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Problems of unusual hydrogen bonds between proton donors and transition metal hydrides and borohydrides

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The results of experimental and theoretical studies of intermolecular MH...HX and BH...HX hydrogen bonds with the hydride hydrogen atom acting as a proton accepting site are analyzed. Spectral (IR and NMR) criteria for their formation are presented. The spectral, structural, and thermodynamic characteristics of these unusual hydrogen bonds obey the regularities found for classical hydrogen bonds. It was shown that the MH...HX bonds participate in the proton transfer with the formation of nonclassical cationic hydrides and the $[M(\eta^2\text{-}H_2)]^+...A^-$ hydrogen bonds are formed in low-polarity media. Problems arising in this new line of investigations are discussed.

Key words: transition metal hydrides, borohydrides, hydrogen bond; molecular spectroscopy; proton transfer.

Unusual hydrogen bonds, in which the hydride hydrogen atom acts as a proton acceptor, have been found recently and are being studied intensively. Five- and six-membered intramolecular cycles stabilized by H-bonds of the IrH...HX (X = N, O) type have been studied.[1—5] NMR spectroscopy data and *ab initio* calculations[2—5] showed that the energy of such an H-bond is equal to 2.5—5.0 and 5—7 kcal mol^{-1}, respectively. According to NMR spectroscopy and X-ray structural analysis data, the H...H distance, *r*(H...H), is 1.7—1.9 Å.

Earlier,[6—8] we have reported the first results of investigations of intermolecular hydrogen bonds between the proton donors and the hydride ligand. We have carried out detailed studies of the MH...HX hydrogen bonds in solution (in both polar and low-polarity media) by IR and NMR spectroscopy taking the interactions between tungsten hydride $WH(CO)_2(NO)(PR_3)_2$,[9] three rhenium hydrides: $ReH_2(CO)(NO)(PR_3)_2$,[10] $Cp^*Re(CO)(NO)H$ ($Cp^* = C_5Me_5$),[11] and $(triphos)Re(CO)_2H$ (triphos = $MeC(CH_2PPh_2)_3$),[12] ruthenium hydride $CpRuH(CO)P(\textit{cyclo}\text{-}C_6H_{11})_3$ [13] and proton donors of different strength as examples. The existence of the ReH...H bond in the crystal of a $ReH_5(PPh_3)$ adduct with indole was proved by neutron diffraction.[14,15] It has been shown that the MH...HX bonds are hydrogen bonds of medium strength (4—7 kcal mol^{-1}) and the H...H distance is close to that for the intramolecular H-bonds of this type.[2—5]

The formation of hydrogen bonds with the hydride hydrogen atom is not a specific feature of transition metal hydrides; it can also occur for hydrides of main group elements. The possibility of formation of the EH...HX bond was discussed taking borohydrides as examples.[16] The analysis of aminoborane structures from the Cambridge crystallographic database showed that shortened (shorter than the sum of the van der Waals radii) H...H distances are characteristic of 18 compounds. We have proved that the hydride hydrogen atom in solution is a center of formation of intermolecular hydrogen bonds between the proton donors and borohydrides (Et_3NBH_3, $(EtO)_3PBH_3$, and BH_4^-).[17]

In this work, spectral (IR and NMR) criteria for the formation of unusual MH...HX and BH...HX hydrogen bonds are presented, a comparative analysis of their properties and those of classical H-bonds is performed, and the first examples of participation of MH...HX hydrogen bonds in the proton transfer resulting in the formation of non-classical cationic hydrides $[M(\eta^2\text{-}H_2)]^+$ are considered. Finally, problems arising at the first stages of development of this new area of knowledge are discussed.

