Theoretical Studies of the Acidity of the Dihydrogen Complexes *trans*-[LM($H_2PCH_2CH_2PH_2$)$_2$(η^2-H_2)]$^{n+}$

Zhitao Xu, Ian Bytheway,[†] Guochen Jia*, and Zhenyang Lin*

Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

Received December 7, 1998

The acidity of transition-metal dihydrogen complexes of the general type *trans*-[LM($H_2PCH_2CH_2PH_2$)$_2$(η^2-H_2)]$^{n+}$ (M = Ru, Os; L = H^-, CH_3^-, F^-, CF_3^-, CN^-, Cl^-, Br^-, CO, NCH, NH_3, PH_3; n = 1, 2) has been modeled by calculating deprotonation energies using the B3LYP density functional method and effective core potentials. Calculated DP energies correlate well with experimental pK_a values. For anionic L with strong σ-donor properties the DP energies are higher and acidities lower, due to significant destabilization of the conjugate hydride. When L is neutral, the complexes are dicationic and have much lower DP energies. The acidities of these complexes are governed by the π-accepting ability of L, as the less positively charged conjugate hydride can be stabilized through metal(d) → π^* back-donation. The effect of the metal center on acidity is also dependent upon the electronic properties of L. Dihydrogen complexes of Ru with L that is either a σ-donor or π-acceptor are less acidic when compared with those of Os. The effect of a strong σ-donor leads to greater destabilization of the Ru conjugate hydrides, while the π-accepting property of L preferentially stabilizes the Os conjugate hydrides.

Introduction

Acidity is an important property in inorganic chemistry which affects reactivity,[1] catalytic activity,[2] and other processes in which proton transfer is important.[3] With the discovery of η^2-coordinated metal−dihydrogen complexes[4,5] it is natural that the acidity of such complexes, corresponding to the reaction

$$[LM(\eta^2\text{-}H_2)X_4]^{n+} \rightleftharpoons [LMHX_4]^{(n-1)+} + H^+ \qquad (1)$$

has attracted considerable interest, evidenced by the large number of acidity measurements that have been performed.[6−9]

The acidities of classical hydride (and polyhydride) complexes which do not contain an η^2-H_2 coordinated ligand are normally understood in terms of “electron richness” and the metal−hydride bond strength.[1] Systems which are electron rich are usually less acidic because the proton is not easily removed. For a series of analogous transition-metal hydride complexes, the acidities decrease down a group because of the increasing strength of the metal−hydride bond as the metal atom gets heavier. Available data indicate that most of the dihydrogen complexes follow the same trend in their acidities; however, some exceptions are known. For example, the complex [HRu(dppe)$_2$(η^2-H_2)]$^+$ (dppe = bis(diphenylphosphino)ethane) is less acidic than the analogous Os complex.[6,7] Additional H−H interactions were suggested as one of the possible factors for this behavior, as these are expected to decrease the acidity.[6]

In this paper, the acidities of complexes with the formulas *trans*-[LM($H_2PCH_2CH_2PH_2$)$_2$(η^2-H_2)]$^{n+}$ have been considered in terms of the relative stability of a dihydrogen complex (the acid) and its conjugate hydride (the conjugate base). Using quantum-chemical methods, the factors influencing the relative stability of metal−dihydrogen complexes, *trans*-[LM($H_2PCH_2CH_2PH_2$)$_2$(η^2-H_2)]$^{n+}$ (M = Ru, Os; L = H^-, CH_3^-, F^-, CF_3^-, CN^-, Cl^-, Br^-, CO, NCH, NH_3, PH_3; n = 1, 2), and the conjugate hydrides have been evaluated.

[†] Present address: Department of Chemistry, University of Western Australia, Nedlands, WA 6907, Australia.

(1) (a) Angelici, R. J. *Acc. Chem. Res.* **1995**, *28*, 51. (b) Kristjánsdóttir, S. S.; Norton, J. R. In *Transition Metal Hydrides: Recent Advances in Theory and Experiment*; Dedieu., A., Ed.; VCH: New York, 1991. (c) Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41.

(2) (a) Campbell, I. M. *Acidity and Properties of Major Industrial Acids*; Chapman & Hall: London, 1992. (b) Fraissard, J. In *Acidity and Basicity of Solids: Theory, Assessment and Utility*; Petrakis, L., Ed.; NATO ASI Series; Kluwer Academic: Dordrecht, The Netherlands, 1994.

