Tetrahydridoborate Complexes

Competition between the Hydride Ligands of Two Types in Proton Transfer to \([\{(k^3-PCH_3C(CH_2CH_2PPh_2)_3\}RuH(\eta^2-BH_4)\}^+\) cation. The experimentally determined basicity factor \(E_j(RuH)\) of the Ru-bound hydrido ligand of 1.43 is among the highest determined for ruthenium hydridoborates. Such high basicity leads to very easy proton transfer to the Ru ligand for strong alcohols (HFIP and PFTB). An alternative reaction pathway involving the migration of the bridging hydride (BH_4^-) to the ruthenium center is suggested for weaker proton donors (MeOH and TFE).

Introduction

Recently, the catalytic and noncatalytic hydrolysis and alcoholysis of simple boron hydrides have received increasing attention owing to the potential of these materials for chemical hydrogen storage.\(^1\) There have been several reports on the mechanisms of the alcoholysis of Me_2NBH_3\(^2\) and the alcoholysis\(^2b\) and hydrolysis\(^3\) of the BH_4^- anion. Transition metals also promote hydrogen evolution from these species through B–H bond activation owing to the formation of σ complexes with the metal center.\(^3\) Tetrahydridoborate metal complexes are frequently reported catalysts or intermediates of amineborane dehydrogenation\(^5\) and other processes accompanied by hydrogen transfer.\(^6\) The hydride–proton interactions, also known as dihydrogen bonds (DHBs), have a great influence on the reactivity of boron hydrides in these reactions.\(^7\)

The treatment of metal tetrahydridoborate complexes with acids results in the loss of the BH_4^- ligand and the formation of mono- or dinuclear species.\(^8\) The data obtained in our studies of the interactions of alcohols with copper and ruthenium tetrahydridoborates (Scheme 1) show the increase of BH_4^- reactivity entailed by complexation to metal centers.\(^9\) The presence of various hydride sites in these complexes [terminal B–H (BHterm), bridging B–H–M (BHbr), and terminal M–H bonds] leads to the formation of a large variety of dihydrogen-bonded complexes, but only a few of the conceivable DHB complexes are real intermediates of the alcoholysis process.\(^9\) As part of our investigations into noncovalent interactions (hydrogen and dihydrogen bonds) and the reactivity of transition-metal tetrahydridoborates towards alcoholysis (Scheme 1),\(^9\) herein we report a combined computational (DFT) and spectroscopic (VT FTIR, NMR) analysis of the interactions of the mixed hydrido–tetrahydridoborate ruthenium(II) complex \([\{(Triphos)RuH}(\eta^2-BH_4)\}^+\) cation. The experimentally determined basicity factor \(E_j(RuH)\) of the Ru-bound hydrido ligand of 1.43 is among the highest determined for ruthenium hydridoborates. Such high basicity leads to very easy proton transfer to the Ru ligand for strong alcohols (HFIP and PFTB). An alternative reaction pathway involving the migration of the bridging hydride (BH_4^-) to the ruthenium center is suggested for weaker proton donors (MeOH and TFE).

Results and Discussion

Variable-Temperature Spectroscopic Study of Interactions with Alcohols

The IR spectrum of hydride 1 shows two well-resolved bands in the region of terminal BH stretching vibrations (ν_{BHterm}; Fig-
The formation of DHB complexes of 1 with proton donors (MFE, TFE, and HFIP) in CH$_2$Cl$_2$ leads to the appearance of the low-frequency ν$_{\text{OH}}$ band of the proton donors (Δν$_{\text{OH}}$ = –285 to –401 cm$^{-1}$, Table 1). The Δν$_{\text{OH}}$ values measured in the presence of excess hydrides allow the determination of the enthalpies of DHB formation (ΔH$_{\text{exp}}$, Table 1).[7b,12] In turn, the ΔH$_{\text{exp}}$ values give the basicity factor (Equation (2))[13] for the Ru–H hydrido ligand of 1: $E_j$ (RuH) = 1.43 ± 0.02. A comparison with other ruthenium(II) hydride complexes shows that 1 features the highest value reported to date (Figure 2). Consequently, this relatively large basicity of the Ru–H hydrido ligand leads to its easy protonation in the presence of an excess of fluorinated alcohols even at low temperatures (vide infra).

