Studies on the Mechanism of Metal-Catalyzed Hydrogen Transfer from Alcohols to Ketones

Oscar Pàmies and Jan-E. Bäckvall*[a]

Abstract: The mechanism of metal-catalyzed hydrogen transfer from alcohols to ketones has been studied. Hydrogen transfer (H-transfer) from (*S*)-α-deutero-α-phenylethanol ((*S*)-**1**) to acetophenone was used as a probe to distinguish between selective carbon-to-carbon H-transfer and nonselective transfer involving both oxygen-to-carbon and carbon-to-carbon H-transfer. The progress of the reaction was monitored by the decreasing enantiomeric excess of (*S*)-**1**. After complete racemization, the alcohol was analyzed for its deuterium content in the α-position, which is a measure of the degree of selectivity in the H-transfer. A number of different rhodium, iridium, and ruthenium complexes (in total 21 complexes) were investigated by using this probe. For all rhodium complexes a high degree of retention of deuterium at α-carbon (95–98%) was observed. Also most iridium complexes showed a high degree of retention of deuterium. However, the results for the ruthenium complexes show that there are two types of catalysts: one that gives a high degree of deuterium retention at α-carbon and another that gives about half of the deuterium content at α-carbon (37–40%). Two different mechanisms are proposed for transition-metal-catalyzed hydrogen transfer, one via a monohydride (giving a high D content) and another via a dihydride (giving about half of D content). As comparison non-transition-metal-catalyzed hydrogen transfer was studied with the same probe. Aluminum- and samarium-catalyzed racemization of (*S*)-**1** gave 75–80% retention of deuterium in the α-position of the alcohol, and involvement of an electron transfer pathway was suggested to account for the loss of deuterium.

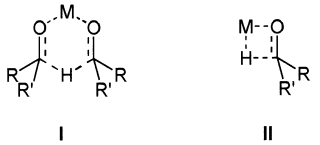
Keywords: homogeneous catalysis · hydrogen transfer · reaction mechanisms · transition metals

Introduction

Ever since the discovery of the Meerwin–Ponndorf–Verley reaction[1] in which a ketone is reduced by an alcohol in the presence of an aluminium alkoxide, the use of metallic compounds to promote hydrogen transfer between alcohols and carbonyl compounds has been widely studied in organic synthesis.[2, 3] More recently, transition-metal-catalyzed versions of these reactions have been developed.[4, 5] Today, the asymmetric transfer hydrogenation[5b, 6] of prochiral ketones is one of the most attractive methods for synthesizing optically active secondary alcohols, which form an important class of intermediates for fine chemicals and pharmaceuticals.[7] The product alcohols are obtained under relatively mild conditions in high yields and good enantioselectivities.[5b, 6] Transition-metal-catalyzed hydrogen transfer has also been used by us[8] and others[9] to racemize alcohols through reversible dehydrogenation in the presence of a lipase to obtain a dynamic kinetic resolution of secondary alcohols.

We have studied the mechanism of ruthenium-catalyzed hydrogen transfer and found that the presence of base in $[RuCl_2(PPh_3)_3]$-catalyzed reactions has a dramatic effect on the rate.[4, 10, 11] More recently, we have shown that the role of the base is to generate a highly active ruthenium dihydride species, $[RuH_2(PPh_3)_3]$.[12]

From a mechanistic point of view, two general pathways have been proposed for hydrogen transfer: 1) direct hydrogen transfer (Figure 1, **I**) and 2) a hydridic route (Figure 1, **II**). The



I II

Figure 1. Intermediates **I** and II proposed for the two general pathways: direct hydrogen transfer (**I**) and a hydridic route (**II**).

direct hydrogen transfer, proposed for the Meerwein–Ponndorf–Verley (MPV) reduction,[1, 3] is a concerted process that

