The UV–vis spectrum of complex **2** shows peaks at 280 (ϵ = 4.87 × 10^3), 356 (1.1 × 10^3), 488 (5.9 × 10^1), and 747 nm (19.5 M^{-1} cm^{-1}). Complex **3** gives bands at 249 (1.24 × 10^4), 478 (1.4 × 10^3), and 755 nm (1.2 × 10^3 M^{-1} cm^{-1}). The bands at 280 and 249 nm in complexes **2** and **3** are assigned to the ligational bands[17] due to EDTA. The characteristic peaks at 356 nm in complex **2** and 478 nm in complex **3** are due to a $1\pi^*$–d LMCT transition from S_2^{2-} and S^{2-} groups, respectively, to Ru(IV). As expected these transitions are observed at lower energy[23] as compared to O_2^{2-} and O^{2-} because of a larger size of $1\pi^*$ orbitals of sulfur as compared to oxygen.

The reaction of complex **2** or **3** in a 1:1 EtOH–water mixture in the absence of excess sulfur takes place in a stoichiometric manner with the formation of cyclohexene sulfide and complex **1**. In the presence of excess sulfur, however, the reaction becomes catalytic. A mechanism for the sulfur atom transfer to cyclohexene is shown in Scheme I.

The product cyclohexene sulfide was isolated from the reaction mixture by fractional distillation under reduced pressure so that the temperature did not exceed 80 °C. The fraction boiling between 70 and 75 °C at 21 mm of Hg pressure was collected. The product was characterized by ^1H NMR and IR spectral analysis. The ^1H NMR spectrum of the product gave peaks at δ 3.2 (broad singlet, 2 H, C1 H and C2 H) δ 2.2 (broad singlet, C3 2 H, C6 2 H) and δ 1.38 (multiplet, C4 2 H, C5 2 H), which is in agreement with the spectrum taken for authentic sample of cyclohexene sulfide prepared by following the reported procedure.[24] The IR spectrum of the product gave characteristic strong bands at 1360, 1020, and 885 cm^{-1} for the episulfide ring. Reaction 1 proceeds at 80 °C with a turnover rate of the product cyclohexene sulfide of about (7 mol/mol of catalyst)/h. The reaction is 1 order of magnitude slower than the O atom transfer reaction of cyclohexene to the epoxide catalyzed[17] by Ru(III)–EDTA in the presence of O_2. This is expected on the basis of a weaker electrophilicity of S as compared to O.

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Insertion Reaction of Acetone-d_6 into the Os–H Bond of $[OsHCl(CO)(P^iPr_3)_2]$: Experimental Evidence for the Hydrogen-Transfer Mechanism from Alcohols to Ketones

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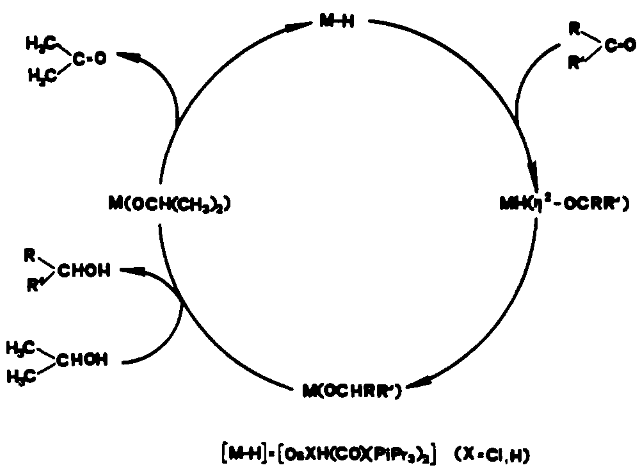
Transfer hydrogenation reactions catalyzed by transition-metal complexes have received a great deal of attention.[1,2] However, direct experimental evidence for possible reaction intermediates remains scarce, and no detailed proof of the mechanism has as yet been obtained.

