

Ab Initio Calculations of pK_a Values of Transition-Metal Hydrides in Acetonitrile

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A well-defined ab initio protocol was developed which could be used to calculate the pK_a values of a variety of transition-metal hydrides in acetonitrile with a precision of 1.5 pK_a units. The gas-phase energies were calculated using a two-layer ONIOM method where the core layer was handled by the CCSD(T) theory. In addition, the C-PCM solvation model previously developed for small organic molecules was confirmed to be reliable for predicting the solvation energies of bulky organometallic complexes. Using the protocol, we studied the structure–property relationships for the acidities of the Fe-, Co-, and Ni-group metal hydrides. It was found that the pK_a values of these hydrides varied considerably with respect to the metal centers. The third-row metal hydrides always appeared to be the least acidic, as compared to the first- and second-row metal hydrides. On the other hand, the relative acidity between the first- and second-row metal hydrides was strongly dependent on the chemical formulas of the metal complexes. Finally, linear correlations were observed between the pK_a values of metal hydrides and the NBO (natural bond orbital) charges carried by the chelating phosphorus atoms.

1. Introduction

Transition-metal hydrides are important intermediates in a large range of stoichiometric and catalytic processes such as hydrogenation and hydroformylation.¹ They display a broad reactivity pattern, some of them behaving as hydride donors, whereas others may act as protonating reagents or may transfer hydrogen through a radical mechanism. It has been widely hypothesized that the difference in the reactivity of transition-metal hydrides can be related to the thermodynamic differences of the M–H bonds. As a result, in recent years considerable efforts have been made to measure the energies associated with the formation and rupture of the M–H bonds of various types of transition-metal hydrides.

Generally speaking, the M–H bond in a transition-metal hydride can be cleaved in three different pathways, as shown in the reactions²



The first reaction is a deprotonation reaction, and its free energy change (or the pK_a value of L_nM-H^+) can be determined by measuring the equilibrium constant for the proton-transfer

reaction between L_nM-H^+ and a base whose pK_a value is known. The second reaction is a homolytic cleavage reaction, and its free energy change can be calculated from the pK_a value of L_nM-H^+ , the one-electron reversible oxidation potential of L_nM , and the reduction potential of the H^+/H^\bullet couple through a thermodynamic cycle. Finally, the third reaction is a hydride transfer reaction, and its free energy change can be calculated from the pK_a value of L_nM-H^+ , the two-electron reversible oxidation potential of L_nM , and the reduction potential of the H^+/H^- couple.

It is evident that the pK_a value of L_nM-H^+ is fundamentally important for the studies of all the three cleavage pathways of an M–H bond. Accordingly, many experimental studies have been performed to measure the pK_a values of various transition-metal hydrides.^{2,3} An alternative is to develop an ab initio computational protocol that can reliably predict the pK_a value of any transition-metal hydride from scratch. Once such a computational protocol is available, it will be straightforward to quantitatively predict which transition-metal complexes will be protonated under a given set of conditions. This is clearly important, because whether the reactant in a catalytic cycle is

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a transition-metal hydride or its deprotonated analogue can have significant chemical consequences. Furthermore, it is worth noting that not all the transition-metal hydrides are readily amenable to experimental characterization even in the far future. Due to this reason, in some research work it may become necessary to use a theoretical method to estimate the pK_a values of some transition-metal hydrides.

The above analysis suggests that the ability to predict the solution-phase acidity of transition-metal hydrides using a coherent theoretical protocol would be valuable to both mechanistic organometallic chemists and synthetic organic chemists.⁵ Unfortunately, despite the strong need, this protocol has not been available, due to the following three reasons. First, well-defined transition-metal hydrides soluble in organic solutions are usually sizable molecules carrying bulky ligands. It is difficult to balance the cost and performance of an ab initio method for these massive molecules. Second, it has been a significant challenge in theoretical chemistry to calculate the thermodynamic properties of transition-metal complexes with confident accuracy.⁴ Third, and perhaps most limiting, very little is known about whether we can accurately calculate the solvation energies of transition-metal complexes in organic solutions.⁶

2. The ONIOM Method and Geometry Optimization

In the present study a two-layered ONIOM method is utilized.⁷ The metal atom, the hydride, and all other atoms directly coordinating to the metal are placed in the core layer, whereas the remaining atoms constitute the outside layer. The ONIOM energy of the whole system is calculated using the equation

$$E(\text{ONIOM}) = E(\text{high level, core}) + E(\text{low level, real}) - E(\text{low level, core}) \quad (4)$$

where $E(\text{high level, core})$ is the energy of the core layer calculated using a high-level method, $E(\text{low level, real})$ is the energy of the whole system calculated using a low-level method,

and $E(\text{low level, core})$ is the energy of the core layer calculated using the low-level method. Three different density functional methods (B3LYP, B3PW91, and B3P86) are examined for the core layer with the LANL2DZ+p basis set. The low-level method is fixed as HF/LANL2MB.

