Structure and Bonding in Hartwig Stretched η^3-Hydridoborate σ-Complex of Niobium(III)

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Ab initio calculations at the SCF, MP2, CASSCF, and CASPT2 levels of theory with basis sets using atomic pseudopotentials have been carried out for the stretched η^3-hydridoborate σ-complex of niobium, [Cl$_2$Nb{H$_2$B-(OH)$_2$}], in order to investigate the nature and energetics of the interaction between the transition metal and the η^3-hydridoborate ligand. The geometry of the complex [Cl$_2$Nb{H$_2$B(OH)$_2$}] and its fragments [Cl$_2$Nb]$^+$ and [H$_2$B(OH)$_2$]$^-$ were optimized at SCF and CASSCF levels. These results are consistent with [Cl$_2$Nb{η^3-H$_2$B-(OH)$_2$}] being a Nb(III) complex in which both hydrogen and boron of the [η^3-H$_2$B(OH)$_2$]$^-$ ligand have a bonding interaction with the niobium preserving stretching B−H bond character. The calculated values of DEF (energy required to restore the fragment from the equilibrium structure to the structure it takes in the complex) for [Cl$_2$-Nb]$^+$ are 5.35 kcal/mol at SCF, 3.27 kcal/mol at MP2, 4.80 kcal/mol at CASSCF, and 2.82 kcal/mol at CASPT2 and for [H$_2$B(OH)$_2$]$^-$ 21.13 kcal/mol at SCF, 23.85 kcal/mol at MP2, 20.69 kcal/mol at CASSCF, and 23.48 kcal/mol at CASPT2. Values of INT (stabilization energy resulting from the coordination of distorted ligand to the metal fragment) for the complex [Cl$_2$Nb{H$_2$B(OH)$_2$}] are −239.35 kcal/mol at SCF, −260.00 kcal/mol at MP2, −230.76 kcal/mol at CASSCF, and −252.60 kcal/mol at CASPT2. For the complex [(η^5-C$_5$H$_5$)$_2$Nb{H$_2$B-(OH)$_2$}], calculations at the SCF and MP2 levels were carried out. Values of INT for [(η^5-C$_5$H$_5$)$_2$Nb{H$_2$B(OH)$_2$}] are −169.93 kcal/mol at SCF and −210.62 kcal/mol at MP2. The results indicate that the bonding of the [η^3-H$_2$B(OH)$_2$]$^-$ ligand with niobium is substantially stable. The electronic structures of [Cl$_2$Nb{H$_2$B(OH)$_2$}], [(η^5-C$_5$H$_5$)$_2$Nb{H$_2$B(OH)$_2$}], and its fragments are analyzed in detail as measured by Mulliken charge distributions and orbital populations.

In recent years, there has been considerable interest in the investigation of synthesis, structure, and reactivity of transition metal boryl and borane σ-complexes.[1−18] These complexes have been invoked as intermediates in a number of catalytic systems including metal-catalyzed hydroboration of unsaturated substrates and diboration of alkynes, alkenes, dienes, and allenes.[19−34] Although theoretical studies regarding metal−boryl bond energies and the mapping of the reaction coordinate for the proposed catalytic cycles have been reported,[35−42] accurate theoretical investigations which address the nature of the chemical bond

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in transition metal boryl complexes are still in an infant stage. The M–BR$_2$ bond is covalent (shared electron) and not a donor acceptor bond.[43]

