

Spectral Features of Unconventional Hydrogen Bonds and Proton Transfer to Transition Metal Hydrides*

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The spectral (low temperature IR, NMR, UV-Vis) changes accompanying the formation of the new unconventional hydrogen bonds (HB): to a metal atom and to a hydride ligand of transition metal hydrides, and allowing to distinguish the different ways of proton transfer *via* these types of H-bonds are summarized. The spectral and theoretical results show, that HB of the first type (M...HX) and of the second (MH...HX) type induce proton transfer respectively to the metal atom and to the hydride ligand, producing classical and nonclassical cationic hydrides. The spectral evidence of ion pairs formation stabilized by HB with anions is presented.

Key words: IR, UV, NMR spectra, new hydrogen bonds, proton transfer, organometallic hydrides

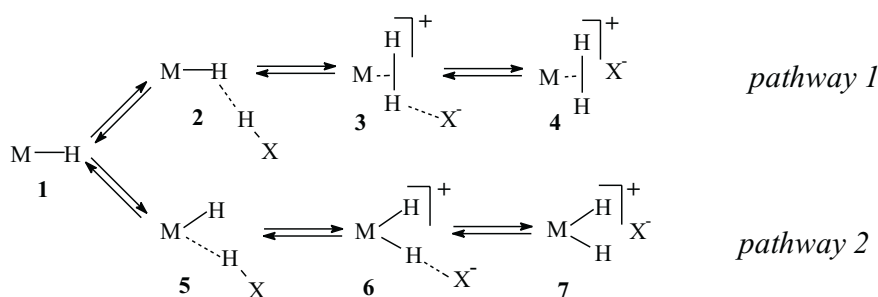
1. Introduction

Several reviews published in the recent years on the nature, spectral and thermodynamic properties of the unconventional hydrogen bonds (HB) demonstrate that this topic is of keen interest [1–6]. The first type of the unconventional HB – the hydrogen bond to the d-lone electron pair of a transition metal atom (M...XH) – was discovered by us in 1990 [7] and studied actively by our [2,8,9] and other groups for numerous transition metal complexes [3,10,11]. The second unusual hydrogen bonding to hydride hydrogen (MH...HX) was found in 1995–96 [12,13]. The term “dihydrogen bond” (DHB) was proposed by Crabtree [5] and “hydridic-protonic bond” introduced by Morris [4], but the first term is in most common use. The first aim of the investigations was to prove, that these intermolecular interactions with various proton donors (alcohols, phenols, indole, carbonic acids) are really HB's. Numerous studies demonstrated significant similarity of the main qualitative and quantitative characteristics, the nature, the structure and the spectral features of both new and classical HB [1,2,6]. The M–H bond of transition metal hydrides possesses two potential sites of HB formation: the hydrogen and the metal atom. Therefore, the problem of the preferable direction of a proton donor attack called for a new methodology of spectral investigations. The peculiarities of the new HB spectral manifestations as well as their partici-

*Dedicated to Prof. M. Szafran on the occasion of his 70th birthday.

pation in proton transfer were actively studied. It was natural to suggest that the new HB's precede proton transfer similar to organic bases, where hydrogen bonding is the first step of protonation. The existence of competition between the two sites of HB and the two pathways of proton transfer (Scheme 1) leading to cationic classical (7) or nonclassical (named also as "dihydrogen complex" or " $\eta^2\text{-H}_2\text{-complex}$ ") (4) hydrides was proposed.

Scheme 1



Determination of the thermodynamic parameters of molecular HB, ion pair and free cation formation, and the energy profiles calculations are out of the frame of this paper (for the review see [1,2,6]). Here we analyze the results concerning IR and NMR spectral features of the novel HB (2, 5) and of the species formed after proton transfer, keeping in mind the M–H bond dichotomy and the possibility of two pathways for proton transfer according to Scheme 1.

2. Spectral criteria of MH...HX and M...HX HB formation

A decrease in the intensity (A) of the $\nu_{\text{OH}(\text{free})}$ IR band of proton donor and the appearance of the low frequency broad intense $\nu_{\text{OH}(\text{bonded})}$ band are characteristic of both classical and unconventional HB formation. Moreover, the changes of spectral parameters ($\Delta\nu_{\text{OH}} = \nu_{\text{OH}(\text{free})} - \nu_{\text{OH}(\text{bonded})}$, $\Delta\nu_{1/2}$ and $\Delta A_{(\text{bonded})}$) similarly increase with the strength of proton donors in both cases. The formation of HB manifests itself in ^1H NMR spectra by downfield shifts of the H(O) signal in the same conditions. So, these changes are diagnostic of HB formation but provide no information concerning its type, *i.e.* the site of coordination.