$$E_j = \frac{\Delta H_j}{\Delta H_{\text{term}}}$$

Table 1. Spectral [cm$^{-1}$] and energetic [kcal/mol] characteristic of the DHBs between 1 and different proton donors in CH$_2$Cl$_2$.

| Proton donor | ρ | ν$_{\text{OH}}$ (free) | ν$_{\text{OH}}$ (bond) | Δν$_{\text{OH}}$ | ΔH$_{\text{exp}}$
<table>
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<tr>
<td>MFE</td>
<td>0.78</td>
<td>3612</td>
<td>3327</td>
<td>–285</td>
<td>5.1</td>
</tr>
<tr>
<td>TFE</td>
<td>0.89</td>
<td>3602</td>
<td>3233</td>
<td>–369</td>
<td>6.1</td>
</tr>
<tr>
<td>HFIP</td>
<td>1.05</td>
<td>3652</td>
<td>3251</td>
<td>–401</td>
<td>6.4</td>
</tr>
</tbody>
</table>

[a] Acidity factor of the proton donor as defined in refs.[11,14] [b] The hydrogen-bond formation enthalpy calculated as –ΔH$_{\text{exp}}$ = 18(ΔH$_{\text{term}}$/[Δν$_{\text{OH}}$])(176/720).[7b,12]

In CH$_2$Cl$_2$, the DHB complexes can be observed in the low-temperature IR spectra (190–230 K) in the presence of 5 equiv. of MFE or smaller amounts of stronger (more acidic) alcohols (4 equiv. of TFE, 2 equiv. of HFIP or 1 equiv. of (CF$_3$)$_3$COH (PFTB)). This trend is in agreement with the increase of DHB strength (–ΔH$_{\text{exp}}$) with the proton-donating ability of the alcohol. The further addition of these alcohols causes new transformations and the appearance of new bands. Above 250 K, the bands of 1 disappear, and two new overlapping bands with similar widths (Δν$_{1/2}$ = 72 cm$^{-1}$) and intensities (ε = 180 m$^{-1}$ cm$^{-1}$) appear at ν = 1950 (ν$_{\text{BHterm}}$) and 1885 cm$^{-1}$ (ν$_{\text{BHbr2}}$ + ν$_{\text{RuH}}$), together with a new band at ν = 1625 cm$^{-1}$ (ν$_{\text{RuHbr1}}$, Δν$_{1/2}$ = 54 cm$^{-1}$, ε = 470 m$^{-1}$ cm$^{-1}$). These new bands belong to the dimetallic [(Triphos)Ru$_2$(μ$_2$-η$^2$-BH$_2$)$_2$]$^+$ cation (3), in which the borohydride ligand bridges two [(Triphos)RuH]$^+$ fragments (Scheme 2, Table 5).[8c]

The addition of alcohols in a small excess to a CH$_2$Cl$_2$ solution of 1 at 200 K leads to the appearance of a new ν$_{\text{RuH}}$ band at lower frequency (Figure 1). An increase of the alcohol strength [from FCH$_2$CH$_2$OH (MFE) to CF$_3$CH$_2$OH (TFE) and (CF$_3$)$_2$CHOH (HFIP)] leads to an increase of the low-frequency ν$_{\text{RuH}}$ band. Above 230–250 K, these bands decrease in intensity owing to the protonation of 1. In CH$_2$Cl$_2$, the ν$_{\text{RuH}}$ bands are much lower in THF than in CH$_2$Cl$_2$, and this spectral picture of DHB formation (–Δν$_{\text{OH}}$) was reported previously for the solid-state spectra.[10a] We assign these bands to ν$_{\text{RuH}}$ and ν$_{\text{BHbr}}$ respectively.

Figure 1. IR spectra of 1 (0.05 M, dashed line) in the ν$_{\text{BHterm}}$ (a) and ν$_{\text{BHbr}}$/ν$_{\text{RuH}}$ (b) regions in the presence of 1 equiv. of TFE in CH$_2$Cl$_2$ at 190–290 K, l = 1.0 mm. The shaded area is masked by the strong solvent absorption.

