

Review

# Novel types of hydrogen bonding with transition metal $\pi$ -complexes and hydrides<sup>1</sup>

Elena S. Shubina, Natalia V. Belkova, Lina M. Epstein \*

*A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Science, Vavilov str. 28, Moscow B-334, 117813, Russia*

Received 24 July 1996; accepted 26 September 1996

## Abstract

This review deals with the results of investigations of novel types of hydrogen bond involving transition metal complexes, namely H-bonds with a metal atom ( $XH \cdots M$ ) and those with the hydride hydrogen atom ( $XH \cdots HM$ ) as a base, as well as those with cationic hydrides as proton donors with organic bases ( $[MH]^+ \cdots B$ ). Spectral, thermodynamic and structural characteristics of intra- and intermolecular hydrogen bonds are described. The influence of the nature of the metal atom, and of electronic and steric properties of ligands on the proton donor ability of the metal atom and hydride hydrogen are discussed. Studies of proton transfers occurring through intermediate hydrogen bonds are also analysed. © 1997 Published by Elsevier Science S.A.

*Keywords:* Hydrogen bond; Transition metal  $\pi$ -complexes and hydrides; Proton transfer

## 1. Introduction

Proton transfer reactions proceeding through hydrogen bonding are widespread and fundamental in chemistry and biochemistry. The modern concepts of nature, structure and spectral manifestations of hydrogen bonds were formed on the basis of the large of data on the interaction between organic acids and bases. Tremendous success was achieved for them in determining the structures of intra- and intermolecular hydrogen bonds, the energetics of ion-molecular H-complex formation in the gas phase, as well as in the determination of correlations between hydrogen bond characteristics and acid-basic properties [1–4].

In recent years most attention has been paid to the investigation of hydrogen bonding with transition metal complexes or hydrides and its participation in proton transfer reactions. So it is extremely important to find out whether the numerous catalytic processes involving transition metal complexes can proceed through intermediate hydrogen-bonded complexes. Hydrogen bonds with different ligands have been examined extensively. Hydrogen bonds with  $\pi$ -ligands have been investigated since the 1970s [5–8]. The large series of works by

Lokshin and co-workers concerned the study of the interaction of fluorinated alcohols and HCl with carbonyl and nitrozyll containing half-sandwich transition metal  $\pi$ -complexes [9,10] was continued by Poliakoff and co-workers [11]. These low temperature IR investigations in liquid xenon solution enabled the detection and study of previously unknown hydrogen bonding with the oxygen atom of terminal CO- and NO-groups. Fairly strong H-bonds of proton donors with alkoxy [12] and phenoxy [13] ligands were studied in solution and in the solid state. The nature of the hydrogen bonds with ligands named above is similar to the hydrogen bonds which are typical for organic bases, since lone pairs of sp-electrons of heteroatoms or  $\pi$ -electrons of unsaturated and aromatic fragments are acting as proton acceptors. Braga and co-workers, after an analysis of the structural data in the Cambridge database, concluded that H-complexes with such proton donor and acceptor ligands as COOH, OH, CH, COOR and CO have structural properties which are similar to those of related organic solids [14].

Recently, new types of hydrogen bonds, which are characteristic only of organometallic compounds, were found and investigated. First of all these are hydrogen bonding to transition metal atoms ( $XH \cdots M$ ) (1). In contrast to organic bases, in this case d-electrons are proton acceptors. Another surprise presented by

\* Corresponding author.

<sup>1</sup> Dedicated to the memory of Professor Yu.T. Struchkov.

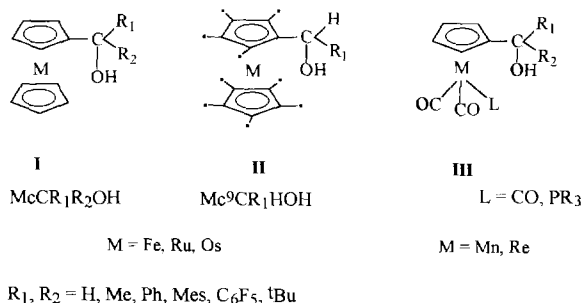
organometallic chemistry in recent years were hydrogen bonds formed with transition metal hydrides. The particular characteristic of transition metal hydrides is their dual reactivity: they can be the source of both protons and hydride ions. Two extreme cases of hydride ligand participation in hydrogen bonding were found: they can react as a proton donor ( $[\text{MH}]^+ \cdots \text{B}$ ) (2), in the case of cationic hydrides, and as an acceptor of protons ( $\text{MH} \cdots \text{HX}$ ) (3). Since hydrogen has no lone pair of electrons, the last, type **III**, bond is exceptional. It is these new types of hydrogen bond and their spectral, thermodynamic, and structural features, as well as their participation in proton transfer, to which this review is dedicated.

## 2. Hydrogen bonding to transition metal atoms of the $\text{XH} \cdots \text{M}$ type

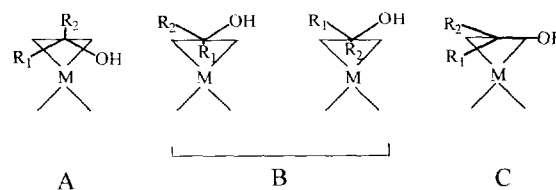
### 2.1. Intramolecular hydrogen bonding to a metal atom

In over 20 years (1970–90) of numerous IR and NMR investigations intermolecular hydrogen bonding to transition metal atoms had not been observed [5–10]. At the same time, intramolecular hydrogen bonding with transition metal atoms was found in molecules of  $\pi$ -complexes of Cr [15], Fe [16–18], Ru, Os [17] and Rh [19,20]. Contradiction between the data obtained raised the question of whether intramolecular hydrogen bonding to a metal atom was the result of the influence steric factors.

This question was answered on the basis of a systematic investigation of  $\alpha$ -carbinols (**I–III**) by IR spectroscopy in combination with conformational calculations by molecular mechanics methods accomplished in the Yu.T. Struchkov's laboratory by Epstein and co-workers [21–30].



All carbinols were shown to be divided into two groups. In the first group intramolecular hydrogen bonding formation is governed by conformational preference. This includes carbinols containing small-size metal



Scheme 1.

atoms of the first transition row or compounds with metal possessing reduced basicity due to electron accepting ligands. The hydrogen bond with a metal atom is formed in this case only if the conformation of (A) with an OH-group position under the cyclopentadienyl ring is energetically favourable (Scheme 1).

The second group includes carbinols containing electron-rich metal atoms of the second and third transition rows. All carbinols of this group form hydrogen bonds with metal atoms regardless of conformation preference.

The best illustration for this statement are the primary carbinol examples (**I–III**,  $\text{R}_1 = \text{R}_2 = \text{H}$ ) possessing no energetically preferable conformations. Therefore, the presence of molecules with intramolecular hydrogen bonding of the  $\text{OH} \cdots \text{M}$ -type in dilute solutions is not connected with the influence of steric factors. In this situation, bands of intramolecular hydrogen bonds in the IR spectra appear only for metallocenylcarbinols of Os and Ru (**II**) [22] and for norbornadienylcyclopentadienylrhodium derivatives [19,20] (second group) while no such bands appear for ferrocenylcarbinols (**I, II**) [21] and carbinol derivatives (**III**) (first group) [23]. Hydrogen bonding to Fe, Mn, Re could be observed in tertiary carbinols or in secondary ones with bulky substituents [23,24,27].

These compounds appeared to be excellent models, enabling one to vary the proton accepting ability of the basic centre (metal atom), proton donor properties of OH-groups and the geometry of the hydrogen-bonded cycles. This allowed separation of the influence of the metal atom nature and determination of the correlation between spectral characteristics and the structure of these compounds [28–30]. The problem of the estimation of the enthalpy of intramolecular hydrogen bonds ( $-\Delta H$ ) is rather complicated.  $\Delta H$  values obtained from the dependence of formation constants on temperature include not only the energy of hydrogen bonding but a conformational component  $E_{\text{conf}}$ . The values of  $E_{\text{conf}}$  could be large and their assessment by conformational calculations is approximate, therefore it is not expedient to determine  $\Delta H$  from the combination of  $E_{\text{conf}}$  and  $\Delta H_{\text{exp}}$  as in Ref. [31]. It is convenient to use  $\Delta\nu_{\text{OH}}$  values as a measure of the relative strength of intramolecular hydrogen bonding of the  $\text{OH} \cdots \text{M}$  type [19–24,28–30].<sup>2</sup>

<sup>2</sup>  $\Delta\nu_{\text{OH}} = \nu_{\text{OH free}} - \nu_{\text{OH bonded}}$ .

### 2.1.1. The nature of the metal atom and the relative strength of intramolecular hydrogen bonding $\text{OH} \cdots \text{M}$

The relative strength of intramolecular hydrogen bonding  $\text{OH} \cdots \text{M}$  for all isostructural carbinols increases down the group parallel to the row of metal atom basicity  $\text{Mn} < \text{Re}, \text{Fe} \ll \text{Ru} < \text{Os}$  [28–30]. Perfect linear dependencies were found between values of  $\Delta\nu_{\text{OH} \cdots \text{M}}$  for carbinols (I) and (II) with different R (Fig. 1). Proton acceptor properties of the metal atom in carbinols increase sharply (twofold) on passing from the first to the second transition row, and to a lesser extent to the third row: 0.56(Fe):1(Ru):1.24(Os). It is interesting that for  $\beta$ -carbinols  $\text{Mc}(\text{CH}_2)_2\text{OH}$  ( $\text{M} = \text{Fe}, \text{Ru}$ ), forming six-membered cycles the same ratio was obtained:  $\Delta\nu_{\text{OH} \cdots \text{Fe}}/\Delta\nu_{\text{OH} \cdots \text{Ru}} = 0.565$  [28–30].

### 2.1.2. Conditions of intramolecular $\text{OH} \cdots \text{M}$ hydrogen bond retention in the solid state

The most common type of hydrogen bonding in crystalline carbinols is intermolecular hydrogen bonding of the  $\text{OH} \cdots \text{O}$  type [14]. There is little knowledge about structures of  $\alpha$ -carbinols containing intramolecular hydrogen bonding with metal atoms. Intramolecular contacts  $\text{M} \cdots \text{H}$  and  $\text{M} \cdots \text{O}$  are assumed on the basis of X-ray data obtained by Struchkov and co-workers for the following carbinols:  $\text{FcCHOH}(\text{ArCo}_4(\text{CO})_9)$  [23],  $\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{C}(\text{OH})(\text{PhC}_4\text{O}_2)$  [32],  $\text{C}_5\text{H}_5\text{RhC}_7\text{H}_5\text{C}(\text{OH})\text{Me}$  [20], and by Lecomte et al. for

$[\eta^5\text{-C}_5\text{H}_4(\text{CH}_2)_3]\text{Fe}[\eta^5\text{-C}_6\text{H}_3\text{C}(\text{OH})\text{PhEt}]$  [33]. The  $\text{M} \cdots \text{O}$  and  $\text{M} \cdots \text{H}$  distances are 3.45–3.57 Å and 2.9–3.03 Å respectively, i.e. less than the sum of the van der Waals radii.