Transition metal hydrides with the electron rich central atoms could form not only DHB, but also HB of OH...M type similarly to organometallic complexes with the same metals [8–11]. Therefore, it is necessary to determine what a site takes part in HB formation. Recently the spectral criteria of both types of H-complexes have been developed, involving the changes of the ligand stretching vibrations (CO, NO, M–Hal, M–H) in IR spectra.

a). The appearance of a new low-frequency ν_{M-H} band (or shoulder) in addition to new high-frequency bands (or shoulders) for the other ligand stretching vibrations indicate that the hydride ligand being the proton-accepting site, *i.e.* DHB is formed (MH...HX).

The experimental evidence was confirmed by theoretical calculations (see the references in the reviews [1,2,5,6]).

b). The spectral criterion for the metal atom being the proton-accepting site (HM...HX) is the appearance of new high-frequency bands (or shoulders) for all the ligands stretching vibrations of the organometallic hydrides.

The IR spectral changes accompanying HB formation of different types are summarized in Table 1. The formation of HB with a metal atom (M...HX) for the organometallic complexes with carbonyl ligands $Cp^*M(CO)L$, ($M = Co, Rh, Ir$; $L = CO, PR_3$) was confirmed by high-frequency shift of ν_{CO} bands ($+15 \div 20 \text{ cm}^{-1}$) in contrast to low-frequency shifts characterizing HB to this ligand (CO...HX) [1,9–11]. The high-frequency shoulder for ν_{MH} band of the tungsten tetrahydride [14] and the high-frequency shift for ν_{MH} band of the rhenium trihydride [15] upon addition of CF_3COOH or alcohols were observed in IR spectra indicating hydrogen bonding to the metal atoms. IR spectra of [triphos]Ru(CO)H₂ ([triphos] = [MeC(CH₂PPh₂)₃]) in excess of R^FOH in CH₂Cl₂ at 190 K demonstrate the example of DHB determination. The $\nu_{Ru-H(\text{bonded})}$ band is shifted to the low-frequency range by (-20 cm^{-1}) (from 1871 cm^{-1}) and the high-frequency ν_{CO} band appears shifted by $+15 \text{ cm}^{-1}$ (from 1934 cm^{-1}) [20].

However, there are some hydrides with very weak or not observable ν_{MH} bands. The conclusion about DHB formation can be made in these cases by NMR spectra. For example, DHB formation of proton donors with $Cp^*ReH(CO)(NO)$ [17] and [triphos]Re(CO)₂H [18] were established by NMR examination.

c). The main NMR spectral criteria of DHB are a small upfield shift of the hydride atom signal and a decrease of the relaxation time (T_{1min}).

The HB formation process is fast in the NMR time scale resulting in the coalescence of the free and bonded M–H signals even at 190 K. The upfield drift of the broad average signal depends on temperature and concentration of alcohol and it usually consists of $-0.2 \div -0.8 \text{ ppm}$ at 200 K in the presence of an excess of proton donors [4,6,18–20]. The MH...HX study in liquid freons allowing to reach very low temperatures (down to 90 K) [17,21] solved this problem. For example, the NMR study of the system $Cp^*ReH(CO)(NO)/R^F OH$ in freon mixture (CDF₃/CDF₂Cl) at 96 K made it possible to observe two signals (at $\delta_{MH} = -7.54$ and -8.87) corresponding to the free Re–H of the initial hydride and the of DHB complex [17]. It is noteworthy that the de-coalescence of the OH resonance into the three signals corresponding to the free alcohol, ReH...HO and NO...HO complexes was revealed in full agreement with IR findings.

Table 1. IR, NMR spectral changes accompanying HB formation of different types for various organometallic hydrides (L = CO, NO, Cl) [1,9–11,14,15,17–21].

Hydride + ROH	$\Delta\nu_{\text{MH}}$ (cm^{-1})	$\Delta\nu_{\text{L}}$ (cm^{-1}) (L = CO, NO, Cl)	^1H NMR $\Delta\delta_{\text{H-M}}$ (ppm) ($T_{1\text{min}}(\text{init})/T_{1\text{min}}(\text{DHB})$)
M...HO	+10 ÷ +20	+10 ÷ +25	
MH...HO	-15 ÷ -20	+10 ÷ +15	Up-field shift +0.2 ÷ +0.8 (1.5 ÷ 2.0)
ML...HO	+10 ÷ +20	-20 ÷ -35	

A decrease of the spin-lattice longitudinal relaxation time ($T_{1\text{min}}$) of the hydride signal is a very sensitive criterion for DHB formation. Moreover, the T_1 measurement is considered as a reliable approach for determination of an H...H distance. Thus a proton donor closer to H–M induces a faster relaxation (shorter T_1) for the hydride signal. The short H...H distance calculated on the basis of a standard approach is actually shorter than the sum of the van der Waals radii of H (2.4 Å) and lies within the 1.7–2.0 Å interval (typical for DHB interactions) [4,6,16,19,20].

