriately chosen bases (reaction 2).



We applied density functional theory in conjunction with various continuum solvation models to compute the free enthalpy of reaction 2 for a set of $[\text{ML}_2]^{2+}$ complexes and compare the obtained results with those from equilibrium measurements.^{6c} The level of agreement we found between

(8) (a) Miertus, S.; Scrocco, E.; Tomasi, J. *Chem. Phys.* **1981**, *55*, 117. (b) Barone, V.; Cammi, R.; Tomasi, J. *Chem. Phys. Lett.* **1996**, *255*, 327. (c) Cossi, M.; Scalmani, G.; Rega, N.; Barone, V. *J. Chem. Phys.* **2002**, *117*, 43. (d) Barone, V.; Impropa, R.; Rega, N. *Theor. Chem. Acc.* **2004**, *111*, 237.

(9) (a) Klamt, A.; Schüürmann, G. *J. Chem. Soc., Perkin Trans. 2* **1993**, 799. (b) Andzelm, J.; Kölmel, C.; Klamt, A. *J. Chem. Phys.* **1995**, *103*, 9312. (c) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995. (d) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. *J. Comput. Chem.* **2003**, *24*, 669–681.

(10) (a) Takano, Yu.; Houk, K. N. *J. Chem. Theory Comput.* **2005**, *1*, 70. (b) Fu, Y.; Liu, L.; Li, R.; Guo, Q. *J. Am. Chem. Soc.* **2004**, *126*, 814. (c) Pliego, J. R.; Riveros, J. M. *J. Phys. Chem. A* **2002**, *106*, 7434. (d) Lopez, X.; Schaefer, M.; Dejaegere, A.; Karplus, M. *J. Am. Chem. Soc.* **2002**, *124*, 5010. (e) Baik, M.; Schaefer, C. K.; Ziegler, T. *J. Am. Chem. Soc.* **2002**, *124*, 11167.

(11) For representative examples from recent mechanistic studies, see: (a) Marino, T.; Russo, N.; Toscano, M. *J. Am. Chem. Soc.* **2005**, *127*, 4242. (b) Casey, C. P.; Johnson, J. B.; Singer, S. W.; Cui, Q. *J. Am. Chem. Soc.* **2005**, *127*, 3100. (c) Nowroozi-Isfahani, T.; Musaei, D. G.; McDonald, F. E.; Morokuma, K. *Organometallics* **2005**, *24*, 2921. (d) Schubert, G.; Pápai, I. *J. Am. Chem. Soc.* **2003**, *125*, 14847.

Table 1. Investigated Systems for Reaction 2^a

M	L	B	pK _a (BH ⁺)	K ₂	ΔG ₂	ΔG _{H⁺} ^o
Ni	dmpe	NEt ₃	18.5	0.49	+0.4	50.8
	depe	<i>p</i> -anisidine	11.3	0.00052	+4.5	56.0
	dmpp	<i>p</i> -bromoaniline	9.6	0.016	+2.5	60.4
Pt	dmpe	TMG	23.3	0.089	+2.8	42.0
	depe	NEt ₃	18.5	1.7	-0.3	51.0

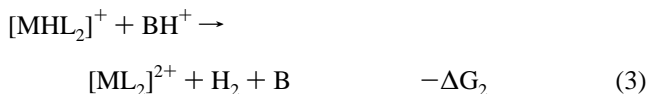
^a The pK_a values refer to those measured in acetonitrile (see ref 6c); K₂ denotes the equilibrium constant values for reaction 2 as obtained from ref 6c; ΔG₂ = -RT ln K₂ = -1.37 log K₂; ΔG_{H⁺}^o is calculated using eq 7. Free enthalpies are given in kcal/mol.

theory and experiment encouraged us to investigate the possibility of calculating hydricities directly according to reaction 1.

