ELSEVIER

Coordination Chemistry Reviews 231 (2002) 165–181

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

New types of hydrogen bonding in organometallic chemistry

Lina M. Epstein, Elena S. Shubina *

A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov Street, 28, 119991 Moscow, Russia

Received 6 December 2001; received in revised form 13 March 2002

Contents

Abstract

The review summarizes the experimental and theoretical advances in the elucidation of the nature, the structure, the spectral and energetic characteristics of the new types of hydrogen bonds (HB) specifically for organometallic compounds: cationic hydride as a proton donor ($[MH]_{+}\cdots OP(X^{-})$) and a metal atom ($M\cdots HX$) or hydride ligand ($MH\cdots HX$) as a proton acceptor. The main features of new unconventional and classical HB appear to be similar. The influence of different factors on HB and full proton

---

* Corresponding author. Tel.: +7-95-135-6448; fax: +7-95-135-5085

E-mail address: shu@incos.ac.ru (E.S. Shubina).

PII: S0010-8545(02)00118-2

transfer is analyzed. Investigations of HB participation in proton transfer reactions as intermediates as well as approaches to experimental energy profiles of protonation are presented.

Keywords: Hydrogen bonding; Proton transfer; Metal hydrides; Organometallic complexes

1. Introduction

Hydrogen bonding plays a key role in chemical, catalytic, and biochemical processes as well as in supramolecular chemistry and chemical engineering [1]. During the last 10 years, new types of hydrogen bonding specific for organometallic compounds were found and studied actively. This review is devoted to the spectral, structural, and thermodynamic features of new types of hydrogen bonds and their place in the general concept of hydrogen bonding. It also considers participation of hydrogen bonded complexes as intermediates of proton transfer reactions in organometallic chemistry.

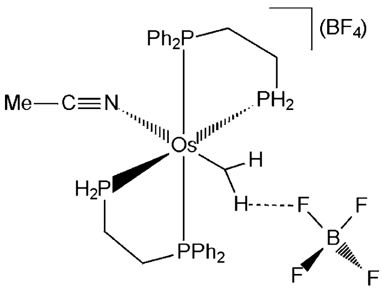
2. Classification of the new types of hydrogen bonds in organometallic chemistry

The new types of hydrogen bonds (HB) in organometallic chemistry can be divided into three types according to the site of coordination and the role of the organometallic species in a hydrogen bonded pair. The short description of these new HBs and the history of their discovery are presented in this part of the review.

2.1. Cationic organometallic hydrides as proton donors in hydrogen bonds

Many neutral hydrides are known to be strong acids. The relative acidities of classical and nonclassical hydrides or dihydrogen complexes, discovered by Kubas [2], have been collected by Norton [3], Morris [4], and Jia et al. [5]. So, it was quite natural to suppose that there might be molecular HB between M–H bonds of neutral transition metal hydrides and neutral bases (B), as hydrogen-bonded intermediates (M–H···B) of deprotonation, analogous to HB of organic acids. However, attempts to find hydrogen bonding between $HCo(CO)_4$, which is a rather strong acid, and a series of nitrogen and oxygen-containing organic bases were not successful [6]. In 1994–1995 it was found that a cationic hydride can be a proton donor forming an ionic ($MH^+\cdots X^-$) or ion-molecular ($MH^+\cdots B$) hydrogen bond [7]. The ionic type of HB was observed for cationic hydrides $(Cp_2^*OsH)^+$ and $(WH_5(dppe)_2)^+$ as proton donors and trifluoroacetate anion as a proton acceptor (X^-). The ion-molecular ($MH^+\cdots B$) interaction was established for phosphine oxides (B) which are excellent proton acceptors combining great ability to form hydrogen bonds with weak basicity. It was found that the process does not stop at hydrogen bond formation but is accompanied by reversible partial proton transfer in the case of the strongest base $(Me_2N)_3PO$. IR spectral manifestations of the process were observed in the ν_{MH} and ν_{PO} regions. Subsequently, IR studies of the system $[IrH_2(PPh_3)_2L_2]BF_4$ and PPh_3PO in the solid state were performed by Peris and Crabtree [8a]. The authors demonstrated the same changes in both the M–H and PO stretching regions. The existence of intramolecular HB $WH^+\cdots OC$ interactions was presented in the work [8b]. Another confirmation of such HB was obtained from the analysis of the Cambridge Structural Database made by Braga et al. [8c]. It was shown that the HB interaction can include nonclassical hydride as the proton donor. The X-ray structure determination for the dicationic complex $[Os(\eta^2\text{-}H_2)(CH_3CN)(dppe)_2](BF_4)_2$ was recently reported by Morris [9a] (Scheme 1). It reveals that a fluorine of one of the two BF_4^- anions accepts a hydrogen bond from the dihydrogen ligand with an H···F distance of about 2.4 Å, which is less than the sum of the van der Waals radii of hydrogen (1.2 Å) and fluorine (1.5 Å). The data obtained by NMR showed that the hydrogen bond formed between the dihydrogen ligand and a counter-anion can influence the relative stability of the tautomers in solution [9b].

The thermodynamic product of protonation of $Ru(dppe)_2H(CN)$ by $HOSO_2CF_3$ in CH_2Cl_2 at −10 °C is believed to be $Ru(dppe)_2(\eta^2\text{-}H_2\cdots OSO_2CF_3)(CN)$. At room temperature, rearrangement occurs to the complex $Ru(dppe)_2(H)(CNH\cdots OSO_2CF_3)$ containing a classical $NH\cdots O$ hydrogen bond. Formation of the ion-pair $\eta^2H_2\cdots X^-$ as an intermediate in the proton transfer from HX to $CpRuHCO(PCy_3)$ will be discussed in Section 6.2. Thus, the first new type ion-molecular or ionic HB involves classical or nonclassical cationic hydrides as proton donors.



Scheme 1.

2.2. Transition metal atoms as proton acceptors

Transition metal atoms possess *d*-type lone pair electrons, so it was assumed that they could act as acceptors in HB like heteroatoms with *sp*-lone pairs. However, attempts to find intermolecular M···HX hydrogen bonds were not successful, although intramolecular H-bonding to transition metal atoms in organometallic compounds had been known for over 20 years (1970–1990) [10]. Such contradictions suggested that the steric factors could cause the intramolecular binding. Thorough IR spectral studies in combination with conformational calculations indicated the rules of intramolecular HB formation as well as the group of carbinols forming H-bonds with metal atom regardless of conformational preference [11]. Thus, the means of a directed search for intermolecular hydrogen bonding to a metal atom were revealed. The first publication devoted to intermolecular hydrogen bonding of 4-fluorophenol with electron-rich second and third row transition metal atoms, namely, Ru and Os atoms of the metallocenes and Rh atoms of norbornadienylcyclopentadienylrhodium derivatives, appeared in 1990 [12]. The interactions between different proton donors with many sandwich and half-sandwich π-complexes (Cp_2M, Cp^*_2M, M = Fe, Ru, Os; Cp^*ML_2, M = Co, Rh, Ir; L = CO, PR_3) as well as with $ML_2(dppe)_2$ (L = CO, 2H) derivatives were studied by IR spectroscopy in common non or low polar solvents by our group [13]. The meticulous IR study of hydrogen bonding of fluorinated alcohols (R^FOH) to the metal center of Cp*MLCO (M = Co, Rh, Ir; L = CO, PPh_3, C_2H_2, N_2) was performed in supercritical media by Kazarian and Polyakoff [14]. Ionic hydrogen bond formation in several salts between the M atom in the anion and NH group in a cation ($M^-\cdots{}^+HN$) was characterized by Brammer et al. in the solid state [15] and in solution [16a,16b]. The spectral and structural investigations of intra- and intermolecular M···HX HB were compiled in our previous review [10], crystal structures of Co···HX were included in Brammer's review [16b], and the comparison of the hydrogen bond (M···HX) with the agostic interaction was presented in [16c]. The nature, strength, and properties of HBs to metal atoms, and their participation as intermediates in proton transfer are discussed in this review.

2.3. Hydride ligands as unconventional proton acceptors

The idea of possible hydrogen bonding between hydride and acid hydrogen atoms was suggested for the first time by Milstein when studying Ir-H(OH)$(PMe_3)_4$. However, in the crystalline structure the H···H distance was found to be 2.40(1) and was interpreted as "too long" for the interaction to be considered as a normal hydrogen bond [17]. Intramolecular hydrogen bonding to hydride, which has neither unshared electrons nor π-density, was discovered by the Morris and Crabtree groups [18,19]. Therefore, the question whether the steric factors could be the cause of the intramolecular H-bond formation arose again. The answer to the question was given very soon. The intermolecular H···H bond in the solid state was established by the Crabtree group using neutron diffraction [20]. Our group provided the spectral, thermodynamic, and structural data for the MH···HX bonding in solution [21]. Recently, a new family of DHB complexes with HB between the NH^+ group of the crown ethers and the hydride ligand of the polyhydride anions was obtained by Morris et al. [22].

The term "dihydrogen bond" was proposed by Crabtree and the term "hydridic–protonic" bond was introduced by Morris. In this review we use the term "dihydrogen bond" (DHB) to distinguish this type of interaction from the other hydrogen bonds. However, the H···H hydrogen bond possesses the same properties as the classical hydrogen bonds. So, one should not treat the dihydrogen bond as something different from other types of hydrogen bonding.

The particular interest in this type of H-bonding was raised because of the actively studied chemistry of nonclassical hydrides. We will describe below the studies of proton transfer leading to nonclassical polyhydrides through DHB intermediates [23,24].

3. The nature and structure of unconventional hydrogen bonds

Different types of calculations were carried out to elucidate the nature, structure, energy, and particular features of the new unconventional hydrogen bonds in comparison with classical types of HBs. Unfortunately, very little information concerning the structure of the new HBs involving metal atoms was reported. The structures of some ionic ($[M]^-\cdots HN^+$) HB were examined [15,16b,16c]. However, structural data concerning neutral M···HX adducts are absent.

3.1. The M···HX-bond

The nature of the intramolecular interaction of M···HO has been examined by Orlova and Scheiner in theoretical studies devoted to the α-metallocenylcarbinols (M = Fe, Ru, Os). These authors also studied the intermolecular interaction in the $Cp_2Os\cdots HOH$ system [25]. The calculations were performed by extended Huckel (EHT) and two levels of DFT (BLYP and B3PW91). An Fe···H interaction is absent and the strength of HB to electron-rich metals increases down the group: Ru···HO < Os···HO, consistent with indications from IR and X-ray [10]. The authors showed that the lone pairs of *d*-electrons behave as lone pairs of the oxygen atom *sp*-electrons. Similar properties were demonstrated, namely elongation of the H–O bond, and the increase of both the positive charge of the bridging hydrogen ($\Delta q = 0.038$) and the negative charge of the metal atom ($\Delta q = -0.041$). The intermolecular HB Os···H–O appears to have linear geometry. The lower O–H bond overlap in this HB is more significant than that in the intramolecular case (0.05 and 0.02, respectively). The problem of the steric requirements observed experimentally was adequately elucidated by calculations [25]. Experimental crystal structures of the salts involving ionic HB between M atom in the anion and NH bond in the cation confirmed the linearity of XH···M fragment [15,16b].

Interaction of the NH and CH ligands with d^8 square planar metals in the axial direction was examined by Crabtree, Eisenstein and Jia using 50 suitable complexes reported in the literature [26]. The linear arrangement of the N–H···M moiety and short distance 2.11–2.81 Å, which is less than the sum of the van der Waals radii ($< \Sigma$vdW), is typical for HBs (three-center four-electron bonds). However, a less demanding linear preference was found for C–H···M (d^8) weak interactions. The structures are intermediate between HB and true agostic C–H···M for d^6 complexes (two-electron, three-center), so that their nature is uncertain.