Figure 2. Basicity factors [E$_j$(RuH)] of various ruthenium(II) hydride complexes.[11,15]
Complex 1 reacts slowly even with the residual water present in CD$_2$Cl$_2$. The signal of H$_2$ is clearly visible in the $^1$H NMR spectra at $\delta$ = 4.57 ppm at 250 K together with several broad low-intensity signals in the hydride region (Figure S6). The reaction slows if the temperature is decreased to 190 K. The addition of 2.5 equiv. of HFIP at low temperatures causes the immediate disappearance of the starting material and the increase of the signals belonging to H$_2$ evolution products (Figure 3; the spectra in the downfield region are given in Figure S6). The wide pseudodoublet ($J = 26$ Hz) centered at $\delta = -4.92$ ppm belongs to the dimetallic cation and is temperature-invariant (Figure 3) in agreement with previous reports.[8c] Another broad resonance (unresolved pseudodoublet) is observed at $\delta = -8.07$ ppm and disappears as the temperature increases together with the doublet of triplets at $\delta = -6.42$ ppm ($^2J_{H,P_{cis}} = 16$ Hz, $^2J_{H,trans} = 100$ Hz). These signals integrate as 2:1 and presumably belong to the BH$_{br}$ and RuH ligands of the same species, which could be [(Triphos)RuH($\eta^2$-H$_2$BH$_2$)]. The latter is found as a stable minimum by DFT calculations (vide infra). Another signal, the doublet of doublets at $\delta = -7.77$ ppm ($^2J = 18$, 50 Hz), could belong to the BH$_{br}$ hydrogen atoms in [(Triphos)Ru(OR)($\eta^2$-H$_2$BH$_2$)], which forms as a result of Ru–H protonation and H$_2$ evolution from [(Triphos)Ru($\eta^2$-H)$_2$-(\(\eta^2$-H$_2$BH$_2$))]$^+$ (vide infra). As the temperature increases from 190 to 250 K, the ratio of these three species changes in favor of dimetallic cation (Figures S8 and S9).

**Theoretical Calculations**

Ab initio calculations of the reaction mechanism were performed at the DFT/M06 level of theory for the model compound 2, in which the phenyl substituents of the Triphos ligand were replaced with methyl groups. No significant changes to the geometry or electron-density distribution of the borohydride fragment were found for the model (Figure S10, Tables S1 and S2). Previously, such an approach was successfully applied in the investigation of the DHB intermediates and alcoholsysis reactions of (Triphos)Cu($\eta^1$-BH$_4$)[9a] and [(PP$_3$)RuH($\eta^1$-BH$_4$)].[9b]

**Structures of the DHB Complexes**

The geometry optimizations (DFT/M06) of the DHB complexes revealed five possible types of coordination of the proton donor to 2 (Scheme 3): monodentate complexes with coordination to...
Scheme 3. Types of DHB complexes 2·HOR. The key distances [Å] and angles [°] are given for HOR = TFE.

a terminal BH ligand (Ia), a Ru–H–B bridge (Ib), or a terminal RuH hydride (Ic) and bifurcated DHB complexes IIab/IIba (with a different balance of interactions with BHterm and Ru–H–B bridge) and Ic (with primary coordination to RuHterm and a secondary interaction with the Ru–H–B bridge). However, the actual number of DHB complexes depends on the alcohol (see Table S3). All five local minima were found only for TFE. For the weakest alcohol, MeOH, four possible DHB intermediates were found: a monodentate complex (Ia) and three bifurcated complexes (IIab, IIba, and Ic). For stronger proton donors such as HFIP, optimization only gave monodentate DHB complexes (Ia, Ib, and Ic).

The structural parameters for all of the optimized DHB complexes are gathered in Table S3. The monodentate DHBs involving RuH (Ic type) feature the shortest H···H distances (1.533–1.577 Å) and almost linear O–H···H(B) angles (161–166°). The bifurcated complexes (IIab and Ic) have short H···H distance and almost linear O–H···H angles (167–176°) for the primary contact (1.705–1.817 Å). The DHB formation causes typical elongations of the O–H bonds of the proton donors and of the B–Hterm or Ru–H bonds involved in DHB formation, and the elongations are larger for stronger bonds.

