Ab Initio Calculations of Thermodynamic Hydricities of Transition-Metal Hydrides in Acetonitrile

Xiu-Juan Qi,[†] Yao Fu,[*,†] Lei Liu,[*,‡] and Qing-Xiang Guo[†]

Departments of Chemistry, University of Science and Technology of China, Hefei 230026, and Tsinghua University, Beijing 100084, China

Received March 14, 2007

Theoretical hydricities calculated by different methods are compared with all the available experimental values for the Co- and Ni-group metal hydrides in acetonitrile. It is found that the B3P86 method employing a sufficiently flexible basis set in combination with the C-PCM solvent model can accurately predict the hydricity with a precision of 2.0 kcal/mol. The same method can also accurately predict the acidities of the metal−hydrogen bond and the redox potentials of the corresponding metal hydrides with precisions of 1.9 pK_a units and 0.07 V, respectively. On the other hand, an ONIOM method where the core layer is treated with the CCSD(T) method fails to predict the hydricity of transition-metal hydrides, possibly because the electronic effects of the outer layer are not accurately estimated with the low-level theory in the ONIOM partitioning scheme or because the basis sets in the ONIOM methods are not sufficiently flexible. As to the periodical trends, it is found that for the Co-group metal hydrides, the hydricities increase in the order second row < third row < first row. For the Ni-group metal hydrides, the hydricities increase in the order second row ≈ third row ≪ first row. As to the effects of the phosphine ligands, it is found that a dual-parameter equation can quantitatively predict the hydricities, where the two parameters are the NBO charge of the phosphorus and the natural bite angle of the diphosphine. Finally, no correlation is found between the hydricity and the metal−hydrogen vibration frequency or the hydrogen chemical shift. Therefore, it is not reliable to use any vibrational spectrum or proton NMR method to estimate the hydricity of transition-metal hydrides.

1. Introduction

Transition-metal hydrides play an important role in a variety of stoichiometric and catalytic reactions such as hydrogenation and hydroformylation.[1] The behavior of the M−H bond in these compounds has been intensively studied for many years with the aim of understanding its different modes of cleavage, which can release a proton, a hydrogen atom, or a hydride ion.[2] Among the three cleavage modes, the heterolytic cleavage of the M−H bond to produce a hydride ion is generally believed to be the most relevant to the applications of transition-metal hydrides in synthesis and catalysis.[3] For this reason, a considerable amount of recent attention has been directed to the measurement of the standard Gibbs free energy change ($\Delta G^{\circ}_{\mathrm{H}^-}$) of the following reaction:[4]

$$\mathrm{L}_m\mathrm{MH}^{n+} \rightarrow \mathrm{L}_m\mathrm{M}^{(n+1)+} + \mathrm{H}^- \ (\mathrm{L} = \text{ligand}) \qquad (1)$$

This free energy change, named the thermodynamic hydricity, quantitatively describes the hydride donor ability of the M−H bond. Many previous studies have shown that quantitative values of $\Delta G^{\circ}_{\mathrm{H}^-}$ for transition-metal hydrides are useful for predicting (1) the stability of the hydrides to acids of different strengths, (2) the ability of the hydrides 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.

Up to now, two experimental methods have been developed to measure the hydricities of transition-metal hydrides. One method measures the equilibria between transition-metal hydrides and acceptor molecules such as triarylcarbonium ions whose hydride acceptor ability has been determined. The other method is based on a thermodynamic cycle that uses the pK_a values of the metal hydrides and the two-electron oxidation potentials of the conjugate bases of the hydrides to calculate the free energy of hydride transfer. Using these two methods, DuBois et al., Aresta et al., and several other groups recently measured the hydricities of a number of hydrides of Ni, Pd, Pt,

---

[*] To whom correspondence should be addressed. E-mail: fuyao@ustc.edu.cn (Y.F.), leiliu@ustc.edu.cn (L.L.).

[†] University of Science and Technology of China.

[‡] Tsinghua University.

(1) (a) Kristjánsdóttir, S. S.; Norton, J. R. In *Transition Metal Hydrides: Recent Advances in Theory and Experiment*; Dedieu, A., Ed.; VCH: New York, 1991; pp 309−359. (b) Crabtree, R. H. *The Organometallic Chemistry of the Metals*; Wiley: New York, 2001.

(2) Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41.

(3) (a) Miedaner, A.; DuBois, D. L.; Curtis, C. J.; Haltiwanger, R. C. *Organometallics* **1993**, *12*, 299. (b) DuBois, D. L.; Berning, D. E. *Appl. Organomet. Chem.* **2000**, *14*, 860.

(4) (a) Berning, D. E.; Noll, B. C.; DuBois, D. L. *J. Am. Chem. Soc.* **1999**, *121*, 11432. (b) Berning, D. E.; Miedaner, A.; Curtis, C. J.; Noll, B. C.; DuBois, M. C. R.; DuBois, D. L. *Organometallics* **2001**, *20*, 1832. (c) Curtis, C. J.; Miedaner, A.; Ellis, W. W.; DuBois, D. L. *J. Am. Chem. Soc.* **2002**, *124*, 1918. (d) Ellis, W. W.; Miedaner, A.; Curtis, C. J.; Gibson, D. H.; DuBois, D. L. *J. Am. Chem. Soc.* **2002**, *124*, 1926. (e) Ciancanelli, R.; Noll, B. C.; DuBois, D. L.; DuBois, M. R. *J. Am. Chem. Soc.* **2002**, *124*, 2984. (f) Price, A. J.; Ciancanelli, R.; Noll, B. C.; Curtis, C. J.; DuBois, D. L.; DuBois, M. R. *Organometallics* **2002**, *21*, 4833. (g) Ellis, W. W.; Ciancanelli, R.; Miller, S. M.; Raebiger, J. W.; DuBois, M. R.; DuBois, D. L. *J. Am. Chem. Soc.* **2003**, *125*, 12230. (h) Curtis, C. J.; Miedaner, A.; Raebiger, J. W.; DuBois, D. L. *Organometallics* **2004**, *23*, 511. (i) Ellis, W. W.; Raebiger, J. W.; Curtis, C. J.; Bruno, J. W.; DuBois, D. L. *J. Am. Chem. Soc.* **2004**, *126*, 2738. (j) Raebiger, J. W.; Miedaner, A.; Curtis, C. J.; Miller, S. M.; Anderson, O. P.; DuBois, D. L. *J. Am. Chem. Soc.* **2004**, *126*, 5502. (k) Miedaner, A.; Raebiger, J. W.; Curtis, C. J.; Miller, S. M.; DuBois, D. L. *Organometallics* **2004**, *23*, 2670. (l) Raebiger, J. W.; DuBois, D. L. *Organometallics* **2005**, *24*, 110.