The comparative theoretical analysis of the interaction between proton donors and the anionic $Co(CO)_4^-$ and the isoelectronic neutral $Ni(CO)_4$ as proton acceptors has recently been provided by Alkorta, Elguero and Rozas [27]. The calculations carried out by the hybrid DFT–HF method (B3LYP/6-311++G**), as well as the atoms in molecules (AIM) and natural bond orbital (NBO) methods, demonstrated the linearity of M···HX hydrogen bond. The M···H distances are less than ΣvdW: 2.20–2.78 Å for the Co complex and 2.57–2.91 Å for the Ni ones. The HB energies of the anionic Co complexes are much stronger than those of Ni neutral analogues. The energy values of HB with a stronger proton donor HF are −11.26 and −1.23 kcal mol^{-1}, respectively. The values of the protonation energies (−313.9 and −174 kcal mol^{-1}) showed that the anionic compound $Co(CO)_4^-$ is significantly more basic. Therefore it is not strange that the “ionic” HB complex $Co(CO)_4^- \cdots HNEt_3$ is more stable than “neutral” $Co(CO)_4H \cdots NEt_3$ by 5.9 kcal mol^{-1}. This result is in agreement with the experimental data [6] and in disagreement with the previous calculations [28] in which the authors fixed the positions of both the Co and N atoms during the optimization of the complexes. The NBO analysis shows that the charges are transferred from organometallic bases to the HB donor as in the case of organic bases. The electron density (ρ) of $M(CO)_4^- \cdots HX$ complexes calculated by AIM at the bond critical points ($\rho_{BCP} \times 10^{-2}$ a.u.) is typical for common HB. Very large $\rho_{BCP} \times 10^{-1}$ a.u. in the M–H bonds of the protonated forms indicates their covalent types.

Thus, the XH···M bond shows the features similar to the classical H-bond. The lone pairs of *d*-electrons are the sites of coordination. They are comparable to the *sp* lone pairs of organic bases. Therefore, the mention concerning such HB: “the orbital involved in the electronic donation cannot be a lone pair” in [27] could only be a misunderstanding. The structural properties, namely elongation of the X–H bond, the short H···M distance, and the linearity of X–H···M moiety, are common for the new and the traditional HB.

3.2. *The MH···HX bond*

Theoretical calculations on DHBs were performed extensively during the past years. Three reviews [28–30] covering both experimental and theoretical work were added to those published in 1996–1998 [10,31a,32]. The new reviews by Alkorta et al. [28] and Maseras et al. [29] are only devoted to the theoretical studies, but the review by Custelcean and Jackson [30] includes experimental information concerning the structure, the energetics, and dynamics of DHB. The crystal structures of DHB are collected in a number of reviews [4a,30,31a,32] so that we will not discuss them in detail here.

The main characteristics of DHB nature will be analyzed in Sections 3.3, 3.4, 3.5 and 3.6.

3.3. *The electrostatic component of the total energy is the greatest*

The driving force of DHB formation is the electrostatic attraction between the partly negative hydride hydrogen and the partly positive hydrogen atom of proton donors $MH^{\delta-} \cdots {}^{\delta+}HM$. Bakhmutov and Berke suggested the semiquantitative method for determination of the M–H ionic character on the basis of deuterium quadrupole coupling constants (DQCC) [33]. Theoretical values of the charges for the first row simple transition metal dihydrides (MH_2) were recently reported by Platt [34]. The charges (AIM) of H are negative, varying from $q(ScH_2) = -0.655$ to $q(NiH_2) = -0.149$, respectively. Therefore, the M–H bond becomes less polar and more covalent across the row, but the hydrogen atoms maintain their hydridic character.

The greatest role of the electrostatic energy is similar to that in the classical HB. Liu and Hoffman calculated the H···H interaction for the model systems FH···HLi and HF···HMnL$_n$ concluding that the attractive H···H interaction is mainly electrostatic by the EHT method [35]. Orlova and Scheiner have carried out DFT and HF/3-21 calculations on PH_3 analogous of MH···HX DHB which have been studied experimentally, namely $MH(NO)(CO)_2(PH_3)_2$ (M = W, Mo) [36a,21a],

Table 1
Energy components in kcal/mol for HB and DHB complexes [36a]

Structure	E_{ES}	E_{EX}	E_{PL}	E_{CT}	E_{MIX}	ΔE	Decomposition, CT		Decomposition, PL	
							Accept.	HR	Accept.	HR
HNO.HF	−6.22	3.76	−0.77	−1.74	0.04	−4.94	−1.60	−0.14	−0.68	−0.06
LiH.HF	−13.24	7.95	−2.75	−3.17	0.69	−10.52	−3.05	−0.12	−2.65	−0.38
HNO.H_2O	−3.06	1.69	−0.26	−1.02	−0.02	−2.66	−0.96	−0.06	−0.19	−0.02
LiH H_2O	−10.97	7.88	−1.13	−2.42	0.36	−6.67	−1.48	−0.93	−0.68	−0.36

Cp*ReH(NO)(CO), CpRu(H)(CO)PH_3 [36b,21c,21d], Ru(H)(H)$(PH_2CH_2PH_2)_2$ [36c,24a] interacting with several HX (HF, H_2O, and $HOCF_3$). The Mulliken charges on the H atoms of the HX are naturally positive but on the hydrides may be inappropriate (positive) depending on the basis set but it always become negative during dihydrogen bond formation. For example, the charges in the system Mo(W)H···HF are equal to -0.05 H(M) and $+0.440$ H(F) [36a].

The authors [36a] used Kitaura–Morokuma decomposition analysis of the bond energy contributions for the simple HNO···HX and LiH···HX models comparing the various energetic components in classical and dihydrogen bonds (Table 1). The electrostatic energy (ES) makes the largest contribution to the total energy of the MH···HX bond, like that in classical H-bonds. The conventional (O···HX) hydrogen bond is classified as "ES > CT" since the electrostatic component is more important than the charge transfer (CT) component, while the contribution of the polarization energy (PL) is considerably smaller [36a]. However, the contribution of the polarization energy is considerably larger for the DHB relative to the classical cases. Therefore, the DHB energy might be termed as "ES > PL ≈ CT". It should be noted that the ES component as well as the total energy for the LiH···HX interaction is somewhat larger than that for HNO···HX. This difference is in agreement with our experimental data on the smaller proton accepting ability of the NO ligand relative to the hydride ligand in rhenium dihydride complexes [21a].

Although the subject of this part of the review is DHB with transition metal hydrides, we need to consider the results from theoretical study for the hydrides of the main group elements. The electron rich transition metals, as was mentioned above, can form hydrogen bonds of the M···HX type using *d* electrons. Therefore, the metal and the hydride ligand can compete with each other to form the HB. On the other hand, the interaction with a hydride ligand can be complemented by the participation of *d* electrons in dihydrogen bonding. The investigation of DHB to hydrides of the main group elements (without occupied *d* orbital) as models can elucidate the effect of *d* electrons. The DHB to boron hydrides have been examined significantly more than any other main group element hydrides [31,37]. Limited information concerning DHB formed by hydrides of other elements (E = Al, Ga, Be, Li, Na, Xe) is collected in Ref. [30]. Most of these H-complexes have been studied only theoretically so far.

Many different studies were devoted to the structure and the nature of the $(H_3NBH_3)_2$ dimer. Using the Cambridge Structural Database of aminoboranes, Crabtree et al. considered DHB as an attractive electrostatic interaction with the entire σ-bond B–H because the B atom in the calculation (PCI-80/B3LYP) was determined to be negative ($q = -0.26$) [31b]. Theoretical studies (HF/6-31G) of the $(H_3NBH_3)_2$ dimer as well as DHB of BH_4^- and BH_3NH_3 with proton donors (H_2O or MeOH and of BH_4^- with HCN) allowed us to make other conclusions in agreement with our spectroscopic data [37]. The calculations revealed an attractive electrostatic interaction between the positive hydrogen atom of the proton donor ($q_H = 0.43$–0.47) and the negative hydride atom ($q_H = -0.27$–(-0.15)) involved in the $B\text{–}H^{\delta-}\cdots{}^{\delta+}H\text{–}X$ moiety. A very interesting approach based on the AIM Bader's methodology was applied to DHB by Popelier [38]. The set of criteria used on the basis of the electron density, which successfully described conventional H-bonds (and, as was shown above, H-bonds to the metal atoms [27]), appears to be applicable to DHB too. Boron atoms are stable as electron-deficient atoms in any system and at any level of calculation they have positive charges with the hydridic atoms being negative [38].

3.4. The elongations of the proton donor bond X–H and proton acceptor bond H–M(E) are similar to classical HB of medium strength

The elongations of the proton donor X–H bond and proton acceptor H–M or H–B bonds were obtained as in the case of classical systems (e.g. C=O···HX) [1c]. The amounts of the stretches of the X–H and M–H bonds are variable and for the systems MH(NO)$(CO)_2(PH_3)_2$/HX (M = W, Mo) they may be as large as 0.04 Å [36a]. The X–H and B–H bonds also stretch out during the BH···HX bonding [37]. N–H bonds involved in the H···H DHB are longer in the dimers $(NH_3EH_3)_2$ (E = B, Al, Ga) than those in the monomers by about 0.01 Å by calculations at the MP2/

Table 2
B3PW91 and HF/3-21 results for some DHB

Complex	$R_{H\cdots H}$ (Å)	ΔR_{HX} (Å)	$-E_{HB}$ (kcal mol^{-1})	Ref.
$Mo(NO)(CO)_2(PH_3)_2H\cdots HF$	1.378	0.040	11.1	[36a]
$Mo(NO)(CO)_2(NH_3)_2H\cdots HOH$	1.647	0.013	13.1	[36a]
$Cp^*Re(CO)(NO)H\cdots HOH$	1.770	0.006	0.9	[36a]
$CpRu(CO)(PH_3)H\cdots HOCF_3$	1.458	0.042	9.8	[36b]
$LiH\cdots HF$	1.611, 1.371^{a}	0.021	10.93, 12.62^{a}	[41]
$HMgH\cdots HF$	1.582^{a}	0.012^{a}	6.02^{a}	[41]
$CpRu(CO)(PH_3)H\cdots HOC(CF_3)_3$	1.654	0.017	9.7 [5.6 in heptane]	[42]
$CuH\cdots HF$	1.692^{a}	0.013^{a}	6.8	[43]

[a] Results of MP2/6-311++G** methods.

cc-pVDZ level [39]. Ab initio calculations (MP2/6-311+G(d,f)) were performed recently for the new complex of the rare gas dihydride XeH_2 with water [40]. This DHB complex $HXeH\cdots HOH$ has a planar geometry with an elongated O–H bonded group. Some examples of ΔR_{HX} values are presented in the Table 2.

The short $H\cdots H$ distances calculated by different theoretical methods for different systems are as a rule in the range: 1.61–2.1 Å $<\Sigma vdW = 2.4$ Å. This range, except for some small values (1.35–1.40 Å) which appeared owing to a poor basis set, is close to the values obtained by crystal structure studies by X-ray and neutron diffraction, as well as in solution NMR experiments (T_{1min}) (see below). For example, the short $H\cdots H$ distance (1.781 Å) calculated for $(H_3NAlH_3)_2$ is less than that for $(H_3NBH_3)_2$ (1.990 Å) [39]. The data concerning the computed $H\cdots H$ bond length and the energy of the DHBs in some $MH\cdots HR$ complexes are listed in Table 2.

