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The Catalyst Precursor, Catalyst, and Intermediate in the Ru^{II}-Promoted Asymmetric Hydrogen Transfer between Alcohols and Ketones**

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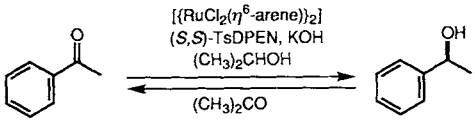
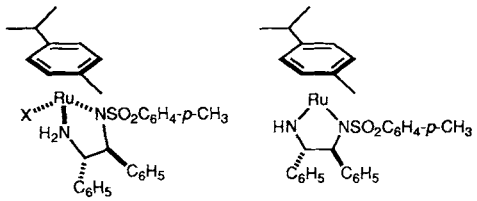
Well-designed chiral Ru^{II}–arene complexes catalyze the asymmetric transfer hydrogenation of ketones or imines with stable organic hydrogen donors such as 2-propanol[1, 2] and formic acid.[3] In these reactions certain derivatives of 1,2-diamines and β-amino alcohols can serve as excellent chiral modifiers and lead to high reactivity and enantioselectivity. For example, when a 0.1 M solution of acetophenone in 2-propanol containing $[\{RuCl_2(\eta^6\text{-arene})\}_2]$, (1*S*,2*S*)-*N*-*p*-toluenesulfonyl-1,2-diphenylethylenediamine ((*S*,*S*)-TsDPEN), and KOH (ketone:Ru:diamine:KOH = 200:1:1:2 molar ratio) was allowed to stand at 28 °C for 10 h, (*S*)-1-phenylethanol was obtained in up to 97% *ee* and in 98% yield [Eq. (a)].[1a] We here disclose the



(a)

molecular structures of a preformed catalyst precursor **1**, the true catalyst **2**, and the reactive intermediate **3** for this asymmetric transfer hydrogenation using 2-propanol. The functions of the added KOH and the NH moiety in the TsDPEN auxiliary



1: X = Cl
3: X = H

2

have also been clarified. Here we describe a very rare catalytic system in asymmetric transformations for which both the true catalyst and the reactive species have been isolated in a pure state.[4] The success can be attributed to the reversible reactions with different but comparable energy profiles.

First, the catalyst precursor **1** was prepared as orange crystals in >90% yield by reacting $[\{RuCl_2(\eta^6\text{-}p\text{-cymene})\}_2]$, (*S*,*S*)-TsDPEN, and KOH (Ru:diamine:KOH = 1:1:1 molar ratio in CH_2Cl_2 at room temperature) or, more effectively, triethylamine (Ru:diamine:NEt_3 = 1:1:2 in 2-propanol at 80 °C). The single-crystal X-ray analysis illustrated in Figure 1 indicates

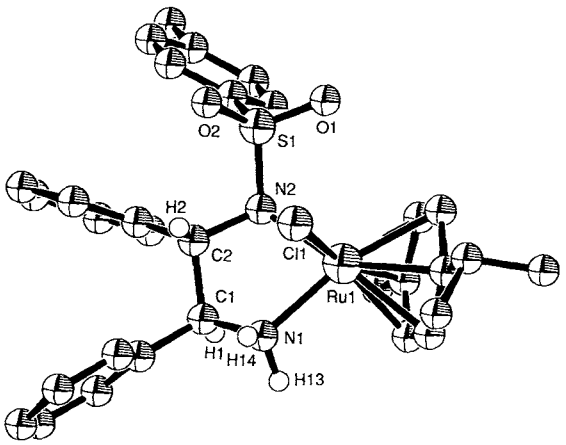


Figure 1. Molecular structure of **1** in the crystal. All hydrogen atoms except for the proton of the amine ligand and those at the carbon atoms in the chelate backbone and one crystal water molecule have been omitted for the sake of clarity. Selected distances [Å] and angles [°]: Ru–Cl 2.435(4), Ru–N1 2.117(9), Ru–N2 2.144(8), RuCl···HN 2.57; N1-Ru-N2 79.4(3), Ru-N1-C1 112.8(7), Ru-N2-C2 111.6(6).

that this 18-electron Ru^{II} complex has a distorted octahedral coordination environment with η^6-arene, amino, sulfonamido, and chloro ligands.[5] The chirality of (*S*,*S*)-TsDPEN forming a δ-configurated five-membered ring determines the (*R*) configuration at the Ru center.[6] Noteworthy is the very short Cl···HN distance of 2.57 Å (expected van der Waals separation, 3.0 Å), which is ascribed to an intramolecular hydrogen bond.[7] The ^{1}H NMR spectrum confirmed that **1** exists as a single diastereomer in $CDCl_3$ solution.