Using X-ray data and results of conformational calculations we have developed the specific spectral criteria enabling one to identify the presence of an intramolecular hydrogen bond with a metal atom in the solid state [26].

Firstly,  $\nu_{\text{OH}}$  bands assigned to the intramolecular hydrogen bond do not obey the linear dependence between half-widths ( $\Delta\nu_{1/2}$ ) and shift values  $\Delta\nu_{\text{OH}}$  evaluated for intermolecular hydrogen bonds of the  $\text{OH} \cdots \text{O}$  type. Secondly, bands assigned to vibrations  $\nu_{\text{OH} \cdots \text{M}}$  of chelates broaden on passing from crystal to solution. This is compatible with common changes of half-widths under less ordered conditions [34]. Thirdly, for intramolecular hydrogen bonds, either considerably smaller  $\nu_{\text{OH}}$  bands shifts to higher frequencies or even low frequency shifts on melting are observed.

The fundamental role of steric effects for crystals has been estimated by analysis of spectra of all compounds investigated in the scope of the above approaches. It turned out that hydrogen bonding to a metal atom in a crystal is not retained if there exists no favourable conformation with an OH-group turned towards the metal atom (A), regardless of their relative strength in solution. For example, spectra of primary carbinols of Ru, Os [22,28] and Rh [20] in solution reveal bands of chelates ( $\Delta\nu_{\text{OH}} = 110\text{--}180\text{ cm}^{-1}$ ), but only  $\nu_{\text{OH} \cdots \text{O}}$  bands are observed for solid samples [25–28].

The existence of conformation (A) energetically favourable for hydrogen bonding  $\text{OH} \cdots \text{M}$  is a necessary but insufficient condition for the retention of this bonding in the solid state. The realisation of an intramolecular hydrogen bond  $\text{OH} \cdots \text{M}$  competing in a crystal with a strong intermolecular hydrogen bond  $\text{OH} \cdots \text{O}$  depends on the proton accepting ability of the metal atom. For example, in the case of  $\text{Mc}^9\text{CHROH}$  crystals: for  $\text{M} = \text{Os}$  ( $\text{R} = \text{Me}, \text{Ph}, \text{C}_6\text{F}_5$ ) only molecules with intramolecular hydrogen bonding  $\text{OH} \cdots \text{Os}$  exist; for  $\text{M} = \text{Ru}$ , in addition to chelates, there exist associates with  $\text{OH} \cdots \text{O}$  hydrogen bonding; for  $\text{M} = \text{Fe}$  almost all molecules are associated [26,28–30]. In solution, chelate cycles are observed in all these compounds, but the relative strength, as mentioned above, decreases in the sequence  $\text{Os} > \text{Ru} \gg \text{Fe}$ . Similarly, in cationic carbinols formed by protonation of aldehydes, intramolecular hydrogen bonding with ruthenium, osmium [35] and rhodium [36] atoms, in contrast to iron, is retained in the solid state as well [35].

The disclosure of intramolecular hydrogen bond formation rules, as well as the dependence of its strength on the nature of the metal atom, revealed the means for a directed search for  $\text{OH} \cdots \text{M}$  intermolecular hydrogen bonding.

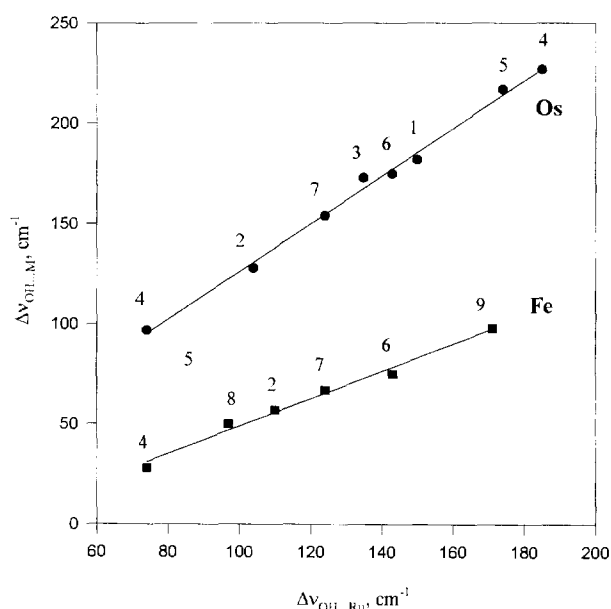


Fig. 1. Correlations of  $\Delta\nu_{\text{OH} \cdots \text{M}}$  ( $\text{M} = \text{Fe}, \text{Os}$ ) with  $\Delta\nu_{\text{OH} \cdots \text{Ru}}$  for metalocenylcarbinols  $\text{McR}_1\text{R}_2\text{OH}$  and  $\text{Mc}^9\text{CHR}_1\text{OH}$ .  $\text{Mc}^9\text{CHR}_1\text{OH}$ :  $\text{R}_1 = \text{H}$  (1),  $\text{Me}$  (2),  $\text{Ph}$  (3),  $\text{C}_6\text{F}_5$  (4),  $\text{Mes}$  (5)  $\text{McR}_1\text{R}_2\text{OH}$ :  $\text{R}_1/\text{R}_2 = \text{Ph}/\text{Ph}$  (6),  $\text{H}/\text{Ph}$  (7),  $\text{H}/\text{Me}$  (8),  $\text{Mc}(\text{CH}_2)_2\text{OH}$  (9)  $\Delta\nu_{\text{OH}}(\text{Fe}) = (0.56 \pm 0.01)\Delta\nu_{\text{OH}}(\text{Ru})$ ,  $r = 0.995$ ;  $\Delta\nu_{\text{OH}}(\text{Os}) = (1.24 \pm 0.01)\Delta\nu_{\text{OH}}(\text{Ru})$ ,  $r = 0.998$  [30].

## 2.2. Intermolecular hydrogen bonding of the OH...M type

Intermolecular hydrogen bonding OH...M was detected when highly basic  $\pi$ -complexes of second and third row transition metals were used, namely in the interaction of 4-fluorophenol with Ru and Os atoms of their metallocenes and with norbornadienylcyclopentadienylrhodium derivatives [37]. In recent years, intermolecular hydrogen bonding of different proton donors with d-electrons of Groups VI and VIII transition metals in Os, Ru metallocenes ( $Cp_2M$ ; IV) and decamethylmetallocenes ( $Cp_2^*M$ ; V) [29,30,38,39], Co, Rh, and Ir half-sandwich  $\pi$ -complexes  $CpML_2$ ,  $Cp^*ML_2$  ( $L = CO, C_2H_4, N_2, PMe_3, PPh_3$ ; VI) [40–43] and molybdenum and tungsten complexes of  $ML_2(dppe)_2$  ( $L = H_2, N_2, CO$ ; VII) type were investigated and characterised [44,45].

Intermolecular hydrogen bonding was studied by IR spectroscopy in common low polar and non-polar solvents by us [38,39,43–45], as well as in liquid xenon and supercritical liquids by Kazarian and co-workers [40–42]; see also the review by Poliakoff et al. [46]. Interaction of proton donors with all the organometallic bases studied induces the appearance of bands of hydrogen bonded complexes OH...M in the  $\nu_{OH}$  range. The sensitivity of these bands to the nature of the metal atom allowed one to assign them to  $\nu_{OH...M}$  vibration. The values of shifts which characterise the strength of intermolecular hydrogen bonding vary in the range 200–500  $cm^{-1}$ , increasing down the group  $Co < Rh < Ir$  [40–43],  $Ru < Os$  [38,39],  $Mo < W$  [44,45]. For complexes with carbonyl and dinitrogen ligands, the formation of hydrogen bonding with a metal atom was confirmed by high frequency shift of  $\nu_{CO}$  and  $\nu_{NN}$  bands in contrast to the low frequency ones characteristic for hydrogen bonding with ligands [9–11]. The amount of experimental data is sufficient to allow one to analyse the properties of this hydrogen bonding type, to elucidate some regularities of their formation, and to discuss the similarity of hydrogen bonding of a proton donor with metals and organic bases and their particular characteristics.

### 2.2.1. The resemblance between new hydrogen bonding to transition metal atoms (OH...M) and the usual one to organic bases (OH...B)

The analogy between some characteristics of hydrogen bonding with d-electrons of metal atoms and with sp-electrons of heteroatoms in organic bases has been revealed.

*Isotopic ratio  $\nu_{OH...M}/\nu_{OD...M}$* : for metallocenes of the iron subgroup [38], and for the half-sandwich carbonyl complexes of rhodium and iridium [40–42], this is 1.35, as in the case of common H-bonds.

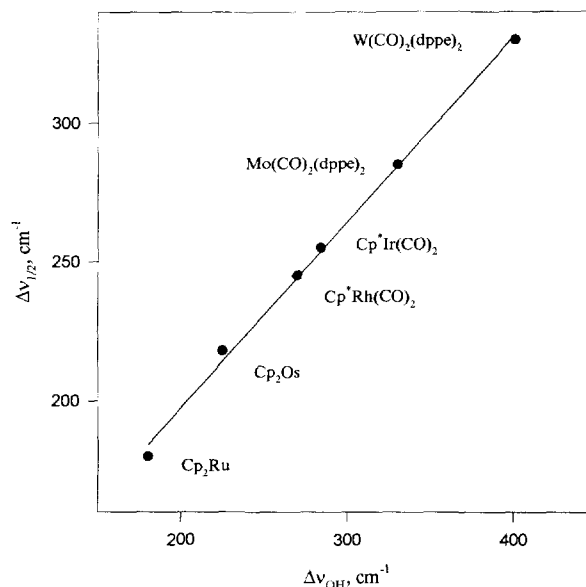


Fig. 2. Correlation of  $\Delta\nu_{1/2}$  (OH bonded) with  $\Delta\nu_{OH}$  for the systems PhOH-transition metal complexes in  $CH_2Cl_2$  solutions ( $r = 0.997$ ).