Electronic Structures

The analysis of the molecular electrostatic potential (MEP) of 2 (Figure 4) reveals that the electron density is localized on the BH4− and RuH fragments with two minima (Vmin) of −42.0 and −50.2 kcal/mol, respectively. The Vmin value for BH4− in 2 is lower than that for (Me3P)2Cu(η2-BH4). The higher energy of Vmin at the RuH site is in agreement with the shorter DHB to the RuH ligand.

Despite the presence of multiple short contacts in some DHB complexes, the intermolecular bond critical points (3, –1) were revealed only for closest contacts with the most linear O–H···H(B) fragment (Figure 5, Table S10). The electron-density values at the (3, –1) critical points (ρc) vary from 0.01 to 0.04 a.u. and grow with the interaction strength (Table S10). The deviation of the DHB geometry from linear caused by the additional interaction is reflected by the increased ellipticity value, which changes from ε = 0.08 for the RuH···HO complex Ic to 0.38 for Ibc (Table S10).

Figure 4. MEP maps [at a distance of 1.5 times the van der Waals (vdW) radii; the red–green–blue (RGB) scale shows −0.07 to 0.05 a.u.] for (a) 2 and (b) (Me3P)2Cu(η2-BH4). The MEP minima Vmin [kcal/mol] are marked as red spheres.

Figure 5. Molecular graphs for the bifurcated DHB complexes 2-TFE.
Frequency Analysis

Frequency analysis for the model complex 2 gives the stretching vibrations of the BHterm groups (νBHterm as and νBHterm s) at \( \tilde{\nu} = 2550 \) and 2470 cm\(^{-1}\), respectively, whereas the νBHdir s and νRuH vibrations were found at \( \tilde{\nu} = 1804 \) and 1821 cm\(^{-1}\) (Figure 6). Another band, νBHdir as, is located at lower frequency (1737 cm\(^{-1}\)) and has very low intensity, which prevents its observation in the IR spectrum.

The DHB formation leads to low-frequency shifts of the stretching vibrations of the bands involved.\(^{[7,16]}\) The computed low-frequency shifts of the νOH vibrations correlate with the O–H bond elongation (Table S6). As expected, the low-frequency shifts of the νYOH term bands by \(-18\) to \(-70\) cm\(^{-1}\) was computed for the DHB complexes with the BHterm ligand (Ia, IIab/IIba). However, the low-frequency shift of νRuH band (by \(-42\) to \(-59\) cm\(^{-1}\)) was found only for monodentate Ic with coordination to the RuH site. In particular, these changes correspond to the experimentally observed spectra. The νBHdir stretching vibrations shift to higher frequency by \(11–38\) cm\(^{-1}\) for Ic and Ibc and by \(41–100\) cm\(^{-1}\) for the others. Such frequency changes are also in agreement with the experimentally observed spectral changes (vide supra).

Taken together with the formation energies of the DHB complexes (Tables 2 and S8), all of the computational data obtained clearly show that the most energetically favorable DHB complexes Ibc and Ic with the participation of RuH ligand should be the intermediates of the reactions with alcohols.

Mechanism of the Proton Transfer Reaction

The calculations of the proton transfer mechanism were performed at the DFT/M06 level of theory for the model compound 2 with single-point solvent model based on density (SMD) correction (CH\(_2\)Cl\(_2\)) for the gas-phase optimized species and optimization with SMD correction. The key activation barriers obtained this way are gathered in Table 3. The calculations revealed several possible reaction pathways, which differ by the structure of the DHB intermediate, the corresponding transition state (TS), and the activation energy. The proton transfer to the BHterm site (denoted as the BHdir and BHanch pathways) was found to be the least feasible reaction pathway, as for copper(I) tetrahydridoborates.\(^{[9b,9c]}\) Therefore, the details of these pathways are given in the Supporting Information. The other pathways have comparable reaction barriers; therefore, it is difficult to choose the preferred one. They involve versatile species, which will be discussed briefly below, but eventually come to the same kinetic product, that is, \([\text{Triphos}^{5\text{Me}}]\text{RuH}\eta^2\text{-H}_2\text{BHOR}]^+\).