Investigated Reactions and Experimental Background

First, we briefly summarize the basic ideas of the method proposed by DuBois et al. in their recent work^{6c} for measuring the hydride donor abilities of transition metal hydrides. As described in ref 6c, the equilibrium measurements for the heterolytic cleavage of H_2 were carried out at room temperature using acetonitrile as a solvent and hydrogen at 1.0 atm pressure. Since the position of equilibrium in reaction 2 depends strongly on the pK_a value of BH⁺, an appropriate base had to be chosen to reach detectable equilibrium in a reasonable time period. Of the reactions reported by DuBois et al., we have investigated five systems in our present study, for which the measured equilibrium constants and the reaction free enthalpies are listed in Table 1. The structures and the notations used for the chelating ligands and the bases are shown in Chart 1.

The free enthalpy of reaction 2 (ΔG₂) can be used to determine the thermodynamic hydride donor ability of cationic hydrides using the thermodynamic cycle defined by reactions 3–5.



On the basis of this cycle, the ΔG_{H⁻}^o value for a given hydride is obtained from eq 7, where 76.0 kcal/mol refers to

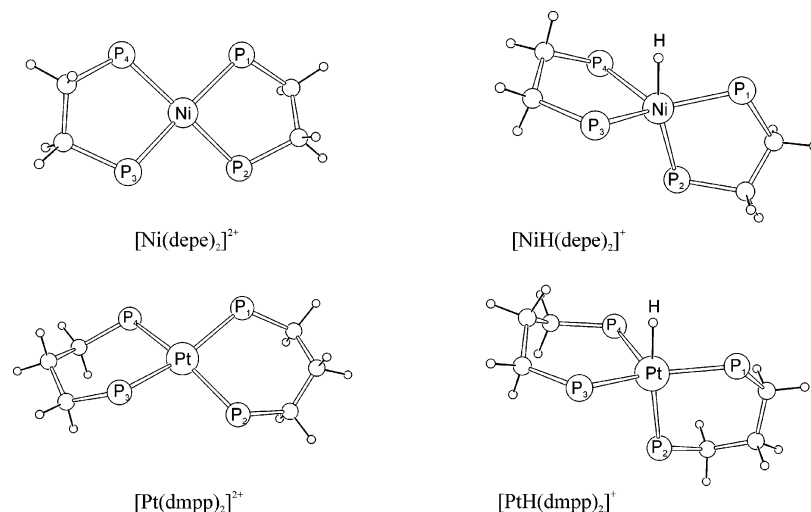


Figure 1. Geometry-optimized structures of selected cationic $[\text{ML}_2]^{2+}$ and $[\text{MHL}]^{2+}$ complexes (alkyl substituents on P atoms are omitted for clarity).

the experimental free enthalpy of the heterolytic cleavage of H_2 in acetonitrile (reaction 5).

$$\Delta G_{\text{H}^-}^{\circ} = -\Delta G_2 - 1.37pK_{\text{a}}(\text{BH}^+) + 76.0 \text{ kcal/mol} \quad (7)$$

The experimental hydride donor abilities determined from eq 7 are shown in the last column of Table 1.

Computational Details

Geometry optimizations for the species involved in reaction 2 were carried out at the B3LYP/SDDP level of density functional theory using the Gaussian 03 package,¹² where B3LYP is the applied hybrid functional^{13–15} and SDDP refers to a basis set including the Stuttgart-Dresden relativistic small core ECP basis set for rhodium and the Dunning/Huzinaga DZ + polarization all-electron basis set for the lighter atoms.^{16–19} The harmonic vibrational frequencies were then calculated at the same level, which were used to estimate the zero-point energy (ZPE) and thermal contributions to the gas-phase Gibbs free energies (G_{g}) of the reaction components. The thermal corrections to G_{g} were calculated for standard conditions ($T = 298 \text{ K}$ and $p = 1.0 \text{ atm}$).

(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Lyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Camml, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc.: Pittsburgh, PA, 2004.

(13) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(14) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(15) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

(16) Dolg, M.; Stoll, H.; Preuss, H.; Pitzer, R. M. *J. Phys. Chem.* **1993**, *97*, 5852.

(17) Dunning, T. H., Jr. *J. Chem. Phys.* **1970**, *52*, 2823.

(18) Dunning, T. H., Jr.; Hay, P. J. In *Methods of Electronic Structure Theory*, Vol. 3; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977.

(19) Schaefer, H. F., III. *J. Chem. Phys.* **1985**, *83*, 5721.