10.1021/om0702429 CCC: $37.00

Chart 1. Chemical Structures of the Phosphine Ligands

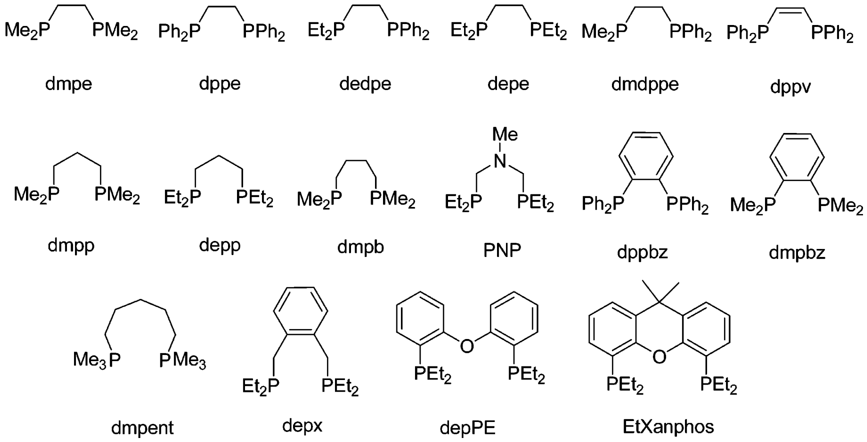


Table 1. Theoretical ΔG°_H Values Calculated by Different Methods[a]

hydride	ΔG°_H (exptl)	ΔG°_H (theor) method 1	method 2	method 3	method 4	method 5
$[HNi(dmpe)_2]^+$	50.7	50.0	51.5	51.3	51.4	51.1
$[HNi(dppe)_2]^+$	62.7	55.4	65.9	64.8	64.3	64.8
$[HPd(depe)_2]^+$	43.2	45.9	48.3	47.4	47.1	45.0
$[HPt(dmpp)_2]^+$	50.7	50.7	50.7	50.7	50.7	50.7
$[HPt(depe)_2]^+$	44.2	44.8	45.2	45.1	45.0	45.3
$[HPt(PNP)_2]^+$	54.7	40.4	49.7	49.4	49.1	53.6
rmse		6.6	3.2	3.0	2.9	1.3

[a] In method 1, the gas-phase energies are calculated by the ONIOM(CCSD(T)/LANL2DZ+p:B3P86/LANL2MB)//ONIOM(B3P86/LNAL2DZ+p:HF/LANL2MB) method. In method 2, this is done by using the ONIOM(CCSD(T)/BS1:B3P86/LANL2DZ)//ONIOM(B3P86/LANL2DZ+p:HF/LANL2MB) method, where BS1 means that the basis set for transition metals is LANL2DZ+p and the basis set for other elements is 6-31+G*). In method 3, this is done by using the B3P86/BS1//ONIOM(B3P86/LNAL2DZ+p:HF/LANL2MB) method. In method 4, this is done by using the B3P86/BS2//ONIOM(B3P86/LNAL2DZ+P:HF/LANL2MB) method, where BS2 means that the basis set for transition metals is LANL2DZ+p, the basis set for P is 6-311+G**, and the basis set for other elements is 6-31+G*. In method 5, this is done by using the B3P86/BS2//B3P86/LANL2DZ+p method. Noteworthily, the solvation energies are always calculated by using the C-PCM model (radii, Bondi) at the B3P86/LANL2DZ+p level.

Table 2. Experimental and Theoretical pK_a, E°(II/0), and ΔG°_H Values for the Co- and Ni-Group Transition-Metal Hydrides That Have Been Experimentally Characterized

transition-metal hydride	pK_a(exptl)	pK_a (calcd)	E°(II/0) (exptl)	E°(II/0) (calcd)	ΔG°_H (exptl)	ΔG°_H (calcd)
$[HNi(dmpe)_2]^{+\,a}$	24.4 ± 0.2	23.3	−1.39	−1.31	50.7	51.1
$[HNi(dmpp)_2]^{+\,a}$	24.0 ± 0.3	23.5	−1.11	−1.05	61.2	64.3
$[HNi(depe)_2]^{+\,a}$	23.8 ± 0.2	27.2	−1.22	−1.29	56.0	57.6
$[HNi(dedpe)_2]^{+\,b}$	20.3 ± 0.2	17.8	−1.04	−1.07	59.8	57.9
$[HNi(dppe)_2]^{+\,a}$	14.7 ± 0.3	15.5	−0.79	−0.78	62.7	64.8
$[HNi(dppv)_2]^{+\,b}$	13.2	12.0	−0.68	−0.68	66.4	64.5
$[HNi(depp)_2]^{+\,c}$	23.3	22.6	−0.96	−0.94	66.2	67.0
$[HNi(PNP)_2]^{+\,d}$	22.2	23.3	−0.94	−1.02	66.0	64.4
$[HPd(depe)_2]^{+\,e}$	23.2 ± 0.2	22.5	−1.48	−1.42	43.2	45.0
$[HPd(depPE)_2]^{+\,e}$	18.3 ± 0.5	16.8	−0.83	−0.81	66.4	65.3
$[HPd(depx)_2]^{+\,e}$	19.8 ± 0.2	20.9	−0.98	−1.07	61.5	59.1
$[HPd(PNP)_2]^{+\,d}$	22.1	20.3	−1.21	−1.19	51.1	52.3
$[HPd(depp)_2]^{+\,e}$	22.9 ± 0.2	21.9	−1.22	−1.26	54.7	51.4
$[HPd(EtXantphos)_2]^{+\,e}$	18.5 ± 0.5	18.7	−0.75	−0.62	(70.4)	76.6
$[HPt(depp)_2]^{+\,c}$			−1.40	−1.50	53.9	50.7
$[HPt(dmpe)_2]^{+\,c}$	31.1	31.2	−1.73	−1.74	42.5	42.1
$[HPt(dmpp)_2]^{+\,c}$	30.4	30.4	−1.53	−1.53	50.7	50.7
$[HPt(depe)_2]^{+\,c}$	29.7	33.4	−1.65	−1.74	44.2	45.3
$[HPt(dppe)_2]^{+\,a}$	22.2	18.8	−1.24	−1.08	52.5	55.6
$[HPt(EtXantphos)_2]^{+\,f}$	27.3 ± 0.5	26.4	−0.89	−0.83	76 ± 2	77.7
$[HPt(PNP)_2]^{+\,d}$	27.6	28.3	−1.36	−1.40	54.7	53.6
$HCo(dppe)_2^{\,g}$	38.1	41.9	−1.80	−1.88	49.1	50.0
$HCo(dppbz)_2^{\,h}$					48	50.0
$HRh(dppbz)_2^{\,h}$	35 ± 1.3	35.7	−2.02	−1.98	34	37.2
$HRh(depx)_2^{\,i}$	51.0	48.3	−2.27	−2.22	45	43.3

[a] Experimental data from ref 4a. [b] From ref 4b. [c] From ref 4c. [d] From ref 4h. [e] From ref 4j. [f] From ref 4k. [g] From ref 4e. [h] From ref 4f. [i] From ref 4l.