Hydride Transfer of the Bridging Hydrogen B–H–Ru with Subsequent Proton Transfer (Sn2 Pathway)

This pathway includes the preliminary formation of DHB complexes, which provide the orientation suitable for the subsequent nucleophilic substitution at the boron atom and assist the B–H\(_\text{B}H\) bond activation. The peculiarity of this process is a hydride transfer from B to Ru along the B–H–Ru bond accompanied by the coordination of the alcohol oxygen atom to the boron atom. This process can be treated as a nucleophilic substitution (Sn2) at the boron atom and is facilitated by the presence of the (Triphos)Ru moiety, which activates the B–H bond (see Supporting Information for details). Depending on the orientation of the alcohol molecule in the starting DHB complex, the substitution can proceed in two different ways (Figure 7), that is, as a simple nucleophilic substitution [denoted as the

![Figure 6. Simulated IR spectra of 2 and 2-TFE DHB complexes and dimetallic cation 3 in the regions of the νOH and νRuH stretching vibrations.](Image 48x740 to 72x765)

Table 2. Formation energies of DHB complexes 2-TFE and energy \(E_{\text{ZPE}}\) of the H–H bond (kcal/mol).

<table>
<thead>
<tr>
<th>DHB</th>
<th>ΔE</th>
<th>ΔE_{ZPE}</th>
<th>ΔE_kin</th>
<th>ΔH_{ZPE}</th>
<th>ΔH_{kin}</th>
<th>ΔH_{ZPE}/ΔH_{kin}</th>
<th>E_{theor}^{[\text{IH}]}/E_{theor}^{[\text{HH}]}/E_{theor}^{[\text{HH}]}</th>
</tr>
</thead>
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<td>-12.2</td>
<td>-9.2</td>
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<td>-2.9</td>
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</tr>
<tr>
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<td>-6.7</td>
<td>-5.6</td>
<td>-5.2</td>
<td>1.1/L/1.1</td>
</tr>
</tbody>
</table>

[a] DHB formation enthalpy calculated from the theoretical ΔH(νOH) data with the correlation \(-ΔH = 18[ΔH(νOH)] / [ΔH(νOH)] + 720\). [b] The energies of the H–H interactions were calculated from the correlation between the binding energy \(E_{\text{ZPE}}\) and the value of the density-functional potential energy \(V(r)\) at the corresponding critical point \(3, -1\): \(E_{\text{ZPE}} = 0.5 V(r)^{[17]}\).
BH pathway; $T_{\text{BH}}^{S_{\text{SN}}^{2}}$, $\Delta G_{\text{theor}}^{(298 \text{~K, DCM})} = 29.5 \text{ kcal/mol}$ for TFE, Figure 7a) or as a nucleophilic substitution with participation of the RuH···OH dihydrogen bond [denoted as the RuH pathway; $T_{\text{RuH}}^{S_{\text{SN}}^{2}}$, $\Delta G_{\text{theor}}^{(298 \text{~K, DCM})} = 23.6 \text{ kcal/mol}$ for TFE, Figure 7b].

Figure 7. M06-optimized geometries of the transition states of the hydride transfer reaction driven by oxygen coordination ($S_{\text{Sn}}^{2}$) for the 2-TFE system. The substituents at the phosphorus atoms are omitted for clarity.

The BH pathway (Scheme 4) begins from the DHB complexes with participation of the BHterm ligand (Ila or Ia). The cleavage of the B–Hbr bond and the coordination of the oxygen atom of the proton donor to the boron atom gives (via $T_{\text{BH}}^{S_{\text{SN}}^{2}}$, Figure 7a) two possible intermediates with staggered (INTBHSN2trans) and eclipsed (INTBHSN2cis) conformations. The first one is energetically slightly more favorable (by 1.7 kcal/mol for TFE), but the second one provides conjugation between the BH and OH bonds that is suitable for the subsequent hydrogen evolution. The second transition state ($T_{\text{BH}}^{S_{\text{PT}}}$, Figure 8a) is a four-membered cycle [(O)BH···H(O)], in which proton transfer and the evolution of molecular hydrogen occur in a concerted manner to yield [(TriphosMe)RuH(η2-H2BHOR)].