*Temperature dependence*: this reveals a reversible increase of the amount of hydrogen bonded proton donor molecules with temperature decrease.

*Linear dependence of  $\nu_{OH}$* : the linear dependence between the values of shifts of  $\nu_{OH}$  ( $\Delta\nu_{OH}$ ) and its half-widths ( $\Delta\nu_{1/2}$ ) of the OH...M bands is similar to that obtained for hydrogen bonding with organic bases (Fig. 2).

*Enthalpy of hydrogen bonding ( $-\Delta H$ )*: this can be determined from the empirical correlation equations connecting  $-\Delta H$  with  $\Delta\nu_{OH}$  and integral intensity  $A_{OH}$  obtained by analysis of organic systems [47].<sup>3</sup> Good agreement between the  $\Delta H$  values obtained from the van't Hoff equation and from the correlation of  $\Delta H/\Delta\nu$  was shown for  $(CF_3)_3COH...IrCp^*(CO)_2$ : 28.6  $kJ\ mol^{-1}$  and 28.4  $kJ\ mol^{-1}$  respectively [40]. Hydrogen bonding with transition metal atoms is of medium strength, the enthalpy values being 3–7  $kcal\ mol^{-1}$ . Proton-accepting properties of transition metal atoms can be determined by use of the empirical 'rule of factors' [39,48,49]. As a result of analysis of a large body of spectroscopic and calorimetric data for organic proton donors and bases, Iogansen proposed [48,49] an empirical correlation assuming constant acidic and basic properties in hydrogen bond formation. The general equation for a proton donor  $i$  and acceptor  $j$  is  $\Delta X_{ij} = \Delta X^s P_i E_j$ , where  $\Delta X^s$  stands for either a spectroscopic ( $\Delta\nu, \Delta A$ ) or thermodynamic ( $-\Delta H$ ) factor in a specific solvent.

<sup>3</sup>  $-\Delta H = 18\Delta\nu/(720 + \Delta\nu)$ ,  $-\Delta H = 2.9(\Delta A_{OH})^{1/2}$ , where  $(\Delta A_{OH})^{1/2} = (A_{OH\ bonded})^{1/2} - (A_{OH\ free})^{1/2}$ .

The basicity factor  $E_j$  is characteristic of the proton accepting site,  $P_i$  is the acidity factor for the proton donating site in the hydrogen bond, and  $\Delta X^s$  is that for the standard H-bonded complex (phenol–ether). For the standard complex both the basicity and acidity factors are taken as unity,  $E_j = P_i = 1$ . The values of  $P_i$  and  $E_j$  demonstrate the invariability of proton donor and proton acceptor properties of organic acids and bases in hydrogen bonding. This rule was found to be applicable to hydrogen bonding to metal atoms. Thus,  $\Delta H$  values increase linearly with the proton donating ability  $P_i$  of the proton donors in the order  $\text{PhOH} < (\text{CF}_3)_2\text{CHOH} < 4-\text{FC}_6\text{H}_4\text{OH} < 4-\text{NO}_2\text{C}_6\text{H}_4\text{OH}$  (Fig. 3). For all metals in the compounds investigated the basicity factor  $E_j$  was calculated from the equation  $E_j = \Delta H_{ij} / \Delta H_{11}^s P_i$ .<sup>4</sup> The  $E_j$  values were shown to be independent of the proton donor used. This enabled us to compare the proton accepting ability of organometallic and organic bases. The  $E_j$  factors for all metals, are, as can be seen from Fig. 4, larger than those for  $\pi$ -systems. In general the  $E_j$  factors vary over the range 0.6–1.2, from values less than for benzonitrile to those larger than that for DMSO and near to that for pyridine.

*The influence of the medium:* the sequence of changes in the hydrogen bonding character and  $\Delta H$  is retained in low polar and non-polar media (liquid xenon and supercritical liquids). As in the case of organic bases, the changes in OH values and the enthalpies of formation increase with decrease in solvent polarity. For example, H values (in kilocalories per mole) for  $\text{Cp}_2^*\text{Ir}(\text{CO})_2 \cdots \text{HOCH}(\text{CF}_3)_2$  increase in the series  $4.8(\text{CH}_2\text{Cl}_2) < 5.7(\text{CCl}_4) < 6.1(\text{C}_6\text{H}_{14})$ .

*Is a hydrogen bond of the OH  $\cdots$  M-type linear?*

The applicability of correlations obtained for linear hydrogen bonds with organic bases allowed us to assume the linearity of such hydrogen bonds in solution. Solid hydrogen bonded complexes  $\text{Cp}^*(\text{CO})_2\text{Rh} \cdots \text{HOR}$ ,  $\text{Cp}^*(\text{CO})_2\text{Ir} \cdots \text{HOR}$  ( $\text{ROH} = \text{HOC}_6\text{H}_4\text{NO}_2$ ) isolated from hexane were characterised by IR spectroscopy. The spectral changes of  $\nu_{\text{OH}}$  and  $\nu_{\text{CO}}$  appeared to have the same regularities as in solution. Bands in the range of stretching vibrations of carbonyl groups are high frequency shifted and  $\Delta\nu_{\text{OH} \cdots \text{Ir}} > \Delta\nu_{\text{OH} \cdots \text{Rh}}$ . This allows one to presume the retention of the linearity of hydrogen bonds in solid state. The linearity of ionic-type hydrogen bonds was proved by neutron diffraction study of following salts:  $\text{Et}_3\text{NH}^+\text{Co}(\text{CO})_4^-$  (the  $\text{Co} \cdots \text{H}-\text{N}$  angle =  $180^\circ$ ) [50], and  $[\text{N}^n\text{Pr}_4][\text{cis}-\text{PtCl}_2(\text{NH}_2\text{Me})_2]$  (the  $\text{Pt} \cdots \text{HN}$  angle =  $167^\circ$ ) [51].

<sup>4</sup>The  $\Delta H_{11}^s$  value is solvent dependent and for carbon tetrachloride is  $5.3 \text{ kcal mol}^{-1}$ , for dichloromethane  $-4.6 \text{ kcal mol}^{-1}$ , and for hexane  $-5.7 \text{ kcal mol}^{-1}$  [49].

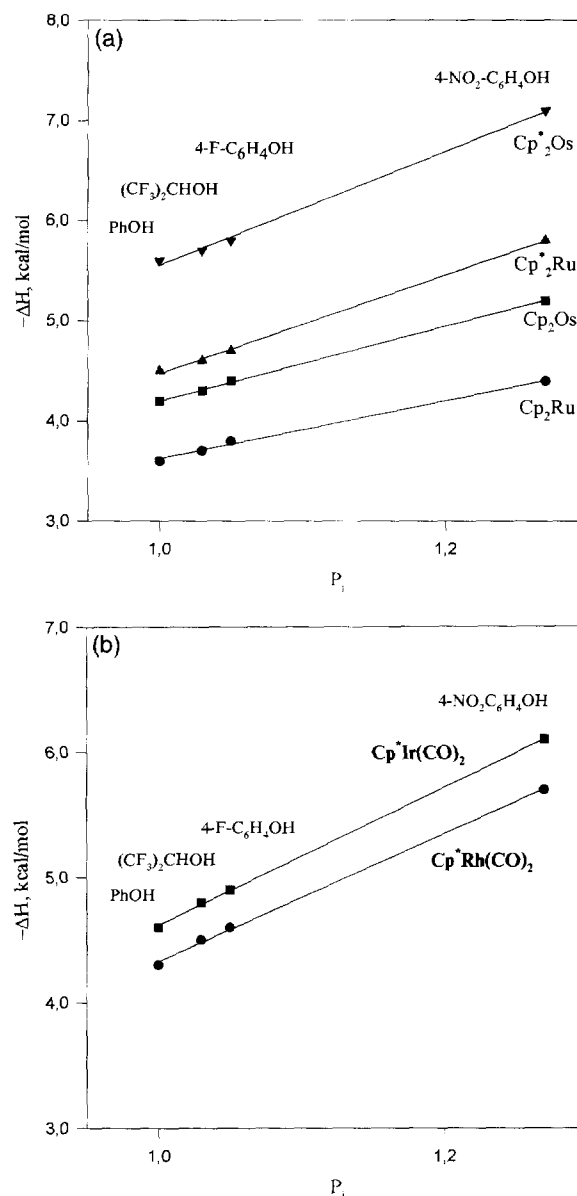


Fig. 3. The  $\text{OH} \cdots \text{M}$  hydrogen bond enthalpies  $-\Delta H$  in  $\text{CCl}_4$  (a) and  $\text{CH}_2\text{Cl}_2$  (b) vs. factor of acidity  $P_i$  for sandwich and half-sandwich complexes.

## 2.2.2. Characteristics of hydrogen bonds with a metal atom

*2.2.2.1. The dependence of basicity factors on the nature of the metal atom.* Basicity factors of transition metal atoms in isostructural compounds increase on moving down the group:  $\text{Ru} < \text{Os}$ ,  $\text{Co} < \text{Rh} < \text{Ir}$ ,  $\text{Mo} < \text{W}$  (Fig. 4). This is the main difference between hydrogen bonds with d-electrons of metal atoms and hydrogen bonds with sp-electrons of heteroatoms where basicity factors decrease down the group:  $\text{N} \gg \text{P} > \text{As}$ ,  $\text{O} > \text{S} > \text{Se}$  [39]. The sequence of proton accepting properties of a metal correlates with the increase of

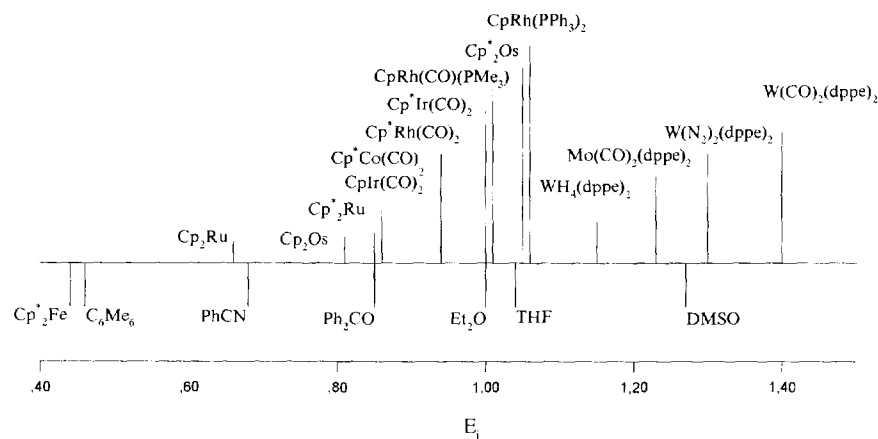


Fig. 4. Scale of  $E_j$  factors of metal atoms in transition metal complexes and organic bases [48,49]. (The values of  $E_j$  were calculated from the data of Refs. [38–45]).

chemical bond strength [52], the sequence of  $pK_a$  [53], and  $\Delta H$  values of protonation [54,55].

