Activation of M—H bond upon the complexation of transition metal hydrides with acids and bases*

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Features of the electronic structure of adducts of transition metal hydride complexes (Cp*M(dppe)H, dppe is the 1,2-(diphenylphosphino)ethane, M = Fe, Ru, Os; CpM(CO)$_3$H, M = Mo, W) with acids and bases were analyzed with the ADF2014 program using energy decomposition analysis (EDA) by the Ziegler—Rauk method combined with the natural orbitals for chemical valence theory (ETS-NOCV). The nature of orbital interactions in the complex determines the reaction pathway: $\sigma_{MH} \rightarrow \sigma^*_{OH}$ interaction leads to the proton transfer to hydride ligand, $n_M \rightarrow \sigma^*_{OH}$ leads to the metal atom protonation, $n_N \rightarrow \sigma^*_{MH}$ implies the metal hydride deprotonation, and $\sigma_{MH} \rightarrow n^*_B$ corresponds to the hydride transfer to Lewis acid. It was shown that M—H bond polarization change has the similar character upon the formation of complexes with Brønsted and Lewis acids. The ease of polarization of M—H bonds in complexes CpM(CO)$_3$H determines their reactivity as proton and hydride ion donors.

Key words: quantum chemical calculations, hydrogen bonds, non-covalent interactions, transition metal hydrides.

Neutral transition metal hydrides can demonstrate different reactivity being formally the sources of hydrogen atom H·, hydride ion H⁻, or proton H⁺.[1,2] This kind of reactivity is not merely typical of metal hydrides as a class of compounds, but is well known in some cases when, depending on the conditions, one and the same hydride complex participates in the reactions of all three types. For example, CpM(CO)$_3$H (M = Cr, Mo, W; Cp = η^5-C$_5$H$_5$), HM(CO)$_5$ (M = Mn, Re) and CpM(CO)$_2$H (M = Fe, Ru, Os) exibit unique reactivity.[3—7]

The hydride transfer from the metal complexes is the key stage of the ionic hydrogenation reactions both in stoichiometric and in catalytic variants. Hydride carbonyl complexes CpM(CO)$_3$H (M = Cr, Mo, W) are used as hydride donors in combination with proton donor, trifluoromethyl sulfonic acid CF$_3$SO$_3$H, in reactions of hydrogenation of substituted alkenes,[8] and also aldehydes and ketones.[9] The proton transfer to an organic substrate competes with the metal hydride protonation with the formation of classical or non-classical hydride.[10] Half-sandwich ruthenium hydride complexes Cp´Ru(P—P)H (Cp´ = η^5-C$_5$R$_5$) are the catalysts of the ionic hydrogenation of imines, imine salts, ketones and aziridinium

cations.[11—13] In this case the cationic complexes [Cp´Ru(P—P)H$_2$]⁺ serve as proton sources, and neutral hydrides Cp´Ru(P—P)H serve as hydride sources.[11]

It is known that hydrides CpM(CO)$_3$H possess relativity high acidity. The pK_a values are 13.3 (Cr), 13.9 (Mo), 16.1 (W)[14] in acetonitrile and ~17 (CpMo(CO)$_3$H) in THF,[15] which are comparable to the acidity values for MeSO$_3$H (pK_a^{MeCN} = 10.0),[14] 2,4-dinitrophenol (pK_a^{MeCN} = 16.0),[14] [HNEt$_3$]⁺ (pK_a^{THF} = 12.5),[15] and cationic hydride complexes (for example, pK_a^{THF} = 12.3 for [Cp*Ru(H)$_2$(PMePh$_2$)$_2$]⁺ and 16.6 for [Ru(H$_2$)H(PMe$_3$)$_4$]⁺).[15]