The Ru complex **1**, which catalyzes the asymmetric transfer hydrogenation of acetophenone in 2-propanol containing

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KOH, is merely a catalyst precursor. This complex has acidic NH_2 protons as confirmed by rapid H/D exchange with CH_3OD. Complex **1** undergoes facile elimination of HCl probably by a D_{cb} mechanism[8] on treatment with one equivalent of KOH in a CH_2Cl_2 – water two-phase system at room temperature to afford the true catalyst **2** as deep purple crystals in 87% yield. This complex reverts back to **1** upon reaction with triethylammonium chloride. The X-ray crystallographic analysis (Figure 2) reveals that **2** is a monomeric, formally 16-electron neu-

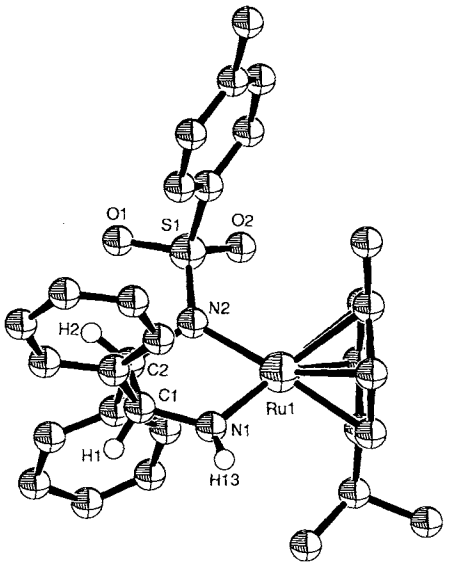
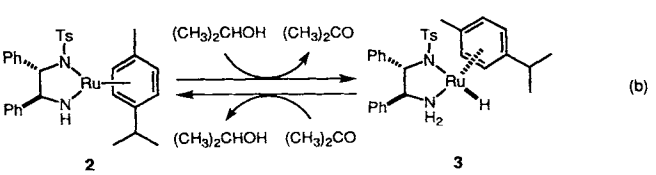


Figure 2. Molecular structure of **2** in the crystal. All hydrogen atoms except for the proton of the amide ligand and those at the carbon atoms in the chelate backbone have been omitted for the sake of clarity. Selected distances [Å] and angles [°]: Ru–N1 1.897(6), Ru–N2 2.065(6), N1–H13 0.88(6); N1-Ru-N2 78.9(2), Ru-N1-C1 121.2(5), Ru-N2-C2 114.9(4).

tral Ru^{II} complex with a square-planar geometry;[5, 9] the metal center is coordinated to two anionic nitrogen atoms and to *p*-cymene, which acts as a bis(three-electron) donor (neutral formalism). The basic skeleton (substituents on the nitrogens and arene neglected) has a mirror plane and the face of the arene ligand is perpendicular to the N1-Ru-N2 plane. Both N1 and N2 have planar geometry. Most notably, the N1–Ru bond (1.897 Å) is shorter than the N–Ru single bond in a Ru^{II}–anilide (2.01–2.16 Å)[10] but longer than the distance in a Ru^{II}–imide complex (1.75 Å) for which an N–Ru triple bond may be assumed.[11] This finding implies significant double bond character for the N1–Ru bond in **2**.[12] The N2–Ru bond in **2** (2.065 Å) is shorter than that in **1** (2.144 Å but substantially longer than the N1–Ru bond in **2** owing to the electronegative tosyl substituent.