The DHBs energy values correspond to a medium strength H-bond. The probable cause of overestimation of the calculated energy for many systems may be a poor basis set or different conditions for the calculations (gas phase) and experimental measurements (DHB in solution or in the solid state). In the calculation of the $XeH\cdots HX$ bond the energy changes from 16.5 to 9 kcal mol^{-1} (from strong to medium) depending on the basis set chosen [40]. The energy values of $Mo(CO)_2(NO)(PH_3)_2H\cdots HF$ obtained by different DFT methods are 10.5–14.7 kcal mol^{-1} [36a] (Table 1). However, the experimental values are less than 7.5 kcal mol^{-1} [21a]. The energy of the $(Cp)Ru(CO)(PH_3)H\cdots HOC(CF_3)_3$ interaction was calculated not only in the gas phase but taking into account the solvent polarity [42]. The ΔE value found for the gas phase is -9.7 kcal mol^{-1}, in n-heptane solution is -5.6 kcal mol^{-1}, and for CH_2Cl_2 solution is -2.4 kcal mol^{-1}. Thus, the calculated interaction energy decreases when the solvent polarity increases. Furthermore, the ΔE value for n-heptane is in reasonable agreement with the experimental ΔH value in the hexane (-7.3 kcal mol^{-1}) [44].

3.5. *The increase in the positive partial charge of the hydrogen atoms ($X–H^{\delta+}$) as well as the negative charge of hydride atom leading to mutual polarization of both components*

An increase in the positive charge of the hydrogen atoms ($X–H^{\delta+}$) and the negative charge of the hydride ($^{-\delta}HM$) or ($^{-\delta}HB$) was observed. The charges increase by the same amount in $BH\cdots HX$ during DHB formation [37a]. For instance, upon dimerization of BH_3NH_3 the charge of H(N) increases from 0.43 to 0.50 and that of H(B) changes from -0.43 to -0.45 (MP2 method) [38]. The examples of the dependence of the polarization during DHB formation for the simple systems $MH\cdots HF$ (M = Cu, Ag, Au) on the calculation methods was demonstrated in [43]. A very small but positive overlap population (0.005–0.021) appears between the H atoms indicating the covalent component of DHB [37a]. The overlap population of the $H\cdots H$ bond in the DHB $MH\cdots HF$ is 0.06 which is about twice as big as the overlap population in the system including the weaker proton donor, namely $MH\cdots HOH$ (M = Mo, W) [36a].

3.6. *The linear arrangement of the $X–H\cdots B$, $X–H\cdots M$ and $X–H\cdots H$ (M) or $X–H\cdots H$ (B) fragments as characteristic of unconventional and classical H-bonds*

The linear arrangement of the fragments $X–H\cdots B$, $X–H\cdots M$ and $X–H\cdots H$ (M) or $X–H\cdots H$ (B) was estimated in the theoretical studies of the classical and the unconventional H-bonds. The first publication of Hoffman showed a linear arrangement of the $X–H\cdots H(M)$ moiety (M = Li, Mn). The $X–H\cdots H$ angles are equal to 179–172° [35]. Crabtree and coworkers discussed originally the interaction between N–H and B–H groups as a bent hydrogen bond from the N–H donor to the B–H σ-bond acceptor [31a,31b], namely featuring bent $N–H\cdots H$ (B) and approximately linear $B–H\cdots H$ (N) fragments. The incorrect conclusion of the theoretical study resulted from the misassignment of the B and N atoms in the X-ray study of the hydride dimer $(BH_3NH_3)_2$. The latest Crabtree, Koetzle et al. neutron diffraction study [31c] cleared up this error and established a linear N–H···H (B) arrangement with a short r(H···H) distance (2.03 Å) as well as a bent B–H···H moiety (106°). Cramer and Gladfelter using HF, DFT or MP_2 methods arrived at another-C_{2h} structure of this dimer with the bifurcated DHB, r(H···H) = 1.990A, N–H···B and B–H···N angles equal to 144.8 and 88.6, respectively [39]. According to results of Popelier [38], there are no large deviations from 180° of the N–H···H angles (less than 15°) in $(BH_3NH_3)_2$. These differences in the theoretical structure for the dimer $(BH_3NH_3)_2$ arise from the different levels of theory and the flat potential energy surface [31a,31b,38,39]. However, the assertion of the authors of the review [30] that the "N–H vector points toward the middle of the B–H bond" is incorrect. DHB is characterized in the best and modern calculations as that close to linear X–H···H and bent M–H···H or B–H···H arrangement [31c,38,43]. For example, the deviations from linearity of the F–H···H fragment in MH···HF (M = Cu, Ag) are less than 14°. The angles M–H···H in these DHBs are bent (about 100°) [43]. Bent M–H···H and B–H···H moieties are very convenient for the interaction with stronger proton donors in which the hydride molecule is susceptible to proton transfer and side-on dihydrogen ligand formation.

3.7. The similarity of the theoretical correlations between H···H distances and energetic parameters

Using high-level ab initio calculations, Grabowski found the relationships between the H-energy and the H···H distance as well as that between the H–F bond length and H···H distance to be similar to the corresponding relationship for the OH···O classical system [41]. Different high–level theoretical calculations of the simple systems: HF···HE (HE = LiH, NaH, BeH_2, MgH_2 et al.) also included the AIM method. A linear relationship was obtained between the electron density critical point for H···H contact (ρ_c) and the DHB energy, thereby creating a new parameter sensitive to the strength of DHB and suitable for its estimation. Unfortunately, there are no experimental data so far to confirm these correlations.

In conclusion, the nature of the hydrogen bonding to a hydride ligand in organometallic and in boron hydrides is similar indicating no *d*-electron effect in the former case. Both types of H···H interactions are similar to conventional hydrogen bonds, the only difference being an increase of the polarization component of the interaction energy for the dihydrogen bond.

4. Spectral definitions of different H-bonding types

4.1. IR, NMR spectral indications of hydrogen bonding

The analogy between unconventional and classical hydrogen bonding is reflected in similar spectral properties. The most typical IR spectral characteristics of conventional hydrogen bond formation are the changes in the XH-stretching vibration bands of the proton donors, namely the appearance of a low frequency broad and intense $\nu_{XH(bonded)}$ band. These changes become more pronounced with an increase of the proton-donating ability (acidity). All spectral characteristics of the $\nu_{XH(bonded)}$ bands, namely the frequency shift $\Delta\nu$ ($\nu_{(free)} - \nu_{(bonded)}$) and the integral intensity enhancement ΔA, increase with the strength of the proton donors [1]. The same situation is observed in the case of organometallic bases [10,14,21,32].

The ^1H NMR spectra of XH-acids in the presence of organic and organometallic bases exhibit downfield chemical shifts of the HX proton signal similar to those observed in the presence of organic bases. This approach is used in most work to establish HB in organometallic chemistry [18,19,16b,21c,32].

4.2. Determination of the coordination site

In order to determine the site of HBs in organometallic complexes such as M atoms and ligands CO, NO, M–Hal M–H and the others, all appropriate ligand stretching vibrations in IR spectra should be investigated. The direct evidence for the hydride ligand being the proton-accepting site in the DHB (MH···HX) is 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. The evidence for the metal atom being the proton-accepting site (M···HX) is the appearance of new high-frequency bands (or shoulders) for all the ligands stretching vibrations of the organometallic complexes.

The formation of HB with a metal atom (M···HX) for the complexes with carbonyl ligands Cp*MLCO, (M = Co, Rh, Ir; L = CO, PR_3) was confirmed by a high frequency shift of ν_{CO} bands (10–20 cm^{-1}) in contrast to the low frequency shifts characteristic of hydrogen bonding directly to the ligand (CO···HX) [13d,14]. Analogous changes occur in the case of ionic HBs. The hydrogen bonded salt $NH^+ \cdots Co(CO)_4^-$ shows ν_{CO} bands shifted to higher frequency relative to those of the free anion $Co(CO)_4^-$ [16].

The formation of a DHB between a fluorinated alcohol (HFIP) and $WH(CO)_2(NO)(PEt_3)_2$ leads to the appearance of a new low-frequency shoulder (at about 1640 cm^{-1}) shifted by 40 cm^{-1} from the initial hydride ν_{W-H} at 1670 cm^{-1} [21a]. In the case of DHB of $[MeC(CH_2PPh_2)_3]Ru(CO)H_2$ with R^FOH the ν_{Ru-H}

band shifts to lower range from 1871 to 1851 cm^{-1} [23d].

The efficiency of these criteria for the determination of the HB sites could be demonstrated using Re hydrides as an example. For NP_3ReH_3 [$NP = N(CH_2CH_2PPh_2)_3$], the high frequency position of the ν_{ReH} bands in the presence of alcohols suggests the existence of hydrogen bonding to the metal atom [45]. The classical hydrogen bonds OH···ON and OH···Cl were observed for $ReH_2(NO)CO(PiPr_3)_2$ and $ReH(Cl)(NO)(CO)(PMe_3)_2$. The bands of ν_{NO} and ν_{ReCl} shift to low frequency ranges ($\Delta\nu$ 20–50 cm^{-1}) [21b,23c]. In the case of $ReH_2(NO)CO(PEt_3)_2$ the coexistence of two types of H-complexes were observed. The low frequency ν_{MH} shoulder and high frequency NO are assigned to XH···HRe DHB. The additional low frequency NO band corresponds to NO···HX [23c]. The same picture in the ν_{NO} range was observed for the interaction of Cp*ReH(CO)(NO) with R^FOH, but an ν_{ReH} band cannot be observed in the IR spectra. In this case, as well as in many others, the conclusion confirming DHB formation can be made by using the NMR spectra (for example $[MeC(CH_2PPh_2)_3]Re(CO)_2H$ [23a] or $CpRuH(CO)PCy_3$ [44]).

NMR spectroscopy is more widely used in DHB studies. The main NMR spectral criteria for DHB bonding are a small upfield shift of the hydride atom signal and a decrease of the relaxation time (T_{1min}). The upfield drift of the broad average signal depends on the temperature and concentration of the alcohol and it usually constitutes of $-0.2 \div -0.8$ ppm at 200 K in the presence of an excess of a proton donor [23a]. Berke et al. studied the HB between $H_2Re(CO)(NO)(PR_3)_2$ and R^FOH in different solvents by NMR and showed the regioselectivity of hydrogen bonding with a weak proton donor. The coordination site is the hydrogen ligand located opposite the nitrosyl group owing to its strong *trans* effect [46].

Unfortunately, H-bond formation is fast on the NMR time scale, resulting in the coalescence of the free and bonded M–H signals even at 190 K. The MH HX study in liquid freons allowing us to reach very low temperatures (down to 90 K) is quite promising [21c]. This approach developed by Golubev and Denisov [47a] turned out to be very effective for organic HB examination [47b]. The NMR study of the system $Cp^*ReH(CO)(NO)/R^FOH$ in a CDF_3/CDF_2Cl mixture at 96 K made it possible to observe decoalescence of the hydride resonance into two signals (at $\delta = -7.54$ and -8.87) corresponding to the free Re–H of the initial hydride and the ReH···HO of HB complex, respectively [21c].

A linear correlation between the hydride signal upfield shift and the quantum exchange coupling was established for polyhydrides by Chaudret and Limbach [24]. This correlation indicates that the quantum exchange coupling can be used as an additional sensor of dihydrogen bond formation, its strength, and geometry. This method was applied for the first time to the interaction of proton donors with $Cp^*RuH_3(PCy_3)$ in d_8-toluene or in a freon mixture [24a]. The value of the hydride signal J_{ab} constant is about 80 Hz for the free hydride which increases to 220 Hz in the presence of the R^fOH excess in both solvents.