Manifestations of MH...HX and BH...HX hydrogen bonds in IR spectra

Changes characteristic of hydrogen bond formation are observed in the regions of X—H (νXH) stretching vibrations in the IR spectra of proton donors in the presence of transition metal hydrides and borohydrides.[9—13,17,18] Thus, the intensities of the νXH bands decrease and broad low-frequency absorption bands of XH groups bonded by hydrogen bonds (νXH_{bond}) appear in the spectra of all proton donors (indole, MeOH, PhOH, trifluoroethyl (TFE), hexafluoroisopropyl (HFIP), and perfluoro-*tert*-butyl (PFTB) alcohols). The values of their spectral characteristics such as shifts

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($\Delta\nu = \nu XH_{free} - \nu XH_{bond}$), half-widths ($\Delta\nu_{1/2}$), and integrated intensities (A) increase as the strengths of proton donors increase. Thus, the νOH_{bond} bands are observed at 3328 cm^{-1} and 3140 cm^{-1} in the spectra of $W(CO)_2(NO)(PMe_3)_2H...HOR$ [9] for phenol and PFTB, respectively. For these compounds, the $\Delta\nu$ values are equal to 295 and 448 cm^{-1}, the halfwidths $\Delta\nu_{1/2}$ increase from 180 to 390 cm^{-1}, and the integrated intensities of the bands increase from $8.3 \cdot 10^4$ to $12.9 \cdot 10^4$ L mol^{-1} cm^{-2}, respectively.[9] The νOH_{bond} bands lie at 3410 cm^{-1} and 3177 cm^{-1} in the spectra of complexes $H_3BH^-...HOR$ for methanol and HFIP, respectively, while the $\Delta\nu$ values change from 214 to 402 cm^{-1}, the $\Delta\nu_{1/2}$ values increase from 91 to 185 cm^{-1}, and the integrated intensities of the bands increase from $3.8 \cdot 10^4$ to $11.8 \cdot 10^4$ L mol^{-1} cm^{-2}, respectively.[17,18]

Studies of IR spectra in the regions of ligand stretching vibrations (νCO, νNO, νMH, and νBH) are of crucial importance for establishing the coordination site. The formation of MH...HX and BH...HX hydrogen bonds results in a decrease in the νMH and νBH frequencies, whereas the stretching bands of the ligands not participating in the formation of hydrogen bonds are shifted to the high-frequency region.[9–13,17,18]

Manifestations of MH...HX and BH...HX hydrogen bonds in NMR spectra

As in the case of organic bases, the formation of hydrogen bonds between XH-acids and hydride hydrogen results in a low-field shift of the proton signal of hydroxyl group. It is of interest that a high-field shift of the signal of hydride hydrogen in the presence of proton donors is reported in all papers;[9,11,12,18,19] its magnitude depends on the concentration of the proton donor and temperature. Thus, the $\Delta\delta$ value for $WH(CO)_2(NO)(PMe_3)_2$/HFIP is 0.72 ppm (at 170 K) for a hydride : alcohol ratio of 1 : 3.[9]

It should be noted that investigations of MH...HX hydrogen bonds in liquid Freons have considerable promise. Previously,[20,21] the efficiency of using Freons which make it possible to reach very low temperatures (down to 90 K) was shown when studying the H-bonds with organic bases. In studies of the interaction between Cp*Re(CO)(NO)H and PFTB in liquid Freons (CDF_2/CDF_2Cl) by ^1H NMR spectroscopy at 96 K, we could separately observe the signals of the hydride hydrogen atom corresponding to both free molecules and the H...H-complex (at δ −7.54 and −8.87, respectively).[11]

Another parameter sensitive to the H...H interaction is the relaxation time ($T_{1,min}$) of the signal of the hydride hydrogen atom; it decreases in the presence of proton donors by a factor of 1.5 to 3. The use of the relationship $r(H...H) = 5.817(\nu\Delta R_{1,min})^{-1/6}$ (where ν/MHz is the frequency of NMR signal and ΔR is the difference between $1/T_{1,min}$ values for the H-complex and initial hydride) makes it possible to determine the $r(H...H)$ distance in the intermolecular hydrogen bonds. The shortened $r(H...H)$ distance was found for systems $WH(CO)_2(NO)(PMe_3)_2$/HFIP (1.77 Å)[9] and (triphos)$Re(CO)_2H$/PFTB (1.83 Å).[12]