Co, and Rh.[4,5] These landmark studies not only improve our understanding about the structures and reactivities of transition-metal hydrides, but also provide important insights into the design of new hydride catalysts for the hydrogenation and hydroformylation reactions.[6−8] Nonetheless, not all the transition-metal hydrides are readily amenable to experimental characterization (as a matter of fact, up to now experimental hydricities have been found for only 25 Co- and Ni-group transition-metal hydrides). Accordingly, the ability to accurately predict the solution-phase hydricities of various transition-metal hydrides with a coherent theoretical protocol should be highly useful to the study of either mechanistic or synthetic organometallic chemistry.

In a recent study we successfully developed an ab initio protocol which could calculate the pK_a values of a variety of transition-metal hydrides in acetonitrile with a precision of 1.5 pK_a units.[9] As a continuation of our previous research, the present study investigates the utilization of ab initio methods to accurately calculate the hydricities of various transition-metal hydrides in acetonitrile. It is noteworthy that Kovács and Pápai reported very recently their use of a density functional theory method to compute the hydricities of three nickel and two platinum hydrides.[10] Compared to the pioneering study by Kovács and Pápai, we have considered substantially more experimental hydricities for both the Co- and Ni-group transition metals in our own study (which cover almost all the existing experimental data). We have also compared the performances of the ONIOM[11] and basis set combination strategies in handling bulky transition-metal hydrides. These efforts allow us to obtain

---

(5) (a) Cheng, T. Y.; Brunschwig, B. S.; Bullock, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 13121. (b) Aresta, M.; Dibenedetto, A.; Amodio, E.; Papai, I.; Schubert, G. *Inorg. Chem.* **2002**, *41*, 6550. (c) Sarker, N.; Bruno, J. W. *Organometallics* **2001**, *20*, 55.

(6) (a) Guan, H. R.; Iimura, M.; Magee, M. P.; Norton, J. R.; Zhu, G. *J. Am. Chem. Soc.* **2005**, *127*, 7805. (b) Guan, H. R.; Saddoughi, S. A.; Shaw, A. P.; Norton, J. R. *Organometallics* **2005**, *24*, 6358.

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

(8) DuBois, D. L.; Blake, D. M.; Miedaner, A.; Curtis, C. J.; DuBois, M. R.; Franz, J. A.; Linehan, J. C. *Organometallics* **2006**, *25*, 4414.

(9) Qi, X.-J.; Liu, L.; Fu, Y.; Guo, Q.-X. *Organometallics* **2006**, *25*, 5879.

(10) Kovács, G.; Pápai, I. *Organometallics* **2006**, *25*, 820.

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

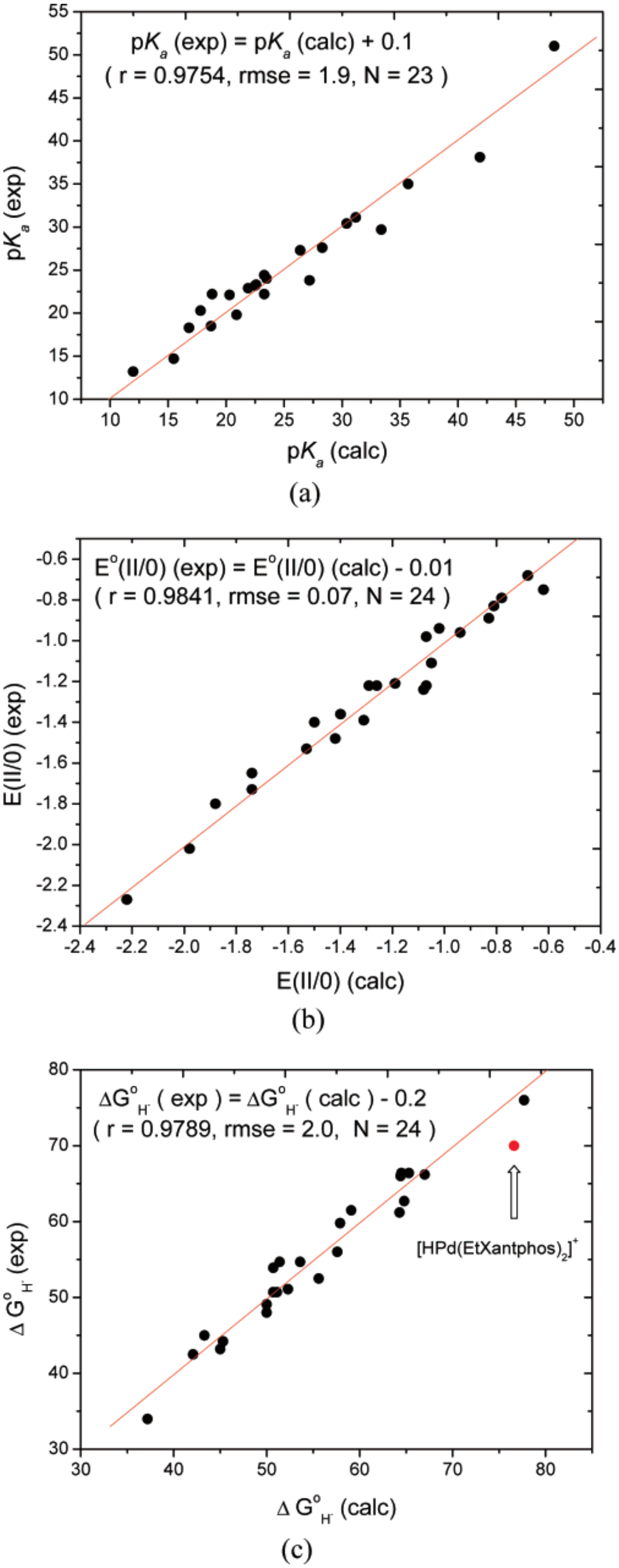


Figure 1. Comparison between the experimental and theoretical acidities (a), redox potentials (b), and hydricities (c) for Co- and Ni-group metal hydrides.

