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Initial Stages in the Rhodium(III)-Catalyzed C–H Bond Activation of Primary Alcohols in Aqueous Solution

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The mechanism of the catalytic H/D exchange in primary alcohol substrates derived from aldopentoses, promoted by a macrocyclic rhodium(III) complex, has been shown to occur by a reversible redox reaction that gives aldehyde and a rhodium–hydride complex. Hydride exchange in the latter complex promotes the introduction of solvent hydrogen in the primary alcohol formed by the reverse reaction. The hydride complex has been crystallographically characterized as a trifluoromethanesulfonate salt that contains the *trans*-[Rh(cyc*b*)(H)(OH_2)]$^{2+}$ (cyc*b* = *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) cation. The hydride complex is stable for extended periods of time in acidic solution in the absence of oxidants. In basic solutions a series of base-catalyzed reactions take place to yield ultimately the same mixture of [Rh(cyc*b*)$(OH)_2$]$^+$ isomers as produced by base hydrolysis of the *trans*-[Rh(cyc*b*)$(Cl)_2$]$^+$ complex.

Introduction

The growing interest in the use of aqueous media for the functionalization of substrates derived from natural products has motivated a significant body of work in recent years. Thus, it was recently demonstrated that aldopentoses in acidic solution and in the presence of the macrocyclic rhodium(III) complex, *cis*-[Rh(cyc*b*)$(OH_2)_2$]$^{3+}$ (cyc*b* = *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, see Figure 1) disproportionates to carboxylic acids and alcohols, both with an unchanged carbon skeleton, as described in the simplified reaction (1).

$$2\ RCHO + H_2O(l) \rightarrow RCOOH + RCH_2OH \quad (1)$$

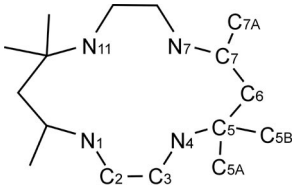

Figure 1. Structure and numbering scheme for the cyc*b* (*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) ligand.

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Furthermore, it turned out that primary alcohol groups under the same catalytic conditions in deuterated water exchanged carbon-bound hydrogen atoms with deuterium.[1]

This latter reaction also takes place for other primary alcohols not generated by disproportionation of the corresponding aldehyde, and this work investigates the introductory steps in this latter C/H-activation reaction.

Results and Discussion

The characterization of the C/H-activation reaction was conducted by treating *cis*-[Rh(cyc*b*)$(OH_2)_2$]$^{3+}$ or *cis*-[Rh(cyc*b*)$(OD_2)_2$]$^{3+}$, both formed by dissolution of *cis*-[Rh(cyc*b*)$(OSO_2CF_3)_2$]CF_3SO_3, in dilute $HClO_4$ and in dilute $DClO_4$, respectively, with the alcohols (ribitol and arabinitol) formerly shown to be formed by disproportionation of the earlier investigated aldopentoses: ribose, arabinose, and lyxose. The reactions were followed in rather concentrated solution by NMR spectroscopic measurements, and in more dilute solutions by mass-spectrometric and UV/Vis-spectrometric measurements in combination with chromatographic analysis.

Identification of Reaction Products

^{13}C NMR spectroscopic measurements in 0.01 M $DClO_4$ showed that the alcohols were initially oxidized to aldehydes. Ribose was formed from ribitol, and a mixture of arabinose and lyxose was formed from arabinitol. This oxidation reaction was accompanied by the formation of the same new rhodium complex for both alcohols. Initially this new complex was characterized by eight ^{13}C resonances

from the 16 carbon atoms of the macrocyclic cyc*b* ligand. During this initial phase of the reaction there were no indications of incorporation of deuterium into either the aldehydes formed or in the alcoholic substrates.

A repetition of the reaction with ribitol in 0.01 M $HClO_4$ gave the same result: formation of ribose and the same new rhodium complex. In the ^1H NMR spectrum of such solutions, however, resonances with large negative chemical shifts in the range between δ = –21 and –24 ppm appeared. This is demonstrated in Figure 2.

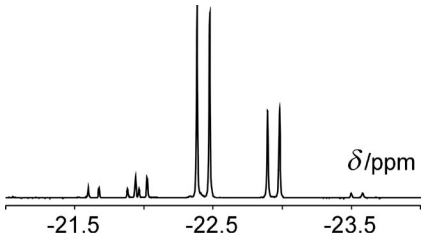


Figure 2. ^1H NMR spectrum of the mother liquor of a reaction mixture of *cis*-[Rh(cyc*b*)$(OH_2)_2]^{3+}$ and ribitol in 0.01 M $HClO_4$ after one week at 70 °C and cooling to room temperature. The dominant doublet at δ = –22.5 ppm, of much reduced intensity relative to the supersaturated solution, corresponds to the structurally characterized *trans*-[Rh(cyc*b*)$(OH_2)(H)]^{2+}$ isomer.