In 1994, Hartwig and De Gala[7] reported the synthesis and characterization (spectral and structural) of niobium complexes [(η^5-C$_5$H$_5$)$_2$Nb{H$_2$BR$_2$}] (R$_2$ = O$_2$C$_6$H$_4$, C$_8$H$_{14}$). Three possible bonding modes (I, II, and III) have been proposed for the complexes [(η^5-C$_5$H$_5$)$_2$Nb{H$_2$BR$_2$}]. The studies involving
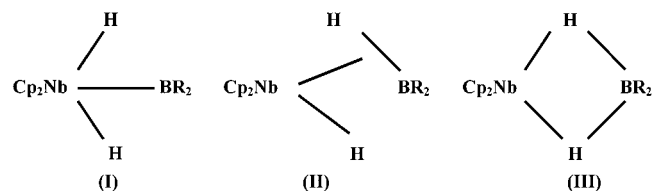
deuterium labeling provided evidence for the equilibrium between the two structures **I** and **III** of the niobocene complex [(η^5-C$_5$H$_5$)$_2$Nb{H$_2$BR$_2$}]. The complex, which exists as a resonance hybrid of the two structures **I** and **III**, contains a stretched [η^3-H$_2$BR$_2$]$^-$ ligand **(IV)** having intermolecular binding to the niobium center through a B–H σ-bond.
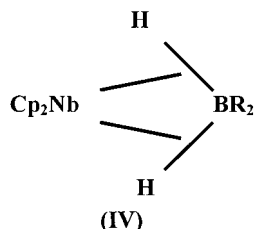
The optimized geometries of isoelectronic endo and exo isomers of tantalum complexes [(η^5-C$_5$H$_5$)$_2$TaH$_2$(Bcat)] are consistent with tantalum boryl complexes rather than tantalum borohydride or hydridoborate complexes.[44] A similar trend has been reported in the reactions of alkylboranes with Rh(I) and Ir(I) hydrides. Alkylboranes reacts with Rh(I) hydrides to afford hydridoborate complexes, while similar reactions with Ir(I) hydrides result in the formation of Ir(III) boryl complexes.[45–47]

Hydrogen atoms in the presence of heavy atoms are commonly not seen to cause scattering problems; therefore accurate experimental determination of its bond distance from heavy atoms by X-ray diffraction is difficult. No neutron diffraction data are as yet available for the complexes of the [H$_2$BR$_2$]$^-$ ligand. Theoretical studies of the complex [η^5-C$_5$H$_5$)$_2$Nb{H$_2$-BR$_2$}] will be useful to better understand the nature of the coordinate bond and electronic structures and to know whether

compounds are best described as Nb(III) hydridoborate or Nb-(V) boryl complexes.

In this paper, I wish to report ab initio calculations at SCF, MP2, CASSCF, and CASPT2 levels of theory for complex [Cl$_2$-Nb{H$_2$B(OH)$_2$}] as a model for [(η^5-C$_5$H$_5$)$_2$Nb{H$_2$BR$_2$}]. In the model compounds, the Cp ligands have been replaced with chlorine atoms. It was shown in other studies that such substitution reduces the computer time but does not affect the essential features of the investigated system.[48–53] For the complex [(η^5-C$_5$H$_5$)$_2$Nb{H$_2$B(OH)$_2$}], calculations at SCF and MP2 levels were also carried out using experimental geometry for the C$_5$H$_5$ ligand.

Computational Details

The quantum chemical calculations reported in this paper have been performed at the closed-shell SCF, second-order Moller–Plesset perturbation (MP2), complete active space SCF (CASSCF), and CASSCF method combined with multiconfigurational second-order perturbation (CASPT2) levels of theory. The CASSCF method is a standard ab initio quantum chemistry tool to evaluate multiconfigurational wave functions.[54] The CASPT2 method computes the first-order wave function and the second-order energy in the full CI space with a CASSCF wave function constituting the reference function.[55] The calculations were carried out with the MOLCAS-4 series of programs.[56]

