

Peculiarities of hydrogen bonding and proton transfer equilibria of organic versus organometallic bases

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Dedicated to Prof. Irina Beletskaya on the occasion of her 75th birthday

Abstract

This review summarizes experimental and theoretical results on hydrogen bonding (HB) and proton transfer processes involving organometallic bases (especially transition metal hydrides) in comparison with organic bases. The competition between different sites for HB and protonation, the proton accepting ability and the HB enthalpy dependence on the atom position in the Periodic Table, proton affinity values and features of proton transfer potential energy profiles are displaying peculiarities of the organometallic bases as proton acceptors.

Keywords: Hydrogen bonding, proton transfer, transition metal complexes, hydrides

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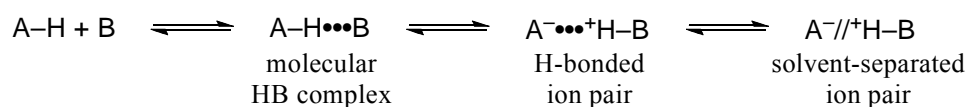
1. Introduction

Hydrogen bonding and proton transfer to organometallic complexes and especially to transition metal hydrides as proton acceptors have attracted considerable attention in the recent decade.^{1,2} This is due to their importance for basic processes such as enzymatic dihydrogen evolution or catalytic ionic hydrogenation.³ Hydrogen bonding is one of the weak interactions often invoked in molecular recognition or supramolecular assembly design.^{4,5} Recent advances in these areas caused a renaissance of studies on hydrogen bonding involving classical organic functional groups. Many of such groups are inserted in compounds containing a transition metal moiety intended to be an active site for e.g., catalytic hydrogenation.⁶ Another area of development in modern organometallic chemistry is the synthesis of water-soluble compounds, which would allow transfer of existing catalytic processes to environmentally friendly aqueous or biphasic media.⁷ This is often achieved by functionalization of ligands via introduction of polar organic groups. In this review, we compare the peculiarities of hydrogen bonding to classical organic bases and to organometallic ones, focusing in the latter case on transition metal hydrides because this important class of compounds is the subject of our research interest during the recent years.

2. Relationship Between the Preferred Site of Hydrogen Bonding and Protonation

2.1 Organic systems

A general reaction scheme embodies the neutral and ionic hydrogen bonded complexes between acid A–H and base B (Scheme 1). The position of equilibrium depends on the relative acidity and basicity of interacting molecules as well as on the properties of the surrounding medium.⁸





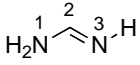
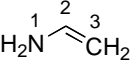
Scheme 1

When the site of hydrogen bond formation coincides with the site of protonation, the intracomplex proton transfer is operative.⁹ However, there are bases with two or more sites

potentially capable to accept a proton, for which it appears to be difficult to determine experimentally the preferred sites (heteroatoms and π -electrons) of H-bonding and protonation.¹⁰ Therefore, a number of *ab initio* calculations of intrinsic basicity has been published.¹¹ But unfortunately, comparison of a basic site with another in order to determine the preferred site of protonation was made without paying attention to the possible formation of hydrogen bonded intermediates.

Recently, the relationship between the preferred H-bonding and proton transfer sites for rather simple organic bases in the gas phase was considered in the very elegant theoretical work by Chan *et al.* employing *ab initio* MP2/6-31+G(d,p) calculations.^{12,13} The authors calculated hydrogen bonding and protonation energies for several potential proton accepting sites in various compounds (some examples are listed in Table 1). The sites for hydrogen bonding and proton transfer are similar for pyrrole and formamidine but contrasting those in furan and vinylamine, with the preferred hydrogen bonding and protonation sites not coinciding. The numerical results show that the preferred protonation site is determined by the stability of the resulting cation and strongly depends on the ability to delocalize the positive charge. On the other hand, the preferred site for hydrogen bonding is influenced by electrostatic interactions; generally, it is the site with the more localized negative charge. Thus, when these conditions are met at different sites, hydrogen bonding and proton transfer may occur at different parts of a molecule.

Table 1. Hydrogen bonding and protonation energies^a ΔE [kcal/mol] for pyrrole, furan, formamidine and vinylamine¹²

Proton source	Interaction site (position)				
HF ^b	1	–	–6.2	–7.8	–10.2
	3	–6.9	–4.9	–16.0	–7.3
H ⁺ ^c	1	–189.9	–167.2	–200.9	–210.6
	2	–207.6	–194.5		
	3	–202.7	–182.5	–231.1	–224.2

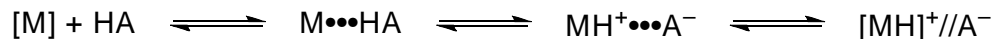
^a Energy at the preferred site is *emphasized*. ^b Hydrogen bonding. ^c Protonation.

2.2 Organometallic systems

Transition metal complexes often bear ligands potentially capable as proton donors or proton acceptors in hydrogen bonding. If formed, such H-bonds would be qualitatively similar to those in traditional organic H-complexes. On the other hand, core transition metals are able to accept a hydrogen bond through their *d*-lone pairs, forming M·HA hydrogen bonds.^{14,15} Hydride ligands possessing a partly negative charge are unusual proton accepting sites forming a so called dihydrogen bond (DHB), M–H·HA. These two types of hydrogen bonding, M·HA and M–H·HA, are unique for transition metal (hydride) complexes and the terms “non-classical” or “unconventional” hydrogen bonding have been coined to address these interactions.³³ Thus, the

dichotomy between different sites of proton donor attacks, classical and non-classical, could arise for transition metal complexes leading to coinciding or different sites of hydrogen bonding and protonation, like in organic bases. The following does not give a comprehensive literature survey for this phenomenon but will provide some examples from the authors' laboratory and from other published works. This section includes mainly experimental data; this area is much less explored by theoreticians probably due to the complexity of systems with transition metal.