Table 3. Theoretical Hydricities (ΔG°_H), NBO Charges (δ_P), Natural Bite Angles (θ), M−H Vibration Frequencies (ν_{M-H}), and Proton Chemical Shifts of Representative Co- and Ni-Group Transition-Metal Hydrides

hydride	ΔG°_H	δ_P[a]	θ[b]	ν_{M-H}[c]	chemical shift of H
$HCo(dmpe)_2$	36.3	0.778	85.9	1870	−14.4
$HCo(dmdppe)_2$	41.8	0.796	85.9	1899	−13.2
$HCo(dmpbz)_2$	41.9	0.800	86.8	1884	−13.7
$HCo(dppe)_2$	50.0	0.814	85.8	1966	−13.9
$HCo(dppbz)_2$	50.0	0.836	85.5	1892	−12.0
$HCo(dmpp)_2$	45.0	0.774	91.9	1884	−14.7
$HCo(dmpb)_2$	45.6	0.763	93.3	1870	−15.6
$HCo(dmpent)_2$	49.3	0.762	95.9	1904	−16.8
$HRh(dmpe)_2$	23.6	0.778	84.4	1921	−7.4
$HRh(dmdppe)_2$	30.1	0.796	84.3	1956	−6.5
$HRh(dmpbz)_2$	29.3	0.800	84.7	1929	−6.9
$HRh(dppe)_2$	38.6	0.814	84.3	1978	−6.0
$HRh(dppbz)_2$	37.2	0.836	83.7	1943	−5.3
$HRh(dmpp)_2$	32.4	0.774	89.6	1935	−7.5
$HRh(dmpb)_2$	36.5	0.763	92.3	1924	−7.8
$HRh(dmpent)_2$	39.8	0.762	94.4	1950	−8.6
$HIr(dmpe)_2$	28.7	0.778	84.5	2030	−6.5
$HIr(dmdppe)_2$	36.1	0.796	84.4	2063	−5.5
$HIr(dmpbz)_2$	36.0	0.800	84.9	2037	−6.1
$HIr(dppe)_2$	48.4	0.814	84.6	2090	−5.0
$HIr(dppbz)_2$	45.6	0.836	83.9	2063	−4.5
$HIr(dmpp)_2$	39.5	0.774	89.8	2047	−6.3
$HIr(dmpb)_2$	43.2	0.763	92.4	2022	−6.4
$HIr(dmpent)_2$	47.9	0.762	94.6	2059	−7.0
$[HNi(dmpe)_2]^+$	51.1	0.778	86.0	1927	−9.6
$[HNi(dmdppe)_2]^+$	54.9	0.796	86.0	1942	−8.2
$[HNi(dmpbz)_2]^+$	55.9	0.800	86.6	1926	−8.8
$[HNi(dppe)_2]^+$	64.8	0.814	85.7	1982	−8.6
$[HNi(dppbz)_2]^+$	67.6	0.836	85.5	1912	−6.6
$[HNi(dmpp)_2]^+$	63.4	0.774	90.9	1977	−10.5
$[HNi(dmpb)_2]^+$	65.0	0.763	92.6	1957	−11.7
$[HNi(dmpent)_2]^+$	68.4	0.762	94.8	1990	−13.0
$[HPd(dmpe)_2]^+$	41.7	0.778	84.3	1960	−3.4
$[HPd(dmdppe)_2]^+$	47.6	0.796	84.3	1979	−2.2
$[HPd(dmpbz)_2]^+$	46.3	0.800	84.4	1970	−3.4
$[HPd(dppe)_2]^+$	55.6	0.814	84.0	1993	−2.1
$[HPd(dppbz)_2]^+$	55.8	0.836	83.6	1958	−1.7
$[HPd(dmpp)_2]^+$	51.2	0.774	88.1	1983	−4.4
$[HPd(dmpb)_2]^+$	57.0	0.763	91.6	2010	−5.2
$[HPd(dmpent)_2]^+$	61.0	0.762	93.6	2039	−6.0
$[HPt(dmpe)_2]^+$	42.1	0.778	84.4	2074	−3.4
$[HPt(dmdppe)_2]^+$	47.9	0.796	84.5	2096	−1.9
$[HPt(dmpbz)_2]^+$	47.2	0.800	84.7	2092	−3.7
$[HPt(dppe)_2]^+$	55.6	0.814	84.3	2154	−2.5
$[HPt(dppbz)_2]^+$	56.1	0.836	83.9	2076	−1.4
$[HPt(dmpp)_2]^+$	50.7	0.774	88.1	2095	−4.3
$[HPt(dmpb)_2]^+$	58.4	0.763	91.8	2106	−4.6
$[HPt(dmpent)_2]^+$	62.5	0.762	93.5	2142	−5.1

[a] δ_P is the NBO charge on phosphorus. [b] θ is the natural bite angle. [c] ν_{M-H} is the stretching vibration frequency of the metal−hydrogen bond.

a more efficient and more accurate theoretical method to compute the hydricities of transition-metal hydrides. Equipped with this newly developed method, we have studied in depth some important mechanistic issues associated with the hydricity by using systematic data not available previously. These include (1) the connection between pK_a and hydricity, (2) the modulation of hydricity by phosphine ligands, and (3) the periodical trends of hydricity.

2. Method Development

Most transition-metal hydrides contain more than 20 non-hydrogen atoms, which precludes the utilization of any high-level (and thereby reliable) theoretical method to directly model the entire species. To compromise the quality and cost of the calculation, a certain division-and-conquer strategy is needed so that the core activity and the environmental influence can be treated separately by different levels of theory. In our previous study on the pK_a values of transition-metal hydrides, we developed a two-layered ONIOM method with an aim to handle the bulky hydrides both accurately and efficiently. Specifically, the ONIOM(B3P86/LANL2DZ+p:HF/LANL2MB) method was found to give satisfactory results for the geometry optimizations, while the ONIOM(CCSD(T)/LANL2DZ+p:B3P86/LANL2MB) method was used to perform the single-point energy calculations. This ONIOM method was found to be capable of predicting the pK_a values of 30 transition-metal hydrides with a precision of 1.5 pK_a units.