All these resonances are seen to be doublets, thereby indicating the presence of hydride directly coordinated to ^{103}Rh, with a nuclear spin of ½ and with $^1J_{Rh,H}$ in the range of 31.0 to 36.8 Hz. The relative intensities of ligand methyl hydrogen atoms to hydride indicated the presence of one hydride ligand in the rhodium complex thus formed.

A summary of these introductory experiments points consequently towards a two-electron oxidation of the primary alcohol accompanied by the reduction of hydrogen with a formal oxidation state of +1 to hydride coordinated to rhodium as described by the simplified formal reaction (2).

$$RCH_2OH + Rh^{3+} \rightarrow RCHO + RhH^{2+} + H^+ \quad (2)$$

At longer reaction times, the earlier characterized disproportionation of the aldehyde products became apparent with the formation of ribonic acid in the ribitol experiments and formation of a mixture of arabinonic acid and lyxonic acid in the arabinitol experiments. It was during this subsequent reaction that the deuteration of the carbon atom of the primary alcohol group took place.[1]

Whereas the reactions with respect to the organic substrate are reasonably clarified, this is not the case for the rhodium complexes. After the initial simple picture with the formation of the new rhodium complex characterized by eight ^{13}C resonances, a significant number of other ^{13}C resonances of low intensity appear at longer reaction times. In combination with the simultaneous formation of a crystalline rhodium-containing precipitate, information from NMR spectroscopic measurements is therefore limited, and eventually all resonances from rhodium complexes disappear in the baseline noise.

The crystalline rhodium complex that precipitated in aqueous solution is soluble in dimethyl sulfoxide. ^{13}C NMR spectroscopic measurements of such solutions show the same pattern of eight ^{13}C resonances from the macrocyclic ligand as are initially seen in the aqueous reaction solutions. The ^1H spectrum of precipitates formed in $HClO_4$ showed further a single doublet in the hydride range with a position of that of the dominating doublet in the aqueous reaction solutions, as verified by the relative intensity variation by the addition of a little dimethyl sulfoxide solution to the aqueous reaction mixture. These observations are both indications that the precipitated complex is identical to the primary reaction product formed by the alcohol reduction of the initial *cis*-diaqua complex.

Mass-Spectrometric Measurements

The formation of a hydride complex was supported by electrospray mass spectrometry of solutions in which *cis*-[Rh(cyc*b*)$(OH_2)_2]^{3+}$ was treated with ribitol or arabinitol in 0.01 M $HClO_4$. Both types of experiments initially showed the exclusive formation of a cation with mass and charge that correspond to the stoichiometric composition [Rh(cyc*b*)$(CF_3SO_3)(H)]^+$, with the coordinated trifluoromethanesulfonate ion originating from the initially dissolved rhodium complex.

At longer reaction times, a more complicated picture emerges and complexes with masses that correspond to coordination of the deprotonated carboxylic acid reaction products are seen.

Mass-spectrometric measurements on dimethyl sulfoxide solutions of the solid reaction product showed a dominating content of the same cation initially formed in the aqueous experiments. The interpretation of such experiments are, however, complicated by redox reactions that take place during evaporation and ionization, and considerable amounts of complexes with coordinated CH_3S^- and HS^- are seen, as are complexes in which the macrocyclic amine ligand has been oxidized to imines and amides still coordinated to rhodium. This latter type of ligand oxidation has previously been characterized in aqueous solutions for other systems including complexes of iridium(III)[2] and chromium(III).[3]

Structure of *trans*-[Rh(cyc*b*)$(OH_2)(H)](CF_3SO_3)_2$

The crystalline solid isolated from the reaction mixtures was characterized by a single-crystal X-ray structure determination. This structural investigation corroborated the conclusions from the NMR spectroscopic measurements and the mass-spectrometric measurements with the presence of a coordinated hydride ligand and identified the solid as *trans*-[Rh(cyc*b*)$(OH_2)(H)](CF_3SO_3)_2$, with the macrocyclic ligand coordinated symmetrically, which accounts for the eight resonances in the ^{13}C spectrum. The structure is

that of a racemic mixture and Figure 3 shows the structure of an enantiomer of the cation. A summary of selected structural parameters is given in Table 1.

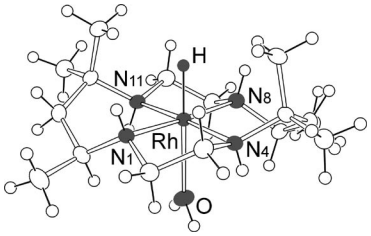


Figure 3. Structure of cation in *trans*-[Rh(cyc*b*)(OH_2)(H)]-(CF_3SO_3)$_2$. Non-hydrogen atoms are drawn as thermal ellipsoids at the 50% probability level and the hydrogen atoms as spheres with a radius corresponding to 0.1 Å.