Using the above ONIOM methods, we have examined their performances for the geometry optimization of 12 transition-metal hydrides or their deprotonated counterparts whose crystal structures are available (see Figure 1; for the structures of the phosphine ligands, see Chart 1). To compare the performances of the three density functionals, we have calculated the average errors and root of mean square errors between the theoretical and experimental bond lengths, bond angles, and dihedral angles (Table 1). It is evident from the results that the B3P86 functional provides the best predictions for all the geometric parameters. Its average errors for the bond lengths (0.029 Å) and bond angles (1.28°) are very low, whereas the average error for the dihedral angle is relatively high (9.1°) because the crystal packing effect is, understandably, not considered in the geometry optimization process.⁸

Some comments are worth noting about the structures of the transition-metal hydrides and their deprotonated counterparts, as we have observed from our calculations and as observed previously by the others in the crystal structures. (1) For $M = \text{Ni, Pd, Pt}$, the structure of $[\text{HM}(\text{diphosphine})_2]^+$ displays a distorted-tetrahedral arrangement of the two diphosphine ligands around the metal center. The $M(\text{diphosphine})_2$ complexes also show the distorted-tetrahedral geometries typical of the d^{10} complexes.⁹ (2) The dihydride complexes $[\text{H}_2\text{M}(\text{diphosphine})_2]^{n+}$ ($M = \text{Co, Rh, Ir; } n = 1, 2$) exhibit a distorted cis-octahedral structure. On the other hand, $[\text{HM}(\text{diphosphine})_2]^{(n-1)+}$ is best described as a distorted-trigonal-bipyramidal complex with one phosphorus atom and the hydride occupying the axial positions.^{2f} (3) For $M = \text{Fe, Ru, Os}$, the geometries of the monohydride (i.e., $[\text{CpMH}(\text{diphosphine})]$) and *trans*-dihydride complexes (i.e., $[\text{CpMH}_2(\text{diphosphine})]^+$) are best described in terms of “three- and four-legged piano stools”, respectively, with the “legs” comprising the phosphine and hydride ligands.^{3f,10}

3. Gas-Phase Acidities

Before we try to calculate of the pK_a value of a transition-metal hydride in acetonitrile, we wish to learn whether we can accurately calculate its gas-phase acidity, defined as the free energy change of the following reaction in the gas phase at 298 K and 1 atm:



Unfortunately, there has not been any experimental value that we could use to evaluate the theoretical predictions. As a result,

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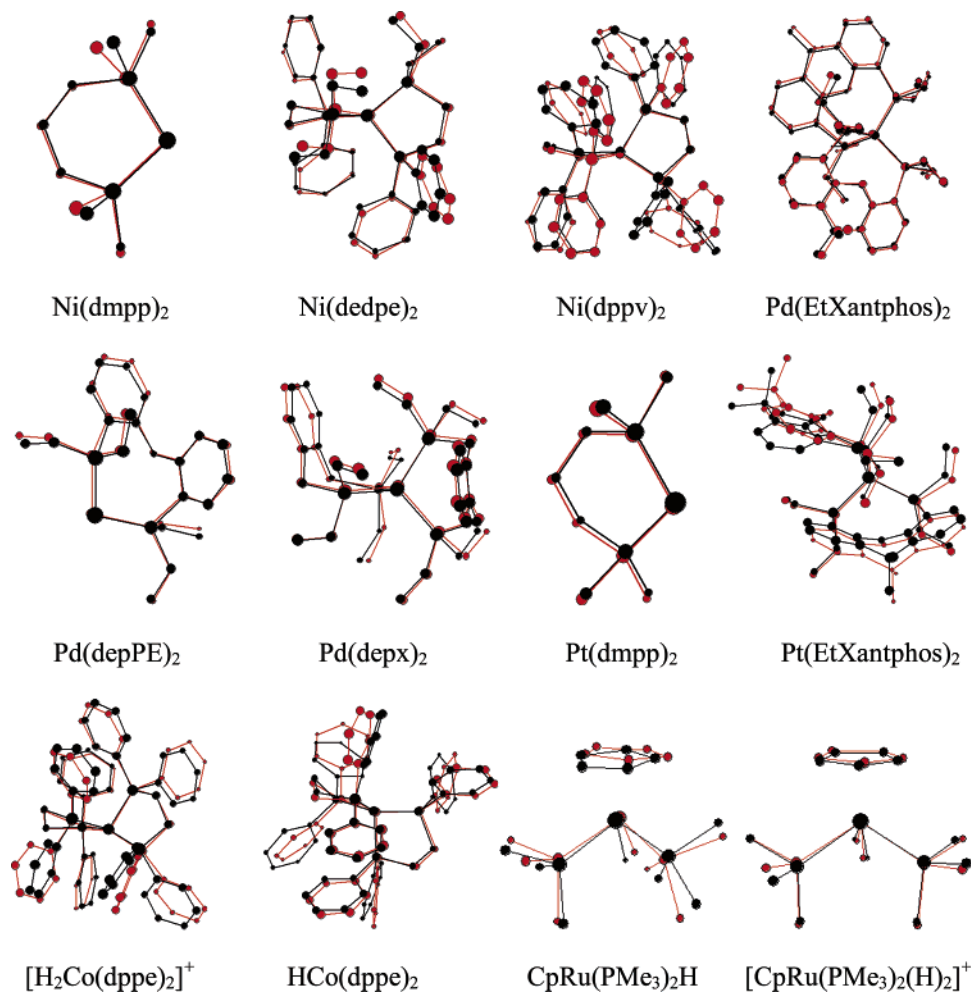


Figure 1. Comparison of the theoretically optimized structures (in red, ONIOM(B3P86/LANL2DZ+p:HF/LANL2MB method) with the experimental crystal structures (in black).