Figure 8. The M06-optimized geometries of the transition states of proton transfer after the $S_{\text{Sn}}^{2}$ reaction in the 2-TFE system.

The RuH pathway (Scheme 5) starts from the DHB complexes with the BHbr ligand (Ilna or Ib). The concerted hydride transfer and B–O bond formation are accompanied by RuH···HO bonding, which makes the energy of $T_{\text{RuH}}^{S_{\text{PT}}}$ a few kcal/mol lower

Scheme 4. The BH pathway.

Scheme 5. The RuH pathway for weak and medium-strength alcohols (MeOH, TFE).
than that of TS$_{BH}$ \_S$^\text{trans}$ (Table 3). The intermediates formed at this stage also exist as two conformers, that is, INT$_{RuH}$ \_S$^\text{trans}$ and INT$_{RuH}$ \_S$^\text{cis}$. As in the BH pathway, the first one, connected by TS$_{RuH}$ \_I$^\text{trans}$ by the intrinsic reaction coordinate (IRC), is energetically more favorable, whereas the second conformer (INT$_{RuH}$ \_I$^\text{cis}$) has a structure close to that of the subsequent TS (TS$_{RuH}$ PT). This barrier is very low (even for weak alcohols), and the proton transfer within the six-membered cycle ([H]RuH--HO(R)B(H); TS$_{RuH}$ PT, Figure 8b) gives the first reaction product, that is, the molecular hydrogen complex [(Triphos$^{Me}$)RuH($\eta^1$-H$_2$)($\eta^1$-HB2OR)], which converts into [(Triphos$^{Me}$)RuH($\eta^1$-H$_2$B2HOR)] (4) through H$_2$ elimination. Moreover, this stage disappears for HFIP, and the formation of the dihydrogen complex [(Triphos$^{Me}$)RuH($\eta^1$-H$_2$)($\eta^1$-H2B2OR)] from the DHB precursor occurs in one step (Scheme 6). A similar pattern was found previously for the protonation of (Triphos$^{Me}$)Cu($\eta^1$-BH$_2$)[9a] and [(PP$_3$)$^\text{Me}$]RuH($\eta^1$-H$_2$)]$^{[9b]}$.

The two pathways, BH and RuH, can be interconnected by rotation around the B–O bond (Scheme 7) to transform INT$_{RuH}$ \_trans into INT$_{RuH}$ \_trans with a very low activation barrier [for MeOH, $\Delta G^{[9c]}_\text{theor}$ (298 K,DCM) = 1.0 kcal/mol for the direct reaction and 5.6 kcal/mol for the reverse process]. Thus, the first reaction step is a concerted hydride transfer and B–O bond formation along the BH$^\text{S(trans)}$ or slightly preferred RH$^\text{S(trans)}$ pathway, which should be followed by almost barrierless proton migration within INT$_{RuH}$ \_trans to form [(Triphos$^{Me}$)RuH($\eta^1$-H$_2$)(\$\eta^1$-H2B2OR)].

Conclusions

The BH$_4^-$ ligand in [(Triphos)RuH($\eta^2$-BH$_4$)] (1) appears to be more tightly bound than that in the related [(PP$_3$)RuH($\eta^1$-BH$_2$)], and this difference results in different NMR spectroscopic and chemical behavior. Although the hydrogen atoms of the BH$_4$ group of [(PP$_3$)RuH($\eta^1$-BH$_2$)] are highly fluxional$^{[9d]}$ no exchange of the terminal and bridging BH atoms was observed in the $^1$H NMR spectrum of 1. Interestingly, the BH$_4^-$hydride atom of [(PP$_3$)RuH($\eta^1$-BH$_2$)] acts as a hydrogen-bond acceptor, whereas the Ru hydrido ligand remains free$^{[9b]}$ despite the relatively high basicity factor of the parent [(PP$_3$)RuH$_2$] hydride...
[E(RuH) = 1.32].\(^{[11]}\) We believe that statistical factors (three BH atoms vs. one Ru hydrido ligand) are not a decisive reason for this phenomenon. Instead, steric factors play a role: the bulky (PP$_3$) group imposes more steric constraints to the Ru-bonded hydrido ligand than to the terminal borohydride ligands. Note that the BH basicity in [([PP$_3$])RuH(η$^1$-BH$_4$)] is lower [E(BH) = 0.98]\(^{[26]}\) than that of free BH$_4^-$ [E(BH) = 1.25]\(^{[18]}\) therefore, the electron density of the tetrahydriborohydride group is depleted upon coordination. Nevertheless, the $E_j$ value is remarkably higher than that determined for the neutral borohydrides [E(BH) = 0.41 and 0.53 for (EtO)$_2$PBH$_3$ and Et$_3$NBH$_3$, respectively].\(^{[18]}\) The electron-density depletion of BH$_4^-$ becomes much stronger for [(Triphos)RuH(η$^1$-BH$_3$)], for which the terminal BH ligands become uncompetitive for hydrogen bonding with alcohols despite their steric accessibility. In turn, the Ru–H ligand becomes quite basic, and the $E_j$(RuH) value of 1.43 is among the highest determined to date for transition-metal hydrides.\(^{[7]}\)