Table 1. Selected structural parameters for the cation in *trans*-[Rh(cyc*b*)(OH_2)(H)](CF_3SO_3)$_2$; see Figure 3.

X	*d*(Rh–X) [Å]	∠(O–Rh–X) [°]	∠(H–Rh–X) [°]
H	1.52(4)	179.5(14)	–
O	2.3175(17)	–	179.5(14)
N1	2.0471(18)	91.32(7)	88.9(13)
N4	2.0598(19)	87.25(7)	93.2(13)
N8	2.0462(19)	91.67(7)	88.1(13)
N11	2.0555(19)	89.30(7)	90.2(13)

This macrocyclic ligand may theoretically exist in 10 possible conformations when coordinated in square-planar complexes.[4] The same number of isomers is clearly possible for octahedral *trans* complexes with identical axial ligands, a number that is doubled when different axial ligands are present. The ligand conformation of the present cation is the given number (9),[4] which has been characterized as one of the low-strain conformations of the theoretically possible coordination modes of this ligand. Experimentally, this conformation has previously been characterized as the so-called α configuration in a square-planar nickel(II) complex of the ligand.[5] Octahedral coordination of this ligand, however, may be expected to favor *cis* coordination,[4] and this expectation has been supported by the characterization of a vast number of *cis* complexes of metal ions including nickel(II), chromium(III), cobalt(III), lead(II), and so on. These complexes are usually folded so as to make the N4 and N11 nitrogen atoms *trans* to each other, but exceptions are known to exist.

The coordination sphere around the rhodium center is similar to that of the previously characterized *trans*-[Rh(cyclam)(H)(Cl)]$^+$ cation[6] (cyclam = 1,4,8,11-tetraazacyclotetradecane), and to the cation in *trans*-[Rh(cyc*b*)Cl_2]-CF_3SO_3,[7] the latter compound being obtained as the dominant product by the reaction between rhodium(III) chloride and the macrocyclic tetraamine ligand.[8]

The rhodium–nitrogen distances are almost identical in these three complexes, and the angular distortions are similar to those normally seen for *trans* complexes of this type of 14-membered tetraaza macrocyclic ligands. The chelate angles are smaller than 90° for five-membered chelate rings and are larger than 90° for the six-membered chelate rings. It is interesting to note that this distortion pattern persists in the present hexamethylated cyclam ligand even though the six-membered chelate rings in this complex adopt the uncommon "twist" conformation as compared to the more common "chair" conformations in both *trans*-[Rh(cyclam)(H)(Cl)]$^+$[6] and *trans*-[Rh(cyc*b*)Cl_2]$^+$.[7]

The presence of a hydride ligand is accompanied by a significant increase of the bond length to the water ligand in the *trans* position to the hydride ligand, a feature well documented in a number of other rhodium complexes such as [Rh(NH_3)$_5$(H)]$^{2+}$[9] and *trans*-[Rh(cyclam)(H)(Cl)]$^+$.

It is additionally noteworthy that the *trans*-ligand conformation in the present complex (see Figure 3) is that obtained by directly "unfolding" the ligand in the *cis*-diaqua complex[8] by the introduction of the hydride ligand in a position *trans* to a replaced water ligand. It is also noteworthy that the two axial methyl groups are both on the hydride side of the RhN_4 plane.

The positions of hydrogen atoms on the coordinating nitrogen atoms and on the water are further corroborated by hydrogen bonding to the trifluoromethanesulfonate oxygen atoms, in which the weakest hydrogen bonds are to the oxygen atoms in the disordered position with lower occupancy.

Stoichiometric Investigations

To further verify the initial reaction stoichiometry, approximately equimolar amounts of ribitol and rhodium complex were reacted at 64 °C in 0.01 M $HClO_4$ and in 0.01 M $DClO_4$. Reactant concentrations were monitored by integration of suitably selected well-separated ^{13}C and ^1H resonances as function of time.

A summary of the results obtained is shown in Figure 4. As seen in the figure, significant similarities as well as differences between the two reaction media exist. The upper left part of the figure shows no difference between the rates at which ribitol disappears in aqueous $HClO_4$ and in aqueous $DClO_4$. In contrast to this behavior, the upper right part demonstrates a significantly faster disappearance of the initial rhodium complex in $HClO_4$ than in $DClO_4$, which corresponds to ribitol/rhodium ratios of 0.56(3):1 in $HClO_4$ and 0.89(8):1 in $DClO_4$, respectively. Obviously, these numbers do not correspond to the 1:1 stoichiometry immediately expected from reaction (2). Consequently the disproportionation of the ribose formed by this reaction plays a more important role in aqueous $HClO_4$ than in aqueous $DClO_4$, which corresponds to a limiting behavior as given by reaction (3).

$$RCH_2OH + 2\ Rh^{3+} + H_2O(l) \rightarrow RCOOH + 2\ RhH^{2+} + 2\ H^+ \quad (3)$$

Both types of experiments are seen to range between the 1:1 stoichiometry of reaction (2) and the 0.5:1 stoichiometry of reaction (3).