Chart 1. Chemical Structures of the Phosphine Ligands

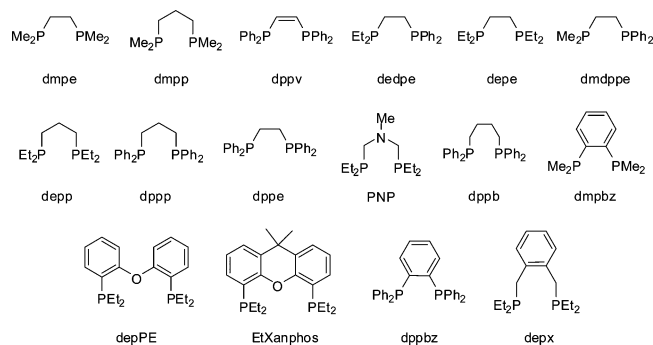


Table 1. Average Errors and Root Mean Square Errors for the Optimized Structures and the Crystal Structures for 13 Transition-Metal Complexes^a

density functional	bond length (Å)		bond angle (deg)		dihedral angle (deg)	
	ae	rmse	ae	rmse	ae	rmse
B3LYP	0.030	0.048	1.40	3.19	13.1	29.4
B3PW91	0.029	0.047	1.44	3.19	11.4	23.0
B3P86	0.029	0.046	1.28	2.04	9.1	20.7

^a Abbreviations: ae, average error; rmse, root mean square error.

we have decided to calculate the gas-phase acidities using the best possible theoretical method that can be accomplished by our HP Superdome Server (32 × 1.5 GHz Itaniumw 2 Madison

CPU). After some test calculations, we determine this method to be ONIOM(CCSD(T)/LANL2DZ+P:B3P86/LANL2MB) for the energy calculation, where the geometry is optimized by the ONIOM(B3P86/LANL2DZ+P:HF/LANL2MB) method. The gas-phase acidities calculated by this method are shown in Table 2 for a collection of transition-metal hydrides whose *pK_a* values in acetonitrile have been experimentally measured. For comparison, we also show the gas-phase acidities calculated by the ONIOM(B3P86/LANL2DZ+P:B3P86/LANL2MB) method, where the geometry is again optimized by the ONIOM(B3P86/LANL2DZ+P:HF/LANL2MB) method.

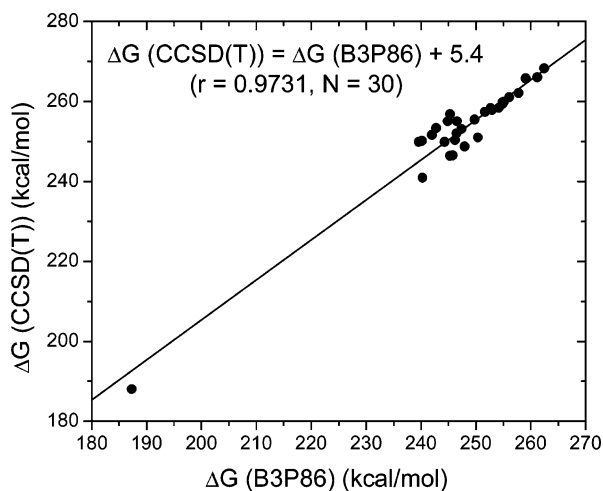
When the results provided by the different methods are compared, it is found that the gas-phase acidities calculated by the CCSD(T) method are lower than the B3P86 predictions for all of the types of transition-metal hydrides. Nonetheless, plotting the CCSD(T) values against the B3P86 data, we find that they correlate reasonably well with each other (Figure 2). The correlation coefficient is as high as 0.9731, and the slope of the correlation is equal to unity. Furthermore, a positive intercept of the plot indicates that the CCSD(T) values are higher than the B3P86 data by about +5.4 kcal/mol in a systematic fashion. Thus, although there is not any experimental value to determine which of the above two methods is more accurate in calculating the absolute gas-phase acidity values, it can be safely concluded at this point that it is trustworthy to use either of the two methods to predict the relative gas-phase acidities between different transition-metal hydrides.¹¹

Table 2. Experimental and Theoretical Gas-Phase Acidities (ΔG_{gas} , kcal/mol) and pK_{a} Values for the Transition-Metal Hydrides That Have Been Experimentally Characterized^a