Table 2. Selected Structural Parameters for $[\text{ML}_2]^{2+}$ Complexes^a

complex	distance (in Å)		angle (in deg)	
	M–P _i	P ₁ –M–P ₂	P ₁ –M–P ₃	
$[\text{Ni}(\text{dmpe})_2]^{2+}$	2.28 [2.21]	85.9 [86.3]	175.0 [177.7]	
$[\text{Ni}(\text{depe})_2]^{2+}$	2.31 [2.23]	85.7 [84.8]	171.7 [180.0]	
$[\text{Ni}(\text{dmpp})_2]^{2+}$	2.29 [2.21]	91.6 [91.5]	143.5 [148.7]	
$[\text{Pt}(\text{dmpe})_2]^{2+}$	2.39 [2.31]	84.1 [84.5]	176.6 [180.0]	
$[\text{Pt}(\text{dmpp})_2]^{2+}$	2.42 [2.31]	88.5 [88.1]	159.7 [171.9]	

^a Numbering of P atoms is shown in Figure 1; average values of experimental data taken from ref 5e are shown in brackets.

The free energies of solvation, hereafter referred to as G_{s} , were obtained from self-consistent reaction field (SCRf) calculations carried out at the B3LYP/SDDP level for the geometry-optimized structures. Three different PCM variants were probed in these calculations that differ in the choice of cavity models. In the PCM-UFF model, the cavity in which the solute molecule resides is defined by the envelopes of atom-centered spheres with atomic radii from the universal force field (UFF) model.²⁰ Hydrogen atoms have individual spheres in this model, whereas in the PCM-UA0 model, the hydrogens are enclosed in the sphere of the heavy atom they are bound to, and the sphere radii are defined according to the united-atom topological model (UATM).²⁰ The cavities used in the PCM-UAHF method are also built from spheres centered on heavy atoms; however, the radii are defined according to the united-atom for Hartree–Fock (UAHF) procedure.²⁰ The dielectric constant in the PCM calculations was set to $\epsilon = 36.6$ to simulate the acetonitrile solvent medium. All SCRf calculations were carried out with Gaussian 03.¹²

Results and Discussion

A. Structure of $[\text{MHL}]^{2+}$ and $[\text{ML}_2]^{2+}$ Complexes. We begin our discussion by reviewing the structures of cationic metal complexes involved in the hydride transfer reactions. Representative structures from the series of investigated diphosphine complexes are illustrated in Figure 1, and selected optimized structural parameters along with available experimental data are given in Tables 2 and 3.

In agreement with crystallographic data,^{5e} the $[\text{M}(\text{dmpe})_2]^{2+}$ and $[\text{Ni}(\text{depe})_2]^{2+}$ cations are predicted to have nearly planar structures, as indicated by trans P–M–P bond angles (P₁–M–

(20) Rappe, A. K.; Kasewit, C. J.; Colwell, K. S.; Goddard, W. A., III; Skiff, W. M. *J. Am. Chem. Soc.* **1992**, *114*, 10024.

Table 3. Selected Structural Parameters for [MHL₂]⁺ Complexes^a

complex	distance (in Å)					angle (in deg)	
	M–P ₁	M–P ₂	M–P ₃	M–P ₄	M–H	P ₁ –M–P ₂	P ₃ –M–P ₄
[NiH(dmpe) ₂] ⁺	2.20	2.25	2.32	2.30	1.451	88.9	90.6
[NiH(depe) ₂] ⁺	2.22	2.27	2.30	2.35	1.448	88.4	91.2
[NiH(dmpp) ₂] ⁺	2.24	2.25	2.26	2.33	1.447	93.7	103.8
[PtH(dmpe) ₂] ⁺	2.33	2.40	2.49	2.46	1.595	85.6	85.2
[PtH(dmpp) ₂] ⁺	2.36	2.41	2.40	2.53	1.592	91.0	98.2

^a Numbering of P atoms is shown in Figure 1.