Another very sensitive criterion for dihydrogen bonding is a decrease of the spin-lattice longitudinal relaxation time (T_{1min}) of the hydride signal. Moreover, the T_1 measurement is a reliable approach for determination of H···H distance. Thus a proton donor closer to H–M induces a faster relaxation (shorter T_1) for the hydride signal. The r(H···H) distance can be calculated by analogy to the method used for η^2-H_2 complex [48]. This method of H···H distance determination has been used by the groups of Morris [18] and Crabtree [19] for a number of compounds containing intramolecular XH···HM DHBs. The authors found short H···H distances of about 1.8 Å in all cases. This approach was also successfully used for intermolecular DHB in solutions of $WH(CO)_2(NO)(PMe_3)_2$/HFIP (1.77 Å) [21a], $H_2Re(CO)_2(NO)(PMe_3)_2$/PFTB (1.85 Å) [20b], $[MeC(CH_2PPh_2)_3]$ $Re(CO)_2H$/PFTB (1.83 Å) [23c], and $[MeC(CH_2PPh_2)_3]Ru(CO)H_2$/HFIP (1.81 Å) [23d].

5. Thermodynamic properties of M···HX and MH···HX bonds

5.1. Methods of estimating M···HX, MH···HX bonds enthalpy values

The enthalpies of intermolecular M···HX, MH···HX hydrogen bonding ($-\Delta H^\circ$) can be determined by means of empirical correlation Eqs. (1a), (2a) and (3a) connecting $-\Delta H^\circ$ with $\Delta\nu_{XH}$ and integral intensity (A_{OH}) obtained by analysis of organic HB systems by Iogansen [49].

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

$$-\Delta H^\circ = 0.30(\Delta\nu)^{1/2} \quad (2a)$$

$$-\Delta H^\circ = 2.9(\Delta A)^{1/2} \quad (3a)$$

Correlation 1a is considered to be more general and applicable in the range of 0–2000 cm^{-1} while, Eq. (2a) is limited to $\Delta\nu > 200$ cm^{-1}. The author considers the best relationship to be 3a. It was found that relationship 3a was valid for different types of H-complexes from homo- and heteroassociates in solution or in the gas phase to polymer chains (or cycles) of hydrogen bonds in crystals and associated liquids in the range $-\Delta H^\circ =$ 0.1–15 kcal mol^{-1}. The correlations between ΔH° and $\Delta\nu$ in Eqs. (1a) and (2a) have a lower accuracy. However, since the measurements of shift values are

Table 3
Thermodynamic characteristics of hydrogen bond formation

[MH]	HX[a]	HB type	solvent	$-\Delta H^{\circ b}$	$-\Delta H^{\circ c}$	$-\Delta S^{\circ c}$	Ref.
$Cp^*Ir(CO)_2$	HFIP	Ir···H	Heptane	5.9(6.0)	6.2	19.1	[14b]
$N(CH_2CH_2PPh_2)_3ReH_3$	TFE	Re···H	CH_2Cl_2	6.3	5.9	13.5	[45]
$WH(CO)_2(NO)(PEt_3)_2$	HFIP	H···H	Hexane	5.1(5.3)	4.9	9.8	[21a]
$ReH_2(CO)(NO)(PMe_3)_2$	PFTB	H···H	Hexane	5.8(6.1)	5.8	6.3	[21b]
			C_7D_{14}		6.2^d	12.4^d	[46]
			Toluene-d_8		3.1^d	10.0^d	[46]
$[MeC(CH_2PPh_2)_3]Ru(CO)H_2$	HFIP	H···H	CH_2Cl_2	6.6	6.7	19.6	[23d]
			CD_2Cl_2		7.1^d	19.0^d	
$CpRuH(CO)PCy_3$	PFTB	H···H	Hexane		7.6	21	[44]
$ReH_2(CO)(NO)(^iPr_3)_2$	PFTB	NO···H	Hexane	4.5	4.5	13.8	[23c]
$ReHCl(CO)(NO)(PMe_3)_2$	PFTB	Cl···H	Hexane	6.0	5.7	9.6	[23c]

[a] HFIP-$(CF_3)_2CHOH$, PFTB-$(CF_3)_3COH$, TFE-CF_3CH_2OH.

[b] $-\Delta H^\circ$ (kcal mol^{-1}) obtained by means of Eqs. (1a), (2a) and (3a).

[c] $-\Delta H^\circ$ (kcal mol^{-1})$-\Delta S^\circ$(e.u.) obtained by van't Hoff's method from IR experiments.

[d] $-\Delta H^\circ$ (kcal mol^{-1})$-\Delta S^\circ$(e.u.) Obtained by van't Hoff's method from NMR experiments.

usually simpler, these proportionalities are widely used for organic bases. All of these equations appeared to be successfully applicable to characterize HB between different proton donors and organometallic complexes. The similarity between the enthalpy values calculated from Eqs. (1a), (2a) and (3a) and those obtained from the temperature dependence of formation constants (van't Hoff's method) proves that the correlation equations are correct for the M···HX and MH···HX bonds (Table 3). It is noteworthy that the thermodynamic parameters obtained from NMR experiments by using the same solvents are in good agreement with those obtained from IR data ($-\Delta H^\circ = 7.1$, 6.7 kcal mol^{-1}, $-\Delta S^\circ = 19.0$, 19.6 e.u., respectively) [23d]. All of the enthalpy values of MH···HX and M···HX complexes correspond to medium strength H-bonds (4–7.6 kcal mol^{-1}). The calculated entropy values ($-\Delta S^\circ = 6.3$–21 e.u.) are in the same range found for H-bonds in organic systems.

The ΔH° values depend on the basicity of organometallic compounds in H-complexes with a common proton donor. For example: the ΔH° values of H-complexes of $Cp^*M(CO)_2$ with PFTB decrease in the row $Cp^*Ir(CO)_2 > Cp^*Rh(CO)_2 > Cp^*Co(CO)_2$ [14a]. The enthalpy values of MH···HX and M···HX depend on the proton donating ability of XH acids MeOH < CF_3CH_2OH < PhOH < $(CF_3)_2CHOH$ < 4-$NO_2C_6H_4$-OH < $(CF_3)_3COH$ [10,21d] and solvents (Table 3). Therefore, this parameter ($-\Delta H^\circ$) is not convenient for comparison of the ability of organometallic compounds to form HB.

5.2. Basicity factors of organometallic bases

A very simple and effective approach for comparison of the proton accepting ability of different sites is the so-called "rule of factors" introduced by Ioganssen as a result of analysis of a large array of spectroscopic and calorimetric data [49,50]. The empirical correlation assumes constant acidic (P_i) and basic (E_j) properties in HB formation. The basicity factors E_j for metal atoms and hydride ligands were calculated from Eq. (4a)

$$E_j = \Delta H^\circ_{ij}/\Delta H^\circ_{11}P_i, \tag{4a}$$

where ($-\Delta H^\circ_{ij}$) is experimental enthalpy data, ($-\Delta H^\circ_{11}$) refers to the phenol diethyl ether pair taken as a "standard", for which the basicity and acidity factors are taken as unity: $P_i = E_j = 1$. P_i values for proton donors are presented in [50].

Therefore, the E_j factors summarized in Table 4 characterize the proton accepting ability of the coordinating sites of organometallic bases. The values of E_j obtained from this rule are really independent of the nature of proton donors and the medium [10,21,23]. The E_j values of the hydride ligands increase with the increasing of the proton accepting ability of the hydride hydrogen over the wide range from 0.6 to 1.6, comparable with the E_j values of the M atoms in organometallic complexes. All of the E_j factor values are considerably larger than those of the aromatic compounds ($E_j < 0.4$) [10]. The most basic hydrides have E_j values greater than DMSO ($E_j = 1.27$) and comparable with pyridine ($E_j = 1.67$) [49a].

The E_j factor is a very good indicator of the electron density distribution in the ground state of the proton acceptor owing to the small changes induced by H-bonding. Complete proton transfer, on the other hand, demands covalent bond formation and a significant electronic and geometric reorganization, so that its parameters (pK_a or $-\Delta H$ of the protonation reaction) depend on the differences between the starting base and the protonation product. Relations of this kind between H-bonding (E_j or $-\Delta H$) and protonation parameters (pK_a or $-\Delta H$ of the protonation) were obtained for

Table 4
Basicity factors of hydrogen bonding sites of organometallic compounds

Compounds	E_j	Ref.	Compounds (site of HB)	E_j	Ref.
(Site of HB) (M) (M)					
$CpCo(CO)_2$	0.62	[14a][a]	$Cp^*Co(CO)_2$	0.84	[14a][a]
Cp_2Ru	0.67	[13c]	Cp^*_2Ru	0.85	[13c]
Cp_2Os	0.81	[13c]	Cp^*_2Os	1.05	[13c]
$CpIr(CO)_2$	0.84	[14a][a]	$Cp^*Ir(CO)_2$	0.99	[14][a]
$CpRh(CO)PMe_3$	1.00	[14a][a]	$Cp^*Rh(CO)_2$	0.94	[14][a]
$Mo(CO)_2(dppe)_2$	1.24	[10]	$W(CO)_2(dppe)_2$	1.39	[10]
$WH_4(dppe)_2$	1.20	[7c]	$N(CH_2CH_2PPh_2)_3ReH_3$	1.45	[45]
(Site of HB) (H) (H)					
$WH(CO)_2(NO)(PPh_3)_2$	0.70	[21a]	$ReH_7(dppe)$	0.54	[20a][a]
$WH(CO)_2(NO)(PO^iPr_3)_2$	0.72	[21a]	$ReH_5(PPh_3)_3$	0.63	[20a][a]
$WH(CO)_2(NO)(PEt_3)_2$	0.87	[21a]	$ReH_2(CO)NO(PMe_3)_2$	0.80	[23c]
$WH(CO)_2(NO)(PMe_3)_2$	0.91	[21a]	$[MeC(CH_2PPh_2)_3]Re(CO)_2H$	0.97	[23a]
CpRuH(CO)PCy3	1.0	[44]	$P(CH_2CH_2PPh_2)_3FeH_2$	1.0	[51]
$RuH_2(dppm)_2$	1.4	[24a][a]	$P(CH_2CH_2PPh_2)_3RuH_2$	1.33	[51]
$[MeC(CH_2PPh_2)_3]RuH_2(CO)$	1.39	[23d]	$P(CH_2CH_2PPh_2)_3OsH_2$	1.60	[51]
Compounds (site of HB)					
Et_2O (O)	1.0	[49a]	Benzene (π-system)	0.38	[10]
DMSO (O)	1.27	[49a]	$ReH_2(CO)NO(PPr_3)_2(NO)$	0.60	[23c]
Py (N)	1.67	[49a]	$ReH(Cl)(CO)(NO)(PMe_3)_2(Cl)$	0.79	[23c]

[a] E_j values were calculated by using $\Delta\nu_{XH}$ values from these references.

organic systems and showed a linear character, but only within a given class of organic bases [52]. It would be very interesting to analyze the relationships between the basicity factor and the parameters associated with the complete proton transfer for different classes of organometallic bases.