An additional sensor of DHB formation, its strength, and geometry for polyhydrides was proposed by Chaudret and Limbach – the increase of the quantum exchange coupling [21,22]. As was shown for the first time the value of the hydride signal J_{ab} constant of $\text{Cp}^*\text{RuH}_3(\text{PCy}_3)$ is about 80 Hz for the free hydride, which increases to 220 Hz in the presence of the R^fOH excess.

3. The spectral features of DHB to di- and polyhydrides

3.1. The ν_{MH} bands assignment in IR and Raman spectra. The site of coordination in the case of di- or polyhydrides containing only phosphine ligands can be determined by such spectral labels as ν_{MH} bands (IR, Raman), δ , and T_1 (NMR). However, several dihydride complexes investigated by us and others exhibit in IR spectra only one broad and weak ν_{MH} band [16,23]. The analysis of IR and Raman spectra of the series of rhenium, molybdenum, and tungsten dihydrides allowed suggesting that only symmetric stretching vibration bands are observed in both spectra [23]. More recently, the results of the *ab initio* calculations were compared with the experimental data for MH_2 (M = Ti, V) [24]. The authors concluded that the two bands of different nature are overlapped and differ in intensity, the intensity of the $\nu_{\text{MH}}^{\text{as}}$ band in this envelope being significantly greater than that of the $\nu_{\text{MH}}^{\text{s}}$ band. Thus, there are some contradictions of the viewpoints concerning the nature of ν_{MH} band. At the same time NMR hydride signals of polyhydrides are, as usual, an average of the fast exchanging.

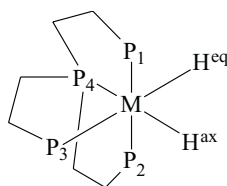
Recently we found the interesting spectral features of the dihydrides and their changes upon DHB formation for $(\text{PP}_3)\text{MH}_2$, where $\text{PP}_3 = \text{P}(\text{CH}_2\text{CH}_2\text{PH}_2)_3$, M = Fe, Ru, Os [25]. Unexpectedly, these dihydrides have two similar and rather intense bands in the ν_{MH} range (1950–1730 cm^{-1}) in the solid state and in solution. The frequencies and intensities (A_{MH}) of the bands are collected in Table 2.

Table 2. The IR bands of ν_{MH} (cm^{-1}) for PP_3MH_2 in CH_2Cl_2 ($A_{\text{MH}} 10^{-4} \text{ l mol}^{-1} \text{ cm}^{-2}$, in brackets) [25] and in the solid state, nujol [26,27].

Hydride	ν_{MH}^1	ν_{MH}^2	$\Delta\nu = \nu_{\text{MH}}^1 - \nu_{\text{MH}}^2$
PP_3FeH_2	1854 (1.0)	1730 (1.0)	124
	1850*	1734*	
PP_3RuH_2	1874 (1.4)	1699 (1.6)	175
	1864*	1722*	142
PP_3OsH_2	1950 (1.1)	1810 (1.3)	140
	1942*	1827*	115

Noteworthy that the intensity of each band is close to the integral intensity of the summary band ν_{ReH} of $\text{ReH}_2(\text{CO})(\text{NO})(\text{PMe}_3)_2$ at 1800 cm^{-1} ($4.5 \cdot 10^{-4} \text{ l M}^{-1} \text{ cm}^{-2}$ in hexane) [20]. These complexes have octahedral geometry (Scheme 2) and the bands could be assigned to symmetric ($\nu_{\text{MH}}^{\text{s}}$) and asymmetric ($\nu_{\text{MH}}^{\text{as}}$) M–H stretching vibrations. But the contradiction for other dihydrides mentioned above [23,24] and the too great difference between the positions of the two ν_{MH} bands ($115\text{--}175 \text{ cm}^{-1}$) forced us to study the polarization Raman spectra for the evaluation of their nature. We carried out Raman depolarization measurements of the ν_{MH} lines in CH_2Cl_2 solution for the most stable Os hydride. The depolarization ratio (ρ) showed that both lines observed in the same positions as of IR bands are strongly and similarly polarized ($\rho = 0.16 \div 0.17$), therefore, they are attributed to symmetrical M–H stretching vibrations ($\nu_{\text{MH}}^{\text{s}}$). The striking difference between the frequencies can be explained by the distinction of the M–H bond strength. Electron donor properties of *trans* ligand are known to decrease the frequency of ν_{MH} (see for example [4]), and the low frequency position of $\nu_{\text{MH}}^{\text{ax}}$ band can be explained by strong *trans* effect of the bridgehead phosphorus atom (P_4) diminishing of M–H^{ax} force constant and bond strength (Scheme 2).