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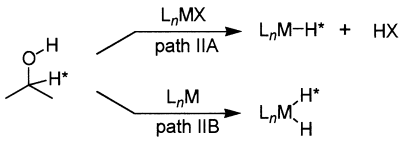
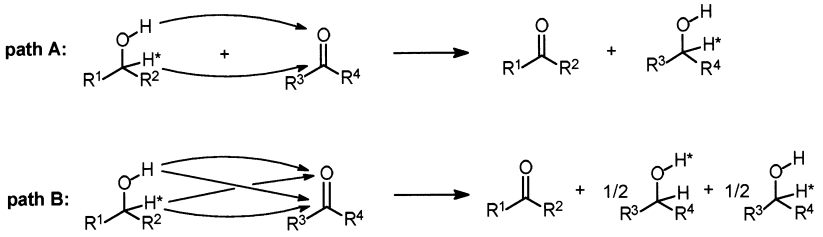
involves a six-membered cyclic transition state (**I**), in which both the hydrogen donor and the hydrogen acceptor are coordinated to the metal center. In the hydridic route, a metal hydride is involved in the hydrogen transfer (**II**). A direct hydrogen transfer is claimed to occur with main group elements, while a hydride mechanism is thought to be involved with transition metal complexes.[6, 13]

For the hydridic route, two different pathways may be involved depending on the origin of the hydride on the metal (Scheme 1). Thus, the metal hydride may arise purely from the C–H of the alcohol (path IIA) or it may originate from *both* the O–H and C–H (path IIB).



Scheme 1. Two different pathways proposed for the hydridic route.

For the second pathway (IIB) any of the hydrides on the metal may add to the carbonyl carbon (cf. Figure 1, **II**). A general question of interest to answer in hydrogen transfer from an alcohol to a ketone is, therefore, whether the hydrogen atoms transferred keep their identity, that is, if O–H is transferred to keto oxygen and C–H to carbonyl carbon (Scheme 2, path A) or if the two hydrogens are scrambled and lose their identity (Scheme 2, path B).



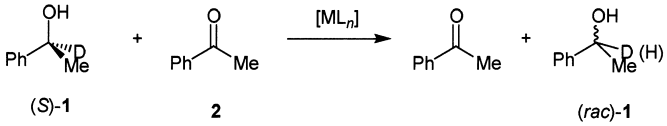
Scheme 2. Possible paths for direct hydrogen transfer.

In a preliminary study we reported on a method how to distinguish between the two pathways in Scheme 2. Two different ruthenium catalysts were compared in hydrogen transfer from an alcohol to a ketone, and it was found that one follows path A, whereas the other follows path B.[14]

A number of transition metal complexes are known to catalyze hydrogen transfer from an alcohol to a ketone.[6, 10] In the present study we have investigated the selectivity of the hydrogen transfer for rhodium, iridium, and ruthenium complexes with various phosphorous, nitrogen, and sulfur ligands by employing the method developed in our laboratory. As a comparison, the corresponding aluminum- and samarium-catalyzed hydrogen transfer reactions were also studied.

Results and Discussion

The method used involves metal-catalyzed hydrogen transfer from enantiomerically pure (*S*)-α-deutero-α-phenylethanol ((*S*)-**1**) to acetophenone (**2**). Since only achiral catalysts are



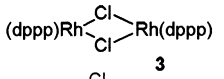
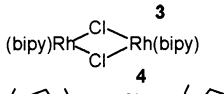
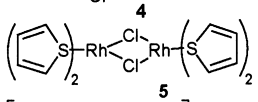
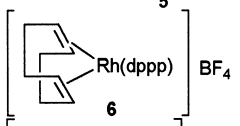
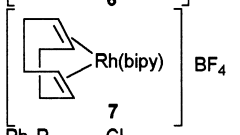
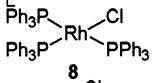
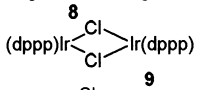
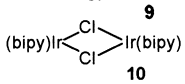
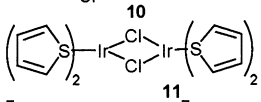
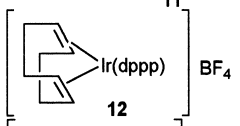
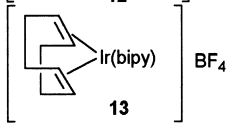
used, the progress of the reaction can be monitored by the racemization of (*S*)-**1**. Analysis of the racemized α-phenylethanol and determination of the deuterium content in the α-position will discriminate between path IIA and path IIB in Scheme 1. Enantiomerically pure deuterated alcohol (*S*)-**1** was prepared as described previously[14] and was >98% deuterated. A control experiment showed that no loss of deuterium was observed when the (*S*)-**1** and **2** were stirred under the reaction conditions without catalyst.