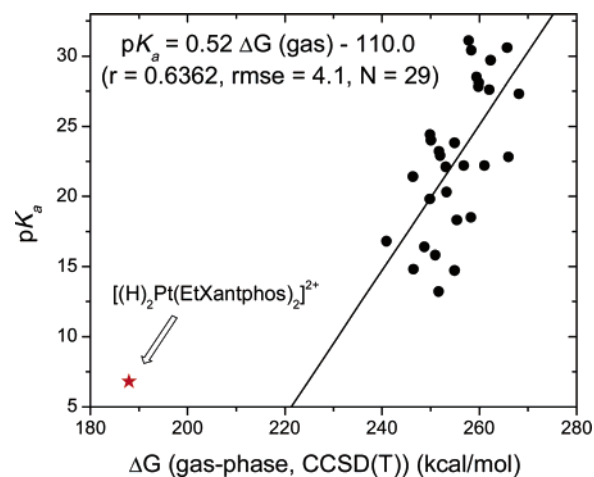
hydride	$pK_{\text{a}}(\text{exptl})$	ref	CCSD(T)/ B3P86 ^c		B3P86/ B3P86 ^d	
			ΔG_{gas}	pK_{a}	ΔG_{gas}	pK_{a}
[HNi(dedpe) ₂] ⁺	20.3 ± 0.2	2c	253.3	19.9	242.8	16.2
[HNi(depe) ₂] ⁺	23.8 ± 0.2	2a	255.0	24.7	246.6	22.5
[HNi(dmpe) ₂] ⁺	24.4 ± 0.2	2a	249.9	22.9	239.6	19.3
[HNi(dmpp) ₂] ⁺	24.0 ± 0.3	2a	250.1	22.7	240.2	19.4
[HNi(dppe) ₂] ⁺	14.7 ± 0.3	2a	255.0	17.3	244.9	13.8
[HNi(dppv) ₂] ⁺	13.2	2c	251.6	14.1	242.0	11.0
[HNi(PNP) ₂] ⁺	22.2	2i	256.8	24.2	245.3	19.8
[HPd(depPE) ₂] ⁺	18.3 ± 0.5	2k	255.4	19.6	249.8	19.5
[HPd(depX) ₂] ⁺	19.8 ± 0.2	2k	249.9	17.6	244.3	17.5
[HPd(EtXantphos) ₂] ⁺	18.5 ± 0.5	2k	258.3	21.3	252.7	21.1
[HPd(depe) ₂] ⁺	23.2 ± 0.2	2k	250.3	22.1	246.2	22.1
[HPd(dmpp) ₂] ⁺	22.9 ± 0.2	2k	252.0	21.7	246.5	21.6
[HPd(PNP) ₂] ⁺	22.1	2i	253.1	21.4	247.4	21.1
[HPt(depe) ₂] ⁺	29.7	2d	257.4	29.9	251.7	30.3
[HPt(depe)(dmpe)] ⁺	27.8	2a	259.8	29.0	254.9	29.3
[HPt(depe)(dmpp)] ⁺	28.1	2a	259.9	28.4	255.1	28.9
[HPt(dmpe)(dmpp)] ⁺	28.5	2a	259.4	29.0	254.9	29.6
[HPt(dppe) ₂] ⁺	22.2	2a	261.0	21.6	256.1	22.0
[HPt(EtXantphos) ₂] ⁺	27.3 ± 0.5	2l	268.2	28.7	262.5	28.5
[HPt(dmpe) ₂] ⁺	31.1	2d	257.8	28.3	253.0	28.7
[HPt(dmpp) ₂] ⁺	30.4	2d	258.4	28.4	254.2	29.3
[(H) ₂ Pt(EtXantphos) ₂] ²⁺	6.8 ± 0.5	2l	188.0	8.2	187.3	11.7
[HPt(PNP) ₂] ⁺	27.6	2i	262.1	28.1	257.8	28.9
[H ₂ Co(dppe) ₂] ⁺	22.8	2f	266.0	25.9	261.2	26.3
[H ₂ Rh(depX) ₂] ⁺	30.6 ± 0.3	2m	265.7	29.9	259.1	29.0
CpRu(dmpe)(H) ₂ ⁺	16.8 ^b	3e	240.9	16.0	240.3	19.5
CpRu(dppe)(H) ₂ ⁺	14.8 ^b	2o	246.5	14.3	245.8	17.7
CpRu(dppp)(H) ₂ ⁺	16.4 ^b	3e	248.7	15.1	248.0	18.6
CpRu(PPh ₃) ₂ (H) ₂ ⁺	15.8 ^b	3e	251.0	16.8	250.4	20.3
CpRu(PMe ₃) ₂ (H) ₂ ⁺	21.4 ^b	3f	246.4	19.8	245.3	23.0

^a It previously was found that the relative pK_{a} values obtained in acetonitrile and benzonitrile were the same within experimental error.²

^b Estimated from the aqueous pK_{a} value using the following equation as provided in ref 1a: $pK_{\text{a}}(\text{in CH}_3\text{CN}) = pK_{\text{a}}(\text{in H}_2\text{O}) + 7.5$. ^c Conditions: gas-phase method, ONIOM(CCSD(T)/LANL2DZ+p:B3P86/LANL2MB)//ONIOM(B3P86/LANL2DZ+p:HF/LANL2MB), solvation model, C-PCM (B3P86/LANL2DZ+p); radii, Bondi. ^d Conditions: gas-phase method, ONIOM(B3P86/LANL2DZ+p:B3P86/LANL2MB)//ONIOM(B3P86/LANL2DZ+p:HF/LANL2MB); solvation model, C-PCM (B3P86/LANL2DZ+p); radii, Bondi.

**Figure 2.** Comparison of the CCSD(T) and B3P86 gas-phase acidities for various types of transition-metal hydrides.

With the gas-phase acidities in hand, we are curious whether there is a good correlation between the gas-phase acidities and the solution-phase pK_{a} 's for the transition-metal hydrides. If this were the case, it would be possible to estimate the pK_{a} value directly from the gas-phase acidity without any further com-

**Figure 3.** Comparison of the theoretical gas-phase acidities (CCSD(T) predictions) and the experimental pK_{a} values in acetonitrile.

plications. Unfortunately, as seen from Figure 3, the correlation is very poor for all of the monocationic transition-metal hydrides (29 species). The correlation coefficient is only 0.6362, whereas the root mean square error is as high as 4.1 pK_{a} units. Furthermore, a dicationic species (i.e., $[(\text{H})_2\text{Pt}(\text{EtXantphos})_2]^{2+}$) dramatically deviates from the correlation plot in Figure 3 and its experimental value (+6.8) differs from the value (−12.2) as expected from the correlation plot about 19.0 pK_{a} units! Thus, it is concluded that there are significant solvation effects on the pK_{a} values of transition-metal hydrides. It is not trustworthy to compare the solution-phase acidities of transition-metal hydrides solely on the basis of their gas-phase acidity values.