Comparative analysis of the properties of unusual and classical H-bonds

The interaction found goes beyond the scope of traditional concepts of hydrogen bonds since the hydride hydrogen, which is a proton accepting site, has neither lone electron pairs (like heteroatoms of organic bases or metal atoms[22]) nor π-electrons (like unsaturated and aromatic compounds). For this reason, there is a need to perform a comparative analysis of the properties of novel EH...HX (E = M, B) complexes and classical hydrogen bonds. The currently available results of experimental[9–13,17,18] and theoretical[10,14,15,18,23–25] works suggest that unusual interactions are characterized by the same properties as classical hydrogen bonds.

1. The isotopic ratios of frequencies $\nu OH...HM/\nu OD...HM$ and $\nu OH...HB/\nu OD...HB$ calculated for a series of H-complexes ($WH(CO)_2(NO)(PEt_3)_2$, $ReH_2(CO)(NO)(PMe_3)_2$, and Cp*Re(CO)(NO)H) with $(CF_3)_2CHOH(D)$[9,22] as well as those for complexes between BH_4^- and BH_3NEt_3 with MeOH(D)[18] are 1.33—1.35, which is the same as in the case of conventional hydrogen bonds of medium strength.

2. Linear dependences between $\Delta\nu$ and $\Delta\nu_{1/2}$ values similar to those for conventional hydrogen bonds were found for H-complexes. For example, the shift and half-width values for borohydrides and metal hydrides interacting with HFIP are related by the following equation: $\Delta\nu_{1/2} = 1.09\Delta\nu - 73$ ($r = 0.991$, $n = 7$).

3. As in the case of classical hydrogen bonds, a reversible equilibrium $HE + XH \rightleftharpoons EH...HX$ is observed. The number of hydrogen-bonded groups increases as temperature decreases.

4. The enthalpies of formation ($-\Delta H$/kcal mol^{-1}) for complexes EH...HX can be determined by empirical correlation equations[26] (1), (2) established for a great number of organic systems, since the calculated $-\Delta H$ values are close to those obtained from temperature dependence of the formation constants (Eq. (3)).

$$-\Delta H^\circ = 18\Delta\nu/720 + \Delta\nu \qquad (1)$$

$$-\Delta H^\circ = 2.9\Delta A^{1/2} \qquad (2)$$

$$-\Delta H^\circ = d\ln K_f/dT \cdot RT^2 \qquad (3)$$

For example, the enthalpies found from Eqs. (1)—(3) for the H-complex $WH(CO)_2(NO)(PEt_3)_2$/HFIP are equal to 5.3, 5.1, and 4.8 kcal mol^{-1}, respectively,[9] while those for complex BH_3NEt_3/HFIP are equal to 3.5, 3.3, and 3.4 kcal mol^{-1}, respectively.[18]

5. Linear dependences between the enthalpies of formation of MH...HX[22] and BH...HX[18] bonds and

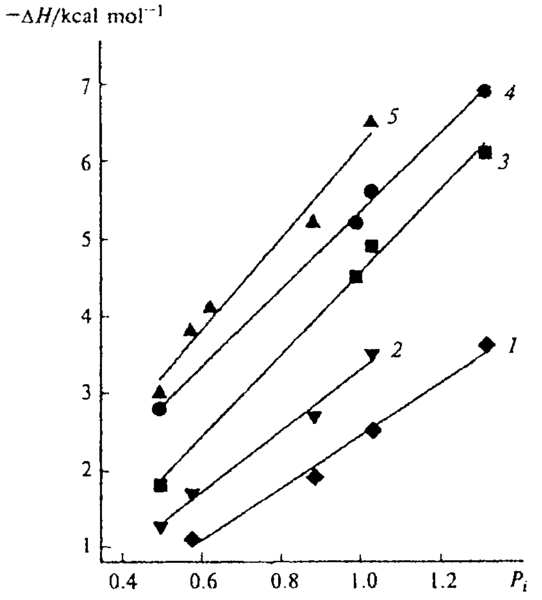

Fig. 1. Dependences of the enthalpies of formation ($-\Delta H$) of MH...HX and BH...HX hydrogen bonds on proton donating properties of XH (P_i): *1* — $BH_3P(OEt)_3$; *2* — BH_3NEt_3; *3* — $ReH_2(CO)(NO)(PMe_3)_2$; *4* — $WH(CO)_2(NO)(PMe_3)_2$; *5* — Bu_4NBH_4.