**2.2.2.2. The dependence of proton accepting ability of a metal atom on electron effects of ligands.** The increase of electron donor ability of ligands leads to an increase in the strength of hydrogen bonding of the  $\text{OH} \cdots \text{M}$  type. Permethylation of the rings in metallocenes increases proton acceptor ability of the metal to a greater extent than the nature of the metal atom. The following succession of  $E_j$  factors was obtained:  $\text{Cp}_2\text{Ru} < \text{Cp}_2\text{Os} < \text{Cp}_2^*\text{Ru} < \text{Cp}_2^*\text{Os}$ . The replacement of carbonyl ligands by phosphine ligands increases the proton acceptor ability of rhodium atom so much that it appeared to be greater than that of iridium. So the sequence of  $E_j$  is as follows:  $\text{CpIr}(\text{CO})_2 < \text{Cp}^*\text{Rh}(\text{CO})_2 < \text{Cp}^*\text{Ir}(\text{CO})_2 < \text{CpRh}(\text{CO})(\text{PPh}_3) < \text{CpRh}(\text{PPh}_3)_2$ . It is interesting that in these cases, as in the case of the replacement of  $\text{H}_2$  ligand by CO ligand, the strength of the hydrogen bond increases:  $\text{MH}_4(\text{dppe})_2 < \text{M}(\text{CO})_2(\text{dppe})_2$  (Fig. 4). It is notable that such effects of isoelectronic ligand groups on metal complex basicity have been found by Angelici and co-workers [54,55].

However, differences in sequences of proton acceptor properties and enthalpy of protonation were found in carbonyl compounds of molybdenum and tungsten  $\text{M}(\text{CO})_2(\text{dppe})_2$ . Basicity factors of the hydrogen bond afford a common increase down the group ( $\text{Mo} < \text{W}$ ), whereas  $-\Delta H$  values of protonation (trifluoromethanesulphonic acid in dichloroethane) changed in the reverse order:  $27.4 \text{ kcal mol}^{-1}$  and  $25.1 \text{ kcal mol}^{-1}$  respectively [55]. Such a contradiction seems to be defined by the cis–trans rearrangement accompanying the protonation reaction. Thus, a hydrogen bonding not causing rearrangement of the base reflects more precisely the electron density distribution in the initial molecule. Consequently, as in the case of organic compounds, hydrogen bond strength characterises just proton accepting ability of the reacting site.

**2.2.2.3. The influence of steric factors of ligands on the formation constants of hydrogen bonding to the metal atom.** The accessibility of the metal centre for the proton donor depends on steric effects of the ligand environment and is reflected in values of the formation constants  $K_{\text{form}}$ . It is clear that in half-sandwich compounds steric effects are smaller than in metallocenes. This is manifested in the decrease of  $K_{\text{form}}$ . Formation constants of hydrogen bonding of metallocenes (**IV**) and their permethylated analogues (**V**) are considerably smaller than those of organic bases with close basicity factors. Moreover  $-\Delta H$  and  $K_{\text{form}}$  values vary in the reverse order, i.e.  $-\Delta H(\text{Cp}_2^*\text{M}) > -\Delta H(\text{Cp}_2\text{M})$  and  $K_{\text{form}}(\text{Cp}_2^*\text{M}) < K_{\text{form}}(\text{Cp}_2\text{M})$ . Molecular mechanics calculations, with and without taking account of hydrogen bond formation, revealed that steric hindrances of methyl groups are responsible for the anomalous order of  $K_{\text{form}}$  changes:  $\text{Cp}_2^*\text{Os} < \text{Cp}_2\text{Os}$  [56].

### 2.3. The competition between metal and ligands as proton accepting sites in hydrogen bonding

Organometallic compounds usually possess several proton acceptor sites and competition arises between them in the formation of a hydrogen bond with a proton donor. At the present time it is difficult to formulate any general rules which could make it possible to predict the site of hydrogen bonding. The following is only an attempt to elucidate several situations already studied.

(1) The coexistence of two types of H-complex: the weaker one with a  $\pi$ -system of Cp rings and the stronger with a metal. Such coexistence was found in the system proton-donor–sandwich  $\pi$ -complexes (**IV**) and (**V**) ( $\text{M} = \text{Ru}, \text{Os}$ ). Steric hindrances, as shown above, considerably reduce the probability of H-bonding of the  $\text{OH} \cdots \text{M}$  type. At the same time, the formation constant for complexes with a  $\pi$ -system, as a rule, are larger than can be expected for weak H-bonds ( $2\text{--}3 \text{ kcal mol}^{-1}$ ) [38,39].

(2) The metallic site in half-sandwich compounds (VI), for example  $\text{Cp}^* \text{M}(\text{CO})_2$  is more accessible; the  $\pi$ -electron density of the Cp ring is diminished due to the electron accepting properties of CO ligands [40–43]. Proton donors with electron-rich metals (Rh, Ir) form only one type of H-bond ( $\text{OH} \cdots \text{M}$ ). Weak proton accepting properties of the metal, in the case  $\text{M} = \text{Co}$  (first transition row), just lead to development of bonding with a  $\pi$ -system [41].

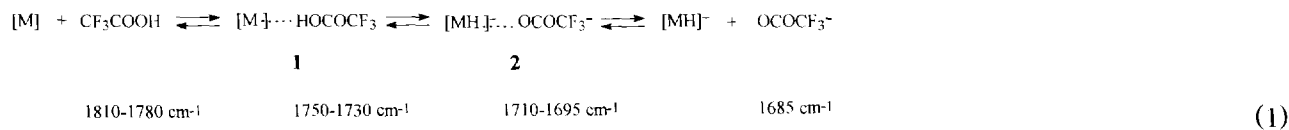
(3) Bridged carbonyl groups are known to be stronger proton acceptors. In bi- ( $\text{M} = \text{Ru}, \text{Rh}$ ) and polynuclear ( $\text{M} = \text{Rh}$ ) complexes they win the competition with the metal [57,58]. By contrast, in the iridium trinuclear cluster containing terminal carbonyl groups the site of coordination is the metal atom [58].

(4) The  $E_j$  values decrease on passing to the left in the period. Metal atoms in  $\text{Cp}^* \text{M}(\text{CO})_3$  ( $\text{M} = \text{Mn}, \text{Re}$ ) [9,10] and even in  $\text{Cp}^* \text{M}(\text{CO})_2 \text{L}$  ( $\text{L} = \text{N}_2, \text{H}_2$ ) [11] do not form complexes with proton donors, the proton accepting site being the oxygen atom of a terminal carbonyl ligand.

(5) Dinitrogen derivatives of tungsten  $\text{W}(\text{N}_2)_2(\text{dppe})_2$  show an interesting type of coordination with proton donors. The site of coordination there appeared to depend on temperature. The simultaneous formation of complexes of both types is observed at ambient temperature. Two bonded  $\nu_{\text{OH}}$  bands appear, and  $\nu_{\text{NN}}$  bands undergo both low frequency ( $\nu_{\text{NN}}$  in a  $\text{OH} \cdots \text{N}$  complex) and high frequency ( $\nu_{\text{NN}}$  in a  $\text{OH} \cdots \text{W}$  complex) shifts. However, only a single  $\nu_{\text{OH}}$  band and a high frequency  $\nu_{\text{NN}}$  band are observed at low temperature (200–220 K) (Fig. 5). Thus, with decreasing temperature, the equilibrium between the two types of hydrogen bonded complex shifts to a more thermodynamically stable one, namely  $\text{OH} \cdots \text{W}$  [44].

#### 2.4. Hydrogen bonding and proton transfer

Proton transfer in low polar media ( $\text{CH}_2\text{Cl}_2$ ) was investigated for organometallic compounds (IV–VII) with trifluoroacetic acid by IR and UV–vis spectroscopy [43,45,59]. The range of carbonyl  $\nu_{\text{CO}}$  and carboxylate  $\nu_{\text{a}(\text{OCO})}$  bands ( $1810\text{--}1600\text{ cm}^{-1}$ ) appeared to be very informative. The spectral criteria for bands assignment of the equilibrium  $\text{RCOOH} \cdots \text{N} \rightleftharpoons \text{RCOO}^- \cdots {}^+ \text{HN}$  were used [60,61]. Spectral evidence



All bands corresponding to every step of the equilibrium above are observed in the case of sterically hindered sandwich compounds [59] and  $\text{WH}_4(\text{dppe})_2$  [45]. The spectral picture is simpler for half-sandwich com-

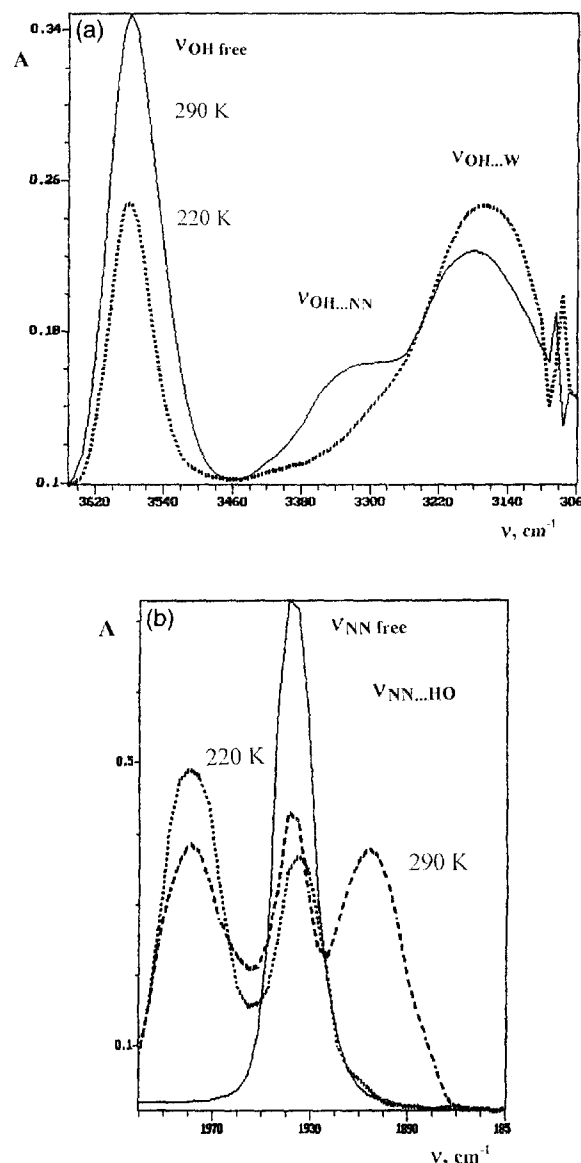


Fig. 5. Variable-temperature IR spectra of  $\text{W}(\text{N}_2)_2(\text{dppe})_2$  with  $(\text{CF}_3)_2\text{CHOH}$  in the range of  $\nu_{\text{OH}}$  (a) and  $\nu_{\text{NN}}$  (b).