4. Procedure for pK_{a} Calculations

The pK_{a} value for the transition-metal hydride $L_n\text{MH}^+$ describes the free energy cost of the reaction $L_n\text{MH}^+ \rightarrow L_n\text{M} + \text{H}^+$ in the solution. Mathematically the pK_{a} value can be calculated by the equation

$$pK_{\text{a}} = -\frac{\Delta G_{\text{gas}} + \Delta G_{\text{solv}}}{2.303RT} = -\frac{\Delta G_{\text{gas}} + \Delta G_{\text{solv}}(L_n\text{MH}^+) - \Delta G_{\text{solv}}(L_n\text{M}) - \Delta G_{\text{solv}}(\text{H}^+)}{2.303RT} \quad (6)$$

where ΔG_{gas} is the gas-phase acidity and ΔG_{solv} is the overall solvation effect, as determined by the solvation energies for the involved species: i.e., $\Delta G_{\text{solv}}(L_n\text{MH}^+)$, $\Delta G_{\text{solv}}(L_n\text{M})$, and $\Delta G_{\text{solv}}(\text{H}^+)$, respectively.¹² As mentioned previously, we have not been able to ascertain the accuracy of the theoretical methods to calculate the absolute value for ΔG_{gas} . Accordingly, we cannot directly utilize eq 6 to calculate the pK_{a} values for transition-metal hydrides. To overcome the problem, we turn to the free energy change ($\Delta G_{\text{exchange}}$) of the following exchange reaction in acetonitrile at 298 K:



in which $[\text{HNi}(\text{dedpe})_2]^+$ is randomly selected as a reference

(11) Similar observations have been reported for the energy calculations concerning other transition-metal complexes. See: de Jong, G. T.; Bickelhaupt, F. M. *J. Chem. Theory Comput.* **2006**, *2*, 322 and references cited therein.

compound. Thus, the pK_a value for L_nMH⁺ can now be calculated by

$$\begin{aligned} \text{p}K_a(\text{L}_n\text{MH}^+) &= \text{p}K_a([\text{HNi}(\text{dedpe})_2]^+) - \frac{\Delta G_{\text{exchange}}}{2.303RT} \\ &= \text{p}K_a([\text{HNi}(\text{dedpe})_2]^+) - \frac{\Delta\Delta G_{\text{gas}} + \Delta\Delta G_{\text{solv}}}{2.303RT} \quad (8) \end{aligned}$$

where $\Delta\Delta G_{\text{gas}}$ and $\Delta\Delta G_{\text{solv}}$ are the relative gas-phase acidity and relative solvation effect values between L_nMH⁺ and [HNi(dedpe)₂]⁺.

In the previous section we have learned that $\Delta\Delta G_{\text{gas}}$ values between different transition-metal hydrides can be reliably calculated by different methods. We hypothesize that $\Delta\Delta G_{\text{solv}}$ can also be calculated with sufficient accuracy (which will be tested below). Therefore, the only missing element in eq 8 is the pK_a value for [HNi(dedpe)₂]⁺. Although this value has been experimentally determined to be 20.3,^{2c} we cannot assert that this particular reported value must be correct. As a result, we temporarily assume that the pK_a value for [HNi(dedpe)₂]⁺ is an unknown number. Our present mission is to find the best theoretical method to minimize the root square error between the theoretical predictions and all the available experimental data, as defined in

$$\text{rmse} = \sum_i \frac{(\text{p}K_a(\text{theor})_i - \text{p}K_a(\text{exptl})_i)^2}{30} \quad (9)$$

where $i = 1-30$ for all the transition-metal hydrides shown in Table 2.

For a given combination of theoretical methods (i.e., gas-phase method + solvation method), the only variable that remains unknown in eq 9 is the pK_a value for [HNi(dedpe)₂]⁺. Without much difficulty, it can be mathematically proven that in order to achieve the lowest rmse value in eq 9, we will have

$$\text{p}K_a([\text{HNi}(\text{dedpe})_2]^+) = \frac{1}{30} \sum_i \frac{\Delta\Delta G_{\text{gas}} + \Delta\Delta G_{\text{solv}}}{2.303RT} \quad (10)$$

where again $i = 1-30$ for all of the compounds shown in Table 2. At this point, we eventually establish a clear-cut procedure to calculate the pK_a values, which is composed of the following

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steps: (1) randomly select a reference compound from a collection of experimental data, (2) choose theoretical methods to calculate $\Delta\Delta G_{\text{gas}}$ and $\Delta\Delta G_{\text{solv}}$, (3) use eq 10 to obtain the pK_a value for the reference compound (note that the number “30” in eq 10 should be changed to match the actual size of the collection of experimental data), and (4) finally, use eq 8 to calculate the pK_a value for any compound.

It is worth noting that the above procedure is not only applicable to the pK_a's of transition metal hydrides but also legitimate for the pK_a's of any groups of compounds in any solvent system. It, in fact, is a general procedure for the pK_a calculation which can be utilized anywhere as long as there is a collection of experimental values available. The fundamental idea behind this general procedure is to calibrate the theoretical method against a set of experimental data. The performance of the theoretical method derived from this procedure will depend on the overall quality of all the available experimental values.

5. Solvation Models

Having obtained a feasible procedure to calculate the pK_a values, our next task is to examine the performances of different solvation models in calculating $\Delta\Delta G_{\text{solv}}$. Although a number of theoretical methods can be employed to calculate the solvation energies, we decide to focus on the dielectric continuum methods, because they are easier to handle and more broadly applicable.¹³ To save time, we have tested only two of the most recent dielectric continuum methods, which are denoted as the IEF-PCM (integral equation formalism model)¹⁴ and C-PCM (polarizable conductor calculation model)¹⁵ methods, respectively. Furthermore, as to the construction of the solvent-inaccessible cavities in which the solute molecule resides, we have tried two different types of atomic radii: i.e., the UA0 radii¹⁶ and the Bondi radii.¹⁷ Thus, altogether we have examined four combinations of solvation models.