DFT calculations revealed a variety of DHB complexes of [(Triphos)RuH(η$^2$-BH$_4$)] with alcohols. Those with the preferential coordination at the RuH site (lcb and ic) are thermodynamically favorable (by 3–5 kcal/mol in CH$_2$Cl$_2$) in comparison with the complexes involving BH$_{term}$ ligands. This observation is in good agreement with the experimental spectra, which suggest that the formation of RuH–HO bonds precedes the protonation of 1, and H$_2$ evolution lead to the loss of boron and the formation of the dimetallate [(Triphos)RuH$_2$(μ$_1$-η$_1$$^2$-BH$_3$)]$^+$ cation (3). On the basis of the DFT calculations, the preferred reaction pathway depends on the alcohol strength. In agreement with the slow reaction of 1 with MeOH in CH$_2$Cl$_2$,\(^{[8c]}\) the activation barriers found for this alcohol are over 25 kcal/mol. In this case, the reaction should follow the RuH$_{sol}$ pathway, in which the concerted hydride transfer and B–O bond formation are accompanied by RuH–HO bonding. In the next step, H$_2$ is formed almost without a barrier to afford the first substitution product [(Triphos)RuH(μ$_1$-η$_1$-BH$_2$OR)] (4). For strong alcohols, the proton transfer to the Ru–H moiety features a very low barrier and yields [(Triphos)Ru(OR)(η$^2$-H$_2$BH$_3$)]. Indeed, the starting hydride 1 disappears instantaneously from the reaction mixture, as shown by NMR spectroscopy. The alkoxide complex [(Triphos)Ru(OR)(η$^2$-H$_2$BH$_3$)] formed at this stage isomerizes slowly into the kinetic product, 4. The introduction of the alkoxide substituent at the boron atom increases the BH hydridicity and facilitates the next protonation to yield the final reaction product, [(Triphos)RuH$_2$(μ$_1$-η$_1$$^2$-BH$_3$)]$^+$(RO) $\cdot$ B$^\cdot$.

**Experimental Section**

**General Considerations**: All manipulations were performed under a dry argon atmosphere by standard Schlenk techniques. Commercially available argon (99.9 %) was additionally purified from traces of oxygen and moisture by sequential passage through a Ni/Cr catalyst column and 4 Å molecular sieves.

HPLC-grade solvents (Acros Organics) were used for sample preparation after additional purification by standard procedures. DCM and THF were dehydrated over CaH$_2$. All solvents were freshly distilled under argon before use. Deuterated solvent (CD$_2$Cl$_2$) was dried with CaH$_2$ and degassed by three freeze–pump–thaw cycles before use. The fluorinated alcohols MFE, TFE, HFIP, and PFTB were obtained from P&M (Moscow, Russia) and Fluca Analytical; they were dried with anhydrous K$_2$CO$_3$ and distilled under argon before use. Other reagents from Sigma–Aldrich were used as received.