Because of the unique nature of the Ru–N1 bond, **2** shows distinct dehydrogenative activity for methanol, ethanol, and 2-propanol. For instance, when the purple complex **2** was treated with 2-propanol at room temperature in the *absence of base*, rapid elimination of acetone took place to produce the yellow ruthenium hydride species **3**, which gives rise to a ^{1}H NMR signal at $\delta = -5.47$ in [D_8]toluene [Eq. (b)]. The kinetically



(b)

controlled reaction was highly stereoselective giving the (*R*)-configurated, octahedral Ru^{II} complex,[6] whereas its diastereomer was formed in <1% yield according to ^{1}H NMR spectroscopy. The major stereoisomer **3** was isolated as the hydrate in 70% yield as yellow needles by recrystallization from wet CH_3OH. When the purple complex **2** was mixed with *tert*-butyl alcohol neither the color nor the ^{1}H NMR spectrum changed. The Ru complex **3** was also obtained by reaction of **2** and molecular hydrogen in toluene at room temperature, but only at 80 atm. The single-crystal X-ray analysis indicates that this ruthenium hydride is structurally similar to the chloride complex **1** except for the orientation of the tosyl substituent (Figure 3).[5] The distorted octahedral complex possesses a δ-configurated, five-membered chelate ring (N1–Ru 2.110 Å,

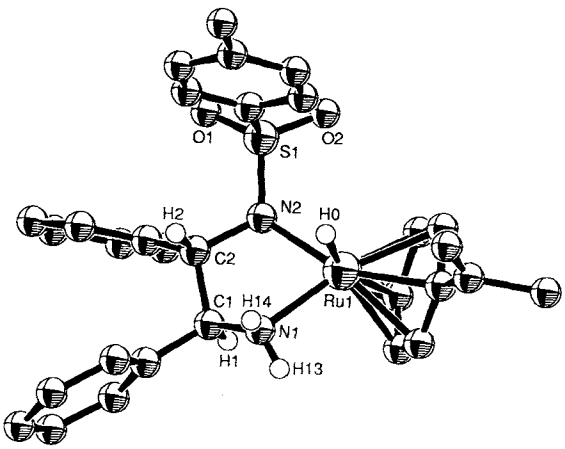


Figure 3. Molecular structure of **3** in the crystal. All hydrogen atoms except for the hydride at ruthenium, the two protons of the amine ligand, and those at the carbon atoms in the chelate backbone, as well as two water molecules in the lattice have been omitted for the sake of clarity. Selected distances [Å] and bond angles [°]: Ru–H0 1.40(1), Ru–N1 2.110(1), Ru–N2 2.139(9), N1–H13 0.90(1), N1–H14 0.7(1), RuH0···H14N1 2.29; N1-Ru-N2 78.3(4), Ru-N1-C1 108.7(7), Ru-N2-C2 113.0(7).

N2–Ru 2.139 Å), an η^6-arene ligand, and a hydrido ligand (Ru–H 1.40 Å). The distance between H0 on Ru and H14 on N1 is short (2.29 Å; van der Waals separation 2.4 Å), indicating a possible hydrogen bonding interaction.[13] One water molecule is hydrogen bonded to H14 on N1, while the second water molecule within the lattice is disordered. Treatment of **3** with a tenfold excess of acetone led instantaneously to the 16-electron species **2** and 2-propanol [Eq. (b)].

The purple complex **2** indeed catalyzes the asymmetric reduction of acetophenone in 2-propanol without KOH to afford (*S*)-1-phenylethanol in up to 95% *ee*. The yellow hydride **3** behaves in the same manner under catalytic conditions. The catalytic activity and stereoselectivity are identical to those observed with the complex formed in situ.[1a] Thus, under the conditions of Equation (a), KOH is necessary only for the generation of the catalyst **2** via the precursor **1**. The isolation of **3** confirms that the Ru-catalyzed transfer hydrogenation takes place by way of a metal hydride rather than the metal alkoxides presumed for the Meerwein–Ponndorf–Verley type reaction.[14] The extent of the enantioselectivity in the acetophenone reduction is independent of the bulkiness or chirality of the hydrogen donors. Methanol, ethanol, 2-propanol, and (*R*,*S*)-, (*R*)-, and (*S*)-2-butanol all gave (*S*)-1-phenylethanol in the same enantiomeric purity, 95 ± 0.5% *ee*, indicating that **3** is the common intermediate. Reduction of acetophenone with $(CH_3)_2CDOH$ (0.996 D at C2) catalyzed by **2** gave (*S*)-$C_6H_5CD(OH)CH_3$ (0.936 D at

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C1) in 95% *ee* as expected. Experiments using mixtures of $(CH_3)_2CHOH$ and $(CH_3)_2CDOH$ revealed a k_H/k_D value of 1.5 ± 0.1 (^1H NMR and GCMS). Because of microscopic reversibility, the (*S,S*)-TsDPEN-based complex **2** dehydrogenates (*S*)-1-phenylethanol in acetone more readily than the (*R*) enantiomer, allowing efficient kinetic resolution of the racemate.[2] Notably, the reductive formation of **3** from **2** is consistently diastereoselective, regardless of the structure of the hydrogen-donating alcohol.