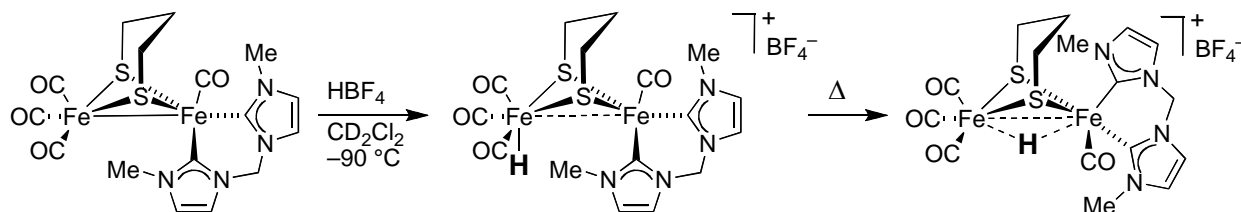
2.2.1 Proton transfer to the metal. Protonation of a core metal atom by strong acids (like $\text{CF}_3\text{SO}_3\text{H}$ or $\text{HBF}_4 \cdot \text{Et}_2\text{O}$) yielding a terminal hydride is widely known.^{4,16} We have shown for the Group VIII metallocenes (Cp^*_2M) that weaker acids form a hydrogen bond to the metal in the first step (Scheme 2).¹⁵ Additional H-bonding to Cp and Cp* rings has been observed by IR spectra in CCl_4 but does not lead to proton transfer.¹⁶ The mechanism of the proton transfer process (but without additional interaction with the Cp* ring) was determined for semi-sandwich complexes $\text{Cp}^*\text{M}(\text{CO})_2$ ($\text{M} = \text{Rh}, \text{Ir}$) in CCl_4 solution¹⁸ and for $\text{Cp}^*(\text{CO})_2\text{Ir}$ in supercritical Xe.¹⁹



Scheme 2

An XH·M bond with anionic $[\text{Co}(\text{CO})_3\text{L}]^-$ ($\text{L} = \text{CO}, \text{PPh}_3$) and neutral $[\text{Ni}(\text{CO})_4]$ bases serving as proton acceptors was observed experimentally⁴⁴ and elucidated theoretically.²⁰

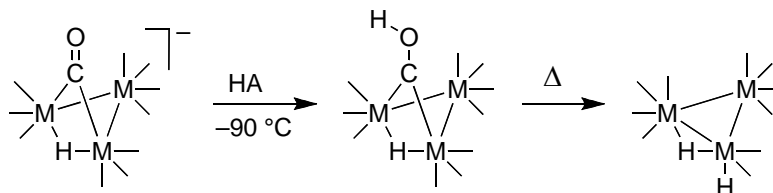
In polynuclear complexes, the barrier of proton transfer to a terminal site is lower than for a bridging site. The protonation of $\text{Cp}(\text{CO})_2(\mu\text{-PPh}_2)\text{WPt}(\text{CO})(\text{PPh}_3)$ by HBF_4 is an early example:²¹ the proton initially binds to the terminal position at tungsten, then the kinetic product $[\text{Cp}(\text{CO})_2(\mu\text{-PPh}_2)(\text{WH})\text{Pt}(\text{CO})(\text{PPh}_3)]^+$ slowly isomerizes to the more stable hydride-bridged product $[\text{Cp}(\text{CO})_2(\mu\text{-PPh}_2)(\mu\text{-H})\text{WPt}(\text{CO})(\text{PPh}_3)]^+$. Examples of iron hydrogenase active site mimicking complexes, $\text{Fe}_2[\mu\text{-S}(\text{CH}_2)_2\text{S}](\text{CO})_2(\text{PMe}_3)_4$,^{22a} $\text{Fe}_2[\mu\text{-S}(\text{CH}_2)_3\text{S}](\text{CO})_4(\text{dppe})$,^{22b} and $\text{Fe}_2[\mu\text{-S}(\text{CH}_2)_3\text{S}](\text{CO})_4(\text{I}_{\text{Me}}\text{-CH}_2\text{-I}_{\text{Me}})$ ^{22c} have been reported recently: At low temperature (-90°C) protonation by HBF_4 gives unstable terminal hydrides; upon warming they convert into stable bridging hydride complexes (Scheme 3).



Scheme 3

2.2.2 Metal vs. ligand protonation. The low barrier for protonation of oxygen or nitrogen bases entails that proton transfer to the ligand is more facile than the thermodynamically preferred

protonation of the metal.²³ Thus, the kinetic protonation site of Group VIII metal carbonyl clusters $[(\mu\text{-H})\text{M}_3(\text{CO})_{11}]^-$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$)²⁴ is the carbonyl oxygen (Scheme 4). The nature of the thermodynamic protonation product depends on the metal. For osmium, the CO-protonated species transform rapidly into terminal hydride at $-80\text{ }^\circ\text{C}$;^{24c,d} for ruthenium, this rearrangement occurs at higher temperatures.^{24b} The unstable iron analogue gives $\text{Fe}_3(\text{CO})_{12}$ above $-30\text{ }^\circ\text{C}$.^{24a}