(3) Muller, A.; Ratajczak, H.; Junge, W. In *Electron and Proton Transfer in Chemistry and Biology*; Studies in Physical and Theoretical Chemistry 78; Diemann, E., Ed.; Elsevier: Amsterdam, 1992.

(4) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *100*, 451.

(5) For review papers, see: (a) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913. (b) Morris, R. H.; Jessop, P. G. *Coord. Chem. Rev.* **1992**, *121*, 155. (c) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120.

(6) (a) Chin, B.; Lough, A. J.; Morris, R. H.; Schweitzer, C. T.; D'Agostino, C. *Inorg. Chem.* **1994**, *33*, 6278. (b) Cappellani, E. P.; Drouin, S. D.; Jia, G.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T. *J. Am. Chem. Soc.* **1994**, *116*, 3375−3388.

(7) (a) Schlaf, M.; Lough, A. J.; Maltby, P. A.; Morris, R. H. *Organometallics* **1996**, *15*, 2270. (b) Maltby, P. A.; Schlaf, M.; Steinbeck, M.; Lough, A. J.; Morris, R. H.; Klooster, W. T. *J. Am. Chem. Soc.* **1996**, *118*, 5396.

(8) (a) Rocchini, E.; Mezzetti, A.; Rüegger, H.; Burckhardt, U.; Gramlich, V.; Zotto, A. D.; Martinuzzi, P.; Rigo, P. *Inorg. Chem.* **1997**, *36*, 711. (b) Jia, G.; Lee, H. M.; Williams, I. D.; Lau, C. P.; Chen, Y. *Organometallics* **1997**, *16*, 3941. (c) Forde, C. E.; Landua, S. E.; Morris, R. H., *J. Chem. Soc., Dalton Trans.* **1997**, 1663. (d) Gusev, D. G.; Hübener, R.; Burger, P.; Orama, O.; Berke, H. *J. Am. Chem. Soc.* **1997**, *119*, 3716.

(9) Luther, T. A.; Heinekey, D. M. *Inorg. Chem.* **1998**, *37*, 127.

10.1021/om980993y CCC: $18.00

Table 1. Calculated Deprotonation Energy (DP, kcal/mol) and Bond Lengths (*d*, Å) for the Model Complexes along with Available Experimental Data

			dihydrogen			hydride		exptl dihydrogen complex			
M	L	DP	d_{M-H}	d_{M-L}	d_{H-H}	d_{M-H}	d_{M-L}	X[a]	pK_a	d_{H-H}[c]	ref
Ru	H^-	262.7	1.884	1.603	0.803	1.635	1.700	dppe	14.0	0.89	6b,7b
	CH_3^-	262.1	1.852	2.177	0.813	1.636	2.251				
	F^-	257.2	1.748	2.021	0.848	1.619	2.195				
	CF_3^-	254.6	1.880	2.082	0.800	1.628	2.160				
	CN^-	251.0	1.829	2.019	0.815	1.627	2.108				
	Cl^-	247.9	1.736	2.453	0.855	1.614	2.593	dppe	6.0	0.99	6a
	Br^-	245.5	1.740	2.602	0.853	1.611	2.746				
	NH_3	157.4	1.736	2.203	0.850	1.613	2.332				
	NCH	155.4	1.739	2.075	0.846	1.625	2.168				
	PH_3	153.5	1.802	2.386	0.822	1.629	2.450				
	CO	146.8	1.861	1.916	0.802	1.656	1.982	dppp	ca. −6.0	8a	
Os	H^-	259.1	1.804	1.646	0.862	1.664	1.711	dppe	12.7	0.99 (0.97)	6b, 7b
	CH_3^-	259.0	1.772	2.203	0.887	1.666	2.254				
	F^-	255.4	1.675	2.049	1.015	1.652	2.205				
	CF_3^-	251.5	1.804	2.108	0.853	1.661	2.154				
	Cl^-	249.1	1.635	2.500	1.202	1.636	2.599	dppe	7.4	1.19 (1.22)	7b
	CN^-	248.8	1.775	2.035	0.874	1.659	2.088				
	Br^-	246.6	1.628	2.658	1.272	1.635	2.747	dppe	5.4	1.19	7b
	NH_3	159.1	1.687	2.223	0.957	1.640	2.311				
	NCH	156.3	1.711	2.061	0.919	1.648	2.111	dppe[b]	ca. −2	7a	
	PH_3	152.2	1.757	2.402	0.880	1.661	2.414				
	CO	143.9	1.836	1.916	0.830	1.695	1.949	dppp	−5.7	8a	

[a] The experimental bidentate ligand. [b] In the experimental complex, L = NCMe. [c] The H−H distances were calculated from *J*(HD) measurements. Values in parentheses are from the neutron diffraction.