Preliminary kinetic investigations proved the isolated complexes **2** and **3** to be the true catalyst and intermediate, respectively, in the hydrogen transfer reaction following Equation (b). The reaction of $(CD_3)_2CO$ with $(CH_3)_2CHOH$ (0.37 to 1.9 M) and **2** (0.45×10^{-2} to 4.0×10^{-2} M) at 23 °C was monitored by following the disappearance of the methyl resonance of $(CH_3)_2CHOH$ in the ^1H NMR spectra. We found that the rate of acetone reduction is first order in $[(CH_3)_2CHOH]$ and first order in [**2**]. By reversing the deuteration, the acetone dependence could be measured. The reduction of $(CH_3)_2CO$ with $(CD_3)_2CHOH$ catalyzed by **3** (or **2**) was found to be zero order in $[(CH_3)_2CO]$ (saturation kinetics) at high concentration (> 0.4 M), thus, $-d[2\text{-propanol}]/dt = k[\mathbf{2}][2\text{-propanol}]$, where $k = 2.5 \times 10^{-3}\ M^{-1} s^{-1}$, whereas at low concentrations of acetone (0.19 to 0.39 M) the rate is first order with respect to $[(CH_3)_2CO]$. These results demonstrate that the reaction of **2** with 2-propanol is the turnover-limiting step in the steady-state hydrogen transfer [Eq. (b)] and that the reverse reaction of **3** with acetone is more facile.

In summary, the Ru-catalyzed hydrogen transfer between alcohols and ketones occurs reversibly and is promoted by the bifunctional metal/ligand catalysts **2** and **3** possibly via a six-membered cyclic transition state.[1d] The interconversion between these 16- and 18-electron Ru complexes takes place by the action of an alcohol or ketone either directly or via a very short-lived intermediate. No other complexes that limit the rates are involved.

Experimental Section

All operations were conducted under an atmosphere of dry argon and standard Schlenk-type glassware was used.

1: A mixture of $[\{RuCl_2(\eta^6\text{-}p\text{-cymene})\}_2]$ [15] (1.53 g, 2.5 mmol), (*S,S*)-TsDPEN [16] (1.83 g, 5.0 mmol), and triethylamine (1.4 mL, 10 mmol) in 2-propanol was heated at 80 °C for 1 h. The orange solution was concentrated and the resulting solid was collected by filtration. The crude compound was washed with a small amount of water and dried under reduced pressure to give complex **1**. Yield 2.99 g (94%). Recrystallization from 99% methanol afforded orange crystals. Decomp > 100 °C; IR (KBr): $\tilde{\nu}$ [cm^{-1}]: 3272, 3219, 3142 (H–N), 3063, 3030 (H–C_{arom}), 2963, 2874 (H–C_{aliph}); FD-MS: m/z (%) = 636 (1) [M^+], 600 (30) [M^+ – HCl], 308 (15), 260 (40), 134 (15), 106 (100); ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.32, 1.34 (each d, ^3J(H,H) = 7 Hz, 3H; $CH(CH_3)_2$), 2.19 (s, 3H; CH_3 in *p*-cymene), 2.28 (s, 3H; CH_3 in *p*-Ts), 3.07 (m, 1H; $CH(CH_3)_2$), 3.26 (m, 1H; NH*H*), 3.54 (m, 1H; *H*CNH_2), 3.66 (d, ^3J(H,H) = 11 Hz, 1H; *H*CN-*p*-Ts), 5.68, 5.70, 5.72, 5.86 (each d, 1H; CH_{arom} in *p*-cymene), 6.61 (m, 1H; NH*H*), 6.29–7.02 (14H; *p*-$CH_3C_6H_4$–$SO_2NCH(C_6H_5)CH(C_6H_5)NH_2$). Anal. calcd. for $C_{31}H_{35}ClN_2O_2RuS$: C 58.53, H 5.54, N 4.40, Cl 5.57, Ru 15.89; found: C 58.37, H 5.44, N 4.36, Cl 5.75, Ru 15.83.