The solvation energies are calculated by the B3P86/LAN2DZ+p method for all four combinations of solvation models. Following the procedure described above, we first select [HNi(dedpe)₂]⁺ as the reference compound. Second, we calculate the relative gas-phase acidities (pertinent data shown in Table 2) and relative solvation energies (data available in the

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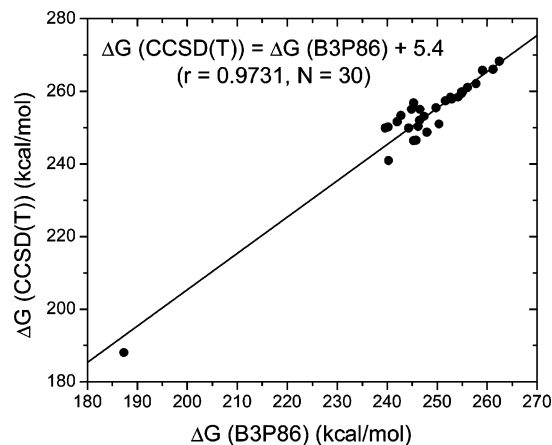
Table 3. Comparison of the Performances of Different Theoretical Methods in the pK_a Calculations for Transition-Metal Hydrides

	CCSD(T) ^a				B3P86 ^a C-PCM ^b
	IEF-PCM ^b		C-PCM ^b		
radii	Bondi	UA0	Bondi	UA0	Bondi
pK_a ([HNi(dedpe) ₂] ⁺)	19.8	21.1	19.9	21.1	16.2
correlation coeff	0.9659	0.9273	0.9664	0.9302	0.9021
rmse	1.5	2.2	1.5	2.2	2.6

^a Gas-phase method. ^b Solvation model.

Supporting Information) using four different solvation models. Third, using the CCSD(T) gas-phase data and the solvation energies from the four solvation models, we calculate the pK_a values for [HNi(dedpe)₂]⁺ to be 19.8, 21.1, 19.9, and 21.1, respectively. These values are compared to the experimental value (20.3). Finally, on the basis of $\Delta\Delta G_{\text{gas}}$, $\Delta\Delta G_{\text{solv}}$, and pK_a ([HNi(dedpe)₂]⁺), we calculate pK_a values for all the other transition-metal hydrides listed in Table 2. The comparisons between these predicted values and the experimental data are shown in Table 3.

As seen from Table 3, the performances of the IEF-PCM and C-PCM models are close to each other when the same scale of atomic radii is used. Nevertheless, the Bondi radii are found to provide significantly better predictions than the UA0 radii, as suggested by both the correlation coefficient and rmse value. Thus, the optimal theoretical protocol of the pK_a calculations for the transition-metal hydrides is finally determined to be composed of the following methods. (a) The gas-phase acidities are calculated by the ONIOM(CCSD(T)/LANL2DZ+p:B3P86/LANL2MB)//ONIOM(B3P86/LANL2DZ+p:HF/LANL2MB) method. (b) Solvation model = C-PCM (B3P86/LANL2DZ+p);

**Figure 4.** Comparison of the theoretical and experimental pK_a values in acetonitrile.

radii = Bondi. (c) The final pK_a value is calculated using eq 8, where pK_a ([HNi(dedpe)₂]⁺) = 19.9. The correlation coefficient for the pK_a values predicted by this method is as high as 0.9664 for 30 species whose pK_a 's span a wide range, from about 5 to 30 (Figure 4). The corresponding rmse error is equal to 1.5 pK_a units. Furthermore, as shown in Figure 4, both the monocationic and dicationic species stay in the same correlation plot. All of the results demonstrate that the solvation effect on the pK_a values has been well predicted by the present theoretical protocol.

It is worth mentioning that we have also examined the performance of the ONIOM(B3P86/LANL2DZ+p:B3P86/LANL2MB) method for the gas-phase acidity calculations. As shown in Table 3, the correlation coefficient for the B3P86 predictions is 0.9021, whereas the rmse error equals 2.6 pK_a

Table 4. Comparison of the pK_a Values for Transition-Metal Hydrides with Different Metal Centers and Diphosphine Ligands

Ligand	Me ₂ P	PMe ₂	Ph ₂ P	PPh ₂	Me ₂ P	PPh ₂	Me ₂ P	PMe ₂	Ph ₂ P	PPh ₂
dmpbz	0.778	0.778	0.814	0.814	0.788	0.805	0.800	0.800	0.836	0.836
dmppe										
dmpbz										
dppbz										

Hydride	pK_a	Hydride	pK_a	Hydride	pK_a
[Cp*Fe(H) ₂ (dmpe)] ⁺	19.7	[Cp*Ru(H) ₂ (dmpe)] ⁺	24.6	[Cp*Os(H) ₂ (dmpe)] ⁺	32.6
[Cp*Fe(H) ₂ (dppe)] ⁺	17.0	[Cp*Ru(H) ₂ (dppe)] ⁺	21.2	[Cp*Os(H) ₂ (dppe)] ⁺	28.7
[Cp*Fe(H) ₂ (dmdppe)] ⁺	18.4	[Cp*Ru(H) ₂ (dmdppe)] ⁺	22.8	[Cp*Os(H) ₂ (dmdppe)] ⁺	30.5
[Cp*Fe(H) ₂ (dmpbz)] ⁺	18.0	[Cp*Ru(H) ₂ (dmpbz)] ⁺	22.8	[Cp*Os(H) ₂ (dmpbz)] ⁺	30.4
[Cp*Fe(H) ₂ (dppbz)] ⁺	15.4	[Cp*Ru(H) ₂ (dppbz)] ⁺	19.5	[Cp*Os(H) ₂ (dppbz)] ⁺	27.3