Hydrogen bonds between organic acids and bases XH$^{\delta+}\cdots^{\delta-}$Y precede the proton transfer. Transition metal hydrides can also serve as acids and bases in the formation of hydrogen bonds.[16,17] The hydride ligand is expected to have the H$^{\delta+}$ positive charge as an acid, while the hydride complexes (proton acceptors in hydrogen bond) are characterized by the opposite polarization of metal—hydrogen M—H$^{\delta-}$ bond. It was shown experimentally that CpM(CO)$_3$H complexes serve as proton donors in hydrogen bonding with organic and organometallic bases, which precede the proton transfer.[18,19] At the same time, it is known[8,20] that protonation by strong acids of CpW(CO)$_3$H, like many other basic hydride complexes, leads to the formation of cationic dihydride [CpW(CO)$_3$(H)$_2$]⁺. Therefore, the question arises about

the conditions of M—H bond repolarization entailed by intermolecular interactions with acids or bases. The results of quantum chemical study of the influence of intermolecular interactions on the activation of M—H bond are presented herein on the example of basic complexes of group 8 metals Cp*M(dppe)H (**1**, M = Fe, Ru, Os, dppe is 1,2-(diphenylphosphino)ethane) and hydrides of group 6 metals CpMH(CO)$_3$ (**2**, M = Mo, W) having both acidic and basic properties. The complex geometries were optimized in Gaussian09 (see Ref. 21) by BP86 methods (for Cp*MH(dppe) with the replacement of Ph rings of dppe ligand by hydrogen atoms) and M05 (for CpMH(CO)$_3$), the features of the electronic structure were analyzed with the ADF2014 program[22] using energy decomposition analysis (EDA) by the Ziegler—Rauk method[23—25] combined with the natural orbitals for chemical valence theory (ETS-NOCV).[26]

Calculation Procedure

The approach for analysis of the electronic structure of dihydrogen bonded transition metal hydride complexes was developed by us earlier on the example of complexes Cp*M(dpe)H · TFE (M = Fe, Ru, Os; dpe is diphosphinoetane, model ligand; TFE is trifluoroethanol CF$_3$CH$_2$OH).[27] The results obtained are complemented with data on the polarization of M—H and O—H bonds and are presented in this work to compare the characteristics of intermolecular complexes of different types.

The geometries of the hydrogen-bonded complexes CpMH(CO)$_3$ (**2**, M = Mo, W) with NMe$_3$ determined[18] earlier were used to analyze of the electronic structure of the com-

plexes. The calculation of CpMH(CO)$_3$ complexes with the BH$_3$ Lewis acid was performed in this work. The geometry was optimized in the Gaussian09 program using the M05 density functional method[28] with the basis sets:[29—31] LANL2TZ(f) for Mo and W atoms, 6-311++G(d,p) for hydride atom and BH$_3$ fragment, and 6-31G(d,p) for all the other atoms.

The analysis of charges was performed by the natural orbitals method (NBO).[32,33] The EDA by the Ziegler—Rauk method[23—25] was performed with the use of ADF2014 program package[22] without geometry reoptimization using the M05 functional and TZP basis.[34] The participation of particular orbitals was analyzed with the use of the natural orbitals for chemical valence theory (ETS-NOCV).[26]

When applying the ETS-NOCV scheme, the orbital interaction energy ΔE_{orb} is expressed in terms of NOCV's according to the formula [26,35]

$$\Delta E_{orb} = \sum \Delta E_k^{orb} = \sum v_k [-F_{-k}^{TS} + F_k^{TS}],$$

where F_{-k}^{TS} and F_k^{TS} are the diagonal elements of the Kohn—Sham matrix, corresponding to the orbitals with the $-v_k$ and v_k eigenvalues. The advantage of this approach is that only few orbital pairs make the main contribution to the total energy ΔE_{orb}. The deformation electron density $\Delta \rho_k(r)$ and energy ΔE_k^{orb} of each orbital interaction can be analyzed with the use of this approach as well.