that the hydrogen bonding to a metal atom ( $\text{OH} \cdots \text{M}$ ) (1) precedes proton transfer was obtained. The following equilibrium involving ionic hydrogen bond ( $\text{MH}^+ \cdots {}^-\text{O}$ ) (2) formation after proton transfer appears for all compounds investigated.

pounds [43]. Only bands of molecular- (1) and ionic-type (2) complexes appear due to high formation constants of hydrogen bonding. The temperature dependencies are similar to those described in Ref. [60]. The intensity

increase of the ionic H-complex (2) band on cooling means a shift of equilibrium to a more stable ionic form. This has been proved additionally by the intensity increase of d–d\* transition in the ionic form (UV–vis spectra) with decreasing temperature [39]. Proton transfer was also observed in pure (CF<sub>3</sub>)<sub>2</sub>CHOH, as well as (CF<sub>3</sub>)<sub>2</sub>CHOH or HCl diluted by supercritical xenon in the  $\nu_{\text{CO}}$  range of Cp\*Ir(CO)<sub>2</sub> (2150–1850 cm<sup>-1</sup>) [41,42]. However, only cation [Cp\*Ir(CO)<sub>2</sub>H]<sup>+</sup> and Cp\*(CO)<sub>2</sub>Ir···H–OR<sub>F</sub> (1) [41] have been found. Probably, excess of proton donors increases the polarity of the medium and causes the dissociation of the ionic hydrogen bond. The ionic-type of hydrogen bonded complex (2) was observed in the  $\nu_{\text{CO}}$  range in the presence of small concentrations of CF<sub>3</sub>COOH in CH<sub>2</sub>Cl<sub>2</sub> solution [39]. The same molecular- and ionic-types of H-complex were detected in the reverse process of deprotonation in CH<sub>2</sub>Cl<sub>2</sub> solution. UV–vis spectra and IR spectra in the range  $\nu_{\text{aOCO}}$ ,  $\nu_{\text{CO}}$  of the acid and  $\nu_{\text{MH}^+}$  of protonated salts (Cp<sub>2</sub>\*OsH<sup>+</sup>A<sup>-</sup> and WH<sub>5</sub>(dppe)<sub>2</sub><sup>+</sup>A<sup>-</sup>) mixed with CF<sub>3</sub>COOK in the presence of 18-crown-6 were measured [39,45,59]. The results obtained showed that the proton transfer in protonation and deprotonation processes in a low polar medium proceeded through the system of molecular (1) and ionic (2) hydrogen-bonded complexes.

### 3. Cationic hydrides as proton donors in hydrogen bonding. Hydrogen bond of the [MH]<sup>+</sup>···B type

Acidic properties of transition metal hydrides have been investigated in detail, and for many of them values of pK<sub>a</sub> in water and acetonitrile were determined [62–65]. Many neutral hydrides are strong acids. So, it was natural to assume that deprotonation proceeds through the hydrogen-bonded intermediates formation. However, attempts to detect hydrogen bonding between HCo(CO)<sub>4</sub> as relatively strong acid and nitrogen- and oxygen-containing bases appeared to be unsuccessful [66]. As is shown above, protonation of IV–VI-types of compound, as well as deprotonation of two salts—(Cp\*OsH)<sup>+</sup>A<sup>-</sup>, A = BF<sub>4</sub>, PF<sub>6</sub>, SO<sub>2</sub>CF<sub>3</sub> [59] and WH<sub>5</sub>(dppe)<sub>2</sub><sup>+</sup>A<sup>-</sup> [45]—resulted in the formation of the ionic-type of hydrogen bonding between cationic hydrides and trifluoroacetate anion [MH]<sup>+</sup>···OCOCF<sub>3</sub><sup>-</sup>.

Ion–molecular hydrogen bonding between cationic hydrides and neutral bases [MH]<sup>+</sup>···B has been detected when the bases used contained phosphoryl groups [45,67]. The choice of phosphynoxides (B) as bases was dictated by their greater ability to form hydrogen bonding and their lower basicity compared with nitrogen ones leading directly to deprotonation products. For example, Ph<sub>3</sub>PO is respectively 3 and 7.5 orders of magnitude less basic than pyridine and triethylamine [68] but give formation constants of H-complex with

phenol (log K<sub>PhOH···OP</sub>) 1.5 and 1 orders of magnitude larger [69]. Spectral evidence of hydrogen bonding was successfully observed by IR spectroscopy, both in the range of  $\nu_{\text{MH}}$  and in the range of stretching vibrations of the phosphoryl group  $\nu_{\text{P=O}}$  (1300–1100 cm<sup>-1</sup>). The increase of integral intensity (two times) in the range  $\nu_{\text{OsH}}$  and growth of the low frequency absorption take place in the presence of phosphine oxides. The intensity of the  $\nu_{\text{PO free}}$  in this case decreases and the low frequency band  $\nu_{\text{PO bonded}}$  belonging to H-complex appears. The intensity of bonded bands increases with the growth of proton acceptor properties of the phosphine oxide (Fc<sub>3</sub>PO), indicating the formation of hydrogen-bonded complexes MH<sup>+</sup>···OP. Very interesting results were obtained for HMPTA possessing a basicity close to that of pyridine and extremely high ability to form hydrogen bonds log K<sub>PhOH···OP</sub> two orders of magnitude larger than that of pyridine. In this case the process does not stop at the stage of ion–molecular hydrogen bonding and is accompanied by partial proton transfer to HMPTA. The  $\nu_{\text{OsH free}}$  and  $\nu_{\text{PO free}}$  bands disappear, but the intensity of the bonded bands are abnormally low at ambient temperature. The reverse shift of the equilibrium to ion–molecular hydrogen bonded complexes (MH<sup>+</sup>···B) on cooling is evidenced by the observed rise in both the bonded bands intensities. So, the intensity of  $\nu_{\text{OsH}}$  became five times larger than that of the free band at the same temperature [67]. Analogous hydrogen bonded complexes of triphenylphosphine oxide with cationic dihydrides [IrH<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>L<sub>2</sub>]BF<sub>4</sub> are described by Peris and Crabtree [70]. For these compounds the growth of the  $\nu_{\text{Ir-H}}$  intensity and the appearance of a low frequency  $\nu_{\text{PO···HM}}$  band are observed. Thus, a new type of hydrogen bonding, where cationic hydrides are in the role of proton donor, was detected and shown to be the preceding step for their deprotonation.

### 4. Hydride ligand as proton acceptor in hydrogen bonding of the MH<sup>δ-</sup>···<sup>δ+</sup>HX type

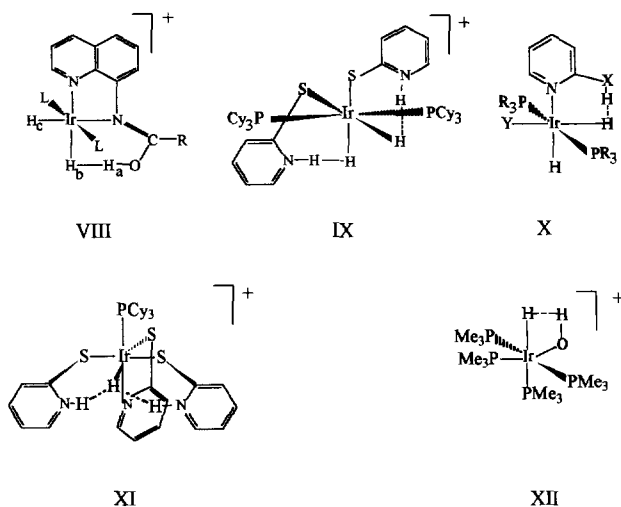
The assumption of a hydride–proton interaction in the transition state was expressed for base-catalysed alcoholysis of silicon triorganohydrides [71]. Later, the intermediate for H/D exchange or H<sub>2</sub> elimination from anionic hydrides of Group VI HM(CO)<sub>4</sub>L<sup>-</sup> was assumed to include such an interaction [72]. The suggestion that the formation of dihydrogen complexes demands the attack of the hydride hydrogen atom was expressed in the review by Jessop and Morris [62].

#### 4.1. Intramolecular hydrogen bonding between hydride ligand and proton donor groups

The existence of intramolecular hydrogen bonding between a hydride ligand and proton donor OH and NH



groups (VIII–XI) was demonstrated simultaneously by the groups of Morris [73,74] and Crabtree [75,76]. The intramolecular MH...HO interaction was detected earlier in the cation  $[\text{IrH}(\text{OH})(\text{PMe}_3)_4]^+$  (XII) by the method of neutron diffraction, the most reliable for locating of H-atoms [77]. However, the distance H...H (2.4 Å) was too large to consider such an interaction as a normal hydrogen bonding.



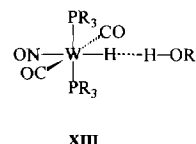
In the work of the Morris and Crabtree groups [73–76], values of 1.7–1.8 Å for the H...H distance were obtained by the less precise X-ray method, but these data coincided with those calculated from  $T_{1\text{min}}$  in NMR. The energy of hydrogen bonding according to experimental assessment is 2.9–5 kcal mol<sup>-1</sup>. For aminopyridines it decreases, depending on the trans ligand, in the sequence H > CO > CN > J > Cl > Br > F. The model ab initio studies showed that formation of hydrogen bonds of this type is determined by a number of factors: the influence of the trans ligand increasing the negative charge on the hydride atom; the energetic preference of the conformation, with the short distance between NH and IrH being optimal for hydrogen bonding; the additional polarisation of the Ir<sup>δ+</sup>–H<sup>δ-</sup> bond on the approach of the N<sup>-δ</sup>–H<sup>+δ</sup> bond [76].