proton donating abilities of XH-acids (Fig. 1) are analogous to linear correlation equations characteristic of H-complexes with organic bases of different classes. The Iogansen "rule of factors"* established for classical hydrogen bonds is also valid for these new hydrogen bonds. The basicity factors (E_j) of the hydride hydrogen are independent of the nature of proton donors and have constant values for a given hydride, analogously to the E_j values for heteroatoms in organic bases[27,28] and metal atoms in metal-containing compounds.[22] This makes it possible to define a scale of basicity factors of the hydride hydrogen for different hydrides and compare the proton accepting properties of the hydride ligand with the proton accepting abilities of the sites of organic bases (Fig. 2).

In all known cases, the basicity factors of the hydride hydrogen in transition metal hydrides are considerably larger than the E_j values for the π-density in unsaturated and aromatic compounds ($E_j < 0.4$). Ruthenium hydride has the greatest proton accepting ability ($E_j = 1.0\pm0.02$), which is close to that of the O atom in diethyl ether ($E_j = 1.0$). Ligands affect strongly the E_j values of the hydride hydrogen. The proton accepting ability of the hydride ligand in $HW(CO)_2(NO)(PR_3)_2$ [9] decreases in the series $PMe_3 > PEt_3 > P(OPr^i)_3 > PPh_3$ ($E_j = 0.91-0.70$) depending on the steric and electronic effects of phosphine ligands. The basicity factor of the hydride ligand in compound (triphos)$Re(CO)_2H$ [12] is equal to 0.97. The decrease in the number of donor ligands reduces substantially the proton accepting ability of hydride hydrogen. For example, the E_j values for complexes $H_2Re(CO)(NO)(PR_3)_2$ are equal to 0.80 and 0.68 for R = Me and Et, respectively,[10] whereas for $Cp^*Re(CO)(NO)H$ [11] $E_j = 0.70$. The close values of basicity factors for the hydride and NO ligands ($E_j = 0.60$ for the latter) lead to a competition between these sites. Taking $H_2Re(CO)(NO)(PR_3)_2$ and $Cp^*Re(CO)(NO)H$ as examples,[10,11] we have established the existence of equilibrium between H-complexes of the types OH...HRe and OH...ONRe.

The BH_4^- anion has the largest basicity factor ($E_j = 1.25$) among all the hydrides investigated (see Fig. 2),[18] which is close to that of such a strong proton acceptor as DMSO ($E_j = 1.27$). The proton accepting ability of the