Rhodium and iridium-catalyzed hydrogen transfer: The results from rhodium-catalyzed reactions of (*S*)-**1** with **2** are given in Table 1 (entries 1–6). The reactions were run at 70 °C, and for the rhodium complexes with phosphorus ligands a quite fast racemization occurred (1–4 h). With sulfur and nitrogen ligands the racemization was slower (entries 2, 3, and 5). For all rhodium complexes studied there is a high selectivity for transfer of deuterium from the α-position of the alcohol to the carbonyl carbon of the ketone (95–98%). The corresponding iridium catalyst precursors, in most cases, also showed a high degree of retention of deuterium in the α-position (Table 1, entries 7–11). For example, with complexes **10**, **11**, and **13** a deuterium content of 96–98% in the α-position was observed after full racemization. However with phosphine ligands (complexes **9** and **12**) some loss of deuterium in the α-position of the alcohol was observed (entries 7 and 10). The rate of hydrogen transfer (racemization) was generally lower for the iridium complexes than for their rhodium analogues.

These results clearly indicate that the monohydride mechanism (path IIA, Scheme 1) is operating for the rhodium and iridium catalysts. Despite the fact that the iridium catalysts show different degrees of deuteration we believe that they also follow the monohydride mechanism. The lower deuterium content of (*rac*)-**1** with the Ir^{I} catalyst precursors containing the 1,3-bis(diphenylphosphinopropane) (dppp) ligand (entries 7 and 10, Table 2) can be explained by aromatic activation of the phosphine ligand by the active catalysts through orthometalation[15] leading to some H/D exchange, as has been previously observed in this reaction.[14]

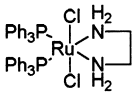
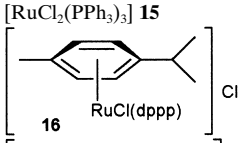
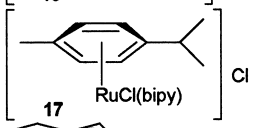
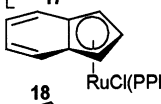
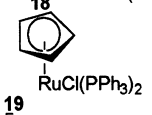
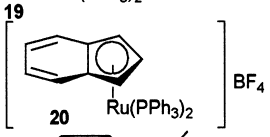
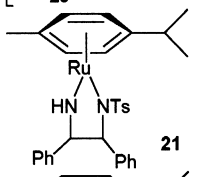
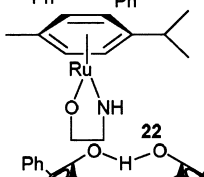
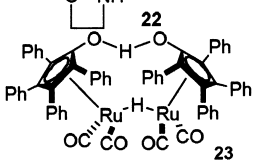
Ruthenium-catalyzed hydrogen transfer: The outcome of the ruthenium-catalyzed racemization of (*S*)-**1** with respect to deuterium content in (*rac*)-**1** varied depending on the type of catalysts precursor employed (Table 2). With dichloride complexes **14** and **15** as catalyst precursors the deuterium content in the α-position of (*rac*)-**1** was 37 and 40%, respectively, after complete racemization (entries 1 and 2). This low degree of deuteration would be best explained by a

Table 1. Deuterium content in (*rac*)-**1** after racemization of (*S*)-**1** by Rh^{I}- and Ir^{I}-catalyzed hydrogen transfer.[a]

Entry	Precursor	Time [h]	% D[b] in (*rac*)-**1**
1	 **3**	4	98
2	 **4**	20	97
3	 **5**	48	98
4	 **6**	3	98
5	 **7**	48	> 95[c]
6	 **8**	1	95
7	 **9**	6	83
8	 **10**	6	98
9	 **11**	48	98
10	 **12**	48	73
11	 **13**	48	96

[a] (*S*)-**1** (0.5 mmol), **2** (0.5 mmol), catalyst (0.01 mmol), NaOH (0.05 mmol), THF (0.75 mL), $T = 70\,^{\circ}C$. [b] % deuterium in the α-position after complete racemization unless otherwise noted. [c] 85% racemization.