So, the same question that arose on studying the hydrogen bonding with metal atom appears: is the formation of such a hydrogen bond determined in general by conformational preference? This is especially because the intramolecular interaction does not demand changes of entropy, whereas intermolecular hydrogen bonding is characterised by a  $-\Delta S$  value in the range 5–20 e.u. [78].

#### 4.2. Intermolecular hydrogen bonding between hydride ligand and proton donors

Intermolecular hydrogen bonding of the MH...HOR type between proton donors (PhOH,

(CF<sub>3</sub>)<sub>2</sub>CHOH, (CF<sub>3</sub>)<sub>3</sub>COH) and tungsten hydrides  $\text{WH}(\text{CO})_2(\text{NO})(\text{PR}_3)_2$  in low polar media was detected and characterised by IR and NMR spectroscopic methods in our common work with Berke and co-workers [79]. These hydrides have highly polarised metal–hydride bonds due to the trans effect of the NO-ligand [80]. Evidence of WH...HO (XIII) hydrogen bonding was obtained from analysis of changes of all the useful bands in the IR spectra ( $\nu_{\text{OH}}$ ,  $\nu_{\text{CO}}$ ,  $\nu_{\text{NO}}$ ,  $\nu_{\text{WH}}$ ) as well as NMR parameters (chemical shifts, coupling constants and relaxation times).



Enthalpy values obtained from equations connecting the shift value  $\Delta\nu_{\text{OH}}$  and the changes of integral intensity  $\Delta A_{\text{OH}}$  with the enthalpy of hydrogen bonds formation [46] and from the temperature dependence of equilibrium constants are close to each other.  $\Delta H$  values are 4–7 kcal mol<sup>-1</sup>, depending on the proton donor strength and on the basicity of phosphine ligand (Fig. 6). The H...H distance obtained from the hydride  $T_{1\text{min}}$  relaxation time (similar to Refs. [73,75,76]) was found to be 1.77 Å (R = Me). It was found that the properties of these unusual OH...HM hydrogen bonds were the same as those for OH...M and OH...B (B = organic base) mentioned above. These are: isotopic ratio of frequencies  $\nu_{\text{OH}\dots\text{H}}/\nu_{\text{OD}\dots\text{H}} = 1.35$ , typical for hydrogen bonds of medium strength; a similar temperature dependence; the constancy of basicity factors for different proton donors. The applicability of empirical correlation equations obtained for linear hydrogen bonds of proton donors with organic bases or metal atoms is in accordance with the assumed linearity of such hydrogen bonds (MH...HOR) in solution. It is noteworthy that these experimental results obtained are also in accordance with ab initio calculations made by Liu and Hoffman [81] for the same intermolecular interaction in the model systems FH...HLi and FH...HMnL<sub>n</sub>. The angle FH...H is practically linear (179.6°), the H...H distances are 1.658 Å and 1.683 Å, and  $\Delta H$  values are 9.29 kcal mol<sup>-1</sup> and 6.65 kcal mol<sup>-1</sup> respectively.

An interesting structure for complex  $[\text{ReH}_5(\text{PMePh}_2)_3 \cdot \text{indol}]$  (XIV) was obtained in the investigation of the interaction between XH proton donors (X = N,O) and polyhydrides by Crabtree and co-workers [82,83]. The unusually precise neutron diffraction study showed that intermolecular asymmetrical three-centre hydrogen bonding NH...H<sub>2</sub>Re exists in this structure in which a proton is bonded with two

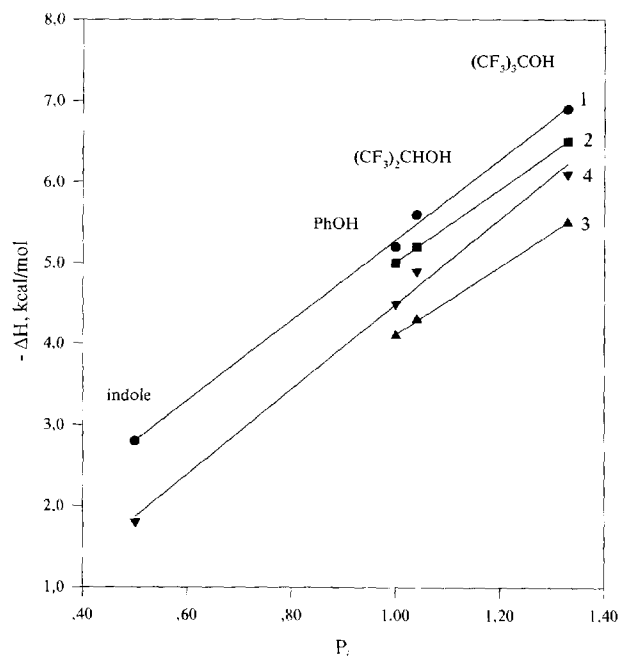
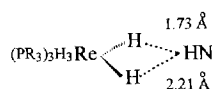


Fig. 6. The  $\text{XH} \cdots \text{HM}$  hydrogen bond enthalpies  $-\Delta H$  vs. factor of acidity  $P_i$  for hydrides of  $\text{HW}(\text{CO})_2(\text{NO})(\text{PR}_3)_2$  ( $\text{R} = \text{Me}$  (1),  $\text{Et}$  (2),  $^i\text{Pr}$  (3)) and  $\text{H}_2\text{Re}(\text{CO})(\text{NO})(\text{PMe}_3)_2$  (4).

hydride ligands; the  $\text{H} \cdots \text{H}$  distances are 1.73 and 2.21 Å.



XIV

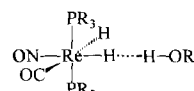
The preference of a three-centre H-bond over the two-centre type was obtained by ab initio calculations with functional density theory [83] for the model  $\text{ReH}_5(\text{PH}_3)_3 \cdot \text{NH}_3$  complex. The  $\text{H} \cdots \text{H}$  distances obtained were 1.92 and 2.48 Å.

IR spectroscopic investigation of interaction products of the rhenium polyhydrides  $[\text{ReH}_5(\text{PPh}_3)_2]$  and  $\text{ReH}_7(\text{dppe})$  and tungsten polyhydride  $\text{WH}_4(\text{PMePh}_2)_4$  with both NH and OH proton donors was performed in the region  $\nu_{\text{XH}}$  for solid films precipitated from solution [82,83]. However, the analysis of spectral data performed by the authors resulted in a number of contradictions. Firstly, the equation  $\Delta H = 1.28(\Delta \nu)^{1/2}$  can be used only for  $\Delta \nu > 200 \text{ cm}^{-1}$ , and hence is inadequate for weak proton donors [46]. Secondly, it is very strange that, even on comparing  $\Delta \nu_{\text{XH}}$  values, independence of the proton accepting ability of the polyhydrides on the partner is not manifested. So, values of  $\Delta \nu_{\text{XH}}$  in the interaction with NH acids are greater for

$\text{ReH}_7(\text{dppe})$  than that for  $\text{WH}_4(\text{PMePh}_2)_4$ . However, the sequence of shift values for H-bonding with OH proton donors is the opposite. Such particular behaviour is difficult to explain by steric factors. It could be associated with a non-equilibrium state of adducts in the films. The authors considered tungsten polyhydride to have the same site of coordination as the rhenium polyhydrides. However, as shown above, changes in the  $\nu_{\text{XH}}$  range of proton donors do not provide the structural information, especially which of the possible sites of coordination is involved in hydrogen bonding.

The problem of defining the coordination site can be simplified as in Ref. [79] by the presence of other ligands possessing characteristic vibrations. The analysis of the changes of the corresponding bands enabled one to detect the  $\text{WH} \cdots \text{HOR}$  bonding. Indirect reason in support of hydrogen bonding with the hydride or metal atom can be the proton transfer leading to the formation of cationic dihydrogen complex in the former case and to the formation of cationic  $(n+1)$  polyhydride in the latter. The proton transfer to  $\text{WH}_4(\text{dppe})_2$  was shown above to result in the formation of salt  $\text{WH}_5(\text{dppe})_2^+ \text{A}^-$  through the system of molecular and ionic H-bonds similar to  $\pi$ -complex adducts. This enables one to consider the metal atom as a hydrogen bonding site.

It turned out that the character of interaction between hydrides and proton donors depends substantially on the metal atom and on the ligand environment. So the interaction of proton donors with rhenium dihydrides  $\text{H}_2\text{Re}(\text{CO})(\text{NO})\text{PR}_3$  possessing a ligand environment similar to tungsten monohydride revealed many surprises [84].



XV

The site of hydrogen bonding in these dihydrides, taking into account the results of Ref. [79] and dihydrogen complex formation after proton transfer [85], could be suggested to be a hydride ligand. However, it appeared that 1:1 adducts, not only of  $\text{OH} \cdots \text{HM}$  type for  $\text{R} = \text{Me}$ , but also of  $\text{OH} \cdots \text{ON}$  type for bulky  $\text{R} = ^i\text{Pr}$  and both types for  $\text{R} = \text{Et}$ , are formed. So the site of hydrogen bonding depends substantially on the steric requirements of the phosphine ligands. Enthalpies of hydrogen bonding with  $\text{ReH}$  turned out to be somewhat smaller than that with  $\text{WH}$  and linearly dependent on proton donor strength (Fig. 6). The question ap-

peared: how can such a variety of complex formation in all cases lead only to one product of protonation, namely the dihydrogen complex? The formation of 2:1 complexes with  $\text{ROH} \cdots \text{HRe}$  bonding with excess of proton donor became the answer. H-bonding hydride ligand always occurs before the formation of the dihydrogen complexes.

The results of model calculations for  $\text{ReH}_2(\text{CO})(\text{NO})(\text{PH}_3)_2 \cdot \text{H}_2\text{O}$  performed by the functional density method are in agreement with the experimental data. The most energetically preferable site of coordination for a sterically unhindered phosphine-containing molecule is the hydride ligand. It is interesting that calculations showed a considerably greater strength in the linear two-centre  $\text{H} \cdots \text{H}$  bond compared than in the three-centre one.

## 5. Conclusion

The review presented shows how fast the category concerning the new field of knowledge—hydrogen bonds specific to organometallic compounds—is proceeding. The use of the combination of spectral methods (IR in combination with UV–vis and NMR) appeared to be highly efficient in studying hydrogen bonding. Three new types of intermolecular hydrogen bond were discovered: hydrogen bonds with a metal atom ( $\text{XH} \cdots \text{M}$ ) and hydride hydrogen ( $\text{XH} \cdots \text{HM}$ ) as bases, as well as between cationic hydride as proton donor and organic bases ( $\text{MH}^+ \cdots \text{B}$ ).