2: A mixture of $[\{RuCl_2(\eta^6\text{-}p\text{-cymene})\}_2]$ [15] (306.2 mg, 0.5 mmol), (*S,S*)-TsDPEN [16] (366.4 mg, 1.0 mmol), and KOH (400 mg, 7.1 mmol) in CH_2Cl_2 (7 mL) was stirred at room temperature for 5 min. On addition of water (7 mL) to the reaction mixture, the color changed from orange to deep purple. The purple organic layer was washed with water (7 mL), dried over CaH_2, and concentrated to dryness to afford deep purple **2** (522 mg, 87% yield). The same complex was prepared by treatment of **1** with one equivalent of KOH in CH_2Cl_2 at room temperature. Decomp > 80 °C; IR (KBr): $\tilde{\nu}$ [cm^{-1}]: 3289 (H–N), 3070, 3017 (H–C_{arom}), 2968, 2920, 2859 (H–C_{aliph}); FD-MS: m/z (%) = 600 (10) [M^+], 305 (5), 260 (25), 134 (20), 106 (100); ^1H NMR (400 MHz, [D_8]toluene, 25 °C, TMS): δ = 1.20, 1.25 (each d, ^3J(H,H) = 7 Hz, 3H; $CH(CH_3)_2$), 2.05 (s, 3H; CH_3 in *p*-cymene), 2.22 (s, 3H; CH_3 in *p*-Ts), 2.53 (m, 1H; $CH(CH_3)_2$), 4.08 (d, 1H, ^3J(H,H) = 4.4 Hz, *H*CNH), 4.89 (s, 1H; *H*CN-*p*-Ts), 5.11, 5.27, 5.28, 5.39 (each d, ^3J(H,H) = 6 Hz, 1H; CH_{arom} in *p*-cymene), 6.64 (br. d, 1H; NH), 6.87, 7.67 (each d, ^3J(H,H) = 8 Hz, 2H; CH_{arom} in *p*-Ts), 7.2–7.7 (m, 10H; *p*-TsNCH(C_6H_5)CH(C_6H_5)NH). Anal. calcd. for $C_{31}H_{34}N_2O_2RuS$: C 62.09, H 5.71, N 4.67, Ru 16.85; found: C 62.06, H 5.77, N 4.66, Ru 16.47.

3: The purple complex **2** (600 mg, 1.0 mmol) was dissolved in 2-propanol (10 mL), and the resulting red solution was stirred at room temperature for 15 min. The solvent was then removed under reduced pressure at room temperature to give a brownish yellow compound, which was washed with cold pentane and recrystallized from methanol to provide orange needles (420 mg, 70% yield). Under vacuum at room temperature the needles turned brown. The same compound **3** was obtained by stirring a toluene solution of **2** (600 mg, 1.0 mmol) under 80 atm H_2 in an autoclave at room temperature for 18 h. Decomp > 60 °C; IR (KBr): $\tilde{\nu}$ [cm^{-1}]: 3335, 3317, 3228, 3153 (H–N), 3060, 3025 (H–C_{arom}), 2960, 2917, 2867 (H–C_{aliph}), 1911 (broad, H–Ru); ^1H NMR (400 MHz, [D_8]toluene, 25 °C, TMS): δ = –5.47 (s, 1H; RuH), 1.53, 1.59 (each d, ^3J(H,H) = 6 Hz, 3H; $CH(CH_3)_2$), 2.29 (s, 3H; CH_3 in *p*-cymene), 2.45 (s, 3H; CH_3 in *p*-Ts), 2.79 (m, 1H; NH*H*), 2.93 (m, 1H; $CH(CH_3)_2$), 3.80 (d, ^3J(H,H) = 8 Hz, 1H; *H*CN-*p*-Ts), 4.02 (m, 1H; *H*CNH_2), 5.15, 5.19, 5.43, 5.58 (each d, ^3J(H,H) = 6 Hz, 1H; CH_{arom} in *p*-cymene), 5.29 (m, 1H; NH*H*), 6.49, 7.59 (each d, ^3J(H,H) = 8 Hz, 2H; CH_{arom} in Ts), 6.9–7.3 (m, 10H; *p*-TsNCH(C_6H_5)CH(C_6H_5)NH_2). Anal. calcd. for $C_{31}H_{36}N_2O_2RuS$: C 61.88, H 6.02, N 4.66, Ru 16.80; found: C 61.79, H 5.94, N 4.70, Ru 16.56.