Attempts to quantify the formation of reaction products proved only to be successful for the hydride/deuteride com-

plex, and the lower right of Figure 4 shows the formation of a hydride complex, as monitored by the intensity of ligand methyl proton resonances, as a function of time in ordinary and in deuterated aqueous perchloric acid. Hydride complexes are rapidly formed in both media and are apparently stabilized at an appreciable level relative to the total amount of rhodium complex: about 42% in $HClO_4$ and 25% in $DClO_4$. It is clear from these experiments that the disappearance of the initial rhodium complex exceeds the formation of rhodium–hydride complex as described by reactions (2) and (3). This apparent stoichiometric disagreement is explained by complex formation between the initial rhodium complex and the ribonic acid produced according to reaction (3). This supposition is supported by the correlation between the disappearance of ribitol and the disappearance of the total amount of initial rhodium complex and hydride complex. Minor differences are apparent between the two reaction media, but a rough 1:1 stoichiometry of the disappearance is seen in the lower left part of Figure 3. This clearly points towards a stoichiometry that, in addition to the redox reactions, is dominated by complex formation with the generated carboxylic acid, which corresponds to the total reaction stoichiometry; see reaction (4).

$$RCH_2OH + 3\ Rh^{3+} + H_2O(l) \rightarrow (RCOO)Rh^{2+} + 2\ RhH^{2+} + 3\ H^+ \quad (4)$$

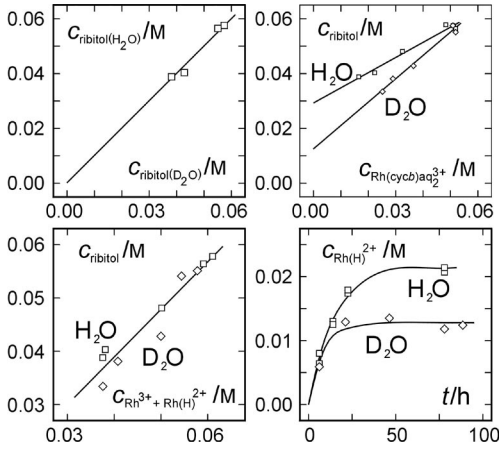


Figure 4. Stoichiometry of the reaction between equimolar amounts of *cis*-$[Rh(cyc\textit{b})(OH_2)_2]^{3+}$ and ribitol in 0.01 M $HClO_4$ or 0.01 M $DClO_4$ at 64 °C; see the text.

Supplementing this determination of the total concentration of hydride/deuteride complexes, the relative amounts of individual hydride complexes were also monitored in nondeuterated solvent. After about 6 h, 93% of the hydride complexes formed correspond to the complex characterized in the solid state, but after about 80 h this relative amount is decreased to 78%. This corresponds to the initial reaction in which formation of the characterized hydride complex is followed by isomerization reactions that give a significant number of other Rh(cyc*b*)(H) isomers.

To further attempt a characterization of these secondarily formed hydride complexes, concentrations of hydrogen ions, trifluormethanesulfonate, and ribonic acid were varied. Such variations gave no well-defined changes in the relative amounts of hydride complexes. In more acidic solution, hydride formation and hydride complex conversions are slower but follow the pattern just described. An increase in the concentration of trifluoromethanesulfonate anion is without effect, contrary to the addition of ribonic acid, which, due to complex formation with the Rh(cyc*b*)-unit, decreases the amount of hydride complexes significantly without apparently changing their relative amounts. These latter experiments point towards isomerization reactions of the initially formed rhodium–hydride complex as being responsible for the significant number of other hydride-containing complexes (Figure 2).

Reactivity of *trans*-$[Rh(cyc\textit{b})(H)(OH_2)]^{2+}$

trans-$[Rh(cyc\textit{b})(OH_2)(H)]^{2+}$ is stable in acidic solution at room temperature for days. At higher temperatures, the dominating reaction is a slow conversion to *cis*-$[Rh(cyc\textit{b})(OH_2)_2]^{3+}$ accompanied by the formation of minor amounts of unidentified complexes. Semiquantitative experiments in aqueous 0.01–0.1 M CF_3SO_3H at 100 °C indicate a half-life (for the disappearance of the hydride complex at these conditions) of about 3.4 h, as monitored chromatographically. In more concentrated solution, as monitored by NMR spectrometry in 0.01 M $HClO_4$, the half-life is about 22 d at 45 °C. This reactivity in acidic solution was not investigated further.