We have recently postulated[3-5] that the hydrogen transfer from propan-2-ol to ketones involves four steps (Scheme I): (i) coordination of the ketone to the coordinatively unsaturated metal center, (ii) formation of an alkoxy metal intermediate by hydrogen migration from the metal to the ketonic double bond, (iii) exchange of the alkoxy group by reaction with the alcohol, which acts as solvent, and (iv) a β-elimination process. We have now found, under noncatalytic conditions, by using the five-coordinate hydrido osmium complex $[OsHCl(CO)(P^iPr_3)_2]$ (**1**) as starting material experimental evidence for the coordination, insertion, and β-elimination steps. Exchange between the hydrogen-bonded alcohol and the coordinated alkoxide has been previously demonstrated.[6] This exchange proceeds most probably via a hydrogen-bonded adduct, some examples of which have been characterized.[7]

Scheme I. Catalytic Cycle for the $OsHX(CO)(P^iPr_3)_2$-Catalyzed Hydrogen Transfer from Propan-2-ol to Ketones



The ^1H NMR spectrum of **1** shows, in C_6D_6, at room temperature a triplet at δ −31.9 with P–H coupling of 14 Hz.[8] In acetone-d_6, this triplet disappears and a broad signal at δ −28.3 is observed.[9] When the temperature is lowered, a new compound is formed by insertion of the coordinated ketone into the Os–H bond. Thus, the ^1H NMR spectrum in acetone-d_6 at −60 °C shows the signals of the phosphine ligands together with a new signal at δ 3.43, which is characteristic of a $OCH(CD_3)_2$ group linked to the metal.[6]

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(9) (a) ^1H NMR data (100 MHz): **2** (acetone-d_6, 27 °C), δ = 2.80 (m; PCH), 1.31 (dvt, J_{H-H} = 7.3 Hz, N = 13.2 Hz, $PCHCH_3$), −28.3 (br, OsH); **3** (acetone-d_6, −60 °C), δ = 3.43 (br, OCH), 2.55 (br, PCH), 1.19 (dvt, J_{H-H} = 6.6 Hz, N = 13.9 Hz, $PCHCH_3$). (b) The broadness of the hydride signal of **2** could be due to the existence of a rapid equilibrium between the coordinated acetone-d_6 and the molecules of the solvent.

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Table I. Kinetic Data for the Hydrogen Transfer from Propan-2-ol to Cyclohexanone Catalyzed by **5**[a]

10^3[catalyst], M	[substrate], M	$10^5 \times$ rate,[b] M s^{-1}	10^2K,[c] M^{-1} s^{-1}
0.8	0.24	0.37	1.9
2.1	0.25	1.16	2.2
2.6	0.25	1.17	1.8
1.3	0.19	0.45	1.8
1.3	0.24	0.70	2.2
1.3	0.32	0.85	2.0
1.3	0.38	1.22	2.4

[a] **5** was generated in situ by reaction of **1** with $NaBH_4$ in propan-2-ol at 83 °C. [b] Initial rate. [c] Average value for K at 83 °C = $(2.1 \pm 0.3) \times 10^{-2}$ M^{-1} s^{-1}.

These spectroscopic observations can be rationalized in terms of a rapid equilibrium between **1**, **2**, and **3** according to eq 1. The

$$\underset{\mathbf{1}}{[OsHCl(CO)(P^iPr_3)_2]} \xrightleftharpoons{(CD_3)_2CO} \underset{\mathbf{2}}{[OsHCl(CO)(P^iPr_3)_2(\eta^2\text{-}(CD_3)_2CO)]} \rightleftharpoons \underset{\mathbf{3}}{[OsCl(OCH(CD_3)_2)(CO)(P^iPr_3)_2]} \quad (1)$$

coordinatively unsaturated species **3**, which dominates at −60 °C, rearranges at higher temperatures to give the 18-electron intermediate **2** by β-elimination. These observations are very similar to those reported for the rhenium isopropoxide $[Re_3(\mu\text{-}O^iPr)_3(O^iPr)_6]$, which exists in equilibrium with a monohydride formed by β-elimination of acetone from one of the terminal alkoxo ligands.[10] The coordination of acetone-d_6 in **2** is strongly supported by the downfield shift of the hydride signal (compared with that of **1**) as has been found for several octahedral hydrido osmium complexes of general composition $[OsHCl(CO)(P^iPr_3)_2L]$.[8,11] The insertion reactions are generally viewed as a concerted process involving a four-center intermediate; thus, for the insertion of the coordinated acetone-d_6 into the Os-H bond of **2**, an Os(η^2-acetone-d_6) bonding is necessary. Other examples of insertion reactions of unsaturated organic substrates into the Os–H bond of **1** have been observed with alkynes (e.g., C_2H_2, MeC_2H, PhC_2H, $C_2(CO_2Me)_2$), which at room temperature lead to the formation of vinyl osmium derivatives.[12,13]