Using the same ONIOM method, we here calculate the hydricity ($\Delta G^\circ_{H^-}$) of Ni- and Co-group transition-metal hydrides. To this end, we define $[Pt(dmpp)_2]^{2+}$ as a reference compound and utilize the following isodesmic reaction:

$$[L_mMH]^{n+} + [Pt(dmpp)_2]^{2+} \rightarrow [L_mM]^{(n+1)+} + [HPt(dmpp)_2]^{+} \quad (2)$$

If the free energy change of the above reaction is calculated to be $\Delta G_{exchange}$ in acetonitrile, the $\Delta G^\circ_{H^-}$ of the hydride $[L_mMH]^{n+}$ will be calculated as

$$\Delta G^\circ_{H^-}(L_mMH^{n+}) = \Delta G^\circ_{H^-}([HPt(dmpp)_2]^{+}) + \Delta G_{exchange} \quad (3)$$

where $\Delta G^\circ_{H^-}([HPt(dmpp)_2]^{+}) = 50.7$ kcal/mol according to the experiment. Noteworthily, the solvation free energy in acetonitrile is calculated by using the C-PCM solvation model[12] (radii, Bondi[13]) at the B3P86/LANL2DZ+p level. This treatment of the solvation effect was shown in our previous work to be the most appropriate for Co- and Ni-group transition-metal hydrides as compared to several other solvation models.

To test the applicability of the theoretical method, we examine the hydricities of six representative metal hydrides (Table 1). To our surprise, it is found that the ONIOM(CCSD(T)/LANL2DZ+p:B3P86/LANL2MB) method fails dramatically in calculating the hydricities, because the rms (root mean square) error of this method amounts to 6.6 kcal/mol, a value beyond the acceptable limit. This observation is troubling to us because we previously found that the same method was capable of predicting the pK_a values of 30 transition-metal hydrides with a precision of 1.5 pK_a units.

To understand the cause of this discrepancy, we first speculate that the ONIOM method may fail in geometry optimization because of the arbitrary division of the chemical bonds. However, after the comparison with the crystal structures and the purely DFT geometries, it is realized that the bond lengths and angles from these different origins agree with each other within about 3.0 pm and 3°, in fact not much worse than the error bars on the crystal structure itself.

The second possibility is that the basis sets in the ONIOM method are not sufficiently flexible because it is known that high-level wave function based correlation methods (e.g., CCSD(T)) need extended basis sets to reach their limits. Thus, we replace the LANL2DZ+p basis set by BS1, which means that the basis set for transition metals is LANL2DZ+p and the basis set for the other elements is 6-31+G* (method 2 in Table 1). Using this method, it is found that the rms error drops significantly to 3.2 kcal/mol. At this point we speculate that a further improvement of the basis set will provide an even better result, which, however, will make it infeasible to use the ONIOM method where the core layer is treated with the CCSD(T) method. To solve the problem, we decide to calculate the whole system by using the B3P86 method with the BS1 or BS2 basis set, which means that the basis set for transition metals is LANL2DZ+p, the basis set for P is 6-311+G**, and the basis set for the other elements is 6-31+G*. Using the geometries optimized by the ONIOM method (i.e., methods 3 and 4), the rms errors are equal to 3.0 and 2.9 kcal/mol, respectively. Using the geometries optimized by the B3P86/LANL2DZ+p method (method 5), the rms error is further decreased to 1.3 kcal/mol.

The above results indicate that the selection of the basis set is more important than the selection of the method level (e.g., CCSD(T) vs DFT) for calculating the hydricities of transition-metal hydrides. This is different from the situation for calculating the pK_a values of transition-metal hydrides, where the ONIOM method was found to be acceptable with relatively fewer flexible basis sets. A possible explanation for the failure of the ONIOM method in calculating hydricities is that the electronic effects of the outer layer are not accurately estimated with the low-level theory in the current ONIOM partitioning scheme. A similar observation of the dramatic failure of the ONIOM method in handling transition-metal complexes was reported recently by Vachet et al.[14]

3. Hydricity, Acidity, and Redox Potential

The B3P86/BS2//B3P86/LANL2DZ+p method is able to calculate the hydricities of six metal hydrides with a precision of 1.3 kcal/mol. Here we examine whether the same method can be used to calculate the hydricities as well as the pK_a values and redox potentials of all the Co- and Ni-group metal hydrides that have been experimentally characterized. Noteworthily no one has previously reported the use of theoretical methods to predict the solution-phase redox potentials of transition-metal diphosphine complexes.

As to the pK_a calculation, we consider the following isodesmic reaction:

$$[L_mMH]^{n+} + Pt(dmpp)_2 \rightarrow L_mM^{(n-1)+} + [HPt(dmpp)_2]^{+} \quad (4)$$

If the free energy change of the above reaction in acetonitrile is calculated to be $\Delta G_{exchange}$, the pK_a of the hydride $[L_mMH]^{n+}$ will be calculated as

$$pK_a(L_mMH^{+}) = pK_a([HPt(dmpp)_2]^{+}) - \Delta G_{exchange}/2.303RT \quad (5)$$

where $pK_a([HPt(dmpp)_2]^{+}) = 30.4$ according to the experiment.

As to the redox potential calculation, we consider the following isodesmic reaction:

$$L_mM + [Pt(dmpp)_2]^{2+} \rightarrow [L_mM]^{2+} + Pt(dmpp)_2 \quad (6)$$

If the free energy change of the above reaction in acetonitrile is calculated to be $\Delta G_{exchange}$, the standard two-electron redox potential (E°(II/0)) of the complex $[L_mM]$ will be calculated as

$$E^\circ(L_mM^{2+}/L_mM) = E^\circ([Pt(dmpp)_2]^{2+}/Pt(dmpp)_2) + \frac{\Delta G_{exchange}}{2 \times 23.06} \quad (7)$$

where $E^\circ([Pt(dmpp)_2]^{2+}/Pt(dmpp)_2) = 1.53$ V according to the experiment.