Table 4. Calculated Free Enthalpies (in kcal/mol) for Reaction 2 Using the PCM-UA0 Solvation Model^a

complex	ΔG_g	G_s				ΔG_s	$\Delta G_2(\text{calc})$	$\Delta G_2(\text{exp})$
		[ML ₂] ²⁺	B	[MHL ₂] ⁺	BH ⁺			
[Ni(dmpe) ₂] ²⁺	–49.9	–105.6	9.2	–12.0	–36.7	45.3	–4.6	0.4
[Ni(depe) ₂] ²⁺	–24.2	–90.1	–1.7	–2.8	–55.9	30.7	6.5	4.5
[Ni(dmpp) ₂] ²⁺	–29.4	–105.3	–3.7	–9.8	–63.2	33.6	4.2	2.5
[Pt(dmpe) ₂] ²⁺	–52.0	–107.2	5.8	–8.6	–35.9	54.5	2.5	2.8
[Pt(dmpp) ₂] ²⁺	–50.8	–104.6	9.2	–8.6	–36.7	47.7	–3.1	–0.3

^a ΔG_g refers to gas-phase calculations; ΔG_s is the signed sum of solvation Gibbs free energies (G_s) of components involved in reaction 2 (the calculated G_s for H₂ is 2.4 kcal/mol). $\Delta G_2(\text{calc}) = \Delta G_g + \Delta G_s$. $\Delta G_2(\text{exp})$ denotes experimental data from ref 6c. For the applied bases, see Table 1.

P₃ in Table 2), which are close to a straight angle in these complexes. On the other hand, the two [M(dmpp)₂]²⁺ complexes exhibit significant tetrahedral distortions, which appears to be more important in [Ni(dmpp)₂]²⁺. The calculated M–P bonds are systematically longer than the experimental values, which might be due to the approximated exchange–correlation energy functional (B3LYP) and also because the effect of counterions is neglected in the gas-phase calculations. The experimental bite angles (P₁–M–P₂) are, however, well reproduced in the calculations.

The geometry-optimized structures of the hydride complexes display a distorted trigonal bipyramidal arrangement of the coordinated ligands with the hydride and one of the phosphorus atoms (P₂ in Figure 1) in the axial positions. Similarly to what we found previously for the [PdH(dppe)₂]⁺ cation,²² the two chelating phosphines in the present hydrides are perpendicular to each other, one of them being coplanar with the M–H bond, whereas the other lies nearly perpendicular to the hydride bond. The calculated M–P distances suggest that this latter phosphine forms a weaker bond with the metal center, which can be attributed to the relatively narrow bite angles in the present chelating ligands that impose distortions from the ideal trigonal structure (with P₁–M–P₂ = 120°) represented by unconstrained [MH(PR₃)₄]⁺ complexes.²³ We note that the M–H bond lengths are not sensitive to the nature of the phosphine ligands; therefore they are not expected to correlate with the hydride donor abilities of the [MHL₂]⁺ complexes.

B. Heterolytic Cleavage of Hydrogen. To monitor the accuracy of various DFT-PCM methods for the estimation of free enthalpies of hydride transfer reactions involving the [ML₂]²⁺ and [MHL₂]⁺ complexes, we calculated the free enthalpy changes for the heterolytic cleavage of H₂ represented by reaction 2. The gas-phase values and the solvation free enthalpies calculated with the PCM-UA0 solvation model are summarized in Table 4, and a comparison of mean absolute deviations (MAD) of the results obtained with three different methods from the experimental data is presented in Table 5.

Table 5. Calculated Free Enthalpies (in kcal/mol) for Reaction 2 Using Various Solvation Models^a

complex	$\Delta G_2(\text{calc})$			$\Delta G_2(\text{exp})$
	PCM-UA0	PCM-UFF	PCM-UAHF	
[Ni(dmpe) ₂] ²⁺	–4.6	0.6	–8.1	0.4
[Ni(depe) ₂] ²⁺	2.5	6.6	–5.7	4.5
[Ni(dmpp) ₂] ²⁺	6.5	13.0	8.9	2.5
[Pt(dmpe) ₂] ²⁺	4.2	6.7	3.1	2.8
[Pt(dmpp) ₂] ²⁺	–3.1	0.4	–5.5	–0.3
MAD	2.4	3.5	5.5	

^a $\Delta G_2(\text{calc})$ values are obtained as described in Table 4. The mean absolute deviations (MAD) of the calculated free enthalpies from the experimental data^{6c} are shown in the last row of the table.