Computational Details

The relative stability of a dihydrogen complex and its conjugate hydride can be related to the deprotonation energy (DP), i.e., the energy required to remove one proton of the coordinated η^2-H_2 ligand. This definition of the DP energy is a thermodynamic one and corresponds to the difference in the energies calculated for the optimized η^2-H_2 complex and its lowest energy conjugate hydride.

In the calculations described here, model complexes have been used. The bidentate ligand dppe (dppe = bis(dipenylphosphino)ethane) or dppp (dppp = bis(diphenylphosphino)propane), commonly used in experimental studies, has been simplified to $H_2P(CH_2)_2PH_2$ and is abbreviated as dpe. The effects of different ligands (L = H^-, CH_3^-, F^-,CN^-, CF_3^-, Cl^-, Br^-, CO, NCH, NH_3, PH_3) on the DP energy have been studied, as has the influence of the metal center, for which Ru and Os were used. Model complexes with both Ru and Os have been used to study the influence of the metal center.

All geometries were fully optimized using the B3LYP density functional method. For elements in the first and second periods the 6-31G basis set was used, while heavier elements were represented by the LANL2DZ effective core potential,[10] which includes a double-ζ basis set to describe the valence electrons explicitly. Additionally, the basis sets of those atoms directly coordinated to the transition metal were augmented by polarization functions: $\zeta_p(H) = 0.11$; $\zeta_d(C) = 0.80$; $\zeta_d(N) = 0.80$; $\zeta_d(P) = 0.34$; $\zeta_d(F) = 0.8$; $\zeta_d(Cl) = 0.514$; $\zeta_d(Br) = 0.389$.[11]

All calculations were performed using the Gaussian 94 program[12] installed on a Silicon Graphics R10000 workstation. The natural bond orbital[13] (NBO) program,[14] as implemented in Gaussian 94, was also used to obtain Wiberg bond indices (bond orders),[15] which are a measure of bond strength, and occupancies. NBO occupancies are used to quantitatively evaluate the occupation number of a given localized bonding/antibonding orbital, which gives information regarding the strengths of interactions among different units within a molecule.

Results

The relative acidities of the various complexes will be discussed in terms of the relative DP energies, which have been calculated using the lowest energy isomer of the conjugate hydride. When L = H^-, CH_3^-, CF_3^-, CN^-, and F^-, the *cis* isomer of the conjugate hydride is found to be more stable than the *trans* isomer.

Calculated values of the DP energy for all the model complexes are listed in descending order in Table 1 together with measured pseudo-aqueous pK_a values.[6,7,8] The pseudo-aqueous pK_a values are obtained in organic solvent but referenced to the pK_a value of an acid in water. We shall simply use the term pK_a values hereafter. The larger the DP energy of the η^2-H_2 complex, the smaller its acidity, and *vice versa*. The effect of different metal centers on the acidity has also been examined by using Ru and Os. The choice of these metals reflects the fact that experimental data are available for the related dihydrogen complexes. For complexes of each metal there are two broad classes of L corresponding to significantly different DP values. Complexes with neutral L have much smaller DP values, indicating higher acidities, while those with anionic L have much greater DP values.

The results for the series of anionic L show that the largest DP energies are calculated for complexes in which L is a σ-donor ligand, while smaller DP values

---

[10] Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

[11] Huzinaga, S. *Gaussian Basis Sets for Molecular Calculations*; Elsevier: Amsterdam, 1984.

[12] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian 94, Revision D.3; Gaussian, Inc., Pittsburgh, PA, 1995.

[13] Reed, A.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

[14] Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. NBO, Version 3.1.

[15] Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083.

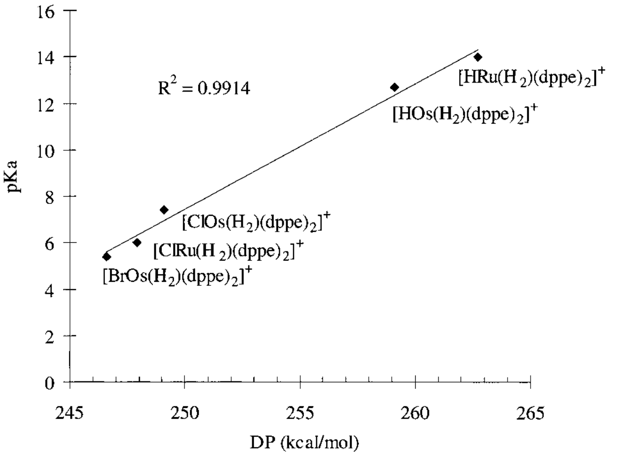

Figure 1. Plot of measured pK_a values against calculated DP energies (kcal/mol). The pK_a values for dicationic complexes are not included in the plot because they are highly acidic and the values were thus measured only approximately.