Results and Discussion

The σ(M—H) molecular orbitals of Cp*MH(dpe) and CpMH(CO)$_3$ complexes have similar structure; the main difference is in the greater electron density shift to the hydride hydrogen in the case of Cp*MH(dpe) (Fig. 1). The M—H bond polarization, pol(M—H), determined
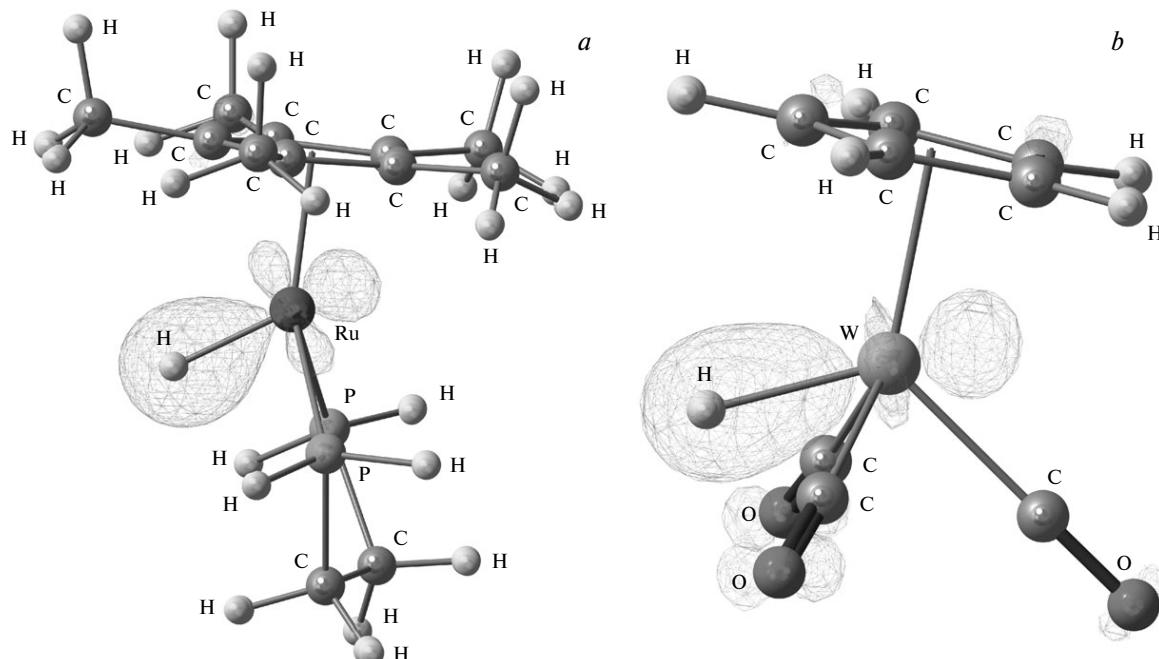
Fig. 1. The σ$_{MH}$ orbitals on the example of complexes Cp*RuH(dpe) (HOMO-5, *a*) and CpWH(CO)$_3$ (HOMO-4, *b*); isosurface at 0.08958 a.u.

here as a portion of electron density on the hydrogen atom relative to the total occupancy of σ_{MH},[27,36] is a little lower than 50% in series of complexes **1** (47.1, 47.6, and 48.7 for **1-Fe**, **1-Ru**, and **1-Os** respectively), but higher than in proton-donor hydride complexes **2** (40.5 and 42.1 for **2**-**Mo** and **2-W** respectively).

The formation of intermolecular complexes with Lewis acids must initiate the metal—hydrogen M—H$^{\delta-}$ bond polarization and precede the hydride transfer, as well as the formation of dihydrogen bond M —H$\cdots$H—X with Brønsted acids indicates the metal—hydrogen M—H$^{\delta-}$ bond polarization. To compare the changes that occur with the M—H bond upon the complexation with acids and bases we compared the electronic structure of dihydrogen-bonded complexes **1** with TFE and classical hydrogen-bonded complexes **2** with NMe$_3$ with the characteristics of adducts of hydrides **2** with the BH$_3$ Lewis acid.

The electronic interaction in the hydrogen bond is described by the electron donation from the occupied orbital of the base to the σ^*_{XH} antibonding orbital of the proton donor[37] which is accompanied by the increase in the positive charge on the acid hydrogen atom and by the increase of negative charge on the interacting atom of the base.[27,36,38] In the case of dihydrogen bond it is the $\sigma_{MH} \to \sigma^*_{OH}$ interaction, and in the case of complex, where the hydride serves as an acid, **2·NMe$_3$**, it is $n_{N:} \to \sigma^*_{MH}$. The quantitative characteristics of $\sigma_{MH} \to \sigma^*_{OH}$ orbital interaction in complexes **1·TFE** were obtained by us earlier[27] and, together with the calculated characteristics of $n_{N:} \to \sigma^*_{MH}$ interaction in complexes **2·NMe$_3$**, are presented in Table 1. The comparison of the

data obtained shows that orbital term makes the contribution of 43—52% into the stabilization of both MH$\cdots$N bond and MH$\cdots$HO bond of the complexes.