Scheme 4

The protonation site of the related ruthenium nitrosyl cluster $[\text{Ru}_3(\text{NO})(\text{CO})_{10}]^-$ depends on the strength of the acid used.²⁵ With $\text{CF}_3\text{SO}_3\text{H}$, the nitrosyl rather than carbonyl oxygen becomes protonated. A weaker acid such as $\text{CF}_3\text{CO}_2\text{H}$ gives $\text{HRu}_3(\text{NO})(\text{CO})_{10}$. The same complex can be obtained from $\text{Ru}_3(\text{CO})_{10}(\text{NOH})$ in the presence of bases stronger than CF_3SO_3^- such as Hal^- , NO_3^- , or CF_3CO_2^- . Deprotonation of the nitrosyl-protonated species as the kinetic proton transfer product eventually yields the thermodynamically more stable metal-protonated form. A similar mechanism could be operative for the above mentioned carbonyl clusters.

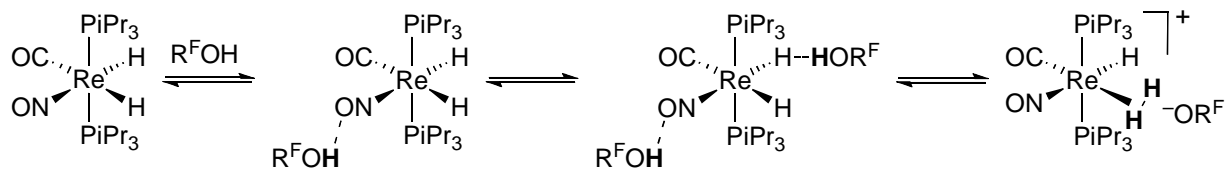
The monocarbonyl and mononitrosyl complexes $\text{CpMn}(\text{CO})(\text{PR}_3)_2$ ($\text{PR}_3 = \text{PPh}_3, \text{PEt}_3, \frac{1}{2}\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$, $n = 1-3$) and $\text{CpM}(\text{CO})_2(\text{NO})$ ($\text{M} = \text{Cr}, \text{Mn}$) form hydrogen bonds $\text{CO}\cdots\text{HA}$ and $\text{NO}\cdots\text{HA}$ [$\text{HA} = (\text{CF}_3)_3\text{COH}, \text{HCl}$] at low temperatures in liquid Xe.²⁶ Proton transfer occurs at the metal, but no $\text{M}\cdots\text{HA}$ hydrogen bonds were found.

2.2.3 Hydride vs. other ligand protonation. The presence of the hydride hydrogen in the metal coordination sphere opens the possibility for another competition: Hydrogen bond and proton transfer can occur at a ligand heteroatom or at a hydride site. In the latter case the protonation product is a cationic dihydrogen complex, $[\text{M}(\eta^2\text{-H}_2)]^+$ (Scheme 5).

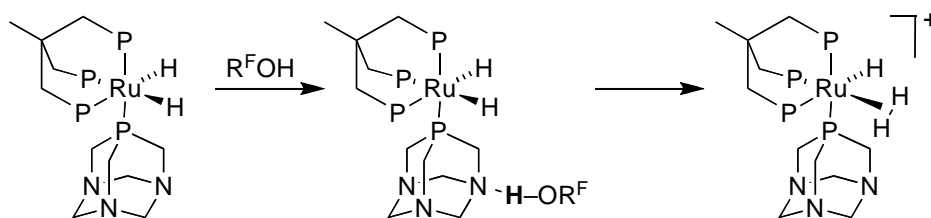


Scheme 5

In addition to dihydrogen bond formation, binding of the proton donor to the carbonyl oxygen of $\text{CpRuH}(\text{CO})(\text{PCy}_3)^{27}$ or to the nitrosyl oxygen in $\text{ReH}_2(\text{CO})(\text{NO})(\text{PiPr}_3)_2^{28}$ or $\text{CpReH}(\text{CO})(\text{NO})^{29}$ was found. But only the latter was the intermediate in the proton transfer process yielding the product of protonation at the hydride site at low temperatures (Scheme 6).

**Scheme 6**

Nitrogen atoms of the water soluble phosphatriaadamantane (PTA) ligand retain their basicity upon coordination to the transition metal atom; therefore, they are prone to interact with proton donors, as in $\text{ReH}_5(\text{PPh}_3)_2(\text{PTA})$ and $[\text{CH}_3(\text{CH}_2\text{PPh}_2)_3\text{RuH}(\text{PTA})]$.³⁰ Formation of the $\text{N}\cdots\text{HA}$ hydrogen bond is the first step in the protonation reaction of both complexes, but the proton transfer products are different: The protonation site in the ruthenium complex is the hydride ligand (Scheme 7); in the rhenium hydride the PTA-ligand nitrogen is protonated.