are calculated for complexes in which L has π-donor properties. The calculated DP values correlate well with the experimentally observed trends in pK_a (see Table 1). The complexes with larger pK_a values (i.e., less acidic) are those for which large DP values were calculated. Similarly, the complexes with smaller pK_a values (i.e., more acidic) are those for which smaller DP energies were calculated. The experimental pK_a values are plotted against the calculated DP energies for complexes with anionic L (Figure 1). Those complexes with neutral L have been excluded from this plot, as they are dicationic, and their measured pK_a values are very low and can be obtained only approximately. The linear correlation, shown in Figure 1, indicates that the DP energy can be used as a measure of acidity in these complexes.

Important structural parameters calculated for all model complexes are also listed in Table 1, which agree with those obtained experimentally,[6-8] as well as with those obtained from other calculations.[16] It should be pointed out that recent theoretical studies have shown that calculations including quantum nuclear motions are necessary to reproduce experimental geometries for some dihydrogen complexes.[17] The H−H bond lengths in the Ru complexes are approximately 0.8 Å for all L, while for the Os complexes the H−H bond lengths spread over a wide range, from 0.83 to 1.27 Å. This range of bond lengths suggests that no clear relationship exists between the H−H separations and the DP values, nor is there a distinct relationship between experimental H−H distances and pK_a values.

Discussion

General Background. Acidity is a thermodynamic property. Stabilizing the dihydrogen complex should decrease its acidity, while stabilizing its conjugate hydride should increase the acidity of the dihydrogen complex. To understand the results of these calculations, the effect of L on the stability of both the dihydrogen complex and its conjugate hydride should be examined. The major difference in the ligand environments between the acid/conjugate base pair is the presence of a very strong σ-donor ligand (H^-) in the conjugate base compared to a rather weak σ-donor (η^2-H_2) in the acid. It is helpful, therefore, to consider the influence of σ-donor, π-donor, or π-acceptor properties separately. Although ligands, in reality, cannot be thought of as belonging to only one of these categories, consideration of these properties should nevertheless provide a useful, albeit simple, mode of analysis.

When L has strong σ-donor properties, it is expected that the conjugate hydride will be destabilized because two strong σ-donor ligands (H^- and L) are present in the same complex. The strong σ-donor hydride ligand in the conjugate base competes for metal coordination and therefore destabilizes the complex. When H^- and L are *trans* to each other, the situation is most competitive and the resulting destabilization effect is commonly known as the *trans* influence.[18] Additionally, as the conjugate hydride is less positive (i.e., the molecule is neutral and does not have an overall positive charge) it will be destabilized by an electron-donating L. The deprotonation energy is therefore high, and the dihydrogen complex is less acidic. Thus, it is expected that increased σ-donor properties of L lead to less acidic dihydrogen complexes.

Theoretical studies[16,19] of η^2-H_2 dihydrogen complexes show that M(d) $\rightarrow$ $H_2(\sigma^*)$ back-donation is important in determining the strength of the M−H_2 interaction. A strong π-donor ligand will result in increased back-donation, which should in turn stabilize the dihydrogen complex. As noted above, a donor ligand will further destabilize the less positively charged conjugate hydride and therefore complexes with L that have stronger π-donor properties should decrease the acidity.

In comparison with the case when L is a π-donor, the relative stability of the dihydrogen complex and its conjugate hydride base should be reversed when L has π-acceptor properties. This is because the less positively charged conjugate hydride is stabilized through the electron-withdrawing property of a π-acceptor, while the dihydrogen complex has weakened M(d) $\rightarrow$ $H_2(\sigma^*)$ back-donation which is a consequence of competition with L for metal d electrons.

In summary, different properties of L have different effects on the relative stabilities of dihydrogen complexes and their conjugate hydride bases. In the following sections, the DP energies for dihydrogen complexes with various types of L are compared and the effects of electronic properties of L are summarized.