Table 2. Deuterium content in (*rac*)-**1** after racemization of (*S*)-**1** by Ru^{II}-catalyzed hydrogen transfer.[a]

Entry	Precursor	Time [h]	% D[b] in (*rac*)-**1**
1	 **14**	6	40
2	$[RuCl_2(PPh_3)_3]$ **15**	4	37[c]
3	 **16**	3	89
4	 **17**	12	98
5	 **18**	0.17	88
6	 **19**	0.17	79
7	 **20**	2	92
8	 **21**	48	92[d]
9		48	91[d]
10	 **23**	24	95[c,d]

[a] (*S*)-**1** (0.5 mmol), **2** (0.5 mmol), catalyst (0.01 mmol), NaOH (0.05 mmol), THF (0.75 mL), $T = 70\,^{\circ}C$. [b] % deuterium in the α-position after complete racemization unless otherwise noted. [c] Ref. [12]. [d] No base added.

dihydride mechanism. On the other hand complexes **17** and **20**–**23** (entries 4 and 7–10) gave a high degree of deuteration (91–98%) in the α-position of the alcohol after complete racemization, indicating a monohydride mechanism for these catalysts. Complexes **16**, **18**, and **19** as catalyst precursors for the racemization of (*S*)-**1** afforded (*rac*)-**1** with a deuterium content of 89, 88, and 79%, respectively. Although there is some loss of deuterium from the α-position of the alcohol the results are also best explained by a monohydride mechanism. The slightly lower deuterium content in (*rac*)-**1** obtained with catalysts **16**, **18**, and **19** can be explained by either exchange with the phosphine ligand by orthometalation,[15] as was suggested for the iridium complexes (vide supra), or by some H/D exchange of the metal deuteride with the solvent or some ligand functionalities as has been recently reported for different ruthenium complexes.[16]

Aluminum- and samarium-catalyzed hydrogen transfer: The results from the racemization of (*S*)-**1** with aluminum and samarium catalysts are given in Table 3. As can be seen there is a loss of deuterium in the α-position from 98% in (*S*)-**1** to 75–80% in (*rac*)-**1** in all cases studied. However, complete retention of deuterium in the α-position would be expected for these catalysts, since it is generally assumed that they occur by direct hydrogen transfer that involves a cyclic transition state (Figure 1, **I**). The results, therefore, suggest partial involvement of some other mechanism in addition to the direct hydrogen transfer mechanism. Ashby[17] has proposed that an electron transfer mechanism can be involved in hydrogen transfer reactions catalyzed by non-transition metals. Thus, the partial loss of deuterium in the α-position (Table 3) may be accounted for by an electron transfer pathway, which would involve radicals.

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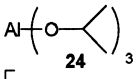
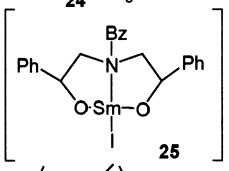
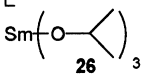
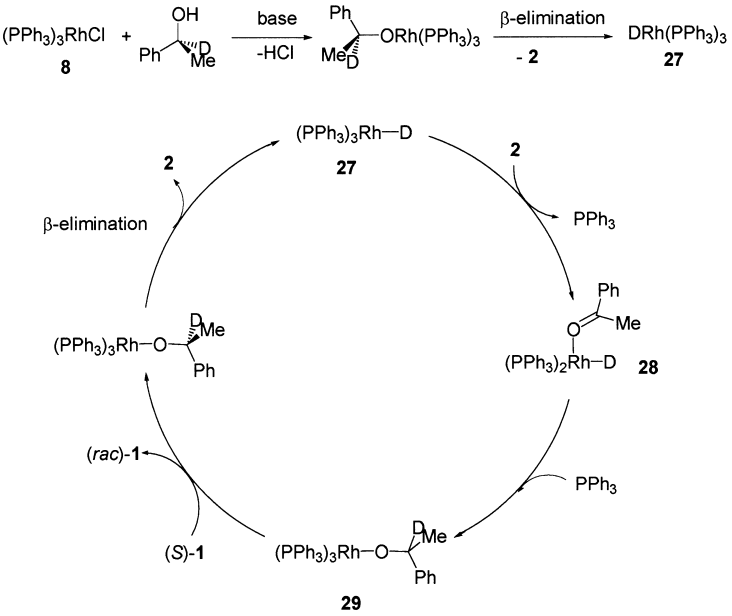
Table 3. Deuterium content in (*rac*)-**1** after racemization of (*S*)-**1** by Al^{III}- and Sm^{III}-catalyzed hydrogen transfer.[a]

Entry	Precursor	Time [h]	% D[b] in (*rac*)-**1**
1	 **24**	18	75
2	 **25**	48	80[c]
3	 **26**	18	76

[a] (*S*)-**1** (0.5 mmol), **2** (0.5 mmol), catalyst (0.05 mmol), THF (0.75 mL), $T = 70\,^{\circ}C$. [b] % deuterium in the α-position after complete racemization unless otherwise noted. [c] 83% racemization.