**Variable-Temperature Infrared Spectroscopy**: The IR spectra were recorded with Nicolet 6700 and Shimadzu IR Prestige-21 FTIR spectrometers with 0.04–0.22 cm CaF$_2$ cells. Low-temperature IR studies in the 190–300 K range were performed with a home-modified cryostat (Carl Zeiss). The accuracy of the experimental temperature adjustment was ±0.5 K. The cryostat modification allowed the transfer of the reagents (premixed at low or room temperature) under an inert atmosphere directly into the precooled cells.

**NMR Spectroscopy**: The NMR spectra were recorded with a Bruker Avance II 500 MHz spectrometer. The $^1$H NMR chemical shifts are reported in ppm relative to tetramethylsilane (TMS) and were calibrated against the residual solvent resonance.

**Complex 1 (Scheme 9)** was synthesized as described previously.\(^{[10]}\)

![Scheme 9. Synthesis of 1.](image)

The measurement of its VT $^1$H NMR spectra at 500 MHz in CD$_2$Cl$_2$ confirmed its stereochemical rigidity and revealed the fine structure of its hydride signals, not reported previously.\(^{[10b]}\) At 190 K, the terminal BH groups give two partially overlapped broad singlets at $\delta_{H} = 5.06$ and 4.96 ppm, whereas the bridging BH groups appear as a broad singlet at $\delta_{H} = −7.42$ ppm. The RuH resonance appears at $\delta_{H} = −4.58$ ppm as a doublet of doublets of triplets ($^3$J$_{H,P}$)$^2$($^2$J$_{H,P}$,$^2$J$_{P,B}$) ($^3$J$_{H,P}$ = 100 Hz, $^2$J$_{H,P}$,$^2$J$_{P,B}$ = 16 Hz, $^2$J$_{H,H}$ = 5 Hz). The minimum longitudinal relaxation times $T_{1\text{min}}$ were found to be 0.389 s for RuH (at $T$ = 240 K) and 0.130 s for BH$_4^-$ (at $T$ = 230 K).

**Computational Details**: Full geometry optimizations were performed with the Gaussian09 (Revision D.01)$^{[19]}$ package at the DFT level with the M06 functional.\(^{[20]}\) A simplified model system (2) was used for the simulation of the proton transfer reaction with the phenyl substituents of the Triphos ligand replaced by methyl groups (Figure S10) to achieve shorter computational times. The effective core potentials (ECPs) and their associated SDD basis set supported with $f$-function polarization were used to represent the innermost electrons of the ruthenium atom.\(^{[21]}\) The basis sets used were 6-311G(d) for the phosphorus atoms\(^{[22]}\) and 6-311++G(d,p) for the BH$_4^-$ fragment, ruthenium-bound hydrogen atom, and the alcohol OH group.\(^{[23]}\) Frequency calculations were performed for all of the optimized complexes in the gas phase and are reported without the use of scaling factors. The nature of all of the stationary points on the potential-energy surfaces was confirmed by a vibrational analysis. The TS structures showed only one negative eigenvalue in their diagonalized force-constant matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration by the IRC method.\(^{[24]}\)

The complex formation energy was calculated in the gas phase with consideration of the basis set superposition error (BSSE, by the Bernardi and Boys method),\(^{[25]}\) and the zero-point vibrational energy (ZPVE) correction was determined from the unscaled harmonic frequencies.\(^{[26]}\)
The inclusion of nonspecific solvent effects in the calculations was performed by the SMD method. The solute cavity was redefined with radii = UAHF, because this atomic cavity was found to be more suitable than the default atom cavity (radii = SMD-Coulomb) defined in the SMD model. The interaction energies were calculated in CH$_2$Cl$_2$ ($ε$ = 8.9) for the gas-phase-optimized geometries. The changes of the Gibbs enthalpies and entropies in the solvent were determined with the corresponding corrections obtained for the gas phase (Equations (3) and (4)).

$$\Delta H_{\text{Solv}} = \Delta E_{\text{Solv}} + \Delta H_{\text{corr}}^{\text{gas}}$$

(3)

$$\Delta G_{\text{Solv}} = \Delta E_{\text{Solv}} + \Delta G_{\text{corr}}^{\text{gas}}$$

(4)

The natural atomic charges and Wiberg bond indices were calculated from the eigenvalues of the Hessian of the electron density at the bond critical point ($\lambda_1 < \lambda_2 < 0$).

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