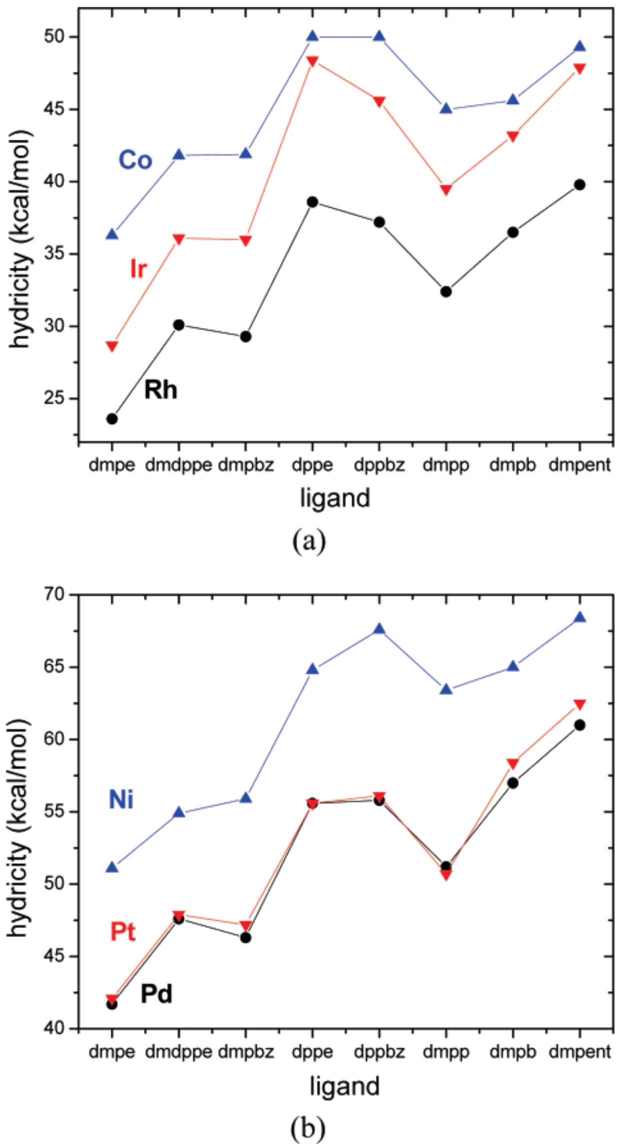
Using the B3P86/BS2//B3P86/LANL2DZ+p method and eqs 3, 5, and 7, we have calculated 25 Co- and Ni-group metal hydrides as shown in Table 2. The detailed chemical structures of the phosphine ligands and their abbreviations are shown in Chart 1. As shown in Figure 1, the theoretical and experimental acidities, redox potentials, and hydricities are in good agreement with each other. The mean signed errors for the acidities, redox

---

[12] (a) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995. (b) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. *J. Comput. Chem.* **2003**, *24*, 669.

[13] Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

[14] Combariza, M. Y.; Fermann, J. T.; Vachet, R. W. *Inorg. Chem.* **2004**, *43*, 2745.



(a)

(b)

Figure 2. Periodical trends for the hydricities of Co-group (a) and Ni-group (b) metal hydrides.

potentials, and hydricitites are −0.1 pK_a unit, +0.01 V, and +0.2 kcal/mol, respectively. The rms errors for the acidities, redox potentials, and hydricities are 1.9 pK_a units, 0.07 V, and 2.0 kcal/mol, respectively.

Despite the good agreement between the theory and experiment for most of the data, we do find one experimental hydricity value to be questionable. As shown in Table 2, the experimental hydricity for $[HPd(EtXantphos)_2]^+$ is 70.4 kcal/mol, while our theoretical value is 76.6 kcal/mol. We argue that this particular experimental value might involve some inaccuracy because the experimental hydricity of $[HPd(depe)_2]^+$ (43.2 kcal/mol) is lower than that for $[HPt(depe)_2]^+$ (44.2 kcal/mol) by only 1.0 kcal/mol. Analogously, the hydricity of $[HPd(EtXantphos)_2]^+$ should not be too much lower than the hydricity of $[HPt(EtXantphos)_2]^+$ (exptl, 76 ± 2 kcal/mol; calcd, 77.7 kcal/mol). This means that our theoretical value (76.6 kcal/mol) appears to be more reasonable.

4. Structure−Activity Relationship

The above results demonstrate that it is reliable to use the theoretical method to predict the hydricities for Co- and Ni-group transition-metal hydrides. This provides us a good opportunity to systematically examine the structure−activity relationships behind these important thermodynamic quantities on the basis of a more complete data sample not accessible in any previous studies. To this end we systematically calculate the hydricities of Co- and Ni-group metal hydrides as shown in Table 3.

4.1. Periodical Trends. DuBois and co-workers reported (mainly on the basis of data for the Ni-group metal hydrides) that the hydricity of metal hydrides in the same group increase in the order second row < third row ≪ first row.[4k] Our theoretical data are consistent with DuBois's observations, but with some modification. As shown in Figure 2, for the Co-group metal hydrides, the hydricities increase in the order second row < third row < first row. For the Ni-group metal hydrides, the hydricities increase in the order second row ≈ third row ≪ first row. Furthermore, it is evident from Figure 2 that the effect of the ligands on hydricity can outweigh that of the metals. Therefore, the above periodical trends hold only under the condition that the same ligand is utilized.

Comparing the Co- and Ni-group metal hydrides, we find that the hydricities of the Co-group metal hydrides vary from about 20 to 50 kcal/mol, whereas the hydricities of the Ni-group metal hydrides vary from about 40 to 70 kcal/mol. The Co-group metal hydrides are significantly more hydridic than the Ni-group ones, presumably because the former compounds are neutral whereas the latter ones are positively charged.

4.2. Effects of Phosphine Ligands. Figure 2 shows that the phosphine ligands dramatically tune the hydricity of the metal hydrides. The origin of the phosphine ligand effects can be partly attributed to the electronic factors, which means that an electron-richer phosphine ligand should make a hydride more hydridic. As shown in Figure 3a, the hydricities of nickel hydrides show a linear dependence on the NBO charge of the phosphorus atom in the series $[HNi(dmpe)_2]^+$, $[HNi(dmdppe)_2]^+$, $[HNi(dmpbz)_2]^+$, $[HNi(dppe)_2]^+$, and $[HNi(dppbz)_2]^+$, which stepwisely replace the alkyl groups on phosphorus by aryl groups. However, the same linear dependence does not apply to $[HNi(dmpp)_2]^+$, $[HNi(dmpb)_2]^+$, and $[HNi(dmpent)_2]^+$, which have electron-richer diphosphine ligands but much higher hydricites as compared to $[HNi(dmpe)_2]^+$.