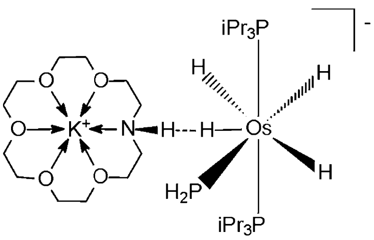
Recently several reviews were published collecting all the data concerning pK_a of different classical hydrides and dihydrogen complexes [3–5]. Different solvents such as MeCN, DMSO, and CH_2Cl_2 were used for the pK_a determination. However, these solvents have significant restrictions (CH_3CN is a better ligand than η^2-H_2 and can substitute H_2; DMSO is an oxidizing solvent; CH_2Cl_2 tends to react with nucleophilic hydrides). The general semiquantitative scale of pK_a^{THF} for many hydrides and dihydrogen complexes was proposed recently by Morris [4b]. It helps to understand the effect of the metal atoms and ligands on the acid strength as well as to unify the various acid–base scales. Angelici and co-workers have ranked the acidity and the bond dissociation energies of about 50 cationic hydrides by protonating neutral metal complexes in CH_2ClCH_2Cl with triflic acid and measuring the enthalpy of the reaction [53]. The basicity factor of the hydrogen bonding of organometallic compounds can be compared with the basicity of the organometallic bases by means of the pK_a value of the conjugate acids. We tried to analyze the pK_a data of the conjugate acids or the $-\Delta H$ values of protonation with the proton accepting ability (E_j) of organometallics. Unfortunately, there are only limited comparable literature data to enable us to estimate the influence of the nature of the metal atom and the ligand environment on E_j, pK_a and $-\Delta H$ of protonation.

5.2.1. The dependence of basicity factors on the nature of metal atom

The effect of the nature of the metal atom can be elucidated by analyzing the E_j factors of complexes with isostructural ligand environments, i.e. E_j factors of transition metal atoms in M···HX HB of the isostructural compounds increase on moving down the group, i.e. Ru < Os, Co < Rh < Ir, Mo < W (Table 4), as well as ΔH values of protonation [53] and pK_a of conjugate acids [3a]. However, differences in the order of E_j and the ΔH were found for the metal carbonyls $M(CO)_2(dppe)_2$, (M = Mo, W). In contrast to E_j values (Mo < W) (see Table 4) the $-\Delta H$ values of protonation change in the reverse order: Mo > W (27.4 and 25.1 kcal mol^{-1}) [53d]. Such a contradiction seems to be caused by *cis–trans* rearrangement accompanying the protonation reaction. Therefore, HB not causing rearrangement of the initial base reflects more precisely the electron density distribution in the initial molecule.

The same trend was established for the E_j of the hydride ligand of the $[P(CH_2CH_2PPh_2)_3]MH_2$ hydrides of the iron subgroup in DHB. The basicity factor E_j increases down the group: 1.0 [H(Fe)] < 1.33 [H(Ru)] < 1.6 [H(Os)] [51]. The pK_a values for the closely related conjugate acids $[MH(H_2)(PMe_3)_4]^+$ (M = Fe, Ru, Os) increase in the same row [54].

Another situation was observed in the case of DHB between anionic hydrides and crown compounds. Using the (aza-crown)potassium cation as a hydrogen-bond



Scheme 2.

donor with $[K(aza\text{-}crown)]^+BPh_4^-$ and the (diazacrown)potassium cation as a dual hydrogen-bond donor, Morris et al. obtained good examples of complexes DHB exhibiting (Scheme 2) [22]. The spectral parameters ($\Delta\nu_{NH}$) and the H···H distances indicate that the DHB strengths of $[K(QNH)]^+[MH_5(P^iPr_3)_2]^-$ and $[K(QNH)]^+[MH_3(CO)(P^iPr_3)_2]$ (M = Ru, Os) decrease down the group (Ru > Os).

The pK_a order of conjugate acids $MH_6(P^iPr_3)_2$, $MH_4(CO)(P^iPr_3)_2$ change in the same order. The authors explain this order of pK_a by the different structures of the Os and Ru neutral hydrides. Thus, the Os complex $MH_4(CO)(P^iPr_3)_2$ has an elongated H–H distance (1.14 Å) while the Ru complex has a short H–H distance (0.88 Å) according to the T_{1min} and J_{HD} data [4b]. The ruthenium dihydrogen complexes are thought to be less acidic than the corresponding osmium complexes owing to the stronger (shorter) H–H bond [4b]. This explains why the dihydrogen complex $Ru(\eta^2\text{-}H_2)_2(H)_2(P^iPr_3)_2$ is less acidic than the classical hexahydride $OsH_6(P^iPr_3)_2$. However, this conclusion cannot explain why the proton accepting ability of ruthenium hydride is larger than that of osmium hydride.

5.2.2. The dependence of basicity factors on the ligand electronic effects

The increase of electron donor ability of ligand leads to an increase of the OH···M bond strength. Permethylation of the rings in metallocenes increases the proton acceptor ability of the metal more than the nature of the metal atom. Thus the following sequence of E_j factors was obtained: $Cp_2Ru < Cp_2Os < Cp_2^*Ru < Cp_2^*Os$. Replacement of carbonyl ligands by phosphine ones increases the proton acceptor ability of the rhodium atom in $CpRh(CO)_2$ so much that it becomes greater than that of iridium. Similar changes are caused by replacement of Cp by Cp*. Thus, the order of E_j is the following: $CpCo(CO)_2 < Cp^*Co(CO)_2 \approx CpIr(CO)_2 < Cp^*Rh(CO)_2 < Cp^*Ir(CO)_2 \approx CpRh(CO)(PPh_3)$ (Table 4). The same sequence is observed for the protonation enthalpy values (ΔH_{HM}) or the pK_a values, namely: $Cp^*Ir(CO)_2 < CpIr(CO)PPh_3$, $CpIr(COD) < Cp^*Ir(COD)$ [53]. Replacement of two hydride ligands by CO ligand leads to the enhancement of E_j factors of metals: $MH_4(dppe)_2 < M(CO)_2(dppe)_2$. The same effect of isoelectronic ligands on metal complex basicity was found by Angelici [53d].

The E_j factor of hydridic hydrogen significantly depends upon the electronic and steric effects of phosphine ligands. The E_j factor for $WH(CO)_2(NO)(PR_3)_2$ increases in the order $PPh_3 < P(O^iPr)_3 < PEt_3 < PMe_3$ as a result of changes of the phosphine ligand, cone angle, and basicity [21a]. A stronger donation is expected to increase the proton accepting properties of the hydride ligand. Note that the first two phosphines give very similar E_j values (0.70 and 0.72), whereas the E_j of the complexes with PEt_3 and PMe_3 is much greater (0.87 and 0.91) [21a].

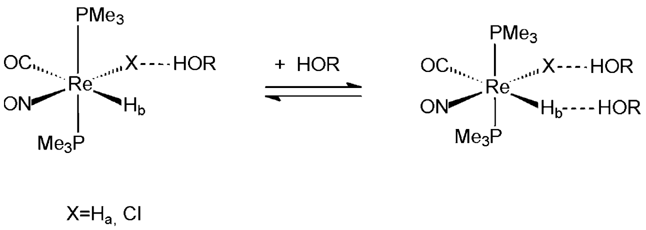
The strengths of DHBs depend on the *trans* effect of the others ligands *trans* to the hydride ligands. Crabtree showed that the H···H interaction energy decreases when a more electron withdrawing ligand is placed *trans* to hydride in the case of intramolecular NH···Hir DHB in 2-aminopyridine. The DHB tends to weaken the H···H bonds in the order F > Cl > Br > I > CN > CO > H [19c].

While ^{1}H-NMR relaxation experiments on MH···HX systems provide the most information on the H···H distance, the analogous ^{2}H-NMR experiments on the corresponding MD···HX systems provide information only on the MD bond polarity. A remarkable sensitivity of the M–D polarity to the *trans* influence of ligands was shown by Bakhmutov and Berke. Thus, the different *trans* effects of NO and CO groups were shown in the case of $Re(CO)(NO)(PR_3)H_2$ hydrides [33]. This effect results in preference of the hydride ligand *trans* to NO-group to form a DHB [46].

6. Hydrogen bonded complexes as intermediates in proton transfer reaction

Protonations of hydride complexes by strong acids [55] leading to both classical and nonclassical polyhydrides, including kinetic investigations [56,57], are widely discussed in the literature. However, a clear understanding of the structural and electronic parameters controlling the site of a proton attack is far from being achieved.

Essential information about proton transfer can be deduced from E_j factor values. Higher E_j values (greater



Scheme 3.

than 0.8) enable us to expect easier proton transfer which can occur in the presence of weaker XH acids such as fluorinated alcohols. Moreover, the site of hydrogen bonding coincides with the site of protonation. Proton transfer from fluorinated alcohols to hydrides having an E_j value of less than 0.8 never occurs even in the presence of large excess of alcohol. As shown above, different types of HB (ReH···H, NO···H, ReCl···H) can form in the interactions of $H_2Re(CO)(NO)(PR_3)_2$ and $(Cl)HRe(CO)(NO)(PMe_3)_2$ with R^FOH [20b,23c]. For the strongest alcohol, PFTB, in high concentration a second hydrogen bonded $H_b \cdots H$-complexes are detected preceding proton transfer (Scheme 3).

Low temperature proton transfer from trifluoroacetic acid induces protonation of the H_b-ligand [46].

6.1. Hydrogen bonds with metal atom and proton transfer

Studies of the XH···M interaction in solution have revealed its important role in the protonation leading to classical cationic hydrides [7,10].

$$\underset{1}{M + HX} \rightleftarrows \underset{2}{M \cdots HX} \rightleftarrows \underset{3}{MH^+ \cdots X^-} \rightleftarrows \underset{4}{MH^+ + X^-} \qquad (1)$$

Proton transfer from trifluoroacetic acid to organometallic compounds $Cp^*M(CO)_2$ ($M = Rh$, Ir), Cp_2^*M Cp2M ($M = Ru$, Os), $MCO_2(dppe)_2$ ($M = Mo$, W), $WH_4(dppe)_2)$ in CH_2Cl_2 was investigated by IR and UV–vis-spectroscopy [7,10]. The range of carbonyl (ν_{CO}) and carboxylate (ν_{OCO}) bands (1810–1600 cm^{-1}) makes it possible to characterize each step of the equilibrium (1). The shift of the equilibrium (1) to the ionic type of hydrogen bonded complex **3** depends on the proton accepting ability of the metal atom ($Ru < Os$, $Rh < Ir$, $Mo < W$). The shift of the equilibrium (1) to the ionic HB **3** occurs on cooling indicating that the ionic form of H-complex is more stable than molecular one **2**. Proton transfer from R^FOH to a metal atom takes place if E_j value is greater than 0.8 (Table 4). Therefore, proton transfer to $Cp^*Ir(CO)_2$ ($E_j = 0.99$) was observed in pure $(CF_3)_2CHOH$, as well as in $(CF_3)_2CHOH$ or HCl diluted by supercritical xenon by using IR study in the ν_{CO} range (2150–1850 cm^{-1}) [14]. However, only the cation $[Cp^*Ir(CO)_2H]^+$ **4** and molecular HB **1** ($Cp^*(CO)_2Ir \cdots H{-}OR_F$) were found [14a]. An excess of proton donors probably increases the polarity of medium and causes the dissociation of the ionic hydrogen bond. The ionic type of hydrogen bonded complex **3** was observed in the ν_{CO} region only in the presence of small concentrations of CF_3COOH in CH_2Cl_2 solution [7]. Proton transfer from $(CF_3)_3COH$ to the metal atom was observed for both $W(CO)_2(dppe)_2$ ($E_j = 1.39$) and $WH_4(dppe)_2$ ($E_j = 1.27$) [7c,10]. Recently it was found that the Re atom in NP_3ReH_3 hydride is a very strong proton accepting site ($E_j = 1.45$), so that the weak acid (CF_3CH_2OH) forms a HB with the metal atom preceding proton transfer and the classical polyhydride formation [45].