Scheme 2



The theoretical calculations by RHF/LanL2DZ method confirmed the experimental assignment. The calculated values of IR frequencies are only slightly different from that observed in IR spectra ($\nu_{\text{MH}}^{\text{eq}} = 1840$ and $\nu_{\text{MH}}^{\text{ax}} = 1746 \text{ cm}^{-1}$ for model Ru dihydride) and the calculated $\nu_{\text{MH}}^{\text{eq}}$ values remain considerably greater than $\nu_{\text{MH}}^{\text{ax}}$ [25]. Therefore, ν_{MH}^1 and ν_{MH}^2 bands of these hydrides (Table 2) were assigned to the stretching vibrations of the equatorial (*cis* to P_4) and axial (*trans* to P_4) M–H bonds and are named below as $\nu_{\text{MH}}^{\text{eq}}$ and $\nu_{\text{MH}}^{\text{ax}}$.

3.2 The changes of ν_{MH} bands by DHB formation. The interesting features of these two bands behavior in the interaction with proton donors of varying strength (2-fluoroethanol (MFE), 2,2,2-trifluoroethanol (TFE), hexafluoro-2-propanol (HFIP) and perfluoro-tert-butanol (PFTB)) were found [25]. The high frequency band of all hydrides ($\nu_{\text{MH}}^{\text{eq}}$) shifts down in an excess of the most weak proton donor –MFE, $\Delta\nu = 6\text{--}12\text{ cm}^{-1}$, but the other band ($\nu_{\text{MH}}^{\text{ax}}$) broadens slightly shifting up and the high and low frequency shoulders are observed in CH_2Cl_2 solution. These changes increase when the alcohol concentration is increased or the temperature is lowered to 200 K. The values of the shifts depend also on the metal nature increasing from Fe to Os, *i.e.* down the group. However, high frequency shifts of the both ν_{MH} bands, as was mentioned above, should be observed in the case of $\text{XH}\dots\text{M}$ hydrogen bonding. Therefore, down shifts of $\nu_{\text{MH}}^{\text{eq}}$ bands indicate clearly that it is the hydride ligand but not the metal atom appears to be the site of HB formation ($\text{XH}\dots\text{HM}$). We could suggest that the $\text{M}\text{--}\text{H}^{\text{ax}}$ ligand, as the most electron-rich center (*trans* for the most electron donating P_4 atom in Scheme 1) is the site of DHB formation selectively. However, the observed changes are more complicated than those predicted by the spectral criteria for this case. So, the participation of both hydride ligands (1) in DHB seemed to be more probable. Note that the spectral changes diminish upon warming (200–270 K) and reverse again when the temperature decreases (270–200 K) demonstrating the reversibility of the process (1).



The involvement of both hydride ligands in DHB formation was supported by DFT calculations. Upon OH proton attack at the axial hydride, an elongation of the $\text{Ru}\text{--}\text{H}^{\text{ax}}$ bond is accompanied by a shortening of the $\text{Ru}\text{--}\text{H}^{\text{eq}}$ bond. A similar changes were calculated when the site of attack was $\text{Ru}\text{--}\text{H}^{\text{eq}}$. The directions of the calculated IR ν_{MH} changes are in agreement with the experimental spectral criteria described above (the bands of bonded MH groups shift down and those of non bonded MH groups shift up). The changes of the distances (Δr) and frequencies ($\Delta\nu$) increase with the alcohol strength as well as the DHB energy difference. The DHB energies for H^{ax} and H^{eq} are very similar for weaker proton donors ($\Delta\Delta E = 0.02\text{ kcal/mol}$ for MeOH) despite the different charges on these hydride atoms and increase for stronger alcohol (for example, $\Delta\Delta E = 3.42\text{ kcal/mol}$ for CF_3OH) [25].

Unfortunately, we could not observe the DHB features in the interaction with stronger acids by IR experiments. Such acids as PFTB, HFIP and even TFE induce partial proton transfer accompanied by the appearance of the new high-frequency bands, $\nu_{\text{MH}}^{\text{eq}}$, of the cationic $(\eta^2\text{-H}_2)^+$ complex as well as by complication of the spectra in the $\nu_{\text{MH}}^{\text{ax}}$ region (see below). DHB process in the interaction with TFE without proton transfer was observed in the coordinating solvent (THF). Even more pronounced spectral changes of both bands than described above for solution in CH_2Cl_2 can be seen in Fig. 1.