Complexes with Anionic L. An interesting feature of Table 1 is that the ordering of calculated DP energies

---

(16) (a) Craw, J. S.; Bacskay, G. B.; Hush, N. S. *J. Am. Chem. Soc.* **1994**, *116*, 5937. (b) Dapprich, S. Frenking, G. *Organometallics* **1996**, *15*, 4547. (c) Bytheway, I.; Backsay, G. B.; Hush, N. S. *J. Phys. Chem.* **1996**, *100*, 6023.

(17) (a) Gelabert, R.; Moreno, M.; Lluch, J. M.; Lledós, A. *J. Am. Chem. Soc.* **1997**, *119*, 9840. (b) Gelabert, R.; Moreno, M.; Lluch, J. M.; Lledós, A. *J. Am. Chem. Soc.* **1998**, *120*, 8168.

(18) Lin, Z.; Hall, M. B. *J. Am. Chem. Soc.* **1992**, *114*, 6102.

(19) (a) Lin, Z.; Hall, M. B. *Coord. Chem. Rev.* **1994**, *135/136*, 845 and references therein. (b) Li, J.; Ziegler, T. *Organometallics* **1996**, *15*, 3844.

Table 2. Result of the Natural Bond Orbital Analyses for the Dihydrogen Complexes and the Conjugated Hydride

			dihydrogen				hydride		
			Wiberg index				Wiberg index		
M	L	DP energy (kcal/mol)	H−H	M−H	M−L	charge η^2-H_2	M−H	M−L	charge H
Ru	H^-	262.7	0.774	0.109	0.632	0.122	0.526	0.522	−0.066
	CH_3^-	262.1	0.732	0.147	0.619	0.155	0.524	0.512	−0.064
	F^-	257.2	0.621	0.255	0.432	0.223	0.572	0.342	−0.049
	CF_3^-	254.6	0.757	0.127	0.659	0.153	0.535	0.550	−0.048
	CN^-	251.0	0.717	0.150	0.648	0.176	0.539	0.548	−0.033
	Cl^-	247.9	0.605	0.240	0.483	0.241	0.634	0.235	−0.058
	Br^-	245.5	0.613	0.228	0.511	0.234	0.621	0.240	−0.051
	NH_3	157.4	0.582	0.269	0.368	0.281	0.652	0.173	−0.023
	NCH	155.4	0.591	0.257	0.416	0.284	0.631	0.252	−0.033
	PH_3	153.5	0.665	0.177	0.570	0.229	0.529	0.304	−0.034
	CO	146.8	0.722	0.141	0.870	0.200	0.466	0.640	−0.106
Os	H^-	259.1	0.652	0.184	0.595	0.146	0.518	0.514	−0.112
	CH_3^-	259.0	0.593	0.241	0.565	0.185	0.514	0.503	−0.107
	F^-	255.4	0.420	0.406	0.391	0.221	0.559	0.352	−0.103
	CF_3^-	251.5	0.642	0.202	0.627	0.188	0.521	0.549	−0.097
	Cl^-	249.1	0.294	0.461	0.395	0.238	0.633	0.273	−0.097
	CN^-	248.8	0.606	0.222	0.631	0.197	0.524	0.570	−0.082
	Br^-	246.6	0.265	0.471	0.404	0.223	0.619	0.279	−0.090
	NH_3	159.1	0.439	0.379	0.345	0.309	0.654	0.203	−0.058
	NCH	156.3	0.487	0.333	0.443	0.296	0.616	0.336	−0.084
	PH_3	152.2	0.560	0.245	0.575	0.258	0.514	0.384	−0.080
	CO	143.9	0.660	0.179	0.943	0.221	0.449	0.798	−0.169

and experimental pK_a values is similar for both Ru and Os dihydrogen complexes:

Ru complexes:	H^-	CH_3^-	F^-	CF_3^-	CN^-	Cl^-	Br^-
Os complexes:	H^-	CH_3^-	F^-	CF_3^-	Cl^-	CN^-	Br^-

← DP Energy Increases

Acidity Increases →

In agreement with the discussion above, complexes with both strong σ-donor and π-donor L are expected to have higher DP energies. The complexes with strong σ-donor characteristics have the highest DP energies, which indicates that the effect of a σ-donor is far more significant in destabilizing the conjugate hydride than that of a π-donor.

The dihydrogen complexes with L = F^- have DP energies closer to those calculated for the complexes containing σ-donor L rather than to those calculated for the complexes where L is either Cl^- or Br^- (i.e., when L is a π-donor). This result is not easily explained and could be due to the difficulty often encountered when calculating the electronic structures of molecules containing the fluorine atoms.[20,21] The puzzling behavior of the complexes with L = F^- may also be due to the very negative charge carried by the F ligand. In a careful theoretical study of the bonding between CO and positively charged atoms, it was found that bond properties for CO were influenced by the charge of the metal center.[22] In light of this finding, it might be expected that the complexes studied here would be affected quite strongly by the negatively charged F^- ligand.