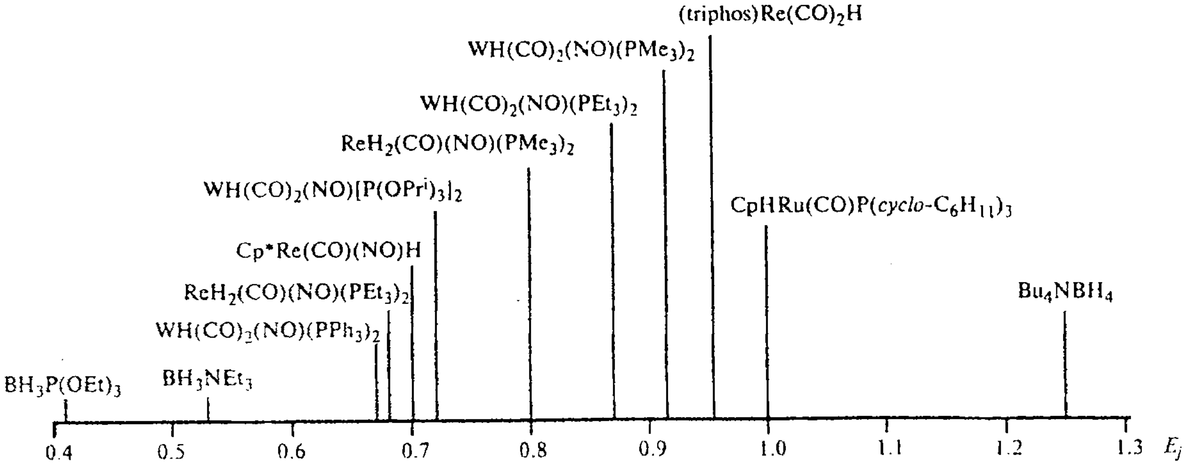

Fig. 2. Scale of basicity factors (E_j) for transition metal hydrides, borohydrides, and organic bases.

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* The empirical "rule of factors" found by Iogansen[27,28] from analysis of hundreds of organic systems demonstrates the constancy of proton donating (P_i) and proton accepting (E_j) properties of partners at the formation of hydrogen bonds: $-\Delta H_{ij} = -\Delta H_{11}P_iE_j$, where $-\Delta H_{11}$ refers to a phenol—diethyl ether pair taken as standard, for which it is assumed that $P_i = E_j = 1$.

hydride hydrogen in neutral borohydrides is minimum (E_j = 0.53 and 0.41 for Et_3NBH_3 and $(EtO)_3PBH_3$, respectively)[18] and is comparable to the E_j value for the O atom in diphenyl ether.

6. The applicability of empirical correlations established earlier for linear hydrogen bonds with organic bases and the results of a number of quantum-chemical calculations of MH...HX [10,23,24] and BH...HX [18] hydrogen bonds are in agreement with the linear arrangement of atoms participating in the formation of unusual dihydrogen bonds. The linearity of FH...H(Li) and FH...H(Mn) fragments has been demonstrated[23] by *ab initio* (HF, 6-31G*) calculations of hydrogen-bonded complexes FH...HLi and FH...HMn(CO)$_5$. The F—H and H—Mn bonds in the latter compound were shown to be lengthened. It was established by density functional theory (DFT) calculations that a linear two-center H-bond (ReH...HO) is energetically preferable to a nonlinear three-center H-bond.[10] It has been found for the model $(H_3P)(NO)(CO)_2ReH_2 \cdot H_2O$ system that the energy of the ReH...HO bond in the linear H-complex is 2.3 times higher than that of the nonlinear three-center complex. *Ab initio* calculations of H-complexes $HM(NO)(CO)_2(PH_3)_2$ (M = Mo, W) with H_2O and HF showed that the H...H—X angles deviate slightly from 180° (they lie in the interval 162°—174° depending on the method of calculations).[24] It is of interest that a deviation of the NH...H(Re) fragment from linearity and weak interaction with the second hydride hydrogen atom is found in the structure of rhenium pentahydride mentioned above.[14,15] Such deviations from linearity and additional interactions caused by the effect of crystal packing are common for many crystalline systems.[29]

It has been found that hydrogen bonds in complexes of H_2O and MeOH with BH_4^- and BH_3NH_3 and in dimer $(H_3NBH_3)_2$ (HF 6-31G calculations) are linear.[18] In all complexes except for $H_3BH...HOH$, the X—H...H(B) angles are equal to 172—178°. The deviation from linearity found for complex $BH_4 \cdot H_2O$ (the H...H—O angle is 154°) is explained by additional interaction between free hydrogen atoms of borohydride and H_2O. It has been shown theoretically[25] that the most energetically preferable structure of complex BH_4^-...HCN is nonlinear. However, not this but the less favorable (by 2.5 kcal mol^{-1}) linear structure exhibits characteristics typical of an H-bond. The linear complex is characterized by the shorter H...H distance (1.7 rather than 2.2 Å), positive H...H-overlap (0.079), and stronger polarization of the partners.[18]