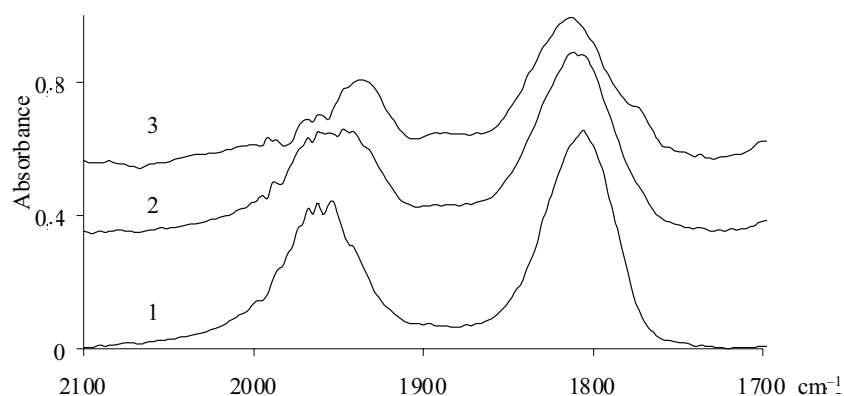


Figure 1. IR spectra in the range of ν_{MH} for $[\text{OsH}_2(\text{PP}_3)]$ ($c = 0.02 \text{ M}$, CH_2Cl_2) at 200 K: without proton donor (1); in the presence of TFE (1:5) at 260 K (2); at 200 K (3).

3.3. DHB by NMR spectral data. In this case NMR studies which was provided by the example of $\text{PP}_3\text{OsH}_2/\text{TFE}$ system occurred to be very informative. The DHB formation was established in a CD_2Cl_2 solution between 200–240 K when the H/H exchange was frozen. The hydride signal in initial complex -6.42 (H^{ax}) shifted up-field to 6.80 by addition of TFE and the second signal -11.68 ppm (H^{eq}) remained practically unchanged (-11.65 ppm) (200 K). The value of $\Delta\delta = -0.41$ is typical for the DHB formation (Table 1). So, the H^{ax} ligand located *trans* to the P_4 -atom with greater proton accepting ability is preferable dihydrogen bonding site. Similar behavior of the two signals were found for the system $\text{H}_2\text{Re}(\text{CO})(\text{NO})(\text{PMe}_3)/\text{PFTB}$ and the better DHB to a stronger polarized H^{ax} atom *trans* to NO ligand as well as the increase of the selectivity of the interaction with more strong acid was established [19]. Additionally the low-temperature ^1H NMR spectrum showed the resonance signal at -7.01 ppm assigned to the (H_2) ligand the product of proton transfer: the $[\text{M}(\eta^2\text{-H}_2)]^+$ complex. The decrease of the initial hydride relaxation time from $T_1(\text{H}^{\text{ax}})$ 0.203 to 0.120 s corresponds well to the above up-field shift of the H^{ax} resonance caused by the H...H bonding. Moreover, the short H...H distance calculated as 1.96 \AA lies within the mentioned above interval, which is typical for DHB complexes [4–6].

Thus, NMR results indicate that hydrogen bond to H^{ax} in the interaction with a stronger acid is preferable and the impact of it (1) is greater ($a > b$) in agreement with the suggestions based on the IR spectra and theoretical data.

4. Spectral criteria of proton transfer

The proton transfer reactions to a metal atom and to a hydride ligand can be expressed as two step processes leading to cationic hydrides *via* DHB or HB to a metal atom by the *pathways 1* and *2*, see Scheme 1.

IR spectra. Proton transfer of the *pathway 2* has been investigated earlier on the examples of the organometallic complexes interaction with different proton donors using the changes of IR $\nu_{\text{M-CO}}$ as well as ν_{CO} and $\nu_{\text{OCO}}^{\text{as}}$ stretching vibration bands of the monochloroacetic or trifluoroacetic acid (TFA) [2,9]. The intense $\nu_{\text{M-CO}}$ bands turned out to be very sensitive spectral indicators of proton transfer: the new $\nu_{\text{M-CO}}$ bands of cations are strongly high-frequency shifted (the $\Delta\nu$ values are $+90 \div +145 \text{ cm}^{-1}$) with respect to the initial band of organometallic complexes. It was shown that the new $\nu_{\text{M-CO}}$ bands assigned to ion pairs stabilized by H-bonds with anion are observed at less high-frequencies than these of the cation **7**. For example, the high frequency shifts ($\Delta\nu$) of the free $\nu_{\text{M-CO}}$ bands of $\text{Cp}^*\text{Ir}(\text{CO})_2$ (**1**) (2004 and 1934 cm^{-1}) in the presence of TFA are equal to $41, 48 \text{ cm}^{-1}$ for HB **5**, $99, 127 \text{ cm}^{-1}$ for **6** and $113 \div 143 \text{ cm}^{-1}$ for **7** [9]. The bands assigned to $\text{M} \dots \text{HX}$ complex **5** decrease in the intensity and disappear upon complete proton transfer. The range of ν_{CO} and $\nu_{\text{OCO}}^{\text{as}}$ bands of TFA are very informative for the elucidation of proton transfer to metal atom *via* **5** and ion pair **6**, especially for complexes without CO ligands [2,9]. The spectral criteria of the equilibrium $\text{CF}_3\text{COOH} \dots \text{M} \rightleftharpoons \text{CF}_3\text{COO}^- \dots \text{M}^+$ were developed on the base of the assignment of acids stretching vibrations provided by Denisov [28] and Szafran with coworkers [29]. The temperature dependence of d-d* transitions of the ionic form (in UV-Vis spectra) was used additionally to prove this equilibrium [2,9]. We suggested that the same spectral features should be characteristic of proton transfer to a metal atom for organometallic hydrides. Up to date it was confirmed at the two examples mentioned above – $\text{WH}_4(\text{dppe})_2$ and $(\text{NP}_3)\text{ReH}_3$ [14,15]. The main criterion of proton transfer to a metal atom (*pathway 2*) for hydrides with only phosphine ligands is a new high-frequency ($\Delta\nu = +60 \div +120 \text{ cm}^{-1}$) shifted $\nu_{\text{M-H}}$ band of the species **6** and **7** (Table 3).