Hydride	pK_a	Hydride	pK_a	Hydride	pK_a
[H ₂ Co(dmpe) ₂] ⁺	33.7	[H ₂ Rh(dmpe) ₂] ⁺	36.7	[H ₂ Ir(dmpe) ₂] ⁺	46.9
[H ₂ Co(dppe) ₂] ⁺	25.9	[H ₂ Rh(dppe) ₂] ⁺	28.5	[H ₂ Ir(dppe) ₂] ⁺	39.2
[H ₂ Co(dmdppe) ₂] ⁺	29.7	[H ₂ Rh(dmdppe) ₂] ⁺	33.4	[H ₂ Ir(dmdppe) ₂] ⁺	43.3
[H ₂ Co(dmpbz) ₂] ⁺	28.9	[H ₂ Rh(dmpbz) ₂] ⁺	33.1	[H ₂ Ir(dmpbz) ₂] ⁺	43.0
[H ₂ Co(dppbz) ₂] ⁺	22.8	[H ₂ Rh(dppbz) ₂] ⁺	25.6	[H ₂ Ir(dppbz) ₂] ⁺	35.7

Hydride	pK_a	Hydride	pK_a	Hydride	pK_a
[HNi(dmpe) ₂] ⁺	22.9	[HPd(dmpe) ₂] ⁺	21.0	[HPt(dmpe) ₂] ⁺	28.3
[HNi(dppe) ₂] ⁺	17.2	[HPd(dppe) ₂] ⁺	13.9	[HPt(dppe) ₂] ⁺	21.6
[HNi(dmdppe) ₂] ⁺	21.5	[HPd(dmdppe) ₂] ⁺	18.7	[HPt(dmdppe) ₂] ⁺	26.8
[HNi(dmpbz) ₂] ⁺	18.9	[HPd(dmpbz) ₂] ⁺	18.0	[HPt(dmpbz) ₂] ⁺	25.9
[HNi(dppbz) ₂] ⁺	15.2	[HPd(dppbz) ₂] ⁺	12.2	[HPt(dppbz) ₂] ⁺	20.6

units. These numbers indicate that the B3P86 method provides much worse pK_a predictions than the CCSD(T) method, which can only be attributed to the worse performance of the B3P86 method in the gas-phase acidity calculations than CCSD(T). Thus, we can confidently conclude now, on the basis of concrete experimental data, that it is more reliable to use the CCSD(T) method to calculate the gas-phase acidities for transition-metal hydrides than to use the density functional theory method.

6. Periodic Trends and Ligand Effects on pK_a Values

The newly developed protocol is used to study the periodical trends and the ligand effects on the hydrides of all the Fe-, Co-, and Ni-group metals. These subjects have been fundamentally important for the organometal field over many years,^{2,3} but the experimental studies have unfortunately remained sluggish to yield sufficient data for organized understandings. For the Fe-group metals, we focus on the *trans*-dihydrides with a chemical formula of [Cp^{*}M(H)₂(diphosphine)]⁺ (see Table 4). For the Co-group metals, we focus on the dihydrides [H₂M(diphosphine)₂]⁺. Finally, for the Ni-group metals, we focus on the monohydride [HM(diphosphine)₂]⁺. The reasons for choosing these particular hydrides are 2-fold: (1) these hydrides are the most frequently encountered ones in literature for each group of metals and (2) experimental crystal structures are available for some of these hydrides for each group of metals, so that it is relatively straightforward to handle their geometries without exhaustive conformation searches and optimizations from scratch. As to the phosphine ligands, we focus on five types of diphosphines: dmpe, dppe, dmdppe, dmpbz, and dppbz (their structures are shown in Table 4; the NBO (natural bond orbital) charges calculated at the B3P86/6-31G level are also shown for the phosphorus atoms). These ligands represent almost all of the commonly used diphosphines, ranging from fully aliphatic diphosphines to fully aromatic diphosphines.

The pK_a values for the transition-metal hydrides shown in Table 4 are calculated using eq 8. It is important to bear in mind that all the calculated pK_a values have an error bar of ±1.5 pK_a units. From Table 4 it can be seen that the pK_a values for the Fe-group metal hydrides range from ca. 15 to 33. When the same diphosphine ligand is utilized, the pK_a values always decrease in the order [Cp^{*}Os(H)₂(diphosphine)]⁺ > [Cp^{*}Ru(H)₂(diphosphine)]⁺ > [Cp^{*}Fe(H)₂(diphosphine)]⁺. Furthermore, for the same metal center the pK_a values decrease in a linear fashion as the NBO charges on phosphorus atoms increase (see Figure 5a). It is worth noting that recently there has been considerable interest in the hydrogenation reactions catalyzed by Cp^{*}Ru(diphosphine)H, where the solution-phase basicity of Cp^{*}Ru(diphosphine)H (or the acidity of [Cp^{*}Ru(H)₂(diphosphine)]⁺) has been found to exert profound, yet not fully understood, effects on the overall catalysis.^{30,18} It remains to be seen whether the theoretical tools developed here would find useful applications in that area.