The inner shells of the atoms (Nb, Cl, O, and B) were described by relativistic pseudopotentials. The (K, L, M, 5s2) core of tantalum, the (K, L) shells of chlorine, and the (K) shells of oxygen and boron were taken into account through nonempirical pseudopotentials of Gaussian form.[57,58] The 4p, 4d, and 5s orbitals of the Nb were represented by an (11s8p7d) primitive set contracted to (3s3p4d).[57] Standard Barandiaran and Seijo bases[58] were used for the 3s and 3p orbitals of chlorine (7s7p/2s4p) and 2s and 2p orbitals of oxygen (5s6p/2s4p) and boron (5s5p/2s3p). The basis sets of Cl, O, and B were augmented with d polarization functions (for chlorine, ζ_d = 0.514; for oxygen, ζ_d = 0.1154; and for boron, ζ_d = 0.388). Contracted basis sets of the atomic natural orbital (ANO) type[59] were used for carbons (10s6p/3s2p) of C$_5$H$_5$ and hydrogens of B(OH)$_2$ and C$_5$H$_5$ (7s/2s), and double-ζ + polarization (7s3p/2s1p) was used for the hydride hydrogens. The coordinate system for the [Cl$_2$Nb{H$_2$B(OH)$_2$}] complex is given in Figure 1.

Results and Discussion

Geometry at the SCF and CASSCF Levels. The optimized geometries of [Cl$_2$Nb{H$_2$B(OH)$_2$}] and its fragments [Cl$_2$Nb]$^+$

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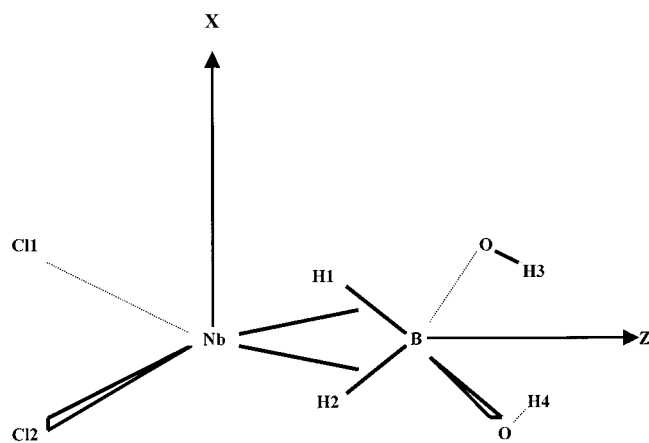
Figure 1. Coordinate System for [Cl₂Nb{H₂B(OH)₂}]. The *Y* axis is out of plane.

Table 1. Geometric Parameters^a for the Optimized Structure of the Complex [Cl₂Nb{H₂B(OH)₂}] and Its Fragments [Cl₂Nb]$^+$ and [H₂B(OH)₂]$^-$

parameter	SCF	CASSCF	exptl^b
[Cl₂Nb{H₂B(OH)₂}]			
bond distances			
Nb−B	2.391	2.418	2.40
Nb−Cl	2.340	2.347	
Nb−H1	1.829	1.842	1.84
Nb−H2	1.829	1.842	1.80
B−O	1.372	1.372	
O−H	0.942	0.942	
B−H1	1.451	1.434	1.38
B−H2	1.451	1.434	1.39
bond angles			
H1/H2−Nb−B	37.30	36.25	35.00
H1−Nb−H2	99.65	98.85	
Cl−Nb−Cl	129.10	126.85	
O−B−O	125.48	125.53	
B−O−H	117.42	117.45	
O1−B−H1	107.19	107.32	
O2−B−H2	107.19	107.32	
[H₂B(OH)₂]$^-$			
bond distances			
B−O	1.502	1.489	
O−H	0.942	0.943	
B−H1/H2	1.255	1.270	
bond angles			
O−B−O	110.23	112.49	
B−O−H	111.89	108.72	
O1−B−H1	109.34	108.30	
O2−B−H2	109.34	108.30	
[Cl₂Nb]$^+$			
bond distance			
Nb−Cl	2.274	2.272	
bond angle			
Cl−Nb−Cl	153.17	148.74	