The deuterated hydride complex exchanges deuterium for hydrogen according to reaction (5).

$$trans\text{-}[Rh(cyc\textit{b})(OH_2)(D)]^{2+} + H_2O(l) \rightarrow trans\text{-}[Rh(cycb)(OH_2)(H)]^{2+} + HOD(l) \quad (5)$$

in acidic solution. In 0.01 M $HClO_4$, the half-life for this process is about 1 d at 45 °C. This type of process has earlier been investigated for *trans*-$[Rh(cyclam)(OH_2)(H)]^{2+}$ in D_2O,[10] a reaction that is base-catalyzed. At 25 °C, this latter reaction proceeds with a second-order rate constant of $1.45(2) \times 10^3\ M^{-1}\ s^{-1}$.

Contrary to its robustness in acidic solution, rapid reactions take place in basic solution. Initially the hydride complex disappears, and this reaction is followed by a number of slower reactions, all of which appear to be accelerated by the base.

The initial reaction was investigated spectrophotometrically and by chromatographic analysis in buffered solutions with pH values between 7 and 11, at an ionic strength of 1 M maintained by the addition of $NaCF_3SO_3$, and at temperatures between 15 and 50 °C. Under such conditions the progress of the reaction in more concentrated solutions is accompanied by evolution of a gas, probably dihydrogen, although this was not identified. To avoid complications from this gas evolution, submillimolar concentrations of rhodium complex were employed for the spectrophotometric measurements. Under these conditions the reaction is of pseudo-first-order in rhodium complex, although at longer reaction times influences from subsequent reactions are

seen. This gave rate constants as a function of pH and temperature as shown in Figure 5. The pH-dependence was analyzed within a stoichiometric reaction scheme involving second-order reactions between rhodium complex and hydroxide and supplemented with a hydrogen-ion-dependent equilibrium as shown in Scheme 1. Quantitative kinetic experiments analyzed by chromatographic analysis verified that the reaction monitored spectrophotometrically was the disappearance of hydride complex.

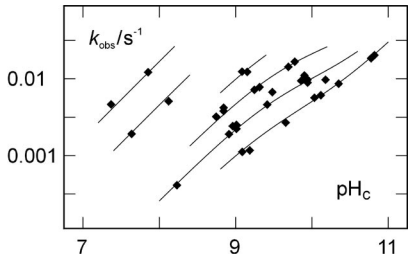
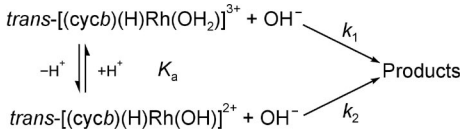


Figure 5. Reactivity of *trans*-[Rh(cyc*b*)(H)(OH_2)]$^{2+}$ in 1 M $NaCF_3SO_3$ between 16.3 and 51.7 °C. The curves are calculated from parameter values at 25 °C of $k_1K_w = 10^{-11.348(14)}$ M^{-1}, $K_a = 10^{-9.67(8)}$ M and $k_2K_aK_w = 10^{-22.1(4)}$ M^{2}s^{-1}; see Scheme 1. Only the activation parameter of the first parameter is sufficiently well defined to be reported: 109.7(15) kJ mol^{-1}. From the ionic product of water, $k_1 \approx 2.8 \times 10^2$ M^{-1}s^{-1} and $k_2 \approx 2 \times 10^1$ M^{-1}s^{-1} may be calculated.



Scheme 1.

In stronger basic solutions, a very complex kinetic behavior that involves a number of consecutive reactions is seen. In a limited hydroxide-concentration window between 0.05 and 0.09 M a pseudo-first-order behavior with rate constants proportional to the hydroxide concentration is observed, as demonstrated in Figure 6. At lower hydroxide concentrations, interference from faster reactions is apparent, and at higher concentrations even slower reactions follow until a mixture of dihydroxo complexes [Rh(cyc*b*)$(OH)_2]^+$ is formed. Eventually, chromatograms (Figure 7) of such reaction mixtures are indistinguishable from those of base-hydrolyzed solutions of *trans*-[Rh(cyc*b*)$Cl_2]CF_3SO_3$, and the reaction monitored is most likely the isomerization between isomers of the *trans*-[Rh(cyc*b*)$(OH)_2]^+$ ion. The chromatograms in Figure 7 indicate a reaction scheme between the dominating product, **A**, formed from the initial hydride complex and the subsequent dominating constituents, **B** and **C**,**D**, as **A** → **B** ⇄ **C**,**D**.