As expected, the gas-phase calculations give huge errors for the reaction free enthalpies. The reactions are predicted to be highly exergonic, since the stabilization of charged species is not taken into account in the gas-phase model. The doubly charged [ML₂]²⁺ species exhibit particularly large solvent effects, as seen from the G_s values, which are all close to –100 kcal/mol. For the B and [MHL₂]⁺ components, the solvation free enthalpies are predicted to be below ±10 kcal/mol; however, the protonated forms of the bases are found to have important solvent effects as well (G_s varies between –30 and –60 kcal/mol). Since the sum of the solvation free enthalpies (ΔG_s according to reaction 2) becomes comparable to ΔG_g for each reaction, the final values of the predicted reaction free enthalpies ($\Delta G_2(\text{calc}) = \Delta G_g + \Delta G_s$) are all close to zero to within a few kcal/mol, which is in line with the results of equilibrium measurements.^{6c}

The mean absolute deviation of the $\Delta G_2(\text{calc})$ values obtained with the PCM-UA0 model from the experimental data is 2.4 kcal/mol, which is surprisingly small considering that the investigated reactions involve metal complexes with varying charges and that $\Delta G_2(\text{calc})$ is a signed sum of relatively large energy values. Table 5 indicates that the other two solvation models (PCM-UFF and PCM-UAHF) provide slightly larger MAD values (3.5 and 5.5 kcal/mol, respectively) and also that the deviations scatter in a wider energy range than those found with the PCM-UA0 method. One cannot, of course, draw any general conclusion for the accuracy of the solvation models from these results, since no systematic investigation of possible sources of errors is provided in the present study; however, for

(21) Barone, V.; Cosi, M.; Tomasi, J. J. *Chem. Phys.* **1997**, *107*, 3210.

(22) Aresta, M.; Dibenedetto, A.; Amodio, E.; Pápai, I.; Schubert, G. *Inorg. Chem.* **2002**, *41*, 6550.

(23) Lin, W.; Wilson, S. R.; Girolami, G. S. *Inorg. Chem.* **1997**, *36*, 3662.

Table 6. Calculated Hydricities (in kcal/mol) Using the PCM-UA0 Solvation Model^a

hydride	$\Delta G_{\text{H}^-}^{\circ}$ (calc)				$\Delta G_{\text{H}^-}^{\circ}$ (exp)
	NEt ₃	TMG	<i>p</i> -anisidine	<i>p</i> -bromoaniline	
[NiH(dmpe) ₂] ⁺	55.2	57.7	53.2	50.9	50.8
[NiH(depe) ₂] ⁺	56.0	58.6	54.0	51.7	56.0
[NiH(dmpp) ₂] ⁺	63.0	65.5	61.0	58.6	60.4
[PtH(dmpe) ₂] ⁺	39.0	41.5	37.0	34.7	42.0
[PtH(dmpp) ₂] ⁺	53.8	56.3	51.8	49.4	51.0
MAD	2.6	4.1	2.1	3.0	

^a $\Delta G_{\text{H}^-}^{\circ}$ (calc) is obtained as $\Delta G_{\text{H}^-}^{\circ} = -\Delta G_2(\text{calc}) - 1.37pK_{\text{a}}(\text{BH}^+) + 76.0$, where $\Delta G_2(\text{calc})$ always refers to the free enthalpy change of reaction 3 with the corresponding base B (the $pK_{\text{a}}(\text{BH}^+)$ values are listed in Table 1). Results obtained with the bases used in the experiments are underlined.

the set of reactions examined here, the PCM-UA0 model gives clearly the most reliable results.

C. Predicting Thermodynamic Hydricities. As suggested by DuBois et al.,^{6c} the hydride donor abilities of cationic hydride complexes can be estimated from eq 7. The $\Delta G_{\text{H}^-}^{\circ}$ values derived from the calculated and experimental ΔG_2 data are listed in Table 6. In principle, for a given $[\text{MHL}_2]^+$ hydride, the calculated $\Delta G_{\text{H}^-}^{\circ}$ should be invariant with respect to the applied bases (see reaction 6); therefore the $\Delta G_{\text{H}^-}^{\circ}$ (calc) values estimated by using different bases in reaction 2 may provide additional information about the accuracy of the DFT-PCM methodology. Table 6 shows that the MAD values of the calculated hydricities from the experimental values vary in the range 2.1–4.1 kcal/mol, indicating that the average error of the B3LYP/SDDP + PCM-UA0 methodology is about 3 kcal/mol.