^{a} Distances are given in Å and angles in deg. ^{b} X-ray crystal structure data for [(η^5-C₅H₅)₂Nb(H₂BR₂)].[7]

and [H₂B(OH)₂]$^-$ are presented in Table 1. Both SCF and CASSCF (two electrons in three active orbitals) calculations give Nb−B, Nb−H1, Nb−H2, B−H1, and B−H2 optimized bond distances for [Cl₂Nb{H₂B(OH)₂}] in good agreement with experimental results observed in the hydridoborate complex [η^5-C₅H₅)₂Nb{H₂BR₂}]. The Nb−B bond distance 2.391 Å at the SCF level is longer than the computed bond distances in metallocene boryl complexes, tungsten (W−B = 2.165 Å) and tantalum (Ta−B = 2.228),[44] despite the smaller size of niobium and is indicative of a Nb−B bond order less than 1.
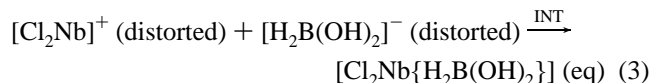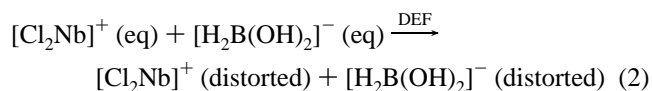
It is noted that the electron correlation effects lengthen the Nb−B coordinate bond distance by about 0.027 Å and the Nb−H1 and Nb−H2 coordinate bond distances by about 0.013 Å. Electron correlation effects on the coordinate bond distances in transition metal complexes seem to depend on the nature of the HOMO. In general, when the HOMO is nearly nonbonding, the metal−ligand distance shortens by electron correlation, and when the HOMO is bonding, electron correlation lengthens the coordinate bond distance. The HOMO of [Cl₂Nb{H₂B(OH)₂}] is bonding in the Nb−B, Nb−H1, and Nb−H2 regions and antibonding in the B−H1 and B−H2 regions. There is large involvement of the niobium d_{z^2} and $d_{x^2-y^2}$ orbitals.

The B−Nb−H1 and B−Nb−H2 bond angles in [Cl₂Nb{H₂B-(OH)₂}] are only 37.30° at the SCF level (36.25° at the CASSCF level), consistent with B−H bonding. The optimized Nb−H1 and Nb−H2 bond distances 1.829 Å at the SCF level (1.842 Å at the CASSCF level) and the B−H1 and B−H2 bond distances 1.451 Å at the SCF level (1.434 Å at the CASSCF level) are longer than the corresponding distances in the titanocene η^2-borane σ-complexes[19] and the η^2-hydridoborate complexes. These results are consistent with [Cl₂Nb{η^3-H₂B(OH)₂}] being a Nb(III) complex in which both hydrogen and boron of the [η^3-H₂B(OH)₂]$^-$ ligand have a bonding interaction with the niobium preserving stretching B−H bond character. Upon coordination of the [η^3-H₂B(OH)₂]$^-$ ligand, the B−O bond distances are shortened by 0.13 Å and the B−H bond distances are lengthened by 0.574 Å.

Binding Energy. The binding energy, which is defined as a stabilization energy caused by coordination of the [H₂B(OH)₂]$^-$ ligand to [Cl₂Nb{H₂B(OH)₂}], is associated with the reaction

$$[Cl_2Nb]^+ \text{ (eq)} + [H_2B(OH)_2]^- \xrightarrow{\Delta E_B} [Cl_2Nb\{H_2B(OH)_2\}] \quad (1)$$
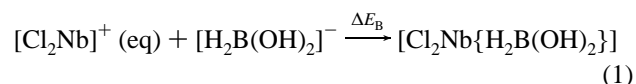
The reactants and product energies that yield ΔE_B were computed at their respective equilibrium geometries. Given that the equilibrium geometries of the fragments [Cl₂Nb]$^+$ and [H₂B(OH)₂]$^-$ in the complex [Cl₂Nb{H₂B(OH)₂}] are different from the free [Cl₂Nb]$^+$ and [H₂B(OH)₂]$^-$ values, the energetics associated with reaction 1 could be analyzed as summarized by the following reactions:
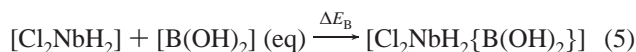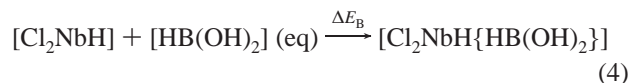
$$[Cl_2Nb]^+ \text{ (eq)} + [H_2B(OH)_2]^- \text{ (eq)} \xrightarrow{\text{DEF}}$$
$$[Cl_2Nb]^+ \text{ (distorted)} + [H_2B(OH)_2]^- \text{ (distorted)} \quad (2)$$