This interpretation of the reactivity in basic solution is supported by data for isomerization between complexes of square planar nickel(II) complexes in combination with estimated relative conformational energies;[4,11] see Figure 8.

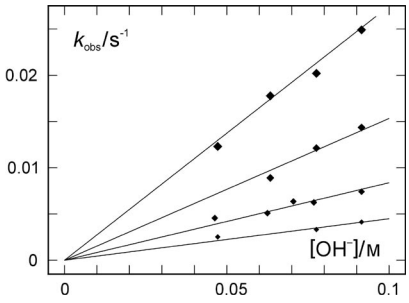


Figure 6. Reactivity of *trans*-[Rh(cyc*b*)$(OH)_2]^+$ isomerization in 1 M Na(OH/CF_3SO_3) between 11.3 and 26.4 °C. The curves are calculated from a second-order rate constant at 25 °C of 0.233(10) M^{-1}s^{-1} and an activation energy of 85(3) kJ mol^{-1}.

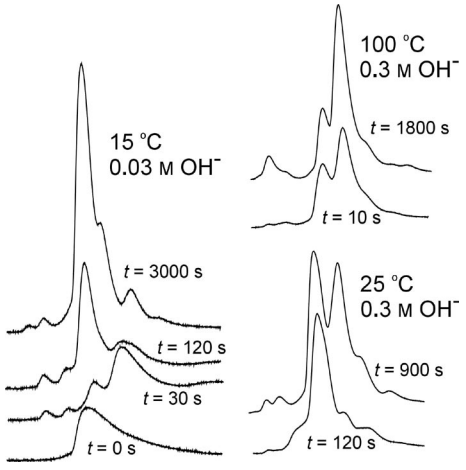


Figure 7. Chromatographic separation of reaction mixtures in basic solution of *trans*-[Rh(cyc*b*)$(OH)_2]^+$ isomers quenched by the addition of acid. The left part of the figure shows the separation behavior of the species of the interconversion quantified in Figure 6 for which the half-life at these reaction conditions is about 300 s. The right part demonstrates the further reactivity at higher hydroxide concentrations and at higher temperatures, which ultimately result in solutions that contain three species, of which two appear dominant.

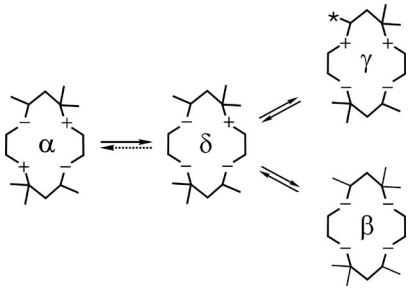


Figure 8. Suggested reaction scheme for the interconversion of low-energy cyc*b*-ligand conformations of *trans*-[Rh(cyc*b*)$(OH)_2]^+$ isomers of the (7*S*,14*S*)-ligand enantiomer. The axial C7-methyl group is indicated by an asterisk. Plus and minus signs at nitrogen atom positions indicate positions of hydrogen atoms relative to the plane of the four nitrogen atoms. Greek letters refer to characterized ligand conformations in square-planar nickel(II) complexes.[11] The γ conformation is that also characterized in a stable *trans*-[Rh(cyc*b*)$-Cl_2]^+$ salt.[7]

Mechanism of Hydrogen-Atom Exchange

An overview of the stoichiometry of the catalytic cycle for the exchange of carbon-bound hydrogen atoms in primary alcohols is given in Figure 9. The significant steps in this cycle are initiated by hydrogen transfer from the primary alcohol group to the rhodium complex, the net result being a redox reaction that results in the formation of aldehyde and an "unfolded" rhodium–hydride complex. Subsequently, the hydride ligand is engaged in equilibration with the hydrogen/deuterium solvent prior to the reversed redox reaction to give the initial organic substrate and the "refolded" initial rhodium complex.

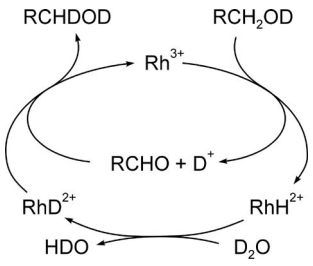


Figure 9. Suggested stoichiometric catalytic cycle for deuteration of primary alcohols in aqueous $DClO_4$. Rh^{3+}, RhH^{2+}, and RhD^{2+} are used as abbreviations for *cis*-[Rh(cyc*b*)$(OD_2)_2]^{3+}$, *trans*-[Rh(cyc*b*)-(H)$(OD_2)]^{2+}$, and *trans*-[Rh(cyc*b*)(D)$(OD_2)]^{2+}$, respectively.