We also note that the trend found for the variation of the experimentally determined hydricities with respect to the nature of the metal atom and the type of ligand L is also reasonably reproduced by calculations: cationic Pt hydrides are always better hydride donors than the corresponding Ni hydrides, and for a given metal, hydride donor abilities follow the dmpe > depe > dmpp order. These trends can probably be related to the electronic structure of the metal center and the σ -donor/ π -acceptor properties of the chelating phosphines similarly to that presented for the oxidative addition of H₂ to various ML₅ type complexes;²⁴ however, such a detailed energy component analysis was beyond the scope of the present study.

The thermodynamic hydricities can be directly computed as the free enthalpy change of reaction 6, i.e., according to eq 8, where G° refers to the sum of gas-phase and solvation free enthalpies of the components ($G^{\circ}([\text{MHL}_2]^+) = G_{\text{g}}([\text{MHL}_2]^+) + G_{\text{s}}([\text{MHL}_2]^+)$, etc.).

$$\Delta G_{\text{H}^-}^{\circ} = G^{\circ}([\text{ML}_2]^{2+}) + G^{\circ}(\text{H}^-) - G^{\circ}([\text{MHL}_2]^+) \quad (8)$$

The calculation of $G^{\circ}([\text{MHL}_2]^+)$ and $G^{\circ}([\text{ML}_2]^{2+})$ is quite straightforward in the present methodology (see Computational Details), which is not the case for the solvation free enthalpy of H⁻.²⁵ We have, therefore, set $G^{\circ}(\text{H}^-)$ to a constant ($G^{\circ}(\text{H}^-) = -404.7$ kcal/mol) that gives the smallest MAD of the calculated hydricities from the experimental data (see Supporting Information for details). The results obtained from the approximated form of eq 8 are collected in Table 7. It is seen that

(24) Tomàs, J.; Lledós, A.; Jean, Y. *Organometallics* **1998**, *17*, 4932.

(25) By definition, no cavity can be associated with H⁻ in the PCM-UA0 and PCM-UAHF formalisms; therefore the solvation free enthalpy of H⁻ cannot be estimated with these methods. Using the B3LYP/SDDP + PCM-UFF methodology, we obtain $G^{\circ}(\text{H}^-) = -387.8$ kcal/mol, which seems fairly inaccurate as compared to the empirical value derived from the experimental data (-404.7 kcal/mol).

Table 7. Hydricities (in kcal/mol) Calculated from the Approximated Forms of Eq 8 Using the PCM-UA0 Solvation Model^a

hydride	$\Delta G_{\text{H}^-}^{\circ}$ (-1)	$\Delta G_{\text{H}^-}^{\circ}$ (-2)	$\Delta G_{\text{H}^-}^{\circ}$ (-exp)
[NiH(dmpe) ₂] ⁺	52.7(1.9)	55.2(4.4)	50.8
[NiH(depe) ₂] ⁺	53.5(2.5)	56.0(0.0)	56.0
[NiH(dmpp) ₂] ⁺	60.4(0.0)	63.3(2.9)	60.4
[PtH(dmpe) ₂] ⁺	36.5(5.5)	38.9(3.1)	42.0
[PtH(dmpp) ₂] ⁺	51.3(0.3)	50.7(0.3)	51.0
MAD	2.0	2.1	

^a $\Delta G_{\text{H}^-}^{\circ}$ (-1) and $\Delta G_{\text{H}^-}^{\circ}$ (-2) are calculated from eqs 9 and 10, respectively. Absolute deviations of the calculated hydricities from the experimental data are given in parentheses.

the mean absolute deviation of the calculated $\Delta G_{\text{H}^-}^{\circ}$ (-1) values from experiment is only 2.0 kcal/mol and the largest deviation is 5.5 kcal/mol, which are both comparable to those found above.