**Scheme 7**

The ^{31}P NMR spectroscopic study of the HBF_4 protonation products of the ruthenium hydride $\text{CpRuH}(\text{PTA})_2$ in water shows the presence of both the nitrogen protonated PTA and the *trans*-dihydrido ruthenium complexes. The equilibrium shifts toward the latter product with lowering pH ($5.9 \rightarrow 3.6$).³¹ In the gas phase, the dihydrido compound *trans*- $[\text{CpRu}(\text{H})_2(\text{PTA})_2]^+$ was found the most stable species (below $[\text{CpRuH}(\text{PTA})[\text{PTA}(\text{H})]]^+$ by 11.4 kcal/mol).³¹ A more recent theoretical work on the H_2 activation by this ruthenium complex³² shows that in water (explicitly included as 3 H_2O) the barrier for proton transfer to nitrogen is $\Delta G^\ddagger = 1.1$ kcal/mol. Proton transfer through the chain of water molecules from $[\text{PTA}(\text{H})]^+$ to the metal forming *trans*- $[\text{CpRu}(\text{H})_2(\text{PTA})_2]^+$ has an activation free energy of 9.1 kcal/mol, and the reaction is endothermic by 1.4 kcal/mol. This result is in agreement with the NMR observation that $[\text{CpRuH}(\text{PTA})[\text{PTA}(\text{H})]]^+$ is the only protonation product in non-buffered water.³¹

The low temperature proton transfer of the related $\text{Cp}^*\text{RuH}(\text{PPh}_2\text{py})_2$ hydride was shown³³ to yield the classical dihydride as well as the DHB species $\text{RuH}\cdot\text{HN}$. According to DFT calculations, the cause of this behavior is the facile protonation of the pyridine nitrogen atoms, which (after possible rotations around $\text{Ru}-\text{P}$ and $\text{P}-\text{C}(\text{py})$ bonds) results in structures with $\text{pyH}^+\cdots\text{py}$ hydrogen bonds. The complete DFT study with all the transition states localized shows comparable energies for hydrogen bonding and protonation and, thus, great competition between non-classical and classical sites of coordination: Ru , $\text{H}(\text{Ru})$, $\text{N}(\text{py})$.

2.2.4 Hydride vs. metal interaction. Molecular complexes of the M·HA type are rarely found in transition metal hydrides. Only two examples are known to date: $\text{WH}_4(\text{dppe})_2$ ³⁴ and NP_3ReH_3 .³⁵ As proton acceptors, hydrides offer a relatively non-encumbered site for protonation, where the proton accepting orbital σ_{MH} (mainly resembled by the spherically symmetrical 1s orbital of the H atom³⁶) is less affected by angular limitations for best interaction with the proton donor. Many examples of protonation of hydride positions by strong acids are known yielding a dihydrogen complex as the kinetically controlled protonation product, even when the classical di- or polyhydride product is thermodynamically favored.³⁷

There are limited experimental data on the competition of classical and non-classical base sites in proton transfer and (especially) hydrogen bonding paired with very little theoretical support. However, it is arguable that the low protonation barrier for classical oxygen or nitrogen containing ligands often renders them the kinetic site of proton attack. The protonation barrier at a hydride or metal atom is higher (see below), but these centers could eventually accept a proton by providing a better delocalization of the positive charge acquired.

3. The Energetics of Proton Transfer to Organic and Organometallic Bases

While the interaction strength in a molecular hydrogen-bonded complex is determined by the proton accepting and proton donating ability of neutral partners, the hydrogen bond strength within a contact ion pair is determined by the acidity and basicity of the cationic and anionic species, respectively. Herein we will use the basicity factor³⁸ E_j as a quantitative measure of the proton accepting property of a base B in hydrogen bonding and the proton affinity PA (taken as $-\Delta H_{298.15\text{K}}$ for the reaction $\text{B} + \text{H}^+ \rightarrow \text{BH}^+$). Correspondingly, in order to characterize the proton donor HA, the acidity factor P_i and PA of the conjugated anion ($-\Delta H_{298.15\text{K}}$ for the reaction $\text{A}^- + \text{H}^+ \rightarrow \text{AH}$) can be used. The next two sections are dealing with the comparison of these features of organometallic and traditional organic bases.

3.1 Proton accepting ability

The strength of non-classical HB has been determined by the same methods as used for classical HB. This shows the similarity in the nature of the bonding. Several examples demonstrate that for non-classical systems $\text{XH}\cdots\text{M}$ the $-\Delta H_{\text{HB}}$ values with the same XH proton donor and the basicity factor^{3,38} E_j increase by going down the Group in the Periodic Table. For example, E_j Cp_2Ru (0.67) < Cp_2Os (0.81), and Cp^*_2Ru (0.85) < Cp^*_2Os (1.05).¹⁸ The same sequence was obtained for DHB, though in this case, the site of coordination is not a metal atom but a hydride hydrogen: E_j PP_3FeH_2 (1.0) < PP_3RuH_2 (1.33) < PP_3OsH_2 (1.66),⁵¹ $\text{Cp}^*\text{Fe}(\text{dppe})\text{H}^{47}$ < $\text{Cp}^*\text{Ru}(\text{dppe})\text{H}$.⁴⁹ For classical systems the dependence of ΔH_{HB} and E_j on the position of the heteroatom in the Periodic Table is opposite: $-\Delta H_{\text{HB}}$ values of the bases involving the Group V–VII heteroatoms as the coordination site decrease by going down the Group: $\text{N} > \text{P} > \text{As}$, $\text{O} > \text{S} > \text{Se}$, $\text{F} > \text{Cl} > \text{I}$.³⁹ This is due to the decrease of the negative charge density with increasing

atomic radii for heteroatoms in contrast to the increase of the electron density at the transition metal atom and concomitantly at the hydride hydrogen by going down the Group.

Interestingly, E_j values determined for organometallic compounds vary in the same range as those for classical oxygen or nitrogen containing bases (see some examples in **Error! Reference source not found.**; a more complete list can be found in ref.²²), whereas all enthalpies of non-classical H-bonds reported to date correspond to the medium strength interaction ($-\Delta H_{\text{HB}} = 4-8$ kcal/mol).¹¹ No strong low barrier H-bonds with shared proton were observed in solution (low polar media), except for the interaction of the ruthenium hydride CpRuH(PP*) (PP* = chiral ferrocenyl diphosphines) with CF₃CO₂H.⁴⁰ However, the evidence based on the short ¹H relaxation time T₁ was questioned by Bakhmutov,⁴¹ who suggested that a short T₁ could result from proton/hydride exchange on the NMR timescale via a short-lived [M-(η²-H₂)]⁺ complex.