This suggested stoichiometric mechanism was corroborated by a few experiments that used other primary alcohols including ethanol, $H_3CC(CH_2OH)_3$, and $C(CH_2OH)_4$. To summarize these experiments: in H_2O formation of the rhodium–hydride complex is seen (see the Exp. Section), and in D_2O deuteration of the primary alcohol group occurs.

This stoichiometric mechanism is similar to the one proposed for the molybdocene-catalyzed H/D exchange in primary and secondary alcohols.[12] Significant differences exist, however, as the suggested catalytic cycle for this latter reaction is suggested to involve *cis* coordination of hydride and oxidized substrate prior to the reverse redox reaction. This mode of reactivity obviously cannot operate for the present system because a *cis* coordination of hydride ligand and the aldehyde reaction partner is highly unlikely to occur in a stable complex, as this would imply significant stereochemical changes that involve the macrocyclic ligand.

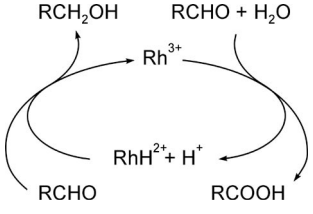


Figure 10. Suggested stoichiometric catalytic cycle for disproportionation of aldehydes in acidic aqueous solution. Rh^{3+} and RhH^{2+} are used as abbreviations for *cis*-[Rh(cyc*b*)$(OH_2)_2]^{3+}$ and *trans*-[Rh(cyc*b*)(H)$(OH_2)]^{2+}$, respectively.

An analogous mechanism may now be envisaged for the rhodium-catalyzed disproportionation of aldehydes, exemplified by the aldopentoses previously investigated. The suggested catalyzed cycle is shown in Figure 10.

Conclusion

H/D exchange in primary alcohol substrates is promoted by the macrocyclic *cis*-[Rh(cyc*b*)$(OH_2)_2]^{3+}$ complex. The exchange occurs by a reversible redox reaction that gives aldehyde and a rhodium–hydride complex. Hydride exchange in the latter complex promotes the introduction of solvent hydrogen into the primary alcohol formed by the reverse reaction. The efficiency of the catalyst, although stable for extended periods of time, is however limited by a series of base-catalyzed isomerization reactions.

Experimental Section

Chemicals: *cis*-[Rh(cyc*b*)$(OSO_2CF_3)_2](CF_3SO_3)$ was prepared according to the literature[7] and was used as the source of *cis*-[Rh(cyc*b*)$(OH_2)_2]^{3+}$ by dissolution in aqueous acid. $NaCF_3SO_3$ was prepared from CF_3SO_3H by neutralization with Na_2CO_3, and recrystallization of the product from water. The D-aldopentoses (Aldrich or Merck) and D-Ribonic γ-lactone (Aldrich) were commercial products. Other chemicals were the best available commercial grades and were used without further purification, except for the NaBr used for chromatographic separations, which was recrystallized from water. The purity of the commercial substrates was controlled by ^1H and ^{13}C NMR spectroscopy using 0.1 M solutions in aqueous 0.01 M $DClO_4$.

Preparation of *trans*-[Rh(cyc*b*)$(OH_2)(H)](CF_3SO_3)_2$: *cis*-[Rh(cyc*b*)-$(OSO_2CF_3)_2]CF_3SO_3$ (100 mg) was dissolved in 0.01 M CF_3SO_3H (1 mL). Ethanol (50 mL) was added, and the resulting solution was kept at 100 °C for 30 min. This resulted in the formation of a white precipitate in a yellowish solution. Cooling to room temperature and chromatographic analysis of the mother liquor indicated an almost complete precipitation of the *trans*-[Rh(cyc*b*)$(OH_2)(H)]$-$(CF_3SO_3)_2$ compound in a yield of about 80%.

The compound may be recrystallized by extraction with 0.01 M CF_3SO_3H at 80 °C, cooling in ice water, and precipitation by the addition of a saturated aqueous solution of $NaCF_3SO_3$. After filtration the compound was washed with a little ice-cold 1 M CF_3SO_3H and then twice with diethyl ether.

^{13}C NMR (62.896 MHz): δ = 18.8 (C7A), 27.6, 27.7 (C5A, C5B), 46.6, 48.3 (C2, C3), 50.7 (C6), 51.7 (C7) and 55.5 (C5) ppm, relative to 39.4 for solvent dimethyl sulfoxide.