Table 3. Natural Bond Orbital Occupancies for the η^2-H_2 Ligand

	Ru		Os	
L	σ_{H-H}	σ^*_{H-H}	σ_{H-H}	σ^*_{H-H}
H^-	1.81	0.06	1.73	0.11
CH_3^-	1.77	0.06	1.67	0.13
F^-	1.67	0.10	1.53	0.24
CF_3^-	1.79	0.05	1.70	0.10
CN^-	1.76	0.06	1.68	0.12
Cl^-	1.65	0.10	*a*	*a*
Br^-	1.66	0.10	*a*	*a*
NH_3	1.62	0.09	1.51	0.18
NCH	1.62	0.09	1.55	0.15
PH_3	1.70	0.07	1.61	0.12
CO	1.75	0.05	1.70	0.07

[a] The NBO analyses suggest that no direct H−H bonding occurs in the Os dihydrogen complexes.

In accord with the accepted ordering[23] of σ-donor ability, overall, the trends in calculated DP energies, as well as observed acidities, indicate that the σ-donor properties of L are the dominant factor. NBO analyses[13] have been used to further examine this factor, along with various Wiberg bond indices[15] (Table 2).

Tables 2 and 3 show the NBO analysis results of the calculations. The H_2 moieties in the dihydrogen complexes and the hydride ligands in the conjugated bases become more positively charged along the series in Table 2. This trend is a result of the decreasing σ-donor ability of L along the series. Table 2 also shows that bond indices of H−H decrease with both DP energies and the σ-donor property of L. A strong σ-donor L competes for metal coordination with other ligands; therefore, decreasing the σ-donor ability of L will increase the M−H interaction. A strong π-donor L increases the metal(d) → $H_2(\sigma^*)$ back-donation and thus also increases the M−H interaction. This can be seen from the M−H bond indices of both dihydrogen complexes and their corresponding conjugate hydrides (see Table 2). The in-

---

(20) (a) Rohlfing, C. M.; Hay, P. J. *J. Chem. Phys.* **1987**, *86*, 4518. (b) Lee, T. J.; Rice, J. E.; Scuseria, G. E.; Schaefer, H. F., III. *Theor. Chim. Acta* **1989**, *75*, 81. (c) Jursic, B. S. *J. Mol. Struct.* **1996**, *97*, 366. (d) Dixon, D. A.; Feller, D. *J. Phys. Chem.* **1998**, *A102*, 8209.

(21) (a) Marsden, C. J.; Wolynec, P. P. *Inorg. Chem.* **1991**, *30*, 1681. (b) Hope, E. G.; Levason, W.; Ogden, J. S. *Inorg. Chem.* **1991**, *30*, 4873.

(22) Lupinetti, A. J.; Fau, S.; Frenking, G.; Strauss, S. H. *J. Phys. Chem.* **1997**, *101A*, 9551.

(23) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry*, 4th ed.; Harper Collins: New York, 1993; p 546.

Table 4. Occupancies of the Ligand π^* Orbitals Derived from the NBO Analyses

M	L	dihydrogen	hydride
Ru	CN^-	0.084	0.082
	CO	0.281	0.282
Os	CN^-	0.094	0.100
	CO	0.344	0.385

creased metal−dihydrogen interaction will in turn lead to higher occupancy of the σ^* orbital of the coordinated H−H ligand and correspondingly smaller occupancy in the H−H σ bonding orbital (see Table 3). For the conjugate hydrides, metal−hydride bond orders increase with decreasing DP energies, indicative of stronger M−H bonding when L has a weaker σ-donor ability.

The complexes with L = F^- are again exceptions to these trends. The H−H bond index in the dihydrogen complex is smaller than would be predicted from the DP energy and has a value similar to those found for the other halide complexes. NBO occupancies for the dihydrogen complex and the results of the NBO analysis for the conjugate hydride are also similar to those found for the complexes when L is either Cl^- or Br^-. These results further suggest that the DP energy calculated for the L = F^- complex is overestimated.