Proton transfer to a hydride ligand and dihydrogen complex formation (**3, 4** in *pathway 1*) accompanied also by an decrease and disappearance of DHB bands in **2**. Unfortunately, the stretching vibrations of the H-H ligand, $\nu_{(\text{H}_2)}$, and the $\nu_{(\text{M-H}_2)}$ bands, are usually not observed in either solution or solid state spectra, as they are too weak and probably masked by more intense $\nu_{\text{C-H}}$ absorptions, for example [20,25]. The IR spectral features of proton transfer for hydrides containing other ligands (CO, NO) are new high frequency bands assigned to their stretching vibrations in cationic dihydrogen complex (Table 3). The $(\eta^2\text{-H}_2)$ -complexes **4** are often unstable and lose H_2 , therefore the studies were carried out at temperatures 250 K to 190 K [13,16,20]. Moreover, using freon mixture as solvent allows to carry out NMR measurements at temperatures down to 100 K [21,22]. For example, IR spectrum at 190–220 K in nonpolar solvent for $\text{ReH}_2(\text{CO})(\text{NO})(\text{PMe}_3)_2$ with CF_3COOH demonstrates proton transfer (*pathway 1*) showing high frequency shifts of the all ligand vibrations: ν_{CO} ($+98 \text{ cm}^{-1}$), ν_{MH} ($+60 \text{ cm}^{-1}$) and ν_{NO} ($+93 \text{ cm}^{-1}$) [16]. The reversibility of the proton transfer *via* DHB was shown by IR and NMR study by the examples of the hydrides of Ru, Re and Os with fluorinated alcohols leading to more stable $(\eta^2\text{-H}_2)^+$ complexes measured at 190–260 K [18,20]. Thus, the spectrum of $[\text{triphos}]\text{Ru}(\text{CO})\text{H}_2$ ($\nu_{\text{CO}} = 1934 \text{ cm}^{-1}$) in excess of HFIP in CH_2Cl_2 reveals the equilibrium between **2** and ionic **3, 4**

forms. Two high frequency shifted ν_{CO} bands are observed relative to initial hydride (1934 cm^{-1}), *i.e.* 1949 cm^{-1} ($+15 \text{ cm}^{-1}$) and 2023 cm^{-1} ($+103 \text{ cm}^{-1}$), respectively [20].

Table 3. Spectral (IR and NMR) characteristics of proton transfer to various transition metal hydrides [1,4,5,9,14–21].

Protonation product	$\Delta\nu_{\text{MH}}^{\text{a}}$, cm^{-1}	$\Delta\nu_{\text{CO}}^{\text{a}}$, cm^{-1}	$^1\text{H NMR}$
$\text{HMH}^+ + \text{OR}^-$	$+80 \div +120$ $(+60 \div +80)^{\text{b}}$	$+90 \div +145$ $(+50 \div +125)^{\text{b}}$	$\Delta\delta > 2.0 \text{ ppm}$ (down shift) $T_1(\text{min}) > 100 \text{ ms}$
$[\text{M}(\eta^2\text{-H}_2)]^+ + \text{OR}^-$	$+50 \div +80$	$+100 \div +120$ $(+60 \div +84)^{\text{b}}$	$T_1(\text{min}) < 50 \text{ ms}$ $J(\text{HD}) = 10\text{--}30 \text{ Hz}$

^a $\Delta\nu = \nu_{\text{cation}} - \nu_{\text{init}}$; ^bin brackets $\Delta\nu = \nu_{\text{ion pair}} - \nu_{\text{init}}$.