6.2. Dihydrogen bonds and proton transfer

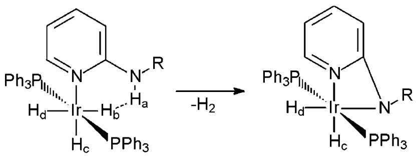
The formation of the MH···HX hydrogen bonds at the first stage of proton transfer reactions, eventually leading to cationic dihydrogen complexes, was shown recently [23,24,44].

$$\underset{1}{MH + HX} \rightleftarrows \underset{2}{MH \cdots HX} \rightleftarrows \underset{3}{M(H_2)^+ \cdots X^-} \rightleftarrows \underset{4}{M(\eta^2\text{-}H_2)^+ + X^-} \rightarrow \underset{5}{[MX] + H_2} \qquad (2)$$

The complete proton transfer from an acid to a hydride complex resulting in the loss of a dihydrogen molecule is a well established phenomenon. The discovery of dihydrogen complexes by Kubas [2a] and the subsequent intensive studies of transition metal hydride protonations have shown that these complexes are intermediates in the proton transfer processes. The existence of stable adducts displaying DHB in solution enables us to suppose that the proton transfer reactions leading to dihydrogen complexes involve these adducts as intermediates (equilibrium 2).

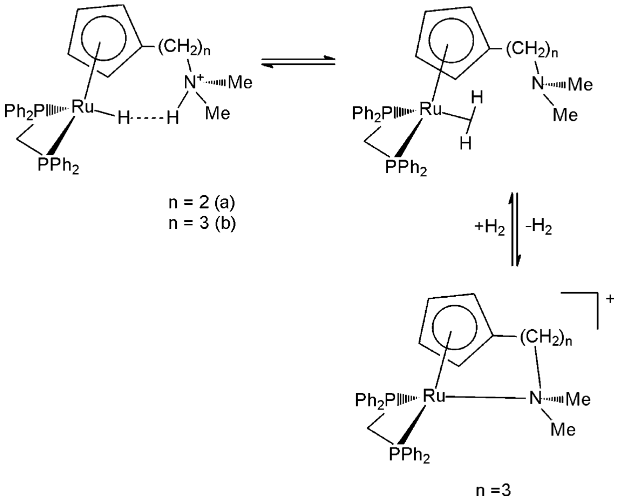
The process, including the intermolecular and intramolecular DHB as the first step of proton transfer from OH and NH acids to an H ligand in transition metal hydrides, was described in several papers [19a,21a,58a]. All of these proton transfer processes are accompanied by the evolution of dihydrogen suggesting the formation of η^2-H_2 complexes on the way of reactions. Activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ of 14 kcal mol^{-1} and -32 6 e.u. were obtained for the transformation, of **1** into **2** (Scheme 4) in the first order reaction.

The highly negative activation entropy suggests an associative process with a highly ordered transition state [19a]. According to Ref. [58a], intramolecular NH···HRu DHB also appeared to mediate proton transfer and subsequent formation of N–Ru bonded chelate structure (Scheme 5). The intramolecular hydrogen bonding complexes were unequivocally characterized by relaxation time T_1 measurements and a spin saturation transfer study [58a].

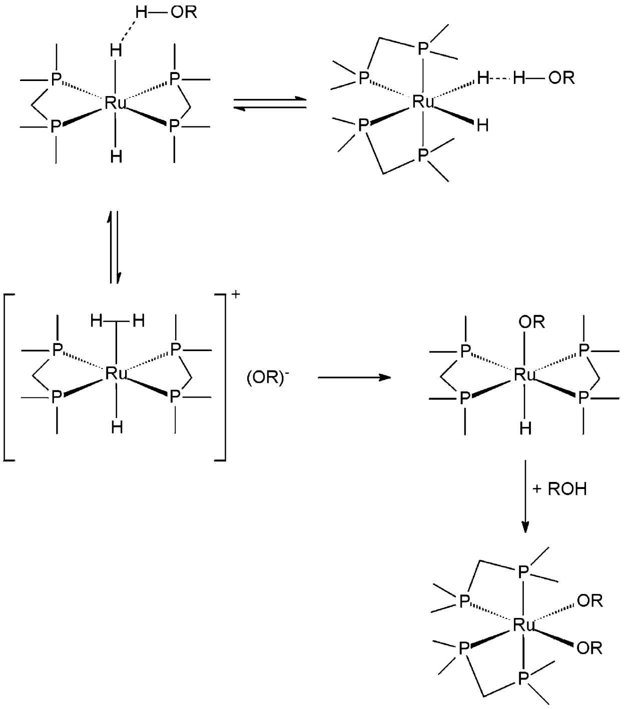


1

Scheme 4.



Scheme 5.



Scheme 6.

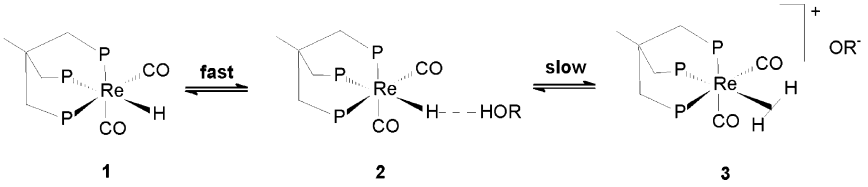
The direct observation of a dynamic equilibrium between H···H bonding and η^2-H_2 complexes resulting from proton transfer for interaction of $RuH_2(dppm)_2$ with PhOH and HFIP was made by Chaudret and coworkers, by NMR spectroscopy [24a] (Scheme 6). The authors noted a considerably larger stability of the η^2-H_2 complex ($\Delta H = 17$ kcal mol^{-1}). However, a fast exchange prevented the NMR spectra from distinguishing the signal from initial hydride and that from the H···H complex.

The existence of the hydrogen bond H···H is supported by IR spectra in the ν_{OH} region. This ruthenium hydride complex exists as a mixture of *cis* and *trans* dihydrogen bonded isomers. However, only the *trans* isomer is formed after proton transfer leading to the dihydrogen complex. In the interaction of $RuH_2(dppm)_2$ with HFIP the complex loses H_2 to give an organyloxy derivative as well as many other hydrides [24a]. A DFT calculation made by Orlova and Scheiner on a HOH···$H_2Ru(PH_2CH_2PH_2)_2$ model confirmed the higher stability of the dihydrogen complex lying 10.7 kcal mol^{-1} lower in energy than the DHB adduct [36c]. The activation energy for the proton transfer was estimated around 10 kcal mol^{-1}.

The effect of the proton donor ability on proton transfer was considered in some theoretical and experimental studies [23a,36b,57b]. Strong acids give η^2-H_2 complexes while weak donors favor dihydrogen-bonded species. The influence of media on proton transfer was discussed by Chaudret, Limbach et al. [24b]. They studied the interaction between Cp*$RuH_3(Cy_3P)$ and various proton donors in toluene, liquid freons, and CD_2Cl_2. Low temperature proton transfer takes place in liquid freons and CD_2Cl_2 in contrast to toluene indicating the important role of solvent dielectric constants in this process [24b]. In addition, Berke et al. [46] have shown that toluene considerably weakens hydrogen bonding between the hydride ligand and a proton donor. In our opinion both dielectric properties of the medium and the competition between hydride and toluene affects formation of the hydrogen bond.

Intermediates in proton transfer reactions in low polar and non polar media can be observed by varying the concentration and strength of proton donors and using the combination of variable temperature IR and NMR studies. The study of the interaction between $[MeC(CH_2PPh_2)_3]Re(CO)_2H$ or $[MeC(CH_2PPh_2)_3]Ru(CO)H_2$ and proton donors (PFTB and HFIP) in CH_2Cl_2 by IR and NMR at low temperature (190–260 K) showed the reversibility of the proton transfer process including the DHB complexes (2) and the dihydrogen complexes (3) (Scheme 7) [23a,23b,23d].

This approach enables us to determine the thermodynamic parameters associated with each step of the reactions using the temperature dependence of the corresponding formation constants [23a,23b,23d]. Enthalpy and entropy values of the interaction of $[MeC(CH_2PPh_2)_3]ReH(CO)_2$ with PFTB were obtained for conversion of **2** to **3** as well as for the overall reaction ($-\Delta H^\circ_{2-3} = 2.3$ kcal mol^{-1}, $-\Delta S^\circ_{2-3} = 8.4$ e.u.; $-\Delta H^\circ_{1-3} = 8.3$ kcal mol^{-1}, $-\Delta S^\circ_{1-3} = 31$ e.u. [23b]). The corresponding values obtained for the $[MeC(CH_2PPh_2)_3]Ru(CO)H_2$ /HFIP system are: $-\Delta H^\circ_{2-3} = 8.6$ kcal mol^{-1}, $-\Delta S^\circ_{2-3} = 42$ e.u.; $-\Delta H^\circ_{1-3} = 16.1$ kcal mol^{-1}, and $-\Delta S^\circ_{1-3} = 65$ e.u. [23d].



Scheme 7.

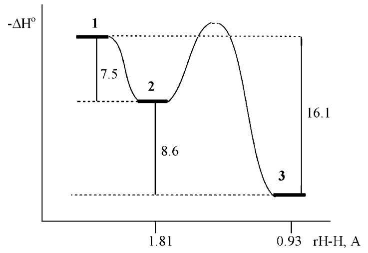


Fig. 1. The scheme of the energy profile for the transformation of $[MeC(CH_2PPh_2)_3]Ru(CO)H_2$ (**1**) into $\{[MeC(CH_2PPh_2)_3]Ru(CO)H(\eta^2\text{-}H_2)\}^+$ (**3**) via $[MeC(CH_2PPh_2)_3]Ru(CO)(H)H\cdots HOCH(CF_3)_2$ (**2**) in CH_2Cl_2 [23d].

Experimental data are summarized in the scheme of energy profile of proton transfer (Fig. 1) in which the abscissa represents the H–H distance obtained from NMR relaxation data. The potential energy surface has two minima. The first one corresponds to the DHB adduct **2** with an H···H bond length of 1.81 Å, while the second one corresponds to the thermodynamically more stable cationic η^2-H_2 complex **3**, with an H–H distance of 0.93 Å. The significant impact of the hydrogen bonding energy into the total energy gain confirms its role as a driving force for proton transfer reactions.

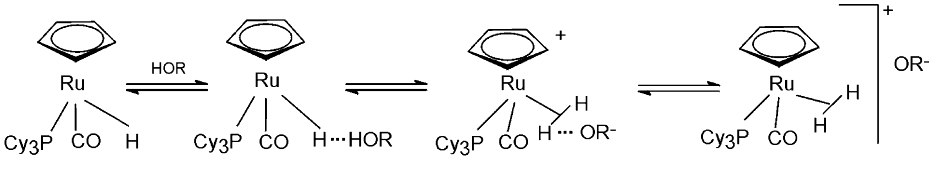
The H-bonded adduct formation is always a diffusion-controlled process so that there is no barrier for this step [1c]. The transition state energy of the conversion of **2** into **3** is shown only qualitatively in Fig. 1. However there are some indications that this step is slow also in the case $RuH_2(dppm)_2$ [24a] and a $Cp^*Ru(Pcy_3)H_3$ [24b]. The upper and lower limits of the rate constants and the barrier value were estimated. It was concluded that the activation barrier of two to three transformation is about 12–13 kcal mol^{-1} [23b]. According to the theoretical studies of proton transfer to Re and Ru hydrides, the proton transfer barriers depend on both the metal complex basicity and the strength of the acid and were predicted to lie in a range from 10 to 0.7 kcal mol^{-1} [36c].