Complex **1** catalyzes the hydrogen transfer from propan-2-ol to cyclohexanone and acetophenone. The NMR spectroscopic observations presented above support Scheme I as the most reasonable mechanistic proposal for these reactions. Interestingly, the addition of $NaBH_4$ gives rise to a significant increase in the catalytic activity. Under these conditions, **1** reacts with $NaBH_4$ to give the tetrahydride **4**.[14] As **4** is coordinatively saturated, activation most probably involves the loss of one dihydrogen molecule per molecule of **4** to produce **5** (eq 2), which is structurally related to **1** and presumably acts as the active catalyst.

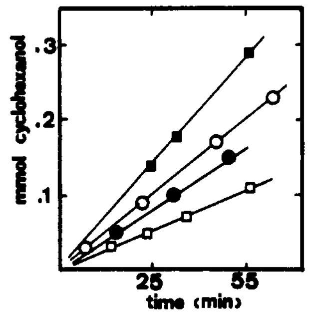

Figure 1. Plots for the formation of cyclohexanol as a function of time for **5**-catalyzed hydrogen transfer from propan-2-ol to cyclohexanone. (**5** was generated in situ by reaction of **1** (1.3×10^{-3} M) with $NaBH_4$ (0.1 mmol) in propan-2-ol at 83 °C). [cyclohexanone]: (□) 0.19 M; (●) 0.24 M; (○) 0.32 M; (■) 0.38 M.

$$\underset{\mathbf{4}}{[OsH_4(CO)(P^iPr_3)_2]} \rightleftharpoons \underset{\mathbf{5}}{[OsH_2(CO)(P^iPr_3)_2]} + H_2 \quad (2)$$

The lability of compound **5** has not allowed us to detect the supposed intermediates in the transfer hydrogenation reactions catalyzed by **1**/$NaBH_4$. However, the kinetic data summarized in Table I and Figure 1 for the formation of cyclohexanol[15] from propan-2-ol and cyclohexanone catalyzed by **5** reveal that the reaction is first order in catalyst and in substrate concentration.[16] The second-order rate law strongly supports the suggestion that the catalytic cycle shown in Scheme I describes not only the mechanism for transfer hydrogenation with **1** as catalyst but also when **5** is the active catalytic species.

Experimental Section

Complex **1** was prepared as described in the literature.[7]

Kinetic Studies. The kinetic measurements were performed under N_2 at 83 °C, following the formation of cyclohexanol as a function of time. The reactions were carried out in a two-necked flask fitted with a condenser and a magnetic stirring bar. The second neck was capped with a Suba-seal to allow samples to be removed without opening the system. In a typical procedure, to a solution of **1** in 2 mL of propan-2-ol was added $NaBH_4$ (3.78 mg, 0.1 mmol) in 2 mL of propan-2-ol. The resulting solution was refluxed for 1 h, and a solution of cyclohexanone in 4 mL of propan-2-ol was injected. The analysis of the products was carried out with a Perkin-Elmer 8500 gas chromatograph. A FFAP on Chromosorb 6 HP 80/100 mesh (3.6 m × 1.8 in) column at 100 °C was used for this analysis. The reaction products were identified by comparison of their retention time with those observed for pure samples. Plots of kinetic data were fitted by using conventional linear regression programs.

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(15) Acetone in a similar amount was formed.

(16) Plots of log rate versus log [catalyst] and log rate versus log [substrate] yield straight lines of slopes 1.0 and 1.2, respectively. A related kinetic study using **1** as the catalyst is precluded by the slowness of the reaction.