Figure 3a indicates that in addition to the electronic factors, some structural factors can also affect the hydricity. In this regard, Norton et al. previously investigated the rate of hydride transfer from ruthenium diphosphine complexes to iminium cations and found that smaller bite angles of the diphosphine ligand favored rapid hydride transfer.[15] Furthermore, DuBois et al. previously studied palladium hydrides carrying diphosphines with variable ligand bite angles.[4j] They found that the ligand bite angle could dramatically change the hydricity of palladium hydrides. Here we plot the hydricities of nickel hydrides against the natural bite angles of the diphosphine ligands. For $[HNi(dmpe)_2]^+$, $[HNi(dmpp)_2]^+$, $[HNi(dmpb)_2]^+$, and $[HNi(dmpent)_2]^+$, we do observe a linear dependence of the hydricity on the natural bite angle (Figure 3b). However, this dependence does not apply to the hydricities of $[HNi(dmdppe)_2]^+$, $[HNi(dmpbz)_2]^+$, $[HNi(dppe)_2]^+$, and $[HNi(dppbz)_2]^+$.

The above results show that both the electronic and structural factors control the hydricity, but neither of them is sufficient to explain the observed variation. Thus, we hypothesize that it is possible to use a dual-parameter correlation to quantitatively

---

[15] Guan, H. R.; Iimura, M.; Magee, M. P.; Norton, J. R.; Janak, K. E. *Organometallics* **2003**, *22*, 4084.

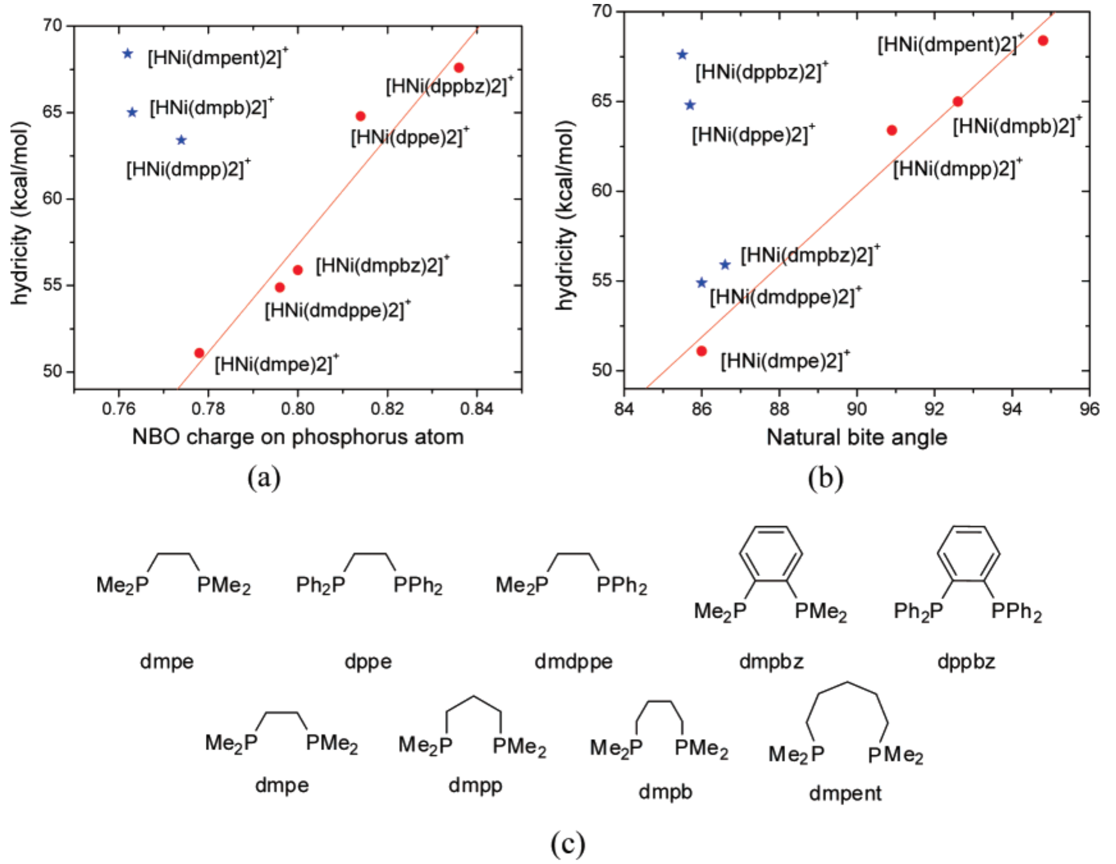


Figure 3. Dependence of the hydricities of nickel hydrides on the electronic and structural factors of the diphosphine ligands.

interpret the ligand effects on hydricities. This provides us the following equations:

$$\Delta G^{\circ}_{\mathrm{H}^-}(\mathrm{Co{-}H}) = -312.3 + 265.4\delta_{\mathrm{P}} + 1.66\theta \qquad (r = 0.9277,\ \mathrm{sd} = 2.1) \quad (8)$$

$$\Delta G^{\circ}_{\mathrm{H}^-}(\mathrm{Rh{-}H}) = -364.1 + 282.8\delta_{\mathrm{P}} + 2.00\theta \qquad (r = 0.9295,\ \mathrm{sd} = 2.4) \quad (9)$$

$$\Delta G^{\circ}_{\mathrm{H}^-}(\mathrm{Ir{-}H}) = -447.0 + 354.6\delta_{\mathrm{P}} + 2.37\theta \qquad (r = 0.9189,\ \mathrm{sd} = 3.2) \quad (10)$$

$$\Delta G^{\circ}_{\mathrm{H}^-}(\mathrm{Ni{-}H}) = -439.6 + 325.6\delta_{\mathrm{P}} + 2.75\theta \qquad (r = 0.9493,\ \mathrm{sd} = 2.4) \quad (11)$$

$$\Delta G^{\circ}_{\mathrm{H}^-}(\mathrm{Pd{-}H}) = -402.5 + 291.8\delta_{\mathrm{P}} + 2.58\theta \qquad (r = 0.9595,\ \mathrm{sd} = 2.2) \quad (12)$$

$$\Delta G^{\circ}_{\mathrm{H}^-}(\mathrm{Pt{-}H}) = -413.3 + 287.7\delta_{\mathrm{P}} + 2.74\theta \qquad (r = 0.9713,\ \mathrm{sd} = 1.9) \quad (13)$$

where δ_{P} and θ are the NBO charge on phosphorus and the natural bite angle, respectively. The correlation coefficients (i.e., the r values) in the above correlations are as high as 0.92–0.97, and the standard deviations (i.e., the sd values) are close to the error bar of the calculation (namely, ~2.0 kcal/mol). Therefore, it is sufficient to use the δ_{P} and θ values to quantitatively predict the hydricities of all the Co- and Ni-group metal hydrides.