The decomposition of orbital interaction energy into the contributions of individual orbitals with the use of natural orbitals for chemical valence theory (NOCV) revealed one prevalent interaction of the trimethylamine HOMO, which is the lone electron pair of nitrogen, with the MH hydride LUMO (Table 2). When using this scheme, only the main orbital interactions are analyzed, that is why the sum of energy contributions of distinct orbitals (see Table 2) is smaller than the total orbital interaction energy ΔE_{orb} (see Table 1). It should be noted that LUMO+1 is the only significant acceptor of electron density for tungsten hydride, while in the stronger complex [Mo]H$\cdots$NMe$_3$ the additional interaction with LUMO+11, which also has a character of σ^*_{MH} orbital, is realized. The LUMO+11 orbital energy in CpMoH(CO)$_3$ is only 3.0 eV higher than the LUMO+1 energy, in spite of the high ordinal number. The interacting orbitals and the resultant deformation electron density are presented in Fig. 2. Thus, [M]H$\cdots$NMe$_3$ complexes from the orbital interaction standpoint are described by the standard orbital model of hydrogen bond, which implies the donation of electron density of the base to the unoccupied orbital σ^*_{XH} of proton donor.

The polarization of O—H and M—H bonds participating in the formation of hydrogen-bonded complexes, *i.e.* the portion of electron density on the hydrogen atom (pol(Z—H), see Table 1), also reflects the nature of interaction. The increase in the proton acceptor pol(M—H)

Table 1. Characteristics of dihydrogen-bonded complexes of Cp*MH(dpe) (**1**) with TFE, hydrogen-bonded complexes of CpMH(CO)$_3$ (**2**) with NMe$_3$ and complexes of **2** with BH$_3$

Com-plex	$-\Delta E_{compl}{}^a$	$-\Delta V_{el}{}^b$	$\Delta E_{Pauli}{}^c + \Delta V_{el}$	ΔE_{orb}	$\%\Delta E_{orb}{}^d$	Δr(M—H)	r(M$\cdots$Y)^e	Angle X—H$\cdots$Y^e /deg	Δq			Δpol^f (%)	
							Å		M	H$_M$	H$_O$	M—H	O—H
		kcal mol^{-1}											
1-Fe·TFE^g	8.2	13.4	3.1	−11.3	46	0.011	1.612	156.8	0.027	−0.067	0.008	9.1	−2.8
1-Ru·TFE^g	8.9	13.7	2.1	−11.0	45	0.011	1.735	147.6	0.003	−0.060	0.012	3.4	−2.6
1-Os·TFE^g	9.3	14.2	1.5	−10.8	43	0.006	1.795	144.7	−0.014	0.044	0.013	2.6	−2.7
2-Mo·NMe$_3$^{h}	9.2	7.3	−3.2	−6.0	45	0.012	2.329	177.7	0.051	0.053	—	−4.4	—
2-W·NMe$_3$^{h}	10.3	6.2	−3.6	−6.7	52	0.005	2.431	170.2	0.036	0.058	—	−2.8	—
2-Mo·BH$_3$^{h}	16.1	16.7	27.2	−43.2	72	0.081	1.500	142.6	0.137	−0.122	—	7.2	—
2-W·BH$_3$^{h}	19.9	18.0	27.4	−47.3	72	0.072	1.498	139.6	0.160	−0.114	—	9.4	—