Scheme 3. Proposed catalytic cycle for the racemization of (*S*)-**1** with catalyst **8**.

Mechanistic considerations

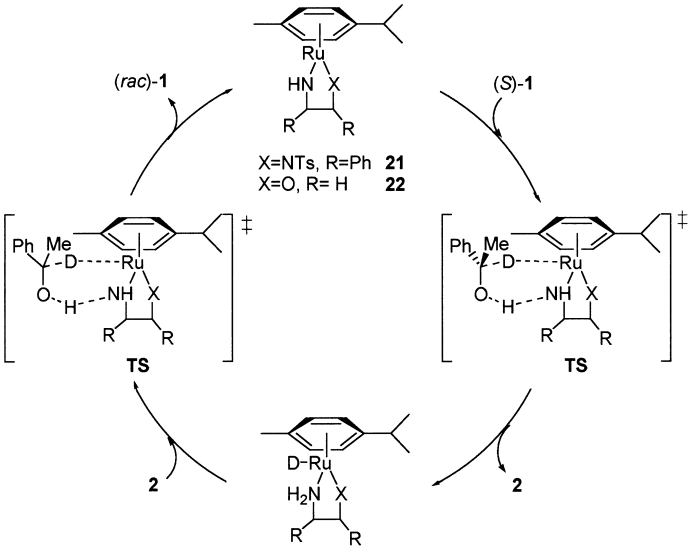
It is generally assumed that transition-metal-catalyzed hydrogen transfer involves metal hydrides as key intermediates. The results presented in Tables 1 and 2 indicate that two different hydridic pathways can be involved in these reactions: 1) a metal monohydride mechanism (path IIA, Scheme 1) and 2) a metal dihydride mechanism (path IIB, Scheme 1).

Metal monohydride mechanism: Hydrogen transfer reactions catalyzed by metal monohydride may proceed by two slightly different pathways. In both pathways the α-C–H is the origin of the hydride (and with the principle of microscopic reversibility the M–H adds exclusively to the carbonyl carbon of the ketone). However the formation of the metal monohydride may involve a) formation of a transition metal alkoxide followed by β-elimination (reversed: insertion of ketone into M–H bond to give metal alkoxide) or b) a concerted pathway with simultaneous transfer of α-C–H to the metal and transfer of O–H to the ligand (reversed: transfer of H^+ from ligand to carbonyl oxygen and M–H to carbonyl carbon). Thus, the latter pathway would not involve the intermediacy of a transition metal alkoxide.

Pathway via transition metal alkoxide: All rhodium (**3**–**8**), and iridium complexes (**9**–**13**) tested and ruthenium complexes **16**–**20** most likely follow the well-established mechanism via a metal alkoxide intermediate and β-elimination.[4, 13] This mechanism is depicted in Scheme 3 for the Wilkinson catalyst **8** as a representative example.

It is well known that chlorides are easily replaced by hydride by an alkoxide displacement/β-hydride elimination sequence.[12] The precursor catalyst **8** is, therefore, rapidly transformed to a monohydride species **27**. Subsequently, insertion of a ketone into the metal hydride bond via **28**[18] results in the formation of alkoxide **29**. Finally, ligand exchange between species **29** and (*S*)-**1** followed by β-elimination completes the catalytic cycle. There is ample support for this alkoxide mechanism,[6] and it has been demonstrated that transition metal hydrides are obtained from β-elimination of the corresponding alkoxide complexes.[19]

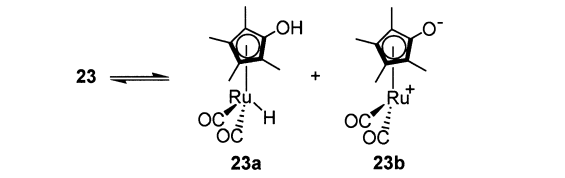
Concerted proton and hydride transfer: This mechanism was first proposed by Noyori[20] for 16-electron Ru complexes **21** and **22** and involves a six-membered transition state (Scheme 4, **TS**).

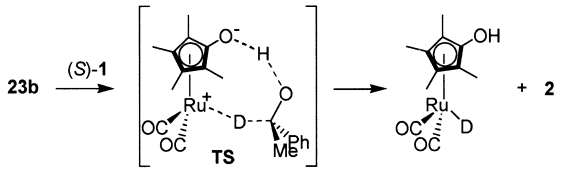


Scheme 4. Proposed concerted proton and hydride transfer mechanism for the racemization of (*S*)-**1** with catalysts **21** and **22**.