7. The electrostatic interaction between the partly positively charged hydrogen atom of the proton donor and the partly negatively charged hydride hydrogen atom ($MH^{\delta-}...^{\delta+}HX$, $BH^{\delta-}...^{\delta+}HX$) is the driving force of the formation of unusual H-bonds. An analysis of contributions to the energy showed[24] that the electrostatic energy makes the largest contribution to the energy of the MH...HX hydrogen bond, analogously to classical H-bonds. Next in magnitude are the contributions of polarization energy and charge transfer. It is of interest that the contribution of polarization energy to the total bond energy of the H...H-complex is considerably larger than that in the case of a classical H-bond. The negative charge on the hydride hydrogen atom and the positive charge on the hydrogen atom of the OH group increase to the same extent (by 0.01—0.07 au) upon formation of the BH...HX hydrogen bond.[18] Redistribution of the electron density is not restricted to this fragment and affects both molecules. It should be noted that changes happening to the proton donor (the molecule of alcohol) are similar to those occurring at the formation of H-bonds with organic bases.

Thus, the experimental and calculated data mentioned above show that the energies of MH...HX and BH...HX interactions lie in the region typical of weak and medium-strength hydrogen bonds. These unusual H-bonds obey the regularities established for classical hydrogen bonds.

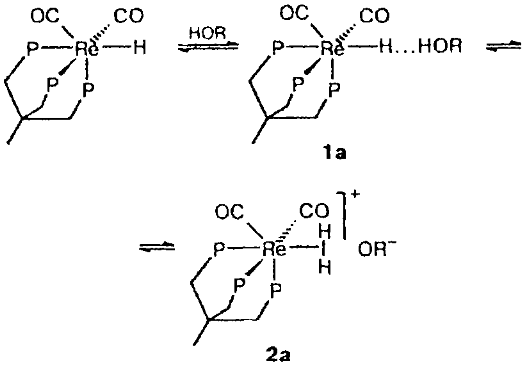
The proton transfer

Protonation of transition metal hydrides is one of the main methods for the synthesis of non-classical cationic hydrides. The hypothesis about the intermediate formation of the H...H hydrogen bond in the protonation reaction resulting in a dihydrogen complex was proposed in Refs. 9, 15, and 22 and was experimentally confirmed in 1997.[12,13,30]

The formation of the H...H bond was shown in studies of the interaction between ruthenium dihydride $(dppm)_2H_2Ru$ and phenol by IR spectra in the νOH region. The dynamic equilibrium involving the proton transfer was established by NMR spectroscopy; however, an attempt to observe individual signals of initial hydride and H-complex failed due to fast exchange.[30] Additionally, the process in this system is complicated by *cis—trans*-isomerization of $(dppm)_2H_2Ru$, whereas the proton transfer is only characteristic of the *trans*-form.

We obtained the first data on the proton transfer in several systems by IR spectroscopy. This method enables one to separately observe individual absorption bands of the initial hydride, the H-complex, and the η^2-H_2-complex. The results of studies of the proton transfer for rhenium and ruthenium hydrides (triphos)Re(CO)$_2$H and CpHRu(CO)P(*cyclo*-C_6H_{11})$_3$ (see Refs. 12 and 13, respectively) will be considered as examples. These hydrides are characterized by the rather high proton accepting ability of the hydride hydrogen which makes it possible to observe the proton transfer in the interaction with fluorinated alcohols. We could expect that relative stability of corresponding η^2-H_2-complexes will allow the studies to be made of equilibria under rather convenient conditions. In fact, we were able to characterize all stages of the equilibrium by studying the νCO region in a wide temperature range.

Thus, the formation of a hydrogen bond between (triphos)Re(CO)$_2$H and PFTB was observed in a small excess of the latter in CH_2Cl_2. In this case, high-frequency shoulders corresponding to the H-complex **1a** appear at 1930 and 1864 cm^{-1} on the ν_sCO (at 1921 cm^{-1}) and ν_{as}CO (at 1856 cm^{-1}) bands of the initial hydride (equilibrium (4)).