^{a} Enegry of complex.
^{b} Contribution of electrostatic interactions.
^{c} Pauli energy.
^{d} $\%\Delta E_{orb} = 100 \cdot \Delta E_{orb}/(\Delta E_{orb} + \Delta V_{el})$.
^{e} Y = H$_O$ for hydride series **1**, N for complexes **2·NMe$_3$**, B for complexes **2·BH$_3$**.
^{f} Bond polarization (pol(Z—H), in % per H) is defined as the portion of electron density on the hydrogen atom bonded to the heavy atom relative to the total electron density on $\sigma_{Z—H}$, Z = M or O; polarization change $\Delta pol(Z—H) = pol(Z—H)^{compl} − pol(Z—H)^0$.
^{g} Geometry optimization by BP86/TZP method, calculation of characteristics by BP86/TZP.
^{h} Geometry optimization at the M05/6-311++G(d,p)/LanL2DZ/6-31G(d,p) level, calculation of characteristics at the M05/TZP level.
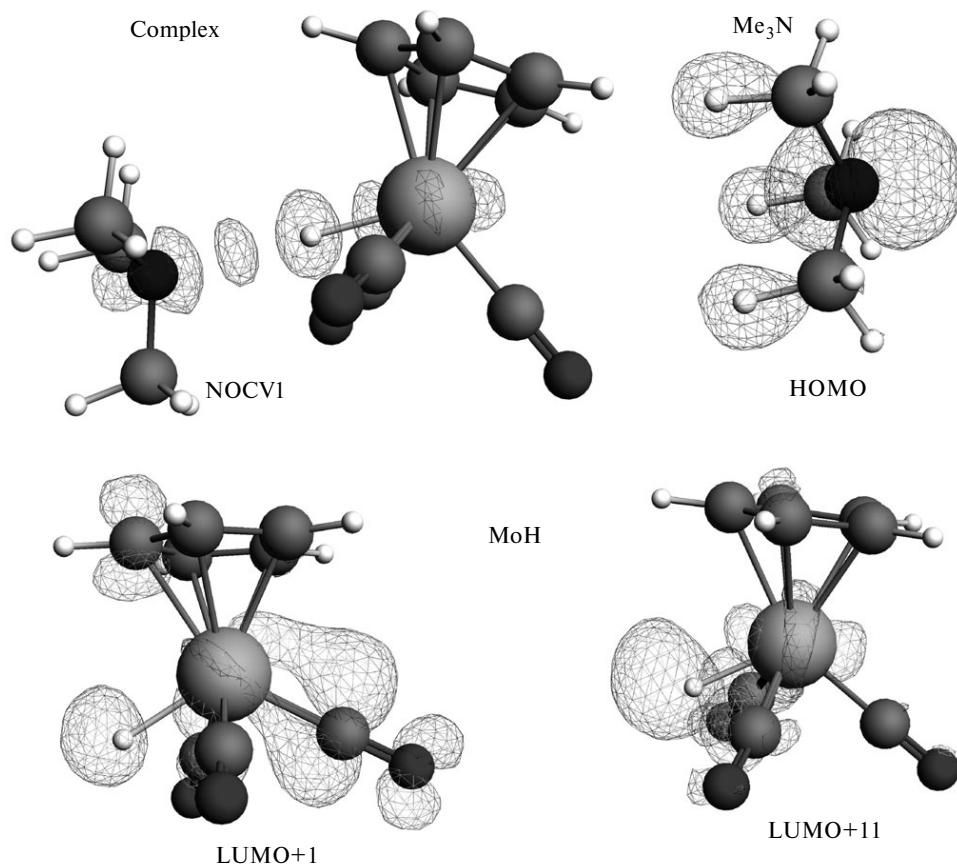
Fig. 2. Deformation electron density upon the formation of the [Mo]H···NMe$_3$ complex (isosurface at 0.001 a.u., $\Delta\rho > 0$ is blue, $\Delta\rho < 0$ is red) and orbitals of fragments that participate in the interaction (isosurface at 0.05 a.u.).
Note. Figures 2 and 3 are availiable in full color in the on-line version of the journal (http://www.springerlink.com).

value and decrease in the proton donor pol(O—H) value is observed in complexes **1·TFE**, *i.e.* the acidity of TFE and hydridity of metal complex increase. The smaller change of the polarization of Ru—H and O—H bonds in comparison with the Fe—H bond is associated with the metal atom participation in the formation of dihydrogen-bonded complexes, which increases on going from 3d- to 4d- and 5d-metals.[27] The polarization of M—H bond in complexes **2·NMe$_3$** decreases similarly, *i.e.* the acidity of the hydride ligand increases, which corresponds to the proton donor behavior during the formation of hydrogen bond.