Kinetic study: The reaction was initiated by adding 2-propanol to a mixture of acetone and **2** at 23 °C. The total volume was maintained at 0.7 mL. When a small amount of acetone was employed, 2-min sonication was necessary to dissolve **2**. The reaction was monitored at 5-min intervals by measuring the integrals of the methyl proton signals in the ^1H NMR spectrum [δ = 1.06 (2-propanol) and 2.04 (acetone)].

The reaction of $(CD_3)_2CO$ and 2-propanol (0.37–1.9 M) with **2** (2.3×10^{-2} M) was monitored over a period of 60 min with 2-propanol conversion in the range of 11 to 20%. The plot of lg(initial rate) versus lg[2-propanol]$_0$ showed a linear dependence, giving n = 1.2 (assumed to be 1, within experimental error). Thus, $-d[2\text{-propanol}]/dt = k_{1obsd}[2\text{-propanol}]$, where $k_{1obsd} = 5.4 \times 10^{-5}\ s^{-1}$ at 23 °C. The reaction of $(CD_3)_2CO$ and 2-propanol (1.87 M) with **2** (0.45×10^{-2} to 4.0×10^{-2} M) was monitored over a period of 60 min with 2-propanol conversion in the range of 6.7 to 28%. The plot of lg(initial rate) versus lg[**2**]$_0$ gave n = 0.8 (assumed to be 1, within experimental error). Thus, $-d[2\text{-propanol}]/dt = k_{2obsd}[\mathbf{2}]$, where $k_{2obsd} = 4.7 \times 10^{-3}\ s^{-1}$ at 23 °C.

The reaction of acetone (0.19–0.39 M) with **2** (1.3×10^{-2} M) in $(CD_3)_2CHOH$ was monitored over a period of 5 min with 2-propanol conversions of up to 40%. The plot of lg(initial rate) versus lg[acetone]$_0$ gave n = 1.0. Thus, $-d[\text{acetone}]/dt = k_{3obsd}[\text{acetone}]$, where $k_{3obsd} = 1.4 \times 10^{-3}\ s^{-1}$ at 23 °C. The initial rate became zero order for acetone concentration > 0.4 M. Thus, $-d[\text{acetone}]/dt = k_{4obsd}$, where $k_{4obsd} = 7.8 \times 10^{-4}\ M\,s^{-1}$.

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[5] a) Crystal structure analysis of **1**·1 H_2O: $C_{31}H_{37}ClN_2O_3RuS$, M_r = 654.23, orange crystal (0.1 × 0.1 × 0.2 mm), orthorhombic, space group $P2_12_12_1$ (no. 19), a = 14.743(5), b = 24.525(9), c = 8.649(9) Å, V = 3127(3) Å^3, Z = 4, ρ_{calcd} = 1.39 g cm^{-3}, $\mu(Mo_{K\alpha})$ = 6.86 m^{-1}. T = 263 K. 3165 Reflections were independent and unique, and 2278 with $I > 3.00\sigma(I)$ ($2\theta_{max} = 50°$) were used for the structure solution. All hydrogen atoms were calculated from ideal geometries, fixed, and included in the calculation of the structural factor. R = 0.050, Rw = 0.060, $w = (\sigma^2(F) + 0.0025F^2)^{-1}$. Crystal structure analysis of **2**: $C_{31}H_{34}N_2O_2RuS$, M_r = 599.75, deep purple crystal (0.1 × 0.1 × 0.1 mm), orthorhombic, space group $P2_12_12_1$ (no. 19), a = 13.899(5), b = 19.084(4), c = 10.672(3) Å, V = 2830(1) Å^3, Z = 4, ρ_{calcd} = 1.41 g cm^{-3}, $\mu(Mo_{K\alpha})$ = 6.58 cm^{-1}. T = 243 K. 3651 Reflections were independent and unique, and 2310 with $I > 3.00\sigma(I)$ ($2\theta_{max} = 55°$) were used for the structure solution. The hydrogen atom at N1 could be localized and was refined isotropically, and the remaining hydrogen atoms were calculated from ideal geometries, fixed, and included in the calculation of the structural factor. R = 0.036, Rw = 0.033, $w = (\sigma^2(F) + 0.0025F^2)^{-1}$. Crystal structure analysis of **3**·2 H_2O: $C_{31}H_{40}N_2O_4RuS$, M_r = 637.77, yellow crystal (0.1 × 0.1 × 0.1 mm), orthorhombic, space group $P2_12_12_1$ (no. 19), a = 15.075(2), b = 18.821(2), c = 11.717(2) Å, V = 3324.1(8) Å^3, Z = 4, ρ_{calcd} = 1.28 g cm^{-3}, $\mu(Mo_{K\alpha})$ = 5.68 cm^{-1}, T =