Usually, owing to their low strength, hydrogen bond formation does not lead to a substantial perturbation of the molecules under investigation. Thus, studies of H-bonding interactions in solution are one reliable way of determining the charge distribution in the molecule and hence the site of electrophilic attack on the transition metal complex. The review presents investigations of complex structures containing intramolecular hydrogen bonds of  $\text{XH} \cdots \text{M}$  and  $\text{XH} \cdots \text{HM}$  types. However, neutron diffraction and X-ray investigations of intermolecular adducts  $\text{XH} \cdots \text{M}$ - and  $\text{MH}^+ \cdots \text{B}$ -types are unknown as is their theoretical investigation.

Cleavage or formation reactions of metal–hydrogen bonds are of crucial importance in catalysis. The elucidation of the role of hydrogen bonding will enable us to understand more clearly the mechanism of many processes concerning the proton transfer. The equilibrium of proton transfer to a metal atom is already established to proceed through the system of hydrogen-bonded complexes of molecular- and ionic-types.

The simultaneous existence of two such types of stable complex is a criterion for the existence of two minima on the potential energy surface. The protonation of hydrides is one of the most general methods of generating of dihydrogen complexes. Detection of hy-

drogen bonding with hydride ligand which precedes protonation reveals the possibility of investigation of the equilibrium between such adducts and dihydrogen complexes. Unfortunately, to date, there are no theoretical researches concerning the potential energy surfaces of proton transfer for any such system.

We hope that this review will stimulate further investigations in this field.

## Acknowledgements

The work of the Epstein group was in part supported by Russian Found of Fundamental Research (Grant Nos. 93-03-4610 and 96-03-34114) and International Scientific Foundation. We gratefully acknowledge Professor M.I. Rybinskaya, Professor H. Berke, Dr. A.Z. Kreindlin and Dr. T.V. Timofeeva for stimulating discussions and all our collaborators for fruitful joint investigations.

## References

- [1] P. Schuster and G. Zundel (eds.), *The Hydrogen Bond*, Vol. 1, Amsterdam, 1976.
- [2] G.A. Jeffrey and W. Saenger, *Hydrogen Bonding in Biological Structures*, Springer, Berlin, 1991.
- [3] L. Legon and J. Millen, *Acc. Chem. Res.*, 20 (1987) 39.
- [4] L.M. Epstein and A.V. Iogansen, *Usp. Khim.*, 59 (1990) 229.
- [5] L.M. Epstein, L.D. Ashkinadze, S.O. Rabcieva and L.A. Kazitsyna, *Dokl. Acad. Nauk SSSR*, 190 (1970) 128.
- [6] L.A. Leites, L.E. Vinogradova, N.A. Ogorodnicova and L.I. Zaharkin, *Zh. Prikl. Spectrosk.*, 16 (1972) 488.
- [7] G. Cerichelli, G. Illuminati, G. Ortaggi and A.M. Giuliani, *J. Organomet. Chem.*, 127 (1977) 357.
- [8] V.G. Alexanyan, Ya.M. Kimmel'feld, R.B. Materikova and G.M. Smirnova, *Zh. Fiz. Khim.*, 54 (1980) 663 (English translation in *Russ. Phys. Chem.*, (1980) 3).
- [9] (a) B.V. Lokshin, S.G. Kazaryan and A.G. Ginzburg, *Izv. Akad. Nauk SSSR Ser. Khim.*, 11 (1986) 2605. (b) B.V. Lokshin, S.G. Kazaryan and A.G. Ginzburg, *Izv. Akad. Nauk SSSR Ser. Khim.*, 4 (1987) 948. (c) B.V. Lokshin, S.G. Kazaryan and A.G. Ginzburg, *Izv. Akad. Nauk SSSR Ser. Khim.*, 2 (1988) 333. (d) B.V. Lokshin, S.G. Kazaryan and A.G. Ginzburg, *Izv. Akad. Nauk SSSR Ser. Khim.*, 3 (1988) 562.
- [10] B.V. Lokshin, S.G. Kazaryan and A.G. Ginzburg, *J. Mol. Struct.*, 174 (1988) 29.
- [11] P.A. Hamley, S.G. Kazarian and M. Poliakoff, *Organometallics*, 13 (1994) 1767.
- [12] (a) S.E. Kogley, C. Schaverien, J.H. Freudenberger, R.G. Bergman, S.P. Nolan and C.D. Hoff, *J. Am. Chem. Soc.*, 109 (1987) 6563. (b) Y.J. Kim, K. Osakado, A. Takenak and A.J. Yamamoto, *J. Am. Chem. Soc.*, 112 (1990) 1096.
- [13] (a) K. Osakado, K. Ohchiro and A. Yamamoto, *Organometallics*, 10 (1991) 404. (b) P.L. Alsters, P.J. Baesjou, M.D. Janssen, H. Kooijman, A. Sichere-Roetman, A.L. Spek and G. Koten, *Organometallics*, 11 (1992) 4124.
- [14] (a) D. Braga, F. Grepioni, P. Sabatino and G.R. Desiraju, *Organometallics*, 13 (1994) 3532. (b) D. Braga, F. Grepioni, K. Biradha, V.R. Pedireddi and G.R. Desiraju, *J. Am. Chem. Soc.*, 117 (1995) 3156.