Complexes with Neutral L. Several calculations were performed for complexes with neutral L, although in general experimental studies of such complexes are not common. These complexes are dicationic and very acidic; for example, $[(NCCH_3)Os(dppe)_2(\eta^2\text{-}H_2)]^{2+}$,[7a] $[(CO)Os(dppp)_2(\eta^2\text{-}H_2)]^{2+}$,[8a] and $[(CO)Ru(dppp)_2(\eta^2\text{-}H_2)]^{2+}$ [8a] have observed pK_a values of −2.0, −5.7, and −6.0, respectively.

Calculated DP energies of these complexes are much lower than those obtained for the complexes with anionic L, which reflects the increased acidity. Regardless of the metal center the ordering of the DP energy, as well as the acidity, is

NH_3 NCH PH_3 CO

← DP Energy Increases

Acidity Increases →

This ordering is related to the increasing strength of π-acceptor properties on going from NH_3 to CO. This is in turn inversely related to the occupancies of the σ^*(H−H) orbitals (Table 3). For complexes with neutral L, compared to cases when L is anionic, the π-accepting properties become dominant in determining DP energies. This is because a neutral L is capable of accepting much more electron density than an anionic L. Evidence for this can be seen in Table 4, where a comparison of the occupancies of π^* orbitals for CN^- and CO shows that the occupancy of the π^*(CO) orbitals is 3−4 times that calculated for the CN^- complex.

Effect of Different Metal Centers. It is of interest to understand what role, if any, the metal atom plays in determining the acidity of these dihydrogen complexes. The differences in DP energies calculated for the complexes with the same L but with different M (Ru or Os), i.e., the value ΔDP = DP(Os) − DP(Ru), are listed in Table 5. Although some of these differences are small, approximately 1 kcal/mol, these values should still be valid, as systematic errors have been canceled. From Table 5, one can see that in some cases DP(Ru) > DP(Os) and in others DP(Ru) < DP(Os). These results suggest that effect of the metal is not uniform and is instead modified by the electronic properties of L.

Table 5. Comparison of the Deprotonation Energies (kcal/mol) of Os and Ru Complexes

	DP		
L	Os complex	Ru complex	DP(Os) − DP(Ru)
H^-	259.1	262.7	−3.60
CH_3^-	259.0	262.1	−3.10
CF_3^-	251.5	254.6	−3.10
CO	143.9	146.8	−2.90
CN^-	248.8	251.0	−2.20
F^-	255.4	257.2	−1.80
PH_3	152.2	153.5	−1.30
NCH	156.3	155.4	0.90
Br^-	246.6	245.5	1.10
Cl^-	249.1	247.9	1.20
NH_3	159.1	157.4	1.70

The complexes of Ru with smaller DP energies contain L = NCH, Cl^-, Br^-, NH_3, which were classified above as neither strong σ-donor nor π-acceptor ligands. The complexes of Ru with larger DP energies have L = H^-, CH_3^-, CF_3^-, CO, CN^-, F^-, and PH_3, which were classified above as either being strong σ-donor anionic ligands or as π-acceptor neutral ligands. These results are consistent with available experimental findings. For example, the pK_a of $[(Cl)Os(dppe)_2(\eta^2\text{-}H_2)]^+$ is 7.4,[7a] while for $[(Cl)Ru(dppe)_2(\eta^2\text{-}H_2)]^+$ it is 6.0,[6a] indicating that the Os complex is less acidic. The pK_a of $[HOs(dppe)_2(\eta^2\text{-}H_2)]^+$ is 12.7,[6b] while for $[HRu(dppe)_2(\eta^2\text{-}H_2)]^+$ it is 14.0,[6b] indicating that the Ru complex is less acidic. When L = CO, the calculated DP energy for the Ru complex is higher than that obtained for the corresponding Os case, although the observed pK_a values of the related complexes $[(CO)M(dppp)_2(\eta^2\text{-}H_2)]^+$ (M = Ru, Os) are quite similar. The acidities of these dicationic complexes are, however, quite high and the measured pK_a values are only approximate (see Table 1). More accurate measurements, if possible, would test this prediction that the Ru complex with CO is indeed less acidic than the Os analogue.

Classical hydride complexes such as $RuH_2(CO)_4$[24] and $[CpRuH_2(PPh_3)_2]^+$ [25] are more acidic than their osmium analogues. Thus, it is surprising to note that $[LRu(dpe)_2(\eta^2\text{-}H_2)]^+$ complexes are less acidic than their osmium analogues when L is a strong σ-donor anionic ligand or a π-acceptor neutral ligand. The unusual order can be related to the effect of strong σ-donating and π-accepting characteristics of the ligands L.