3.2 Proton affinity

The proton affinity (PA, the energy of the reaction $B + H^+ \rightarrow BH^+$) is widely used as a criterion for predicting the A-H...B interaction strength and conditions for hydrogen-bond formation and proton transfer. When a proton donor A-H encounters a proton acceptor B (a base), a hydrogen bonded complex AH...B should be observed if the proton affinity of A is greater than that of B; proton transfer yielding $A^- \cdots H^+ B$ would be expected if the proton affinity of A is smaller than that of B.⁴² Experimental techniques such as high pressure mass spectrometry and ion-cyclotron resonance spectrometry have been developed and actively explored since the 1970's allowing the investigation of acid-base interactions in the gas phase and the determination of PA's of organic bases. These studies demonstrate the difference between the positions of acid-base equilibria in the gas phase and in solution for organic systems,⁴³ and show the unexpectedly large impact of the solvent on substituent effects in hydrogen bonding and proton transfer.⁴⁴ Application of another modern technique, rotational spectroscopy in supersonically expanded jets, led to conclusions about the difference between the structure and nature of the partners in hydrogen bonding and proton transfer in the gas phase and in solution.⁴⁵ Recent developments of computational techniques allow PA calculations by different DFT and ab initio methods^{11b,12,46} in good agreement with experimental data. PA-based theoretical criteria have been developed to predict the formation of neutral or ionic structures in the gas phase.^{42,46}

No acid-base system involving organometallic complexes has been studied by the gas phase methods so far. The PA values for some transition metal hydrides studied in our group were determined by means of quantum chemical (DFT) calculations and are collected in Table 1 together with those of selected organic bases and of conjugated anions of the proton donors used.

Analysis of the data in Table 2 shows that all PA values of organometallic hydrides (243–267 kcal/mol) are larger than those of the reference organic compounds (198–230 kcal/mol) though we chose the strongest organic bases (except Et₂O and ammonia). The PA values of the anions (A⁻), whose conjugated acids were used in the studies of proton transfer to organic (A⁻ = Hal⁻, NO₃⁻; B = R₃N and others) and organometallic (A⁻ = RO⁻) bases, vary in similar ranges. Therefore, the difference in the acidity of AH and the basicity of B (= the normalized proton

affinity difference, NPAD)^{42,53} between A⁻ and B (eq. 1) is less for organometallic systems than for classical ones.

$$\text{NPAD} = (\text{PA}_B - \text{PA}_{A^-}) / (\text{PA}_B + \text{PA}_{A^-}) \quad (1)$$

Table 2. Proton affinity, PA, [kcal/mol] of some organic and organometallic bases (B) and organic conjugated bases (A⁻)^a

A ⁻	PA	B	BH ⁺	<i>E_f</i> (B) ^b	PA
F ⁻	371.5	H ₃ N			204.0
Cl ⁻	330.2	Me ₃ N			226.8
Br ⁻	323.4	Et ₃ N		1.70	234.7
I ⁻	316.6	pyridine		1.67	220.8
NO ₃ ⁻	324.5	Et ₂ O		1.00	198.0
C ₂ H ₅ O ⁻	378.3	Me ₃ PO		1.40	217.4 221.9 ^{c,46}
F(CH ₂) ₂ O ⁻	371.2	Cp*FeH(dppe) ^{47,48}	[Cp*Fe(η ² -H ₂)(dppe)] ⁺	1.35	258.7 ^{c,d} 267.1 ^c
CF ₃ CH ₂ O ⁻	361.7	Cp*RuH(dppe) ⁴⁹	[Cp*Ru(η ² -H ₂)(dppe)] ⁺	1.38	257.1 ^{c,d}
(CF ₃) ₂ CHO ⁻	345.0	Cp*MoH ₃ (dppe) ⁵⁰	[Cp*MoH ₂ (η ² -H ₂)(dppe)] ⁺	1.43	271.0 ^c
CF ₃ CO ₂ ⁻	323.8	PP ₃ RuH ₂ ^{e,36,51}	[PP ₃ RuH(η ² -H ₂)] ⁺	1.33	264.9 ^{c,f}

^a PA is $-\Delta H_{298.15\text{K}}$ for the reaction $A^- + H^+ \rightarrow AH$, or $B + H^+ \rightarrow BH^+$; data from ref.⁵² unless noted otherwise. ^b Basicity factors, see ref.³⁸ for details. ^c *Calculated value*, (dhpe)-model. ^d dhpe = H₂PCH₂CH₂PH₂. ^e PP₃ = P(CH₂CH₂PPh₂)₃. ^f P(CH₂CH₂PH₂)₃.

Thus, we can suggest that proton transfer for non-classical systems in gas phase is easier than for classical bases. This could be due to better delocalization of the acquired positive charge in the presence of transition metal in comparison to traditional organic bases.

3.3 Potential energy profiles for acid-base interaction

3.3.1 Organic systems. Early calculations on H_{3-n}Me_nN·HHal (n = 0–3, Hal = F, Cl, Br, I) have demonstrated that the correlated potential energy surface of these systems typically contains a single minimum.^{42,54} This minimum becomes deeper and shifts progressively from the neutral (molecular) H-complex to the ionic one as the strength of the acid or base increases (Figure 1).