A feature of these complexes and also of complex **23** is that no addition of external base is needed as a co-catalyst, since one of the coordinating sites of the ligand acts as a basic center. The reaction of the basic nitrogen with the deuterated alcohol (*S*)-**1** would result in proton abstraction with concomitant formation of the corresponding Ru^{II}–hydride inter-

mediate. A similar concerted pathway may also take place for ruthenium complex **23**. Recent theoretical studies[21] lend support to formation of a Ru^{II}–hydride intermediate via the six-membered transition state (**TS**) in Scheme 4. Very recently Casey and co-workers provided experimental support for this pathway for **23** (Scheme 5).[22] From kinetic studies it

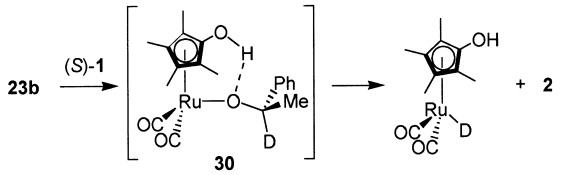




Scheme 5. Pathway proposed by Casey and co-workers for the formation of Ru–hydride species from complex **23** (phenyl groups in the complexes have been omitted for clarity)

was found that there is a combined kinetic isotope effect for the two hydrogens transferred in the process (studied for the addition of **23a** to benzaldehyde), which supports a concerted mechanism. However, it was not possible to exclude a two-step mechanism with nearly equal barriers in the two steps. Although supported by theoretical studies these concerted mechanisms are still under discussion.

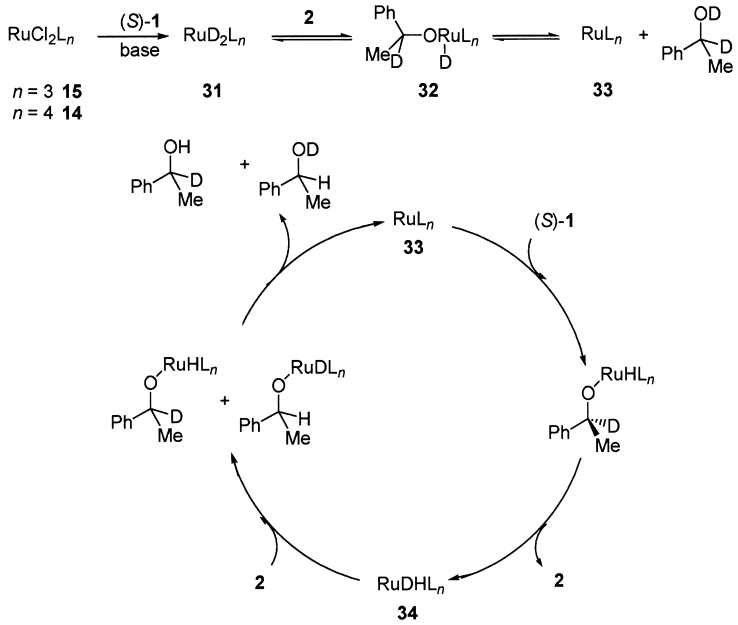
In a two-step mechanism, coordination of the alcohol to the 16-electron catalyst **23b** followed by proton transfer would give the alkoxide intermediate **30**. Subsequent β-elimination would produce the Ru–monohydride species (Scheme 6),



Scheme 6. Proposed pathway involving an alkoxide intermediate for the formation of Ru–monohydride species from **23b** (phenyl groups in the complexes have been omitted for clarity).

and this mechanism has been previously proposed in the transfer hydrogenation with the so-called Shvo catalyst **23**.[11b, 23] This mechanism is supported by the fact that amines, when allowed to react with catalyst **23**, undergo a similar reaction to give amino complexes.[24]