- [15] W.R. Jackson and C.H. McMullen, *J. Chem. Soc.*, 2 (1965) 1170.
- [16] (a) D.S. Trifan and R. Bacskai, *J. Am. Chem. Soc.*, 82 (1960) 5010. (b) E.A. Hill and J.H. Richards, *J. Am. Chem. Soc.*, 83 (1961) 4216. (c) F.H. Hon and T.T. Tidwell, *J. Org. Chem.*, 37 (1972) 1782. (d) A.N. Nesmeyanov, M.D. Reshetova and E.G. Perevalova, *Izv. Akad. Nauk SSSR Ser. Khim.*, 9 (1969) 1939. (e) J. Mirek, S. Rachwal and B. Kawaler, *J. Organomet. Chem.*, 248 (1983) 107.
- [17] A.W. Baker and D.E. Bublitz, *Spectrochim. Acta*, 22 (1966) 1787.
- [18] (a) L.D. Ashkinadze, Yu.N. Polivanov, A.I. Yanovsky, Yu.T. Struchkov, V.N. Postnov and V.A. Sazonova, *Izv. Akad. Nauk SSSR Ser. Khim.*, 7 (1985) 1672. (b) V.N. Postnov, L.D. Ashkinadze, Yu.N. Polivanov and S.N. Grukhanova, *Dokl. Akad. Nauk SSSR*, 288 (1986) 1129.
- [19] (a) I.T. Chizhevskii, N.V. Rastova, N.E. Kolobova, L.E. Vinogradova and L.A. Leites, *Izv. Akad. Nauk SSSR Ser. Khim.*, 6 (1985) 1382. (b) L.E. Vinogradova, L.A. Leites, I.T. Chizhevskii, N.V. Rastova, N.E. Kolobova, A.I. Yanovsky and Yu.T. Struchkov, *Izv. Akad. Nauk SSSR Ser. Khim.*, 7 (1986) 1685.
- [20] L.E. Vinogradova, L.A. Leites, I.T. Chizhevskii, N.V. Rastova, N.E. Kolobova, A.I. Yanovsky and Yu.T. Struchkov, *Metalloorg. Khim.*, 4 (1989) 769 (English translation in *Organomet. Chem. USSR*, (1989) 4).
- [21] E.S. Shubina, L.M. Epstein, T.V. Timofeeva, Yu.T. Struchkov, A.Z. Kreindlin, S.S. Fadeeva and M.I. Rybinskaya, *J. Organomet. Chem.*, 346 (1988) 59.
- [22] E.S. Shubina, L.M. Epstein, T.V. Timofeeva, Yu.T. Struchkov, A.Z. Kreindlin, S.S. Fadeeva and M.I. Rybinskaya, *J. Organomet. Chem.*, 401 (1991) 133.
- [23] E.S. Shubina, L.M. Epstein, Yu.L. Slovokhotov, A.V. Mironov, Yu.T. Struchkov, V.S. Kaganovich, A.Z. Kreindlin and M.I. Rybinskaya, *J. Organomet. Chem.*, 401 (1991) 155.
- [24] E.S. Shubina, A.N. Krylov, T.V. Timofeeva, Yu.T. Struchkov, A.G. Ginzburg, N.M. Loim and L.M. Epstein, *J. Organomet. Chem.*, 434 (1992) 329.
- [25] E.S. Shubina, L.M. Epstein, T.V. Timofeeva, Yu.T. Struchkov, A.Z. Kreindlin, S.S. Fadeeva and M.I. Rybinskaya, *J. Organomet. Chem.*, 345 (1988) 313.
- [26] E.S. Shubina, L.M. Epstein, A.Z. Kreindlin, S.S. Fadeeva and M.I. Rybinskaya, *J. Organomet. Chem.*, 401 (1991) 145.
- [27] M. Gruselle, B. Maleizieux, L.L. Troitskaya, V.I. Sokolov, L.M. Epstein, E.S. Shubina and J. Vaissermann, *Organometallics*, 13 (1994) 200.
- [28] E.S. Shubina and L.M. Epstein, *J. Mol. Struct.*, 265 (1992) 367.
- [29] L.M. Epstein and E.S. Shubina, *Metalloorg. Khim.*, 5 (1992) 61 (English translation in *Organomet. Chem. USSR*, 5 (1992) 31).
- [30] L.M. Epstein and E.S. Shubina, *Khim. Phys.*, 11 (1992) 755.
- [31] R.R. Shagidulin, A.H. Plyamovatii and S.A. Katsuba, *Izv. Akad. Nauk SSSR Ser. Khim.*, 10 (1980) 2262.
- [32] Yu.T. Struchkov, A.S. Batsanov, S. Toma and M. Salisova, *J. Organomet. Chem.*, 329 (1987) 373.
- [33] C. Lecomte, Y. Dusauoy, J. Protas, C. Mois and J. Tirouflet, *Acta Crystallogr. Sect. B*, 29 (1973) 488.
- [34] N.D. Sokolov, *The Hydrogen Bond*, Nauka, Moscow 1981, p. 63.
- [35] M.I. Rybinskaya, A.Z. Kreindlin, A.N. Kiseleva, A.A. Kamysheva, N.V. Kruglova, P.V. Petrovskii, L.M. Epstein, E.S. Shubina, A.N. Krylov and I. Turpeinen, *Izv. Akad. Nauk Ser. Khim.*, (1995) 2486 (*Russ. Chem. Bull.*, 44 (1995) 2382).
- [36] I.T. Chizhevskii, N.V. Rastova, N.E. Kolobova, P.V. Petrovskii, E.I. Fedin, L.E. Vinogradova, L.A. Leites, A.I. Yanovsky and Yu.T. Struchkov, *J. Organomet. Chem.*, 339 (1988) 165.
- [37] L.E. Vinogradova, L.A. Leites, A.Z. Kreindlin, I.T. Chizhevskii, E.S. Shubina and L.M. Epstein, *Metalloorg. Khim.*, 3 (1990) 1192 (English translation in *Organomet. Chem. USSR*, (1990) 5).
- [38] E.S. Shubina, A.N. Krylov, A.Z. Kreindlin, M.I. Rybinskaya and L.M. Epstein, *J. Mol. Struct.*, 301 (1993) 1.
- [39] L.M. Epstein, A.N. Krylov and E.S. Shubina, *J. Mol. Struct.*, 322 (1994) 345.
- [40] S.G. Kazarian, P.A. Hamley and M. Poliakov, *J. Chem. Soc. Chem. Commun.*, (1992) 994.
- [41] S.G. Kazarian, P.A. Hamley and M. Poliakov, *J. Am. Chem. Soc.*, 115 (1993) 9069.
- [42] S.G. Kazarian, M. Jobling and M. Poliakov, *Mendeleev Commun.*, (1993) 149.
- [43] E.S. Shubina, A.N. Krylov, D.V. Muratov, A.A. Fil'chikov and L.M. Epstein, *Izv. Akad. Nauk Ser. Khim.*, 11 (1993) 2002 (*Russ. Chem. Bull.*, 42 (1993) 1919).
- [44] L.M. Epstein, A.N. Krylov, E.S. Shubina, A.P. Borisov and V.D. Makhaev, *XVIIth Int. Conf. Organometallic Chemistry, Sussex, UK, 1994*, p. 313.
- [45] E.S. Shubina, A.N. Krylov, N.V. Belkova, L.M. Epstein, A.P. Borisov and V.D. Makhaev, *J. Organomet. Chem.*, 493 (1995) 275.
- [46] M. Poliakov, S.M. Howdle and S.G. Kazarian, *Angew. Chem. Int. Ed. Engl.*, 34 (1995) 1275.
- [47] A.V. Iogansen, *The Hydrogen Bond*, Nauka, Moscow, 1981, p. 134.
- [48] A.V. Iogansen, *Theor. Experim. Khim.*, 7 (1971) 314.
- [49] A.V. Iogansen, *Theor. Experim. Khim.*, 7 (1971) 302.
- [50] L. Brammer, M.C. McCann, R.M. Bullock, R.K. McMullan and P. Sherwood, *Organometallics*, 11 (1992) 2339.
- [51] L. Brammer, J.M. Charnock, P.L. Goggin, R.J. Goodfellow, A.G. Orpen and T.F. Koetzle, *J. Chem. Soc. Dalton Trans.*, (1991) 1789.
- [52] J.A.M. Simoes and J.L. Beauchamp, *Chem. Rev.*, 90 (1990) 629.
- [53] S.S. Kristjansdottir and J.R. Norton, in A. Dedieu (ed.), *Transition Metal Hydrides*, New York, 1991, p. 309.
- [54] (a) M.K. Rottink and R.J. Angelici, *J. Am. Chem. Soc.*, 115 (1993) 7267. (b) J.R. Sowa, V. Zanotti, G. Facchin and R.J. Angelici, *J. Am. Chem. Soc.*, 113 (1991) 9185. (c) M.K. Rottink and R.J. Angelici, *Inorg. Chem.*, 32 (1993) 3282.
- [55] R.J. Angelici, *Acc. Chem. Res.*, 28 (1995) 51 and references cited therein.
- [56] T.V. Timofeeva, A.N. Krylov, E.S. Shubina and L.M. Epstein, *Izv. Akad. Nauk Ser. Khim.*, (1995) 1925 (*Russ. Chem. Bull.* (1995) 1845).
- [57] B.V. Lokshin, A.G. Ginzburg and S.G. Kazaryan, *J. Organomet. Chem.*, 397 (1990) 203.
- [58] A.N. Krylov, E.S. Shubina, D.V. Muratov, E.V. Vorontsov and L.M. Epstein, *Izv. Akad. Nauk Ser. Khim.*, 11 (1995) 386 (*Russ. Chem. Bull.*, 44 (1995) 378).
- [59] E.S. Shubina, A.N. Krylov, A.Z. Kreindlin, M.I. Rybinskaya and L.M. Epstein, *J. Organomet. Chem.*, 465 (1994) 259.
- [60] G.S. Denisov, G.S. Gusakova and A.L. Smolyansky, *J. Mol. Struct.*, 15 (1973) 377.
- [61] Z. Dega-Szafran, M. Grundwald-Wyspinka and M. Szafran, *Spectrochim. Acta Part A*, 47 (1991) 543.
- [62] P.G. Jessop and R.H. Morris, *Coord. Chem. Rev.*, 121 (1992) 155.
- [63] (a) E.P. Cappellani, S.D. Drouin, G. Jia, P.A. Maltby, R.H. Morris and C.T. Schweitzer, *J. Am. Chem. Soc.*, 116 (1994) 3375. (b) G. Jia and R.H. Morris, *J. Am. Chem. Soc.*, 113 (1991) 875.
- [64] (a) O.V. Ruyn, M. Tilset and V.D. Parker, *J. Am. Chem. Soc.*,

- 112 (1990) 2618. (b) O.V. Ryan, M. Tilset and V.D. Parker, *Organometallics*, 10 (1991) 298. (c) M. Tilset, *J. Am. Chem. Soc.*, 114 (1992) 2740.
- [65] K.W. Kramarz and J.R. Norton, *Prog. Inorg. Chem.*, 42 (1994) 1.
- [66] S.S. Kristjansdottir, J.R. Norton, A. Moroz, R.L. Sweany and S.L. Whittenburg, *Organometallics*, 10 (1991) 2357.
- [67] L.M. Epstein, E.S. Shubina, A.N. Krylov, A.Z. Kreindlin and M.I. Rybinskaya, *J. Organomet. Chem.*, 447 (1993) 227.
- [68] (a) J.F. Coetzee and G.R. Padmanabhan, *J. Am. Chem. Soc.*, 87 (1965) 5005. (b) Matrosov, Ye.H. Tsvetkov, Z.N. Mironova, R.A. Malevannaya and M.I. Kabachnik, *Izv. Akad. Nauk SSSR Ser. Khim.*, (1975) 1333.
- [69] (a) M. Abraham, P. Grelier and D.V. Prior, *Tetrahedron Lett.*, 30 (1989) 2571. (b) L.M. Epstein, E.S. Shubina, A.I. Krylova, V.S. Tolkunova and D.N. Kravtsov, *Izv. Akad. Nauk SSSR Ser. Khim.*, (1987) 572.
- [70] E. Peris and R.H. Crabtree, *J. Chem. Soc. Chem. Commun.*, (1995) 2179.
- [71] (a) K.O. Donnel, R. Bacon, K.L. Chellapa, R.L. Schowen and J.K. Lee, *J. Am. Chem. Soc.*, 94 (1972) 2500. (b) C. Eaborn and J.D. Jenkus, *J. Organomet. Chem.*, 69 (1974) 185.
- [72] P.L. Gaus, S.C. Kao, M.Y. Darensbourg and L.W. Arndt, *J. Am. Chem. Soc.*, 106 (1984) 4752.
- [73] A.J. Lough, S. Park, R. Ramachandran and R.H. Morris, *J. Am. Chem. Soc.*, 116 (1994) 8356.
- [74] S. Park, R. Ramashandran, A.J. Lough and R.H. Morris, *J. Chem. Soc. Chem. Commun.*, (1994) 2201.
- [75] (a) J. C. Lee, E. Peris, A. Rheingold and R.H. Crabtree *J. Am. Chem. Soc.*, 116 (1994) 11014. (b) J.C. Lee, A. Rheingold, B. Muller, P.S. Pregosin and R.H. Crabtree, *J. Chem. Soc. Chem. Commun.*, (1994) 1021.
- [76] E. Peris, J.C. Lee, J.R. Rambo, O. Eisenstein and R.H. Crabtree, *J. Am. Chem. Soc.*, 117 (1995) 3485.
- [77] R.C. Stevens, R. Bau, D. Milstein, O. Blum and T.L. Koetzle, *J. Chem Soc. Dalton Trans.*, (1990) 1429.
- [78] (a) H.H. Jaffe, *J. Am. Chem. Soc.*, 79 (1957) 2373. (b) E.M. Arnett, L. Joris, E. Mitchell, T.S.S.R. Murty, T.M. Gorrie and P. Schleyer, *J. Am. Chem. Soc.*, 92 (1970) 2365. (c) M.C.S. Lopes and H.W. Thompson, *Spectrochim. Acta Part A*, 24 (1968) 1367.
- [79] (a) E.S. Shubina, N.V. Belkova, A.N. Krylov, L.M. Epstein, D.G. Gusev and H. Berke, *XIth FEICHEM Conf. Organometallic Chemistry, Parma, Italy, 1995*, p. 174. (b) E.S. Shubina, N.V. Belkova, A.N. Krylov, E.V. Vorontsov, L.M. Epstein, D.G. Gusev, M. Niedermann and H. Berke, *J. Am. Chem. Soc.*, 118 (1996) 1105.
- [80] H. Berke and P. Burger, *Comments Inorg. Chem.*, 16 (1994) 279.
- [81] Q. Liu and R. Hoffmann, *J. Am. Chem. Soc.*, 117 (1995) 10108.
- [82] E. Peris, J. Wessel, B.P. Patel and R.H. Crabtree, *J. Chem Soc. Chem. Commun.*, (1995) 2175.
- [83] 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 and R.H. Crabtree, *Angew. Chem.*, 107 (1995) 2711; *Angew. Chem. Int. Ed. Engl.*, 34 (1995) 2507.
- [84] N.V. Belkova, E.S. Shubina, A.V. Ionidis, L.M. Epstein, H. Jacobsen, A. Messmer and H. Berke, *Inorg. Chem.*, in press.
- [85] S. Feracin, T. Burgi, V.I. Bakhmutov, I. Eremenko, E.V. Vorontsov, A.B. Vimenits and H. Berke, *Organometallics*, 13 (1994) 4194.