Kinetic Measurements: The kinetics of the reactions of the hydride complex was followed spectrophotometrically with a computer-controlled Perkin–Elmer Lambda-18 spectrophotometer equipped with a Perkin–Elmer digital temperature controller. Absorbance-time data were collected at single wavelengths in the near-UV region. Data up to 3–4 half-lives were used for the rate constants calculations, with pseudo-first-order rate constants, k, calculated by nonlinear regression analysis using the function; see Equation (6).

$$A_{obs}(t) \approx A_{calc}(t) = A_0 + A_1 \cdot e^{-kt} + A_2 \cdot t \quad (6)$$

The reactions were investigated in aqueous solution with the ionic strength kept at 1 M by the addition of $NaCF_3SO_3$. Total concentra-

tions of buffer substances $(HOCH_2)_3CNH_3^+/(HOCH_2)_3CNH_2$, NH_4^+/NH_3, or $H_2NCH_2CH_2NH_3^+/H_2NCH_2CH_2NH_2$ were varied between 0.05 to 0.015 M (see Figure 5), and hydroxide concentrations between 0.05 and 0.09 M (Figure 6). Rhodium concentrations were kept at 0.2 mM.

Solutions for the stoichiometry followed by NMR spectroscopic measurements were prepared by dissolution of *cis*-[Rh(cycb)-$(CF_3SO_3)_2$](CF_3SO_3) and ribitol in 0.01 M $HClO_4$ or 0.01 M $DClO_4$ to give concentrations of about 0.05 M of both reactants. Such stock solution was divided in sealed ampoules and thermostatted at the desired reaction temperatures.

NMR Spectroscopic Measurements: ^1H NMR spectra were recorded at 400.13 MHz with a Bruker Avance 400 instrument. 3-(Trimethylsilyl)-1-propanesulfonic acid, sodium salt hydrate (ACROS) was used as the internal reference. Water suppression by presaturation was applied to the spectra of nondeuterated aqueous solutions. An external deuterium lock was used for such solutions.

The ^{13}C NMR spectra of aqueous solutions were recorded at 75.477 MHz with a Bruker Avance 300 instrument; reference: 1,4-dioxane with $\delta \approx 67.4$ ppm.

All ^1H and ^{13}C NMR spectra used for quantitative comparisons were recorded at identical instrument settings. Relative concentrations of hydride complex were monitored by integration of selected methyl group ^1H resonances for $HClO_4$ or $DClO_4$ solutions, supplemented by integration of the hydride resonance for $HClO_4$ solutions, with relative integrals for the $HClO_4$ solutions that corresponded well to the expected 18:1 ratio. Relative ribitol concentrations were obtained from the relative integrals of ^{13}C resonances; C2, C3, and C4 resonances were used for D_2O solutions; and all C resonances for H_2O solutions. Relative concentrations of the diaquarhodium(III) complex were obtained analogously from the C resonances of the ligand methyl groups.

Routine ^{13}C NMR spectra were recorded at 62.896 MHz with a Bruker AC 250 instrument.

X-ray Crystallography: The crystals of *trans*-[Rh(cyc*b*)(OH_2)-$(H)](CF_3SO_3)_2$ were grown from water. The compound crystallizes as prisms; additional data is as follows: crystal size $0.40 \times 0.21 \times 0.19$ mm^3; monoclinic; space group $P2_1/c$; a = 9.6202(5), b = 19.4920(11), c = 15.0962(8) Å; b = 90.4530(10)°; Z = 4. Data were collected at 120(2) K with Mo-K_α radiation.

CCDC-777383 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] L. Mønsted, O. Mønsted, *Inorg. Chem.* **2005**, *44*, 1950.
[2] L. Mønsted, O. Mønsted, S. Schäffer, K. Simonsen, I. Søtofte, *Acta Chem. Scand.* **1996**, *50*, 973.
[3] J. Chatłas, O. Impert, A. Katafias, P. Kita, G. Wrzeszcz, J. Eriksen, O. Mønsted, A. Mills, *Transition Met. Chem.* **2004**, *29*, 634.
[4] P. O. Whimp, M. F. Bailey, N. F. Curtis, *J. Chem. Soc. A* **1970**, 1956.
[5] N. F. Curtis, D. A. Swann, T. N. Waters, *J. Chem. Soc., Dalton Trans.* **1973**, 1963.
[6] A. Bakac, L. M. Thomas, *Inorg. Chem.* **1996**, *35*, 5880.
[7] A. M. Holm, *M. Sc. thesis*, University of Copenhagen, **1993**.
[8] J. Eriksen, O. Mønsted, L. Mønsted, *Transition Met. Chem.* **1998**, *23*, 783.
[9] B. A. Coyle, J. A. Ibers, *Inorg. Chem.* **1972**, *11*, 1105.
[10] K. Lemma, A. Ellern, A. Bakac, *Inorg. Chem.* **2003**, *42*, 3662.
[11] J. Chen, C. Chung, *Inorg. Chem.* **1986**, *25*, 2841.
[12] C. Balzarek, T. J. R. Weakly, D. R. Tyler, *J. Am. Chem. Soc.* **2000**, *122*, 9427.

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