The [M]H···BH$_3$ complexes are characterized by the stronger coordination of the partner molecule to the hydride ligand in comparison with the hydrogen-bonded [M]H···NMe$_3$ complexes; in this case, the orbital interactions become the main attractive component of the complex formation energy (see Table 1). The main component of the orbital interaction ($\Delta E_{\text{NOCV1}} = -37.8$ kcal mol^{-1} for [W]H) is the donation from the HOMO-2 and HOMO-4 of hydride to the LUMO of the Lewis acid (BH$_3$; see Table 2). The M—H bond orbital is the HOMO-4 of complex **2** (atoms H and M make the contributions of 26% each to the orbital formation), the HOMO-2 is the orbital of the carbon atoms of the cyclopentadienyl ligand with

a small contribution of hydride bond (10% H and 10% W). The second component of the orbital interaction has the smaller energy ($\Delta E_{\text{NOCV2}} = -5.2$ kcal mol^{-1} for [W]H) and the electron density transfer is directed to the opposite side: from the HOMO of BH$_3$ to the LUMO of the transition metal complex (back donation).

The back donation in the [M]H·BH$_3$ complexes can be described as dihydrogen bond BH···H[M] with the participation of the metal hydride LUMO+1 and LUMO+11 as the acceptors similarly to the hydrogen bond in [M]H···NMe$_3$ complexes. The electron density donors are the HOMO and HOMO-2 orbitals of the borane B—H bonds. Since the back donation energy is significantly lower than the energy of the main interaction $\sigma_{\text{MH}} \rightarrow n^*_{\text{B}}$ the geometric characteristics of MH···H(B) fragment differ from the typical ones for hydrogen bonds. The complex geometry is determined by the σ_{MH} orbital overlap with the n^*_{B} orbital located perpendicularly to the plane of the BH$_3$ hydride ligands (Fig. 3).

Thus, the low-energy interactions (hydrogen-bonded or Lewis complexes) activate the M—H bonds involved and stimulate further transformations. At that, the nature of the orbital interactions in the complex will determine the reaction pathway: proton transfer to hydride

Table 2. Major components of the orbital interactions in the complexes [M]H···NMe$_3$ and [M]H···BH$_3$ and participation of orbitals of fragments in the electron density transfer (Δq)

Interaction	E/kcal mol^{-1}	Fragment	Orbital	Δq^*, a.u.
[W]H···NMe$_3$	−4.1 (E_{NOCV1})	Me$_3$N	B3MO	−0.030
		[W]H	HCMO+1	0.013
[W]H···BH$_3$	−37.8 (E_{NOCV1})	BH$_3$	HCMO	0.254
		[W]H	B3MO−2	−0.132
			B3MO−4	−0.087
	−5.2 (E_{NOCV2})	BH$_3$	B3MO	−0.032
			B3MO−2	−0.018
		[W]H	HCMO+1	0.015
			HCMO+11	0.011
[Mo]H···NMe$_3$	−5.1 (E_{NOCV1})	Me$_3$N	B3MO	−0.037
		[Mo]H	HCMO+1	0.017
			HCMO+11	0.015
[Mo]H···BH$_3$	−37.6 (E_{NOCV1})	BH$_3$	HCMO	0.249
		[Mo]H	B3MO−2	−0.122
			B3MO−4	−0.094
	−5.3 (E_{NOCV2})	BH$_3$	B3MO	−0.030
			B3MO−2	−0.010
		[Mo]H	HCMO+1	0.015