The ion pairs stabilized by HB's between an dihydrogen complex and anions **3** as intermediate in the proton transfer reaction was also detected. An intracomplex proton transfer from **2** to **3** was established. The experimental evidence of ion pair formation was the position of the $\nu_{\text{M-CO}}$ **3** band of the hydride $\text{CpRuH}(\text{CO})(\text{PCy}_3)$ depending on the basicity of anions used ($\text{CF}_3\text{COO}^- < (\text{CF}_3)_3\text{CO}^-$) [30,31] (Table 3). The initial $\nu_{\text{M-CO}}$ band observed at 1920 cm^{-1} is shifted to 2020 cm^{-1} ($+100 \text{ cm}^{-1}$) by formation of the free cation **4** in the interaction with strong acid – HBF_4 . The formation of ion pairs **3** induces the low frequency shift of the band of **4** to 1996 cm^{-1} for $[\text{Ru}(\eta^2\text{-H}_2)]^+ \dots \text{OOC}(\text{CF}_3)_3$ and to 1960 cm^{-1} for $[\text{Ru}(\eta^2\text{-H}_2)]^+ \dots \text{OC}(\text{CF}_3)_3$ in solution of CH_2Cl_2 [30].

The proton transfer and ion pairs formation were additionally confirmed by changes of ν_{CO} and $\nu_{\text{OCO}}^{\text{as}}$ stretching vibrations of carbonic acids, for example, CF_3COOH or ClCH_2COOH [18,30,31]. It was pointed out that the dissociation of the ion pair **3** into the free cationic complex **4** in the reaction of $\text{CpRuH}(\text{CO})(\text{PCy}_3)$ with TFA is assisted by the formation of homoconjugated ions $(\text{CF}_3\text{COO}\dots\text{H}\dots\text{OOCF}_3)^-$ characterized by ν_{CO} 1648 cm^{-1} [30]. IR spectra in the ν_{CO} and $\nu_{\text{OCO}}^{\text{as}}$ stretching vibrations of TFA revealed all the species; the DFT calculation is in agreement with the experiment [31]. Norton *et al.* also found that proton transfer from PhNH_3^+ acid to $\text{CpHW}(\text{CO})_2(\text{PMe}_3)$ occurs due to homoconjugated pair formation $[\text{PhNH}_2 \cdots \text{H} \cdots \text{H}_2\text{NPh}]^+$ [32].

There are interesting features of proton transfer to PP_3MH_2 hydrides [25]. The spectral modifications cause the replacement of the initial hydride bands with weaker and broad high frequency shifted bands, $\nu_{\text{MH}}^{\text{eq}}$, assigned to the terminal hydride ligand in cationic forms **3** or **4**. IR bands (1912 cm^{-1} for Ru and 2012 cm^{-1} for Os) coincide with those measured in CH_2Cl_2 for the protonation of the dihydrides with HBF_4 as well as those exhibited by the isolated salts $[\text{MH}_2(\eta^2\text{-H}_2)(\text{PP}_3)]\text{BPh}_4$. Both increasing the alcohol concentration and decreasing the temperature shifted the equilibrium to the right. The complete reversibility of the system was also demonstrated. For example, the high-frequency $\nu_{\text{MH}}^{\text{eq}}$ band of PP_3RuH_2 is shifted from 1874 to 1905 and 1920 cm^{-1} with an increase of alcohol content. It is noteworthy, that at low temperature and high $\text{R}^{\text{F}}\text{OH}$ concentration an extremely broad “continuous” absorption in the range

1850–1650 cm^{-1} was unexpectedly observed (Figure 2). “Continuous” IR absorptions have been previously reported for symmetrical ionic H-bonds and have been explained in terms of important mixing of proton vibrations with different normal modes of the organic base [33,34]. In our case we can suggest analogous interpretation but deeper theoretical and experimental studies are required to elucidate the effect without ambiguity.

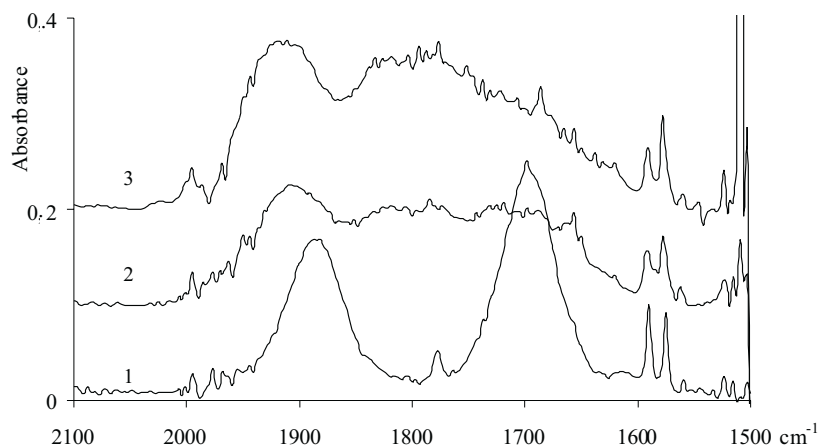


Figure 2. IR spectra in the range of ν_{MH} for $[\text{RuH}_2(\text{PP}_3)]$ at 200 K in THF: without proton donor (1); in the presence of HFIP (1:6) (2), in the presence of HFIP (1:10) (3).