As to the dihydrides of the Co-group metals, it is found that their pK_a values range from ca. 23 to 47. When the same diphosphine ligand is utilized, the pK_a values decrease in the order [H₂Ir(diphosphine)₂]⁺ > [H₂Rh(diphosphine)₂]⁺ > [H₂Co(diphosphine)₂]⁺ (Figure 5b). When the same metal center is concerned, the pK_a values again decrease in a linear fashion as the NBO charges on phosphorus atoms increase. Noteworthy, it was reported previously that the acidities of the Co-group metal hydrides decreased in the order HRh(CO)₄ > HCo(CO)₄ > HIr(CO)₄.^{1,19} Since this order is different from that observed in the present study, we have to conclude that the relative acidity between the first- and second-row metal

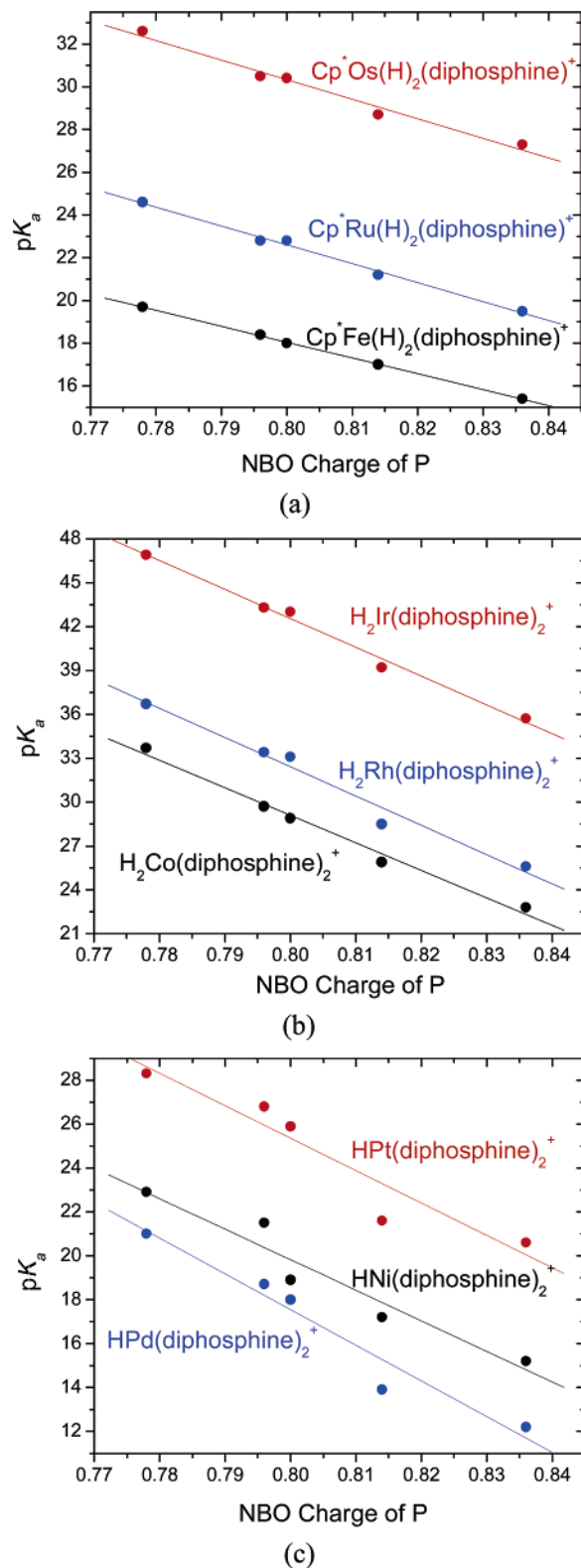


Figure 5. Correlations between the pK_a values and the NBO charges of the phosphorus atoms (note: for dmdppe the average value, i.e., 0.796, is used).

hydrides is strongly dependent on the chemical formulas of the metal complexes. Nonetheless, the third-row metal hydrides always appear to be the least acidic.

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Finally, as to the monohydrides for the Ni-group metals, it was found that their pK_a values range from ca. 12 to 28. For each metal the pK_a values decrease linearly against the NBO charges carried by the phosphorus atoms (Figure 5c). When the same diphosphine ligand is utilized, the pK_a values decrease in the order $[\text{HPt}(\text{diphosphine})_2]^+ > [\text{HNi}(\text{diphosphine})_2]^+ > [\text{HPd}(\text{diphosphine})_2]^+$. This observation is in excellent agreement with DuBois's finding that the acidity decreases in the order second row > first row > third row for the $[\text{HM}(\text{diphosphine})_2]^+$ complexes.^{1,2} Nonetheless, it is important to emphasize that the effect of the ligands on pK_a can outweigh that of the metals, as illustrated by Figure 5c.

6. Computational Methodologies

All the calculations were performed with the Gaussian 03 programs¹⁶ using our HP Superdome Sever (32×1.5 GHz Itanium 2 Madison CPU). Initial geometry optimization was conducted using three ONIOM methods (method for the whole system, HF/LANL2MB; method for the core layer, B3LYP, B3PW91, or B3P86 with the LANL2DZ+p basis set). 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 ONIOM method from the optimized geometries. Zero-point vibrational energy (ZPE) corrections were obtained using unscaled frequencies. Single-point electronic energies were then calculated at the ONIOM methods (method for the core layer, CCSD(T)/

LANL2DZ+p; method for the whole system, B3P86/LANL2mb). Gas-phase acidity was calculated as the free energy change of the deprotonation reaction described in eq 1 in the gas phase. This free energy change was corrected with ZPE, thermal corrections ($0 \rightarrow 298$ 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.

In order to calculate pK_a values, we utilized the IEF-PCM and C-PCM solvation models 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.¹³ 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.

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Supporting Information Available: Tables, text, and figures giving Cartesian coordinates of optimized structures, detailed thermodynamic data, detailed pK_a values predicted by various methods, and a full citation for ref 16. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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