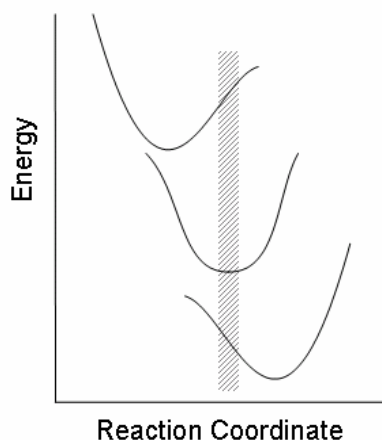


Figure 1. Evolution of a single-well potential energy profile with acid-base strength. The shaded region corresponds to quasi-symmetric $A^{\delta-}\cdots H\cdots B^{\delta+}$ structures.

This trend was reaffirmed in more recent studies, e.g., by calculations on the interaction of HCl or HBr with 4-substituted pyridines,⁵⁵ 4-cyanopyridine with CCl_3COOH ,⁵⁶ of ammonia and amines with HNO_3 ⁵⁷ or other bases with $HHal$.⁴⁶ In the latter study both molecular and ionic H-complexes are minima for the $Me_3PO\cdot HBr$ system, as expected. For ammonia and amines interacting with nitric acid in the gas phase the ionic structures $R_nH_{3-n}NH^+\cdots ONO_2^-$ were found at 11.1 (NH_3) to 3.7 (Me_2NH) kcal/mol above those of molecular H-complexes; they are only saddle points for double proton transfer between nitric acid and the base.⁵⁷

NMR studies on the interaction between HF, HCl, acetic or chloroacetic acid with pyridine or 2,4,6-trimethylpyridine (collidine) in liquid freons⁵⁸ show the gradual proton shift away from A towards B. Simultaneously, the H-complex structure transforms from molecular $A-H\cdots B$ to the quasi-symmetric $A^{\delta-}\cdots H\cdots B^{\delta+}$ and then to the ionic $A^-\cdots H-B^+$ type. The matrix isolation study⁵³ of H-complexes between $H-Hal$ and O or N bases led to the same observation and allowed to propose the so called “vibrational correlation diagram” correlating the low frequency shift of the ν_{AH} stretching vibration (as $\Delta\nu_{AH}/\nu_{AH}$) with NPAD (eq. 1). The results of these studies are in good agreement with the conclusion of ab initio calculations and gas phase measurements.⁵⁹ The proton shifts smoothly from the acid side in the molecular complex to the base side in the ionic complex as the NPAD value decreases.

The strong hydrogen bonds with a hydrogen atom centered between two electronegative atoms in a single minimum potential $A^{\delta-}\cdots H\cdots B^{\delta+}$ have been widely discussed. Nowadays, they are actively studied not only for academic interest but because of their importance in enzymatic reactions.⁶⁰ Both theoretical⁴² and experimental⁵³ approaches predict the structures with a shared proton at NPAD values close to -0.2 , which corresponds to a PA difference of A and B of ca. 125 kcal/mol. Several examples of such bonds are considered in a recent review,⁶¹ most of them belonging to species with intramolecular $[NHN]^+$ hydrogen bridges, where the zero point energy

level is above the barrier. On the other hand, a recent study of 4-cyano-2,2,6,6-tetramethylheptane-3,5-dione reveals a low-barrier double well potential for the O–H...O hydrogen-bonded proton.⁶² In asymmetric complexes, like F...H...N (collidine),^{58c} the proton position does not necessarily coincide with the midpoint between the heavy atoms.^{58b}

A possible second minimum of the ionic H-complex was indicated by gas phase calculations of A–H...B complexes: H₃N...HBr, MeH₂N...HBr,⁶³ and H₂C=N(H)...HO(O)CH.⁶⁴ On the other hand, numerous experimental data for the interaction of various nitro- and halogen-substituted phenols with nitrogen atoms (as in aliphatic amines,⁶⁵ pyridine and its derivatives,⁶⁵ an azomethine base CH₃(CH=CH)₅CH=NHC₄H₉⁶⁶) or oxygen (sulfoxides, phosphine oxides, N-oxides)⁶⁷ bases in solution show the establishment of an equilibrium between molecular and ionic hydrogen bonded complexes, often referred to as “tautomeric” equilibrium. These observations evidence the two minima on the potential energy surface. With increasing acid or base strength the ion pair minimum deepens faster (Figure 2) than the minimum of the molecular complex due to the much stronger electrostatic interaction operating in ionic species. For the same reason the proton transfer equilibrium is very responsive to media effects. The relative stability of the ion pair in comparison with the neutral pair can be fine-tuned by raising the media polarity. Thus, optimization of the adduct CCl₃CO₂H·4-cyanopyridine in the gas phase and in increasingly polar solvents (PCM model) shows not only the gradual shift of the proton toward the base in the molecular complex, but also the progressive stabilization of the ionic complex in chloroform, dichloroethane, and acetonitrile.⁵⁶ These theoretical results were confirmed by IR measurements in the same media⁵⁶ and are in a good agreement with other experiments.⁶⁸

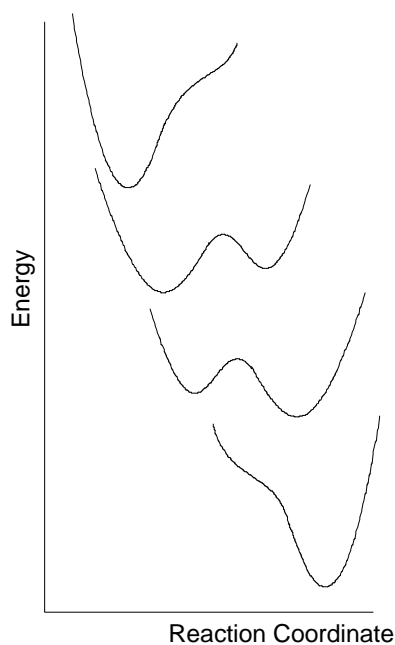


Figure 2. Evolution of a double-well potential energy profile with acid-base strength.