$$[Cl_2Nb]^+ \text{ (distorted)} + [H_2B(OH)_2]^- \text{ (distorted)} \xrightarrow{\text{INT}}$$
$$[Cl_2Nb\{H_2B(OH)_2\}] \text{ (eq)} \quad (3)$$

where DEF is the energy required to restore the [Cl₂Nb]$^+$ and [H₂B(OH)₂]$^-$ from the equilibrium structures to the structures adopted in the complex, and INT is the stabilization energy resulting from the coordination of the distorted [η^3-H₂B(OH)₂]$^-$ ligand to the [Cl₂Nb]$^+$ fragment. Values of DEF for [Cl₂Nb]$^+$ are 5.35 kcal/mol at SCF, 3.27 kcal/mol at MP2, 4.80 kcal/mol at CASSCF, and 2.82 kcal/mol at CASPT2, and for [H₂B(OH)₂]$^-$ they are 21.13 kcal/mol at SCF, 23.85 kcal/mol at MP2, 20.69 kcal/mol at CASSCF, and 23.48 kcal/mol at CASPT2. Values of INT for the complex [Cl₂Nb{H₂B(OH)₂}] are −239.35 kcal/mol at SCF, −260.00 kcal/mol at MP2, −230.76 kcal/mol at CASSCF, and −252.60 kcal/mol at CASPT2. Values of INT for [(η^5-C₅H₅)₂Nb{H₂B(OH)₂}] are −169.93 kcal/mol at SCF and −210.62 kcal/mol at MP2. We note that a large stabilization that is dominated by the charge transfer contributions is predicted.

Table 2. Mulliken Charges for [Cl$_2$Nb{H$_2$B(OH)$_2$}] and Its Fragments [Cl$_2$Nb]$^+$ and [H$_2$B(OH)$_2$]$^-$

	SCF	CASSCF	CASPT2	Δq^a CASSCF	CASPT2
		[Cl$_2$Nb{H$_2$B(OH)$_2$}]			
Nb	+0.652	+0.656	+0.620	−0.602	−0.598
s	0.697		0.692		
p	6.429		6.407		
d	3.222		3.281		
B	+0.676	+0.656	+0.646	+0.182	+0.175
s	0.504		0.512		
p	1.521		1.536		
d	0.299		0.306		
O	−0.522	−0.522	−0.509	+0.214	+0.215
s	1.691		1.684		
p	4.816		4.796		
d	0.015		0.030		
H1/H2	−0.308	−0.309	−0.305	+0.016	+0.017
Cl	−0.316	−0.318	−0.299	−0.189	−0.190
H(O)	+0.482	+0.482	+0.480	+0.169	+0.169
		[Cl$_2$Nb]$^+$			
Nb	+1.276	+1.258	+1.218		
s	0.270		0.340		
p	6.245		6.218		
d	3.209		3.224		
Cl	−0.138	−0.129	−0.109		
		[H$_2$B(OH)$_2$]$^-$			
H1/H2	−0.334	−0.325	−0.322		
B	+0.509	+0.497	+0.471		
s	0.573		0.589		
p	1.722		1.736		
d	0.196		0.204		
O	−0.735	−0.736	−0.724		
s	1.728		1.719		
p	4.993		4.975		
d	0.014		0.030		
H	+0.314	+0.313	+0.311		

^{a} The changes in atomic charges caused by coordination of [H$_2$B(OH)$_2$]$^-$ to [Cl$_2$Nb]$^+$.