Recently Basallote et al. studied the protonation kinetics of $FeH_2\{P(CH_2CH_2PPh_3\}$, $FeH_2(dppe)_2$ and $RuH_2(dppe)_2$ hydrides by strong acids using electrochemical methods. Low rates of proton transfer and η^2-H_2-complex generation (varying from 10^6 to 10^{-1} s^{-1} with activation barriers $\Delta G^\ddagger$ (290 K) of ca. 6.5–12 kcal mol^{-1}) were reported in these papers [57]. However, this method does not provide information about the structure of reaction intermediates but enables the authors to suggest the existence of the different hydrogen bonded complexes in transition state.

Experimental evidence for a stepwise mechanism was obtained in the protonation of $CpRuH(CO)(Pcy_3)$ by different proton donors (Scheme 8) [44]. A new intermediate in the proton transfer reaction was detected during the course of the protonation study. The formation of ion pairs stabilized by hydrogen bonds between the dihydrogen complex and anions (CF_3COO^-, $(CF_3)_3CO^-$) was observed in CH_2Cl_2. The observation of a **3a** intermediate, which is in equilibrium with the DHB complex **2** and the free cation **3** (Scheme 8), greatly contributes to the knowledge of the detailed mechanism of the proton transfer process to transition metal hydrides and is in accord with the concept of proton transfer to metal atoms in organometallic complexes [10].

The rate constants obtained at 200 K in CH_2Cl_2 and at 200–250 K in hexane fall in the range 10^{-4} s^{-1}–10^{-3} s^{-1}, providing barrier heights $\Delta G^\ddagger$ (200 K) of 13.7 kcal mol^{-1} in CH_2Cl_2 [44] and 15.0 kcal mol^{-1} in hexane [42]. The activation enthalpy ($\Delta H^\ddagger = 7.4$ kcal mol^{-1}) and entropy ($\Delta S^\ddagger = -36$ e.u.) for the transformation of a DHB complex into a cationic dihydrogen complex in hexane were determined.

The energetic profile describing the formation of the η^2-H_2-complex via the DHB-adduct was obtained on the basis of the thermodynamic parameters determined by an effective combination of two spectral methods. It is important to note that the formation of the DHB intermediate considerably contributes to the total energy



Scheme 8.

of the proton transfer leading to the dihydrogen complex. It is tempting to suggest a generalization of this type of potential energy surface when the cationic η^2-H_2-complexes are thermodynamically more stable than the DHB-complex.

7. Conclusion

The studies summarized in the review show the significant progress made in this new field of organometallic chemistry. Very important theoretical and experimental information has contributed to understanding the nature of the HBs to metal atoms and DHBs to hydride ligands. Their main characteristics appeared to be the same as those of classical HBs. The enthalpy values of both HB types are in the medium strength range (4–7.5 kcal mol^{-1}). The structures of ionic HBs to the metal atoms and molecular DHBs as well as the ion pairs stabilized by H-bond between dihydrogen cations and anions have been obtained for several cases. Two ways of proton transfer through HBs to the metal atom as well as DHBs to the hydride ligand leading to classical and nonclassical cationic hydrides have been identified. However, although the first type of HBs were found earlier (1990), the thermodynamic data on each step of the proton transfer reactions and the energetic profile of proton transfer were only determined for the second type.

There are a great number of remaining problems requiring further active investigations in the area. There are only a few examples allowing the comparison of the influence of different effects on the proton accepting ability of the metal atom or hydride ligand with the characteristics of the complete proton transfer. It is very important to examine the effects of metal, ligands, and medium on the basicity factors and the energy profile of proton transfer, particularly the height of the proton transfer barrier. Numerous spectral, kinetic, structural and theoretical investigations are still needed to formulate general rules governing proton transfer processes. Such processes play a very important role in catalysis, organometallic, bio-organic, and supramolecular chemistry.

Acknowledgements

The authors are very grateful to Professors V.I. Bakhmutov, M. Peruzzini, H.-H. Limbach, H. Berke, A. Lledós for useful discussions. The authors extremely appreciate the work of their co-workers and collaborators as well as financial support from INTAS (00-00179) and RFBR (02-03-32194).

References

[1] (a) G.A. Jeffrey, W. Saenger, Hydrogen Bonding in Biological Structures, Springer–Verlag, Berlin, 1991;
(b) G.A. Jeffrey, An Introduction to Hydrogen Bonding, Oxford University Press, New York, 1997;
(c) St. Scheiner, Hydrogen Bonding. Theoretical Perspectives, Oxford University Press, New York, 1997.

[2] (a) G.J. Kubas, R.R. Ruan, B.I. Swanson, P.J. Vergamini, H.J. Wasserman, J. Am. Chem. Soc. 106 (1984) 451;
(b) G.J. Kubas, Acc. Chem. Res. 21 (1988) 120.

[3] (a) S.S. Kristjansdottir, J.R. Norton, in: A. Dedieu (Ed.), Transition Metal Hydrides, New York, 1992, p. 309;
(b) S.S. Kristjansdottir, J.R. Norton, A. Moroz, R.L. Sweany, S.L. Whittenburg, Organometallics 10 (1991) 2357;
(c) S.S. Kristjansdottir, A.J. Loendorf, J.R. Norton, Inorg. Chem. 30 (1991) 4470;
(d) R.T. Weberg, J.R. Norton, Am. Chem. Soc. 112 (1990) 1105.

[4] (a) P.J. Jessop, R.H. Morris, Coord. Chem. Rev. 121 (1992) 155;
(b) K. Abdur-Rushid, T.P. Fong, B. Greaves, D.G. Gusev, J.G. Hinman, S.E. Landau, R.H. Morris, J. Am. Chem. Soc. 122 (2000) 9155.

[5] G. Jia, C.-P. Lau, Coord. Chem. Rev. 190 (1999) 83.

[6] S.S. Kristjánsdóttir, A.E. Moody, R.T. Weberg, J.R. Norton, Organometallics 7 (1988) 1983.

[7] (a) E.S. Shubina, A.N. Krylov, A.Z. Kreindlin, M.I. Rybinskaya, L.M. Epstein, J. Organomet. Chem. 465 (1994) 259;
(b) L.M. Epstein, E.S. Shubina, A.N. Krylov, A.Z. Kreindlin, M.I. Rybinskaya, J. Organomet. Chem. 447 (1993) 277;
(c) E.S. Shubina, A.N. Krylov, N.V. Belkova, L.M. Epstein, A.P. Borisov, V.D. Mahaev, J. Organomet. Chem. 493 (1995) 275.

[8] (a) E. Peris, R.H. Crabtree, J. Chem. Soc. Chem. Commun. (1995) 2179;
(b) S.A. Fairshurst, R.A. Henderson, D.L. Hughes, S.K. Ibrahim, C.J. Pickett, J. Chem. Soc. Chem. Commun. (1995) 1569;
(c) D. Braga, F. Grepioni, E. Tedesco, K. Birradha, G.R. Desiraju, Organometallics 15 (1996) 2692.

[9] (a) T.P.M. Schlaf, A.J. Lough, P.A. Maltby, R.H. Morris, Organometallics 15 (1996) 2270;
(b) T.P. Fong, C.E. Forde, A.J. Lough, R.H. Morris, P. Rigo, E. Rocchini, T. Stephan, J. Chem. Soc. Dalton Trans. (1999) 4475.

[10] E.S. Shubina, N.V. Belkova, L.M. Epstein, J. Organomet. Chem. 536–537 (1997) 17.

[11] (a) E.S. Shubina, L.M. Epstein, Yu.T. Struchkov, T.V. Timofeeva, A.Z. Kreindlin, S.S. Fadeeva, M.I. Rybinskaya, J. Organomet. Chem. 401 (1991) 133;
(b) L.M. Epstein, E.S. Shubina, A.N. Krylov, A.Z. Kreindlin, M.I. Rybinskaya, J. Organomet. Chem. 401 (1991) 145;
(c) E.S. Shubina, L.M. Epstein, J. Mol. Structure 265 (1992) 367.

[12] L.E. Vinogradova, A.Z. Kreindlin, L.A. Leites, I.T. Chizevskii, E.S. Shubina, L.M. Epstein, Metalloorg. Khim. 3 (1990) 1192 [(English translation in Organomet. Chem. in USSR 3 (1990) 618]..

[13] (a) L.M. Epstein, E.S. Shubina, Khim. Phys. 11 (1992);
(b) E.S. Shubina, A.N. Krylov, A.Z. Kreindlin, M.I. Rybinskaya, L.M. Epstein, J. Mol. Struct. 301 (1993) 1;
(c) L.M. Epstein, A.N. Krylov, E.S. Shubina, J. Mol. Struct. 322 (1994) 345;
(d) E.S. Shubina, A.N. Krylov, D.V. Muratov, A.A. Fil'chikov, L.M. Epstein, Russ. Chem. Bull. 42 (1993) 1919.

[14] (a) S.G. Kazarian, P.A. Hamley, M. Poliakoff, J. Am. Chem. Soc. 115 (1993) 9069;
(b) S.S.G. Kazarian, P.A. Hamley, M. Poliakoff, J. Chem. Soc. Chem. Commun. (1992) 995;
(c) M. Poliakoff, S.M. Howdle, S.G. Kazarian, Angew. Chem. Int. Ed. Engl. 34 (1995) 1275.

[15] (a) L. Brammer, M.C. McCann, R.M. Bullock, R.K. McMullan, P. Sherwood, Organometallics 11 (1992) 2339;
(b) L. Brammer, J.M. Charnock, P.L. Goggin, R.J. Goodfellow, A.G. Orpen, T.F. Koetzle, J. Chem. Soc. Dalton Trans. (1991) 1789;
(c) I.C.M. Wehman-Ooyeevaar, D.M. Grove, H. Kooijman, P. van der Sluis, A.L. Spek, G. van Koten, J. Am. Chem. Soc. 115 (1992) 9916.

[16] (a) L. Brammer, D. Zhao, F.T. Ladipo, J. Braddok-Wilking, P. Sherwood, Organometallics 15 (1996) 1154;
(b) J.C.M. Rivas, L. Brammer, Coord. Chem. Rev. 183 (1999) 43;
(c) A. Martin, J.Chem. Educ. 76 (1999) 578.

[17] (a) D. Milstein, J.C. Calabrezi, I.D. Williams, J. Am. Chem. Soc. 108 (1986) 6387;
(b) R.C. Stevence, R. Bau, D. Milstein, O. Blum, T.F. Koetzle, J. Chem. Soc. Dalton Trans. (1990) 1429.

[18] (a) A.J. Lough, S. Park, R. Ramachandran, R.H. Morris, J. Am. Chem. Soc. 116 (1994) 8356;
(b) S. Park, R. Ramachandran, A.J. Lough, R.H. Morris, J. Chem. Soc. Chem. Commun. (1994) 2201.

[19] (a) J.C. Lee, E. Peris, A. Rheingold, R.H. Crabtree, J. Am. Chem. Soc. 116 (1994) 11014;
(b) J.C. Lee, A. Rheingold, B. Muller, P.S. Pregosin, R.H. Crabtree, J. Chem. Soc. Chem. Commun. (1994) 1021;
(c) E. Peris, J.C. Lee, J.R. Rambo, O. Eisenstein, R.H. Crabtree, J. Am. Chem. Soc. 117 (1995) 3485.