3.3.2 Energy profiles for transition metal hydrides. The interaction of transition metal complexes and hydrides with proton donors has been much less explored. All experimental and theoretical results acquired to date show the presence of two minima on the proton transfer potential energy surface with the exception of the extreme cases of very weak (e.g., indole,^{28b} H₂O⁶⁹) or very strong (CF₃OH,³⁶ H₃O⁺,^{27b,69,70} HBF₄·OEt₂) proton donors. Thus, one of the first DFT studies^{69a} on the interaction of the model hydride complex MoH(CO)₂(NO)(PH₃)₂ with proton donors HF and H₂O reveals only the molecular H···H complex, whereas the interaction with H₃O⁺ yields only the proton transfer product, [(CO)₂(NO)(PH₃)₂Mo(η²-H₂)]⁺···OH₂ without formation of the DHB intermediate. A similar result was obtained for the interaction of H₃O⁺ with CpRuH(CO)(PH₃)^{27b} and Cp₂NbH₃.⁷⁰ The interaction of proton donors of various strength with several transition metal hydrides has been studied theoretically in more detail,^{27b,36,48,50} and includes studies of the proton transfer energy profiles. Beside the formation of molecular DHB complexes, distinct second minima of the ion pair [M(η²-H₂)]⁺···[OR^F]⁻ were found. Whereas hydrogen bonding is energetically favored in the gas phase, the proton transfer step, as a rule, is endothermic. For example, the interaction energy (ΔE) is -10.0 kcal/mol for the PP₃RuH₂ complex with methanol, whereas the product of proton transfer/hydrogen bonded ion pair [PP₃RuH(η²-H₂)]⁺···[OCH₃]⁻ is 26.4 kcal/mol above the DHB complex.³⁶ For the interaction of the similarly basic hydride Cp*Fe(dppe)H (**Error! Reference source not found.**) with the strong proton donor CF₃CO₂H the process is considerably more favorable. For Cp*Fe(dhpe)H···HO₂CCF₃, the calculated hydrogen bonding energy is -14.5 kcal/mol, whereas the hydrogen bonded ion pair CpFe(dhpe)(η²-H₂)]⁺···[OCOCF₃]⁻ is 10.2 kcal/mol above the corresponding model DHB complex.⁴⁸ Use of the even stronger proton donor CF₃OH (P_ACF₃O⁻ = 329.8 kcal/mol)⁷¹ turned the proton transfer to become exothermic; the [PP₃RuH(η²-H₂)]⁺···[OCF₃]⁻ ion pair was found 4.3 kcal/mol below the preceding DHB complex with ΔE = -22.0 kcal/mol.³⁶

These theoretical results are in good agreement with experimental observations. For numerous hydride-HOR combinations the equilibria between the DHB complex and the proton transfer product [M-(η²-H₂)]⁺[OR]⁻ (Scheme 5) were observed in non-polar or low polar media. This means, though qualitatively, the potential energy profile has a double-well character. Noteworthy, lowering the temperature shifts the proton transfer equilibrium toward the ionic complex. This indicates that the ion pair minima are deeper than those of DHB, thus showing an important difference between gas phase and solution.

The main difficulty in studying double-well systems is finding the conditions for the spectroscopic observation of the equilibrium between molecular H-complex and ion pair. Quantitative data on DHB and proton transfer thermodynamics have been obtained for a limited number of transition metal hydride-fluorinated alcohol systems.¹¹ The proton accepting ability of hydrides varies in a rather wide range, but their H···H bonding enthalpies are within a narrow range (6–7 kcal/mol). This results from the requirement of a weaker proton donor for a more basic hydride in order to simultaneously observe both neutral and molecular forms.

An interesting issue is the nature of the counter anion in the hydrogen bonded ion pair. The 1:1 composition was determined for the hydrogen bonded ion pair $[\text{Cp}^*\text{MH}_4(\text{dppe})]^+ \cdots [\text{OR}]^-$ ($\text{M} = \text{Mo},^{50} \text{W}^{72}$) as the proton transfer product, whereas 1:2 H-bonded ion pairs $[\text{L}_n\text{M}(\eta^2\text{-H}_2)]^+ \cdots [\text{ROHOR}]^-$ were found for the protonated $[\text{Cp}^*\text{MH}(\text{dppe})]$ ($\text{M} = \text{Fe},^{48} \text{Ru}^{49}$) and PP_3MH_2 hydrides ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$).⁷³ A possible rationalization could be the weaker acidity of classical polyhydride species vs. non-classical ones;⁷⁴ the latter can be stabilized by the interaction with a stronger base $[\text{OR}]^-$, thus withstanding deprotonation. This idea is supported by theoretical data obtained for hydrides Cp_2NbH_3 ⁷⁰ and $\text{CpRuH}(\text{CO})(\text{PH}_3)$.^{27b} All attempts to find a minimum for the $[\text{M}(\eta^2\text{-H}_2)]^+ \cdots [\text{OR}]^-$ resulted in DHB complexes, in contrast to the success for $[\text{M}(\eta^2\text{-H}_2)]^+ \cdots [\text{ROHOR}]^-$ systems, where the reduced basicity of $[\text{ROHOR}]^-$ compared to that of $[\text{RO}]^-$ prevents deprotonation of the DHB complex and allows the latter to be a stable species. All experimental studies were performed in low-polar media (dichloromethane, THF), where no ion pair dissociation was detected up to room temperature.