$$\Delta G_{\text{H}^-}^{\circ}(1) = G^{\circ}([\text{ML}_2]^{2+}) - G^{\circ}([\text{MHL}_2]^+) - 404.7 \text{ kcal/mol} \quad (9)$$

Note that the estimation of hydricities according to eq 9 is computationally still rather demanding because it requires the calculation of harmonic vibrational frequencies for $[\text{MHL}_2]^+$ and $[\text{ML}_2]^{2+}$. To provide a simpler protocol, we assumed that the sum of ZPE contributions and thermal corrections to the gas-phase Gibbs free energies in eq 8 is constant to a good approximation in the family of investigated hydrides, so the gas-phase contribution to $\Delta G_{\text{H}^-}^{\circ}$ can be estimated from electronic total energies (E_{o} in eq 10).

$$G_{\text{g}}([\text{ML}_2]^{2+}) - G_{\text{g}}([\text{MHL}_2]^+) \approx E_{\text{o}}([\text{ML}_2]^{2+}) - E_{\text{o}}([\text{MHL}_2]^+) + \text{const} \quad (10)$$

The validity of this assumption, which relies upon the fact that the $[\text{MHL}_2]^+$ complexes undergo similar structural changes in the series, was verified by a new parametrization involving a single constant for the sum of all gas-phase energy corrections (ZPE and thermal) and $G^{\circ}(\text{H}^-)$ as well (eq 11).

$$\Delta G_{\text{H}^-}^{\circ}(2) = (E_{\text{o}}([\text{ML}_2]^{2+}) + G_{\text{s}}([\text{ML}_2]^{2+})) - (E_{\text{o}}([\text{MHL}_2]^+) + G_{\text{s}}([\text{MHL}_2]^+)) - 406.5 \text{ kcal/mol} \quad (11)$$

As indicated by the results shown in Table 7, the accuracy of this procedure is very similar to that represented by eq 9, as the MAD of the $\Delta G_{\text{H}^-}^{\circ}$ (-2) values is 2.1 kcal/mol and the largest deviation amounts only to 4.4 kcal/mol.

D. Calculated Hydricities for [PdH(depe)₂]⁺ and [PdH(dppe)₂]⁺. The reliability of the suggested procedures was further tested on an additional $[\text{MHL}_2]^+$ type hydride, and we also predicted the hydricity of a recently synthesized palladium hydride complex.

The $[\text{PdH}(\text{depe})_2]^+$ cation represents a hydride that is characterized by the smallest natural bite angle in the series of $[\text{PdH}(\text{diphosphine})_2]^+$ complexes investigated recently by DuBois et al.^{6f} In accordance with the trend found for the hydride donor abilities of these hydrides, the measured $\Delta G_{\text{H}^-}^{\circ}$ for $[\text{PdH}(\text{depe})_2]^+$ is fairly low ($\Delta G_{\text{H}^-}^{\circ}(\text{exp}) = 43.2$ kcal/mol). Full geometry optimizations (see Figure 2) and subsequent vibrational analyses were carried out in our study for the $[\text{Pd}(\text{depe})_2]^{2+}$ and $[\text{PdH}(\text{depe})_2]^+$ complexes, and we used both procedures (eqs 9 and 11) to estimate the hydricity of $[\text{PdH}(\text{depe})_2]^+$. The obtained results ($\Delta G_{\text{H}^-}^{\circ}(1) = 43.4$ kcal/mol and $\Delta G_{\text{H}^-}^{\circ}(2) = 43.1$ kcal/mol) indicate that both methods give an excellent agreement with experiment.

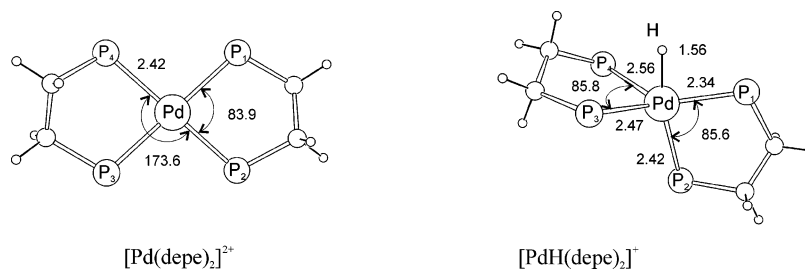


Figure 2. Geometry-optimized structures of $[\text{Pd}(\text{depe})_2]^{2+}$ and $[\text{PdH}(\text{depe})_2]^+$ complexes (ethyl substituents on P atoms are omitted for clarity). Bond distances are shown in angstroms, bond angles in degrees.