4.3. Metal−Hydrogen Vibration. In Table 3 are also shown the stretching vibration frequency of the metal−hydrogen bond in all the hydrides. For Co−H, Rh−H, and Ir−H, the vibration frequencies are 1870−1966, 1921−1978, and 2022−2090 cm^{-1}, respectively. For Ni−H, Pd−H, and Pt−H, the vibration frequencies are 1912−1990, 1958−2039, and 2074−2154 cm^{-1}, respectively. These values do not correlate with the periodical trends in hydricities. Furthermore, for each particular metal we do not find any correlation between the hydricity and the metal−hydrogen vibration frequency. Therefore, it is not reliable to use any vibration spectrum method to predict the hydricity of a transition-metal hydride.

4.4. Chemical Shift of the Hydride Hydrogen. After finding that the hydricity has no correlation with the metal−hydrogen vibration frequency, we wonder whether there is any correlation between the hydricity and the chemical shift of the hydride hydrogen. To this end we use the B3P86/LANL2DZ+p (NMR, GIAO) method to calculate the chemical shifts of the hydride hydrogens in Table 3. It is found that the calculated chemical shifts are in reasonable agreement with the available experimental values. Specifically, the chemical shifts of hydrogen for $\mathrm{HCo(dppe)_2}$, $\mathrm{HRh(dppbz)_2}$, $[\mathrm{HNi(dmpp)_2}]^+$, and $[\mathrm{HNi(dmpe)_2}]^+$ are −14.9, −9.4, −14.3, and 14.0 according to the experiment, whereas our theoretical values are −13.9, −5.3, −10.5, and −9.6, respectively.[4a,e,f,] Using the theoretical values, we find that for each particular metal there is no correlation between the hydricity and the hydrogen chemical shift. Therefore, it is not reliable to use the NMR method to predict the hydricity of a transition-metal hydride.

5. Summary

The thermodynamic hydricity quantitatively describes the hydride donor ability of the metal−hydrogen bond. The ability to accurately calculate hydricity is essential to the use of theoretical methods to study the mechanism of many catalytic processes that involve transition-metal hydrides. Here we systematically compare the theoretical hydricities calculated by different methods and all the available experimental values for the Co- and Ni-group metal hydrides. We have the following conclusions.

(1) It is found that the B3P86 method employing a sufficiently flexible basis set (namely, LANL2DZ+p for transition metals, 6-311+G** for phosphorus, and 6-31+G* for the other elements) in combination with the C-PCM solvent model can accurately predict the hydricity with a precision of 2.0 kcal/mol. The same method can also accurately predict the acidities of the metal−hydrogen bond and the redox potentials of corresponding complexes with precisions of 1.9 pK_a units and 0.07 V, respectively.

(2) An ONIOM method where the core layer is treated with the CCSD(T) method fails to predict the hydricity of transition-metal hydrides. A possible explanation is that the basis sets in the ONIOM methods are not sufficiently flexible because it is known that high-level wave function based correlation methods (e.g., CCSD(T)) need extended basis sets to reach their limits.

(3) As to the periodical trends, it is found that for the Co-group metal hydrides, the hydricities increase in the order second row < third row < first row. For the Ni-group metal hydrides, the hydricities increase in the order second row ≈ third row ≪ first row.

(4) The phosphine ligands tune the hydricity through both the electronic and structural parameters. On the basis of systematic data, we show that it is possible to use a dual-parameter correlation to quantitatively interpret the ligand effects on hydricities, where the two parameters are the NBO charge of the phosphorus and the natural bite angle of the diphosphine.

(5) On the basis of systematic data, we find no correlation between the hydricity and the metal−hydrogen vibration frequency or the hydrogen chemical shift. Therefore, it is not reliable to use any vibrational spectrum or proton NMR method to estimate the hydricity of transition-metal hydrides.

6. Computational Methodologies

All the calculations were performed with the Gaussian 03 programs[16] using our HP Superdome Server (32 × 1.5 GHz Itanium 2 Madison CPU). Initial geometry optimization was carried out using B3P86 and an effective core potential (LANL2DZ) for the inner electrons and its associated double-ζ basis set for the more external ones.[17] In the case of the P atom and transition-metal atoms a d-polarization shell or an f-polarization shell was added.[18] Each optimized structure was confirmed by the frequency calculation at the same level to be the real minimum without any imaginary vibrational frequency. For compounds that have multiple conformations, efforts were made to find the lowest energy conformation by comparing the structures optimized from different starting geometries.

Harmonic vibrational frequencies were calculated using the B3P86/LANL2DZ+p method from the optimized geometries. Zero-point vibrational energy (ZPE) corrections were obtained using unscaled frequencies. Single-point electronic energies were then calculated with the B3P86/BS2 method (BS2, the basis set for transition metals is LANL2DZ+p, the basis set for P is 6-311+G**, and the basis set for the other elements is 6-31+G*). The gas-phase free energy change was corrected with ZPE, thermal corrections (0 → 298 K), and the entropy terms. It is worth noting that all the calculated gas-phase free energies correspond to the reference state of 1 atm and 298 K.

To calculate the hydricity, acidity, and redox potential, we utilized the C-PCM solvation model at the B3P86/LANL2DZ+p level (version, MATRIX INVERSION; cavity, GePol; TSARE = 0.2; radii, Bondi or UA0; $\alpha = 1.0$). The gas-phase geometry was used for all of the solution-phase calculations, because it has been demonstrated in many previous studies that the change of geometry by the solvation effect is usually not significant.[19] It is worth noting that all the calculated solution-phase free energies correspond to the reference state of 1 mol/L and 298 K. Correction terms for the change from 1 atm and 298 K to 1 mol/L and 298 K must be added when the gas-phase and solution-phase free energies are involved in the same equation.

Acknowledgment. This study was supported by the National Natural Science Foundation of China (Grant Nos. 20472079 and 20602034). We also thank the USTC Supercomputer Center for technical support.

Supporting Information Available: Cartesian coordinates of optimized structures and detailed thermodynamic data. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0702429

---

[16] 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.; Iyengar, 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.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, 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.: Wallingford, CT, 2004.

[17] (a) Hay, P. J.; Wadt, W. R. *J. Phys. Chem.* **1985**, *82*, 299. (b) Wadt, W. R.; Hay, P. J. *J. Phys. Chem.* **1985**, *82*, 284.

[18] Höllwarth, A.; Böhme, M.; Dapprich, S.; Ehlers, A. W.; Gobbi, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 237.

[19] (a) Cramer, C. J.; Truhlar, D. G. *Chem. Rev.* **1999**, *99*, 2161. (b) Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, *105*, 2999.