3.3.3 Proton transfer energy barriers. When the potential energy surface has two minima, the question arises about the height of the barrier between them. Studies by Kresge⁷⁵ have demonstrated that proton transfer is rapid when the basic lone pair is localized at one atom and does not change hybridization upon transfer. The lone pair delocalization may slow down the proton transfer of carbon atoms but not in the case of traditional nitrogen bases.⁷⁵ Protonation of typical oxygen or nitrogen bases by acetic acid or phenols requires an activation energy of only about 2 kcal/mol, a value consistent with the barrier to diffusion.^{61,75} In such systems, the protonation reaction is often “encounter controlled”, the proton transfer itself is essentially complete in the transition state, and the observed reaction barrier is influenced by the energy needed to bring the reactants together. For weaker proton donors the equilibrium between the molecular and ionic complexes are observed, e.g., $(\text{CF}_3)_2\text{CHNO}_2$ or $\text{CH}_3\text{CH}(\text{NO}_2)_2$ with NEt_3 ;⁶¹ the proton transfer activation energy is much higher ($\Delta E^\ddagger = 4.7$ and 7.9 kcal/mol, respectively) and increasing with decreasing hydrogen bond strength.

In the case of transition metal hydrides the barriers have been determined for the conversion of the molecular $\text{M-H} \cdots \text{HA}$ complex into the ionic $[\text{M}(\eta^2\text{-H}_2)]^+ \cdots \text{A}^-$. For a fluorinated alcohol HA the experimentally determined activation free energies vary from $\Delta G^\ddagger_{298\text{K}} = 14$ kcal/mol for $\text{Cp}^*\text{FeH}(\text{dppe}) \cdots \text{HOC}(\text{CF}_3)_3$ ⁴⁷ up to over 22 kcal/mol for $\text{WH}(\text{CO})_2(\text{NO})(\text{PR}_3)_2$ ($\text{R} = \text{Me}, \text{Et}$).⁷⁶ Somewhat lower barriers of ca. 6.5–12 kcal/mol have been reported for the reactions of PP_3MH_2 ($\text{M} = \text{Fe}, \text{Ru}$) complexes with stronger acids, HBF_4 or HHal ,⁷⁷ although no dihydrogen bond formation has been observed in this case. Thus, despite the use of proton donors similar to those protonating organic bases, the proton transfer to transition metal hydrides appears to have a higher activation barrier. Calculations show a possible active participation of the second proton donor molecule in the proton transfer process, which strengthens the primary hydrogen bond via a cooperative effect^{27b,36} and lowers the proton transfer barrier.^{27b,48} As expected, the transition from gas phase to solution, and with increasing solvent polarity^{27b,48,50} lowers the barrier as does the use of a stronger proton donor.^{27,47,76}

4. Conclusions

Our previous reviews^{1,2} showed that unconventional attractive interactions of organometallic bases with proton donors are a real hydrogen bond with spectral and structural characteristics similar to classical H-bonds with organic bases. In this account, peculiarities of hydrogen bonding and proton transfer to organometallic bases (especially transition metal hydrides) are considered in comparison with organic bases. In general, organometallic bases as proton acceptors combine HB sites at classical ligands (CO, NO, NR, or Cp groups) with an unconventional site, the core transition metal atom and a hydride ligand. The electron density distribution and steric encumbrance of the metal complex and the ligands will determine the site of protonation. Molecular complexes $M \cdots HA$ are well established for non-hydride compounds of late transition metals but are rare in hydrides (only two cases are known to date). In many cases, classical HB with ligands does not lead to proton transfer. HB and protonation site do not coincide, the proton transfer product is the result of protonation at an unconventional site (metal or hydride). Future theoretical studies on determining the energetic characteristics of different sites in both processes will allow establishing the energetic preference of classical and non-classical sites, thus helping to control and steer protonation reactions along a desirable pathway.

The position of the central metal atom and heteroatom of respective organometallic and organic bases in the Periodic Table determines the proton accepting ability (E_j) and the strength of hydrogen bonding ($-\Delta H_{HB}$): going down the Group, these values feature countercurrent changes for the two types of bases. Another peculiarity concerns proton affinity values, which turned out to be greater for organometallic hydrides than for the strongest organic bases, suggesting an easier proton transfer for the former type of bases.

The potential energy profiles have been little investigated for organometallic bases, mostly for transition metal hydrides. The distinct feature revealed both by theoretical calculations in the gas phase and in solvents as well as by experimental studies is the double-well character of the energy profile with a significant barrier. Qualitative (right shift of the equilibrium upon cooling) and quantitative results (thermodynamic data for intra-complex proton transfer) indicate an exothermic proton transfer step and a deeper ion-pair well in comparison to the H-bond.

A future challenge will be to examine proton transfer processes for a larger number of organometallic systems to elucidate energetics, structure and stability of ion pairs, dependence of proton transfer activation parameters on solvent polarity and coordination ability. Further kinetic, spectral, structural and theoretical investigations are needed to formulate general rules governing proton transfer processes, which are important in various fields including catalysis, bio- and supramolecular chemistry.

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