We also carried out calculations to predict the hydricity of the $[\text{PdH}(\text{dppe})_2]^+$ complex (dppe = 1,2-bis(diphenylphosphino)ethane), which has been synthesized recently,²² and it has been found to act as a proton or hydride donor in a number of hydrogenation reactions.²⁶ The calculation of vibrational frequencies for $[\text{Pd}(\text{dppe})_2]^{2+}$ and $[\text{PdH}(\text{dppe})_2]^+$ complexes, which involve two bulky phosphine ligands, becomes computationally prohibitive; therefore we used eq 11 to estimate the thermodynamic hydricity of $[\text{PdH}(\text{dppe})_2]^+$.²⁷ The relatively low value obtained for the hydricity ($\Delta G_{\text{H}^-}^\circ(2) = 49.6$ kcal/mol) shows that the $[\text{PdH}(\text{dppe})_2]^+$ cation can be considered as a good hydride donor, which is consistent with the observations regarding the reactivity of this species.^{22,26}

Summary and Concluding Remarks

With the primary goal of exploring the applicability of quantum chemical continuum solvation models for reactions involving transition metal complexes with varying charges, we combined density functional calculations with recent implementations of the PCM solvation method to compute the Gibbs free energies for a set of reactions that represent the heterolytic

cleavage of H_2 by cationic $[\text{M}(\text{diphosphine})_2]^{2+}$ species (reaction 2). These reactions have recently been investigated systematically in terms of equilibrium measurements performed in acetonitrile, and accurate thermodynamic data are available for comparison.^{6c} We found a good agreement between the calculated results and the experimental data, as the mean absolute deviations from experiment were shown to be in the range 2.4–5.5 kcal/mol depending on the cavity model used in the PCM calculations.

We also utilized the experimental hydricities as a reference to derive an empirical constant associated with the free enthalpy of the solvated H^- species, which allowed us to calculate hydricities directly according to reaction 6, i.e., without considering a thermodynamical cycle. We showed that the costly vibrational frequency analysis for $[\text{ML}_2]^{2+}$ and $[\text{MHL}_2]^+$ complexes is not necessarily required to obtain reliable $\Delta G_{\text{H}^-}^\circ$ values since the gas-phase contributions can be estimated from the electronic total energies. This latter procedure was applied to predict the hydride donor abilities of two newly synthesized palladium hydrides ($[\text{PdH}(\text{depe})_2]^+$ and $[\text{PdH}(\text{dppe})_2]^+$), which were found to be in line with the experimental findings.

Acknowledgment. Financial support from the Hungarian Research Foundation (OTKA grant: T037345) is greatly acknowledged.

Supporting Information Available: Cartesian coordinates of optimized structures and calculated thermodynamic data for all species involved in the investigated reactions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(26) Aresta, M.; Dibenedetto, A.; Pápai, I.; Schubert, G.; Macchioni A.; Zuccaccia, D. *Chem. Eur. J.* **2004**, *10*, 3708.

(27) The geometries of the $[\text{Pd}(\text{depe})_2]^{2+}$ and $[\text{PdH}(\text{depe})_2]^+$ complexes were optimized in QM/MM calculations using the ONIOM coupling scheme (see ref 28), where the phenyl groups were included in the MM region and the QM core (i.e., the $[\text{PdH}(\text{H}_2\text{P}(\text{CH}_2)_2\text{PH}_2)_2]^+$ model) was described at the B3LYP/SDDP level of DFT. The E_0 total energies for eq 11 were obtained from single-point B3LYP/SDDP calculations carried out for the QM/MM optimized structures, and the G_s values were calculated with the PCM-UA0 method.

(28) Maseras, F.; Morokuma, K. *J. Comput. Chem.* **1995**, *16*, 1170.