* Negative Δq values correspond to the electon density donor, the positive values correspond to the acceptor.
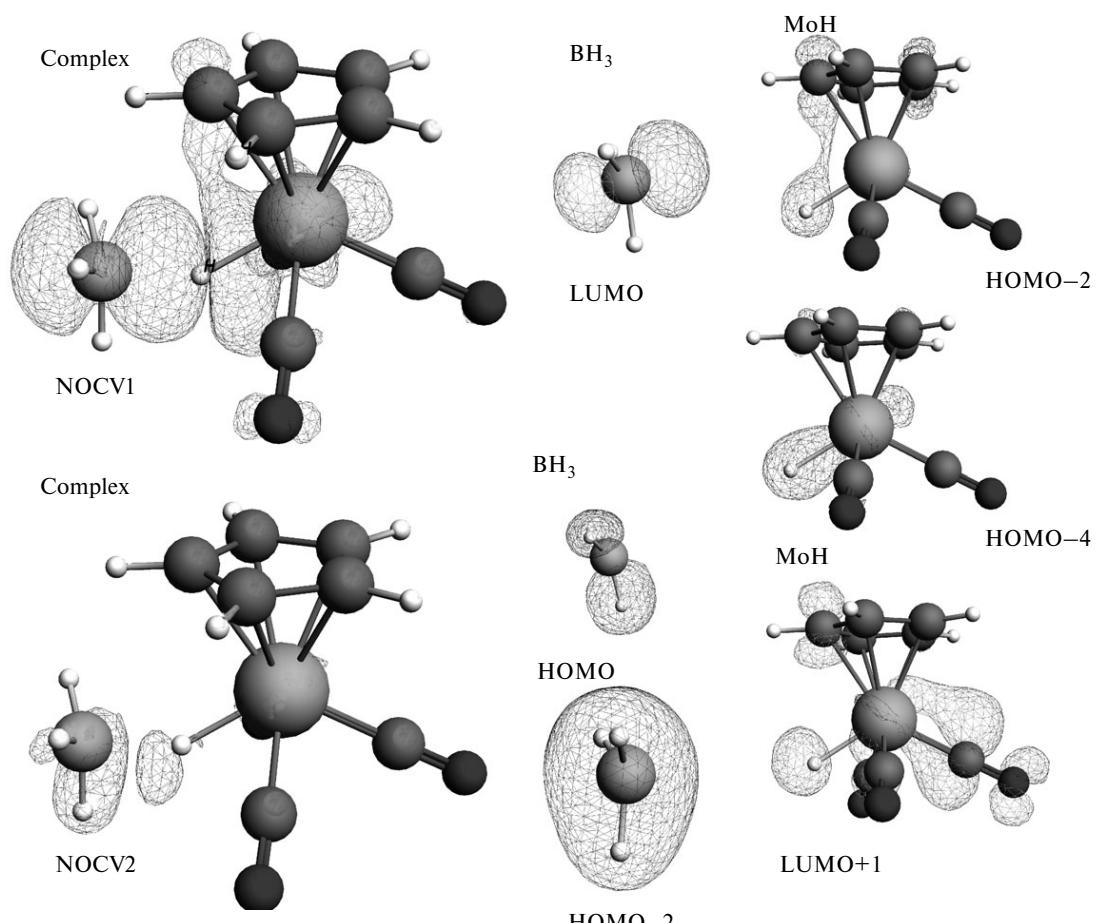
Fig. 3. Deformation electron density upon the formation of the [Mo]H···BH$_3$ complex (isosurface at 0.001 a.u., $\Delta\rho > 0$ is blue, $\Delta\rho < 0$ is red) and orbitals of fragments that participate in the interaction (isosurface at 0.05 a.u.).

ligand in the case of $\sigma_{MH} \rightarrow \sigma^*_{OH}$, metal atom protonation in the case of $n_M \rightarrow \sigma^*_{OH}$, metal hydride deprotonation in the case of $n_N \rightarrow \sigma^*_{MH}$, and hydride transfer to Lewis acid in the case of $\sigma_{MH} \rightarrow n^*_B$. The M—H bond polarization change has the similar character upon the formation of complexes with Brønsted and Lewis acids. The M—H bond polarization increases in comparison with the initial hydrides in the complexes **1·TFE** and **2·BH₃**, which attests an increase in the hydride character of the hydrogen atom and, in the extreme case, can lead to the hydride transfer. The hydride transfer generally does not occur from the dihydrogen-bonded complexes with XH acids due to the easier cleavage of the X—H bond, which is also polarized in the dihydrogen-bonded complex and "prepared" for the proton transfer to give a cation di(poly)hydride or molecular hydrogen complex. Meanwhile, the interaction with Lewis acids leads to the hydride transfer.[39] The unique behavior of the $CpMH(CO)_3$ hydride complexes is determined by the electron density of M—H bond, which is shifted to metal but is easily relocated upon the formation of complexes with Lewis bases and acids.

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