[20] (a) E. Peris, J. Wessel, B.P. Patel, R.H. Crabtree, J. Chem. Soc. Chem. Commun. (1995) 2175;
(b) J. Wessel, J.C. Lee, E. Peris, G.P.A. Yap, J.B. Fortin, J.S. Ricci, G. Sini, A. Albinati, T.F. Koetzle, O. Eisenstein, A.L. Rheingold, R.H. Crabtree, Angew. Chem. Int. Ed. Eng. 34 (1995) 2507;
(c) B.P. Patel, J. Wessel, W. Yao, J.C. Lee, E. Peris, T.F. Koetzle, T.F. Gap, J.B. Fortin, J.S. Ricci, G. Sini, A. Albinati, O. Eisenstein, A.L. Rheingold, R.H. Crabtree, New J. Chem. 21 (1997) 413.

[21] (a) E.S. Shubina, N.V. Belkova, A.N. Krylov, E.V. Vorontsov, L.M. Epstein, D.G. Gusev, M. Niedermann, H. Berke, J. Am. Chem. Soc. 118 (1996) 1105;
(b) N.V. Belkova, E.S. Shubina, A.V. Ionidis, L.M. Epstein, H. Jacobsen, A. Messmer, H. Berke, Inorg. Chem. 36 (1997) 1522;
(c) E.S. Shubina, N.V. Belkova, A.V. Ionidis, N.S. Golubev, L.M. Epstein, Russ. Chem. Bull. 44 (1997) 1349;
(d) L.M. Epstein, E.S. Shubina, Ber. Bunsenges. Phys. Chem. 102 (1998) 359;
(e) E.S. Shubina, N.V. Belkova, E.V. Bakhmutova, L.N. Saitkulova, A.V. Ionidis, L.M. Epstein, Russ. Chem. Bull. 47 (1998) 817.

[22] (a) D.G. Gusev, A.J. Lough, R.H. Morris, J. Am. Chem. Soc. 120 (1998) 13138;
(b) K. Abdur-Rasid, D.G. Gusev, S.E. Landau, A.J. Lough, R.H. Morris, J. Am. Chem. Soc. 120 (1998) 11826;
(c) K. Abdur-Rasid, D.G. Gusev, A.J. Lough, R.H. Morris, Organometallics 19 (2000) 834.

[23] (a) E.S. Shubina, N.V. Belkova, E.V. Bakhmutova, E.V. Vorontsov, V.I. Bakhmutov, A.V. Ionidis, C. Bianchini, L. Marvelli, M. Peruzzini, L.M. Epstein, Inorg. Chim. Acta 280 (1998) 302;
(b) N.V. Belkova, E.V. Bakhmutova, E.S. Shubina, C. Bianchini, M. Peruzzini, V.I. Bakhmutov, L.M. Epstein, Eur. J. Inorg. Chem. (2001) 2163;
(c) N.V. Belkova, E.S. Shubina, E.I. Gutsul, L.M. Epstein, S.E. Nefedov, I.L. Eremenko, J. Organomet. Chem. 610 (2000) 58;
(d) V.I. Bakhmutov, E.V. Bakhmutova, N.V. Belkova, C. Bianchini, L.M. Epstein, M. Peruzzini, E.S. Shubina, E.V. Vorontsov, F. Zanobini, Can. J. Chem. 79 (2001) 479.

[24] (a) J.A. Ayllon, C. Gervaux, S. Sabo-Etienne, B. Chaudret, Organometallics 16 (1997) 2000;
(b) S. Gruendemann, S. Ulrich, H.-H. Limbach, N.S. Golubev, G.S. Denisov, L.M. Epstein, S. Sabo-Etienne, B. Chaudret, Inorg. Chem. 38 (1999) 2550.

[25] G. Orlova, St. Scheiner, Organometallics 17 (1998) 4362.

[26] (a) W. Jao, O. Eisenstein, W. Jao, R.H. Crabtree, Inorg. Chim. Acta 254 (1997) 105;
(b) G. Sini, O. Eisenstein, W. Jao, R.H. Crabtree, Inorg. Chim. Acta 280 (1998) 26.

[27] I. Alkorta, I. Rozas, J. Elguero, J. Mol. Struct. 537 (2001) 139.

[28] I. Alkorta, I. Rozas, J. Elguero, Chem. Soc. Rev. 27 (1998) 163.

[29] F. Maseras, A. Ledos, E. Clot, O. Eisenstein, Chem. Rev. 100 (2000) 615.

[30] R. Custeclean, J.E. Jackson, Chem. Rev. 101 (2001) 1963.

[31] (a) R.H. Crabtree, P.E.M. Siegbahn, O. Eisenstein, A.L. Rheingold, T.F. Koetzle, Acc. Chem. Res. 29 (1996) 348;
(b) T.B. Richardson, S. de Gala, R.H. Crabtree, P.E.M. Siegbahn, J. Am. Chem. Soc. 117 (1995) 12875;
(c) W.T. Klooster, T.F. Koetzle, P.E.M. Siegbahn, T.B. Richardson, R. Crabtree, J. Am. Chem. Soc. 121 (1999) 6337.

[32] R.H. Crabtree, J. Organomet. Chem. 557 (1998) 111.

[33] D. Neitlispach, V.I. Bachmutov, H. Berke, J. Am. Chem. Soc. 115 (1993) 9191.

[34] J. Platt, J. Mol. Struct. 545 (2001) 111.

[35] Q. Liu, R. Hoffmann, J. Am. Chem. Soc. 117 (1995) 10108.

[36] (a) G. Orlova, S. Scheiner, J. Phys. Chem. A 102 (1998) 260;
(b) G. Orlova, S. Scheiner, J. Phys. Chem. A 102 (1998) 4813;
(c) G. Orlova, S. Scheiner, T. Kar, J. Phys. Chem. A 103 (1999) 514.

[37] (a) L.M. Epstein, E.S. Shubina, E.V. Bakhmutova, L.N. Saitkulova, V.I. Bakhmutov, A.L. Chistyakov, I.V. Stankevich, Inorg. Chem. 37 (1998) 3013;
(b) E.S. Shubina, E.V. Bakhmutova, L.N. Saitkulova, L.M. Epstein, Mendeleev Commun. (1997) 83;
(c) I. Alkorta, J. Elguero, C. Foces-Foces, J. Chem. Soc. Chem. Commun. (1996) 1633.

[38] P.L. Popelier, J. Phys. Chem. A 102 (1998) 1873.

[39] C.J. Cramer, W.L. Gladfelter, Inorg. Chem. 36 (1997) 5358.

[40] J. Lundell, M. Petterson, Phys. Chem. Chem. Phys. 1 (1999) 1691.

[41] (a) S.J. Grabowsky, Chem. Phys. Lett. 327 (2000) 203;
(b) S.J. Grabowsky, J. Phys. Chem. A 104 (2000) 5551.

[42] M. Besora, A. Lledós, F. Maseras, N.V. Belkova, L.M. Epstein, E.S. Shubina, in: FIGIPS meeting, Barcelona, (2001) Abstracts, Preliminary communication

[43] R. Minyaev, T. Gribanova, J. Inorg. Chem., Russia 46 (2001) 1521.

[44] N.V. Belkova, A.V. Ionidis, L.M. Epstein, E.S. Shubina, S. Gründemann, N.S. Golubev, H.-H. Limbach, Eur. J. Inorg. Chem. (2001) 2163.

[45] A. Albinati, V.I. Bakhmutov, N.V. Belkova, C. Bianchini, L. Epstein, I. de los Rios, E.I. Gutsul, L. Marvelli, M. Peruzzini, R. Rossi, E. Shubina, E.V. Vorontsov, F. Zanobini, Eur. J. Inorg. Chem. 2002, 1530.

[46] A. Messmer, H. Jacobsen, H. Berke, Chem. Eur. J. 5 (1999) 11.

[47] (a) N.S. Golubev, G.S. Denisov, J. Mol. Struct. 270 (1992) 263;
(b) N.S. Golubev, I.G. Shenderovich, S.N. Smirnov, G.S. Denisov, H.H. Limbach, Chem. Eur. J. 5 (1999) 491.

[48] L.H. Desrosiers, Z.R. Cai, R. Lin, R. Richards, J. Halpern, J. Am. Chem. Soc. 114 (1991) 4173.

[49] (a) A.V. Iogansen, Theor. Exp. Khim. 7 (1971) 314;
(b) A.V. Iogansen, Theor. Exp. Khim. 7 (1971) 302;
(c) A.V. Iogansen, The Hydrogen Bond, Nauka, Moscow, 1981, p. 134;
(d) A.V. Iogansen, Spectrochim. Acta A 55 (1999) 1585.

[50] The ΔH_{11} value is solvent dependent and for carbon tetrachloride is equal to 5.3 kcal mol^{-1}; for dichloromethane, 4.6 kcal mol^{-1}, for hexane, 5.7 kcal mol^{-1} so the enthalpy values to be used in Eq. (4a) should be measured in the corresponding solvent. The P_i

values representing proton acceptor ability of acids are taken from [49a,49b].

[51] E.I. Gutsul, N.V. Belkova, E.S. Shubina, L.M. Epstein, C. Bianchini, M. Peruzzini, F. Zanobini, preliminary data.

[52] (a) L.M. Epstein, A.V. Iogansen, Usp. Khim. 59 (1990) 22;
(b) L.M. Epstein, Usp. Khim. 53 (1979) 1602.

[53] (a) M.K. Rottink, R.J. Angelici, J. Am. Chem. Soc. 115 (1993) 7267;
(b) J.R. Sowa, V. Zanotti, G. Facchin, R.J. Angelici, J. Am. Chem. Soc. 113 (1991) 9185;
(c) M.K. Rottink, R.J. Angelici, Inorg. Chem. 32 (1993) 3282;
(d) R.J. Angelici, Acc. Chem. Res. 28 (1995) 51;
(e) D. Wong, R.R.J. Angelici, J. Am. Chem. Soc. 118 (1996) 935.

[54] D.G. Gusev, R. Hubener, R. Burger, O. Orama, H. Berke, J. Am. Chem. Soc. 119 (1997) 3716.

[55] (a) R.M. Bullock, J.-S. Song, D.J. Szalda, Organometallics 15 (1996) 2504;
(b) C. Nataro, L. Tomas, R. Angelici, Inorg. Chem. 36 (1997) 6000.

[56] (a) K.W. Kramarz, J.R. Norton, Prog. Inorg. Chem. 42 (1994) 1;
(b) E.T. Papish, F.C. Rix, N. Spetseris, J.R. Norton, R.D. Williams, J. Am. Chem. Soc. 122 (2000) 2235.

[57] (a) M.G. Basallote, J. Duran, M.J. Fernandez-Trujillo, M.A. Manez, J.R. de la Torre, J. Chem. Soc. Dalton Trans. (1998) 745;
(b) M.G. Basallote, J. Duran, M.J. Fernandez-Trujillo, M.A. Manez, J. Chem. Soc. Dalton Trans. (1998) 2205;
(c) M.G. Basallote, J. Duran, M.J. Fernandez-Trujillo, M.A. Manez, Inorg. Chem. 38 (1999) 5067.

[58] (a) H.C. Chu, C.P. Lau, K.Y. Wong, W.T. Wong, Organometallics 17 (1998) 2768;
(b) H.C. Chu, Z. Xu, C.P. Lau, S.M. Ng, Z. Lin, Eur. J. Inorg. Chem. (2000) 993.