Metal dihydride mechanism: In this mechanism, both O–H and α-C–H hydrogen atoms of the alcohol are transferred to the metal, generating a metal dihydride species (Scheme 1, path IIB). The results shown in Table 2 indicate that the transfer hydrogenation with catalyst precursors **14** and **15** (entries 1 and 2, Table 2) follows this mechanism. Since chlorides are easily replaced by hydrides,[12] the catalyst precursors **14** and **15** are therefore rapidly transformed to ruthenium dihydride species under hydrogen transfer reaction conditions. In fact, it has been demonstrated that $[RuCl_2(PPh_3)_3]$ (**15**) reacts with isopropanol in the presence of base to produce the corresponding dihydride $[RuH_2(PPh_3)_3]$, which was isolated and characterized.[12] With substrate (*S*)-**1** a dideuterated complex **31** would therefore be formed. This species would react with **2** to give the Ru^0 complex **33** via **32** after reductive elimination. Thus both the ruthenium dihydride and Ru^0 species **33** would be key intermediates in the catalytic cycle of the hydrogen transfer reaction (Scheme 7). In the catalytic cycle, species **33** undergoes oxidative addition of (*S*)-**1** followed by β-hydride



Scheme 7. Proposed catalytic cycle for the racemization of (*S*)-**1** with catalyst precursors **14** and **15**.

elimination to produce **2** and mixed hydride–deuteride species $[HRuDL_n]$ (**34**). Species **34** would add to acetophenone to give two different alkoxide complexes and after reductive elimination, species **33** and the racemic alcohol with the deuterium scrambled between the α- and oxygen-position are formed. Theoretically this mechanism would give about 50% deuterium content in the α-position. However, because the deuterium on the oxygen readily undergoes D–H exchange with traces of water (and solvent) the total amount of deuterium (C–D and O–D) in the racemized alcohol will be less than one equivalent. After several catalytic cycles the deuterium content at the α-carbon will therefore be significantly less than 50%.

Conclusion

The mechanistic study carried out in this work provides new insight into the mechanism of catalytic hydrogen transfer reactions. For transition-metal-catalyzed hydrogen transfer from an alcohol to a ketone, two different pathways can be

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distinguished: one that give selective carbon-to-carbon hydrogen transfer and another that leads to nonselective hydrogen transfer involving both oxygen-to-carbon and carbon-to-carbon hydrogen transfer. The results are best explained by a mechanism involving a metal monohydride in the selective hydrogen transfer reactions and a metal dihydride in the nonselective hydrogen transfer reactions.

Experimental Section

All syntheses were performed by using standard Schlenk techniques under argon atmosphere. Solvents were purified by standard procedures. Complex **15** was purchased from Aldrich. Complexes **18** and **19** were obtained from Strem. All the commercially available compounds were used without further purification. The extent of the racemization was monitored by gas chromatography by using a CP-Chirasil-Dex CB chiral column. ^{1}H NMR spectra were recorded on a Varian Gemini 400 MHz spectrometer with [D]chloroform as solvent. Enantiomerically pure (*S*)-α-deutero-α-phenylethanol ((*S*)-**1**)) was obtained by a previously described method.[14] Dimeric Rh^I and Ir^I complexes **3**–**5** and **9**–**11** were prepared and used in situ according to standard procedures.[25] Cationic complexes **6**[26], **7**[26], **12**[26], **13**[26], **16**,[27] and **17**[27] were synthesized following standard procedures. Cationic Ru^{II} complex **20** was prepared from **18** following similar procedure to the syntheses of Rh and Ir cationic complexes.[26] Wilkinson's catalyst **8**[28] and ruthenium complex **23**[8d] were synthesized according to literature procedures. Complexes **14**[29a] **21**,[20] and **22**[29b] were synthesized following the procedure described by Noyori and co-workers. Racemic *N*-tosyl-1,2-diphenylethylenediamine was synthesized by using the combined methods of Corey et al. and Sheldon et al.[30] Samarium complex **25** was synthesized by following the method previously described by Evans et al.[31] Racemic ligand 3-aza-3-benzyl-1,5-dihidroxy-1,5-diphenylpentane was synthesized by following the procedure of Trost et al.[32]

Racemization by metal-catalyzed hydrogen transfer—general procedure: The catalyst precursor (0.01 mmol) was added to a solution of (*S*)-**1** (61.5 mg, 0.5 mmol) and acetophenone (60 mg, 0.5 mmol) in THF (0.75 mL) in a Schlenk tube. The reaction mixture was heated in an oil bath (bath temperature 70 °C). The reaction was analyzed by chromatography by using a chiral column. When complete racemization of (*S*)-**1** had occurred, the reaction was worked up by filtration over a bed of silica and purified by flash chromatography. The racemic alcohol was analyzed by ^{1}H NMR for its deuterium content in the α-position.

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