The Ru complexes with L which are strong σ-donors have larger DP energies (see Table 5) when compared to the corresponding Os complexes. This result implies that the effect of σ-donor L on DP energies is of more importance for Ru complexes than for the analogous Os complexes. The results of these calculations show that the reduction in the M−L bond index and lengthening of the M−L bond distance on going from a dihydrogen complex to its conjugate hydride (see Table 6) are indeed more significant for Ru complexes. When L has π-acceptor properties, the DP energy is lowered due to the increased stabilization, relative to the dihydrogen com-

---

(24) Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257.

(25) Jia, G.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 875.

Table 6. Reduction of the M−L Bond Index and Lengthening of the M−L Bond Distance (Å) on Going from Dihydrogen Complex to Its Conjugate Hydride

	reduction of M−L bond index		lengthening of M−L bond length	
L	Ru	Os	Ru	Os
H^-	0.110	0.081	0.097	0.065
CH_3^-	0.107	0.062	0.074	0.051
F^-	0.090	0.039	0.174	0.156
CF_3^-	0.109	0.078	0.078	0.046
CN^-	0.100	0.061	0.089	0.099
Cl^-	0.248	0.122	0.140	0.053
Br^-	0.271	0.125	0.144	0.089
NH_3	0.195	0.142	0.129	0.088
NCH	0.164	0.107	0.093	0.050
PH_3	0.266	0.191	0.064	0.012
CO	0.230	0.145	0.066	0.033

plex, of the less positively charged conjugate hydride. The calculated DP energies for the Os complexes are lower than those for the corresponding Ru complexes. This result implies that such a stabilization effect is more important for the Os complexes, which can be understood in terms of the more diffuse d orbitals of Os increasing the stability of the conjugate hydride through increased metal(d) → CO(π*) back-donation. It is understandable that complexes in which L is neither a strong σ-donor nor a π-acceptor ligand follow the normal trend observed for classical hydride complexes because the destabilization of the strong σ-donor and the stabilization of the π-acceptor are not significant.

Conclusion

Using quantum-chemical methods the acidity of transition-metal−dihydrogen complexes has been examined in terms of the relative stability of the complex and its conjugate hydride. The energies required to deprotonate complexes of the general type *trans*-$[LM(H_2PCH_2CH_2PH_2)_2(\eta^2\text{-}H_2)]^{n+}$ (**1**: M = Ru, Os; L = H^-, CH_3^-, F^-, CF_3^-, CN^-, Cl^-, Br^-, CO, NCH, NH_3, PH_3; $n = 1, 2$) were calculated and found to be closely related to observed pK_a values (Figure 1). The effect of L on the acidity is varied and can be related to its electron-donating or -withdrawing properties.

The effect of anionic L on acidity can be understood through their ability to act as σ-donors. For those dihydrogen complexes with a strong σ-donor L (H^-, CH_3^-, and CF_3^-) the DP energies are higher, corresponding to lower acidities, because the destabilization of the conjugate hydride is significant. When L is a weaker σ-donor L or π-acceptor (Cl^-, Br, or CN^-), the corresponding complexes have lower DP energies and formation of the conjugate hydride is therefore more favorable, resulting in greater acidities.

When L is neutral, the complexes are dicationic and have much lower DP energies, corresponding to higher acidities. The acidities of these complexes are governed by the π-accepting ability of L, as the less positively charged conjugate hydride can be stabilized through metal(d) → π* back-donation. In accord with this, the most acidic complexes are those with the CO ligand, which is also the strongest π-acceptor.

The effect of the metal center on DP energy was also examined. Complexes in which L is neither a strong σ-donor nor a π-acceptor ligand follow the normal trend observed for classical hydride complexes, i.e., Os complexes have higher DP energies. When L is anionic and a strong σ-donor, however, the Ru complexes have higher DP energies because the destabilization of the conjugate hydride is significant. When L is neutral and a strong π-acceptor, the Ru complexes also have higher DP energies because the conjugate hydride, when compared to the conjugate hydride of Os, has less metal(d) → L(π*) back-donation. Previously, stronger H−H interaction in $[HRu(dppe)_2(\eta^2\text{-}H_2)]^+$ has been proposed[6b] as one of the possible causes for its lower acidity when compared with $[HOs(dppe)_2(\eta^2\text{-}H_2)]^+$. The results of our calculations suggest that the explanation could be valid for complexes with a strong σ-donor or π-acceptor L.

Acknowledgment. We thank the Research Grant Council of Hong Kong and The Hong Kong University of Science and Technology for financial support.

OM980993Y