Recently, the competition between HB complexes with the metal atom and the hydride ligand was observed for the first time by the example of the Co hydride [35]. IR spectra showed high and low frequency shoulders of ν_{CoH} band simultaneously and preliminary conclusion that there are two H-bonded intermediates determining the nature of the final protonation products: the dihydride or dihydrogen complex (Scheme 1). However, what systems could create conditions for similar equilibria should be elucidated in the future.

UV-Vis spectra. IR and NMR spectra (200–250 K) demonstrating proton transfer from various proton donors *via* DHB to the PP_3MH_2 hydrides do not reveal the ion pair **3** formation [25]. The low temperature electronic spectroscopy was used to solve this problem [36]. The systems of p-nitrophenol/ PP_3MH_2 in THF solution were studied. The new long-wavelength bands at $\lambda_{\text{max}} = 394$ nm appear in the spectra of these systems (instead of 309 nm assigned to the p-nitrophenol). This new band is slightly blue shifted ($\Delta\lambda_{\text{max}} = -28$ nm) in comparison with that exhibited by the “free” nitrophenolate anion ($\lambda_{\text{max}} = 422$ nm). A similar spectral features has been reported for hydrogen bonded ion pairs involving nitrophenols and amines ($\Delta\lambda_{\text{max}} = -20 \div -30$ nm) [37,38]. Therefore, the shorter wavelength absorption in the systems investigated is assigned to the formation of ion pairs **3**.

NMR spectra. NMR spectral evidence of proton transfer is first of all an appearance of the new resonance of ionic form, which is significantly shifted down field in comparison to the initial hydride signal (Table 3). Unfortunately, there is no difference of the direction and $\Delta\delta$ values in dependence on the nature of the cationic form (classical or nonclassical). For example, ^1H NMR spectra of the initial hydrides reveal a signal at $\delta = -12.5$ ppm for $\text{CpRuH}(\text{CO})(\text{PCy}_3)$, proton transfer induces to $\delta = -8.0$ ppm resonance for dihydrogen complex $\text{CpRu}(\eta^2\text{-H}_2)(\text{CO})(\text{PCy}_3)^+$ ($\Delta\delta = 4.5$ ppm) in liquid freons at 150 K [30]. The proton transfer to $\text{CpFeH}(\text{diphosphine})$ and $\text{CpOsH}(\text{diphosphine})$ shifts δ values from $-16.6 \div -14.8$ ppm of initial hydrides down to the similar range $-12.0 \div -11.2$ ppm for cations ($\Delta\delta = 3.6\text{--}4.6$ ppm), though protonation of the Fe derivatives leads to the $\eta^2\text{-H}_2$ complexes (**4**), while osmium hydrides give the cationic classical dihydrides (**7**) [39].

The two other NMR parameters ($T_{1\text{min}}$ relaxation time and J_{HD} coupling constants) allow to deduce the nature of the protonation product (classical or nonclassical) and therefore to distinguish the site of proton transfer. It is well known that $(\eta^2\text{-H}_2)$ complexes usually are characterized by very small $T_{1\text{min}}$ times (< 50 ms) but rather large J_{HD} values ($> 10\text{--}15$ Hz) of the hydride signal (Table 3) [1,4,40].

Conclusions

Summing up, we can say that the main spectral (IR, NMR, UV-Vis) features of the unconventional and classical HB are similar. There can be no doubt now, that the unconventional attractive interactions of transition metal hydrides with proton donors are really hydrogen bonds. Therefore, it is possible to use many spectral approaches found for a great number of organic HB systems in investigations of unconventional HB. The real spectral criteria developed allow to establish the sites of HB – a metal or a hydride atom. The conditions and the spectral evidence of DHB selectivity were found for the dihydrides with different charges and proton accepting ability of hydride ligands. IR and NMR spectra at 190 to 260 K reveal, that HB of the two types are intermediate species along the two pathways of proton transfer, leading to classical and nonclassical cationic hydrides. The elucidation of the conditions, inducing different pathways of proton transfer *via* HB, is at an early stage of development and numerous spectral studies confirmed by theoretical calculations are necessary in the future. However, it is clear that these new unconventional HB are very important for the concept of hydrogen bonding, as well as for the possibility to control the proton transfer reactions.

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