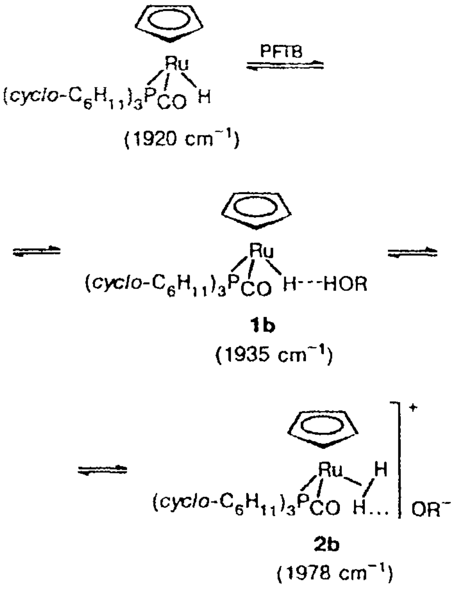
(4)

New bands corresponding to ν_sCO and ν_{as}CO of dihydrogen complex **2a** appear in the IR spectrum obtained in a ten-fold excess of PFTB at low temperature (200 K) at 2004 cm^{-1} and 1935 cm^{-1}, respectively (the latter band overlaps the band of hydrogen-bonded complex **1a**). The IR spectra show that spectral changes in the temperature interval 200—260 K are reversible. The equilibrium is shifted towards the thermodynamically more stable η^2-H_2-complex as temperature decreases. The equilibrium (4) can be shifted to the right using the stronger XH-acids (HBF_4, $ClCH_2COOH$); in this case the intensities of the νCO bands of η^2-H_2-complex **2a** increase while their positions are retained.

The study of IR spectra of ruthenium hydride CpHRu(CO)P(*cyclo*-C_6H_{11})$_3$ in nonpolar medium (hexane) made it possible to clearly observe the νCO bands of all participants of equilibrium (5).

It should be noted that the rate of proton transfer and formation of the η^2-H_2-complex in hexane appeared to be very low at 190—210 K: $(2-8)\cdot 10^{-4}$ s^{-1}. This indicates the presence of a high barrier on the potential energy surface ($\Delta G^{\neq}$ = 15 kcal mol^{-1}).

It is of interest that the position of the νCO band of this hydride in dihydrogen complex (**2b**) was found to be strongly dependent on the nature of the anion. This means that the ionic pairs are stabilized by a rather strong hydrogen bond with the anion. The replacement of anion BF_4^- by CF_3COO^- and $(CF_3)_3CO^-$ leads to a shift of νCO bands of complex **2b** to the low-frequency region in accord with the increasing ability of the anion to form the H-bonds (thus, the νCO in CH_2Cl_2 lie at 2020, 1996, and 1966 cm^{-1}, respectively). It is likely that steric hindrances from the bulky phosphine ligand in complex **2a** hamper the formation of H-bonds between the η^2-H_2-ligand and the anion.



(5)

Thus, we established that the H...H hydrogen bond is involved in the proton transfer resulting in the formation of η^2-H_2-complexes. The ionic pairs were found in low-polarity media stabilized by hydrogen bonds between the dihydrogen complex and the counterion.

There is a great number of "white spots" in the area considered. Further intensive investigations are needed. First of all, it is necessary to establish how the strength of H-complexes depends on the metal position in the Periodic system and ligand environment. Data on the proton transfer are scarce. It is unknown how electronic and steric effects of the ligands and the nature of the metal atom affect the proton transfer. The first results make it possible to raise the questions on the character of the potential energy surface of the proton transfer and how the barrier height depends on the structure of hydrides and properties of the medium. It is also of interest to elucidate how hydrogen bonds affect the equilibrium position between classical and non-classical cationic hydrides. To do this, both experimental and theoretical investigations are needed. The solution of these problems is of importance for an understanding of the specific reactivity of hydrides in reactions involving proton transfer and catalytic processes.

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