The binding energies associated with the reactions

$$[\text{Cl}_2\text{NbH}] + [\text{HB(OH)}_2]\ (eq) \xrightarrow{\Delta E_B} [\text{Cl}_2\text{NbH}\{\text{HB(OH)}_2\}] \quad (4)$$

$$[\text{Cl}_2\text{NbH}_2] + [\text{B(OH)}_2]\ (eq) \xrightarrow{\Delta E_B} [\text{Cl}_2\text{NbH}_2\{\text{B(OH)}_2\}] \quad (5)$$

have also been calculated. Values of binding energies for the η^2-borane σ-complex [Cl$_2$NbH{HB(OH)$_2$}] are −12.08 kcal/mol at SCF, −36.76 kcal/mol at MP2, +5.46 kcal/mol at CASSCF, and −30.53 kcal/mol at CASPT2, and for the boryl complex [Cl$_2$NbH$_2${B(OH)$_2$}] they are −198.76 kcal/mol at SCF, −166.21 kcal/mol at MP2, −53.04 kcal/mol at CASSCF, and −63.19 kcal/mol at CASPT2. The calculated binding energy values indicate that bonding modes **I** and **II** are less stable than structure **IV**.

Coordinate Bond Nature and Electron Distribution. The HOMO of [Cl$_2$Nb{H$_2$B(OH)$_2$}] is bonding in the Nb−B, Nb−H1, and Nb−H2 regions and antibonding in the B−H1 and B−H2 regions. There is large involvement of the niobium d$_{z^2}$ and d$_{x^2-y^2}$ orbitals. The second HOMO has heavy involvement of 1s orbitals of H1 and H2 with bonding combination 4d$_{xy}$ + 1sσ for Nb−H1 and Nb−H2 linkages. The LUMO is mainly Nb 4d$_{yz}$ and 4p$_y$ orbitals with weak antibonding in the Nb−Cl and Nb−B regions. The Mulliken charge distributions of [Cl$_2$Nb{H$_2$B(OH)$_2$}] and its fragments [Cl$_2$Nb]$^+$ and [H$_2$B(OH)$_2$]$^-$ calculated at the SCF level are presented in Figure 2 and Table
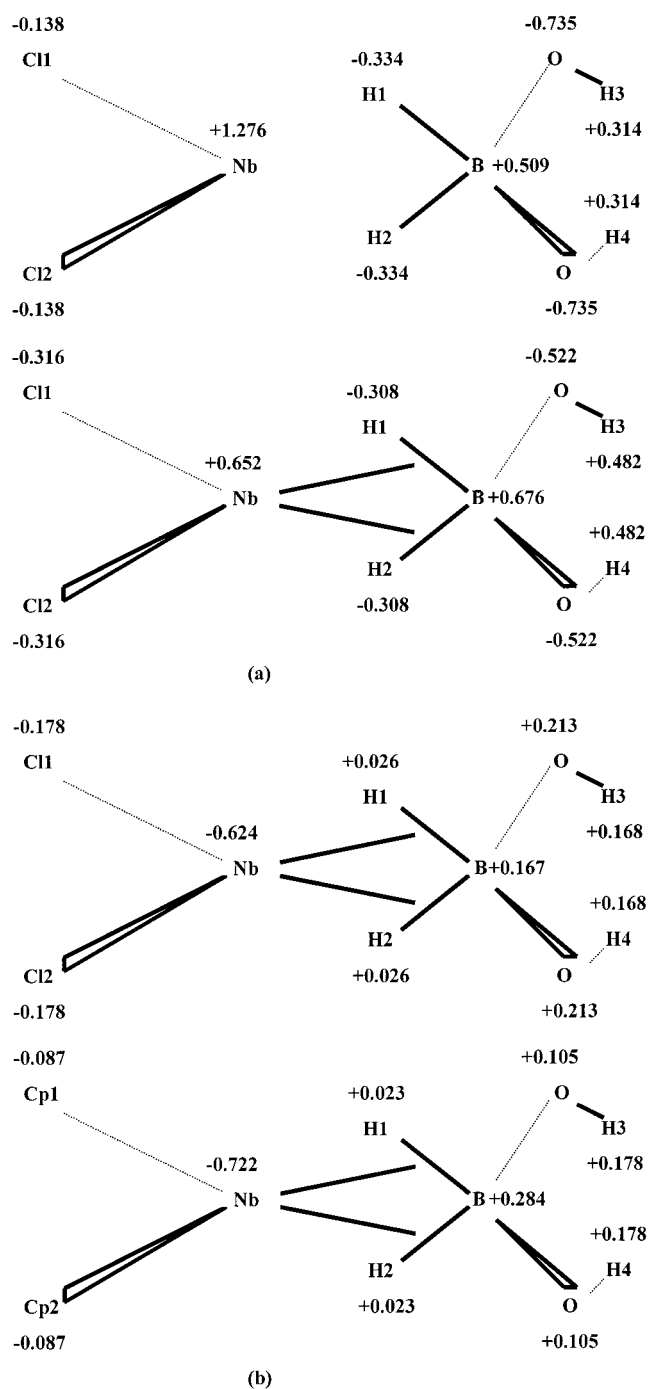
Figure 2. (a) Gross atomic charges for [Cl$_2$Nb{H$_2$B(OH)$_2$}] and its fragments. (b) The changes caused by coordination of [H$_2$B(OH)$_2$]$^-$ to [Cl$_2$Nb]$^+$ and to [(η^5-C$_5$H$_5$)$_2$Nb]$^+$.

2. In the complex [Cl$_2$Nb{H$_2$B(OH)$_2$}], the oxygen and hydride hydrogen atoms become less negative while the boron and hydrogen atoms bonded to oxygen become more positive than in the [H$_2$B(OH)$_2$]$^-$ fragment. We ascribe this to the polarization of [H$_2$B(OH)$_2$]$^-$ (0.98 electron) in the complex under the electrostatic field of the positively charged niobium atom in [Cl$_2$Nb]$^+$. The changes in charges of oxygen and hydrogen atoms of [H$_2$B(OH)$_2$]$^-$, which do not take part in charge-transfer directly, provide the estimate of polarization effect.

In the complex [(η^5-C$_5$H$_5$)$_2$Nb{H$_2$B(OH)$_2$}], the electronic substituent effects of [(η^5-C$_5$H$_5$)$_2$Nb]$^+$ on the [H$_2$B(OH)$_2$]$^-$ ligand are not very different from those of [Cl$_2$Nb]$^+$ (Figure 2b).

Conclusion. In this theoretical work, ab initio calculations at the SCF, MP2, CASSCF, and CASPT2 levels of theory with basis sets using atomic pseudopotentials have been carried out for the stretched η^3-hydridoborate σ-complex of niobium, [Cl$_2$-Nb{H$_2$B(OH)$_2$}], and at the SCF and MP2 levels for [(η^5-C$_5$H$_5$)$_2$Nb{H$_2$B(OH)$_2$}]. The geometry of the complex [Cl$_2$Nb-{H$_2$B(OH)$_2$}] and its fragments [Cl$_2$Nb]$^+$ and [H$_2$B(OH)$_2$]$^-$ were optimized at the SCF and CASSCF levels. Both SCF and CASSCF calculations give Nb$-$B, Nb$-$H1, Nb$-$H2, B$-$H1, and B$-$H2 optimized bond distances for [Cl$_2$Nb{H$_2$B(OH)$_2$}] in good agreement with experimental results observed in hydridoborate complex [η^5-C$_5$H$_5$)$_2$Nb{H$_2$BR$_2$}]. These results are consistent with [Cl$_2$Nb{η^3-H$_2$B(OH)$_2$}] being a Nb(III) complex in which both hydrogen and boron of the [η^3-H$_2$B-(OH)$_2$]$^-$ ligand have a bonding interaction with the niobium creating a stretched B$-$H bond. The calculated binding energy values indicate that bonding modes **I** and **II** are less stable than structure **IV**. The electronic substituent effects of [(η^5-C$_5$H$_5$)$_2$-Nb]$^+$ on the σ-bonding ligand [H$_2$B(OH)$_2$]$^-$ are not very different from those of [Cl$_2$Nb]$^+$.