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243 K. 4282 Reflections were independent and unique, and 2162 with $I > 3.00\sigma(I)$ ($2\theta_{max} = 55°$) were used for the structure solution. The hydrogen atoms at N1 and at Ru could be localized and were refined isotropically, and the remaining hydrogen atoms were calculated from ideal geometries, fixed, and included in the calculation of the structural factor. $R = 0.050$, $Rw = 0.067$, $w = (\sigma^2(F) + 0.0025F^2)^{-1}$. Rigaku AFC7R diffractometer (graphite monochromator, $Mo_{K\alpha}$). The structures were solved with PATTY and DIRDIF94 [5b]. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-179-149. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: Int. code +(1223)336-033; e-mail: deposit@chemcrys.cam.ac.uk), on quoting the full journal citation; b) P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel, J. M. M. Smits, C. Smykalla, *The DIRDIF Program System, Technical Report of the Crystallographic Laboratory*, University of Nijmegen, The Netherlands, **1994**.

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Kinetic Resolution of Racemic Secondary Alcohols by Ru^{II}-Catalyzed Hydrogen Transfer**

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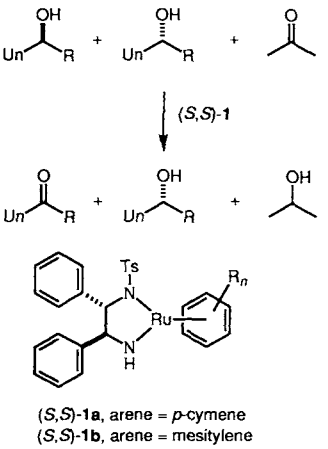
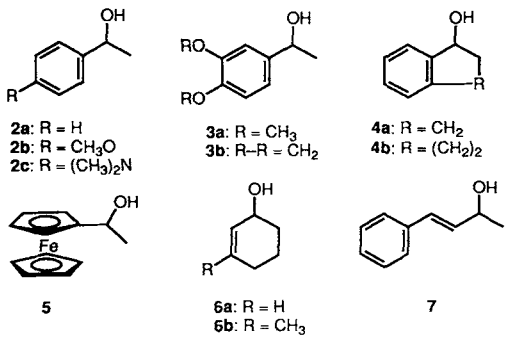
The recent discovery of highly reactive, chiral metal complexes led to rapid advances in catalytic asymmetric transfer hydrogenation.[1–7] Chiral diamine-based Ru^{II} complexes are particularly efficient catalysts for the enantioselective reduction of prochiral ketones under mild conditions using 2-propanol as a hydrogen source.[1, 3, 4] Since this asymmetric reaction is reversible, the efficiency is highly dependent on the redox properties of the alcohols formed[8] in addition to the chiral recognition capabilities of the catalyst. Therefore, high enantioselectivity is not possible in the preparation of alcohols having a high reduction potential such as 2,3-benzo-2-cyclenols and 1-phenylethanols with an electron-donating group on the aromatic ring.[1] Although this is the greatest flaw of this otherwise attractive asymmetric catalysis, the same tendency provides an opportunity for kinetic resolution of such secondary alcohols. However, this is possible only with a suitable catalyst and under suitable reaction conditions. Here, we report on an example of the direct resolution, without derivatization,[9] of simple racemic alcohols by a purely chemical method,[5c, 10–12] which is a useful complement to the asymmetric reduction of achiral ketones.[1–7]

Excellent kinetic differentiation of enantiomeric alcohols is achieved with the novel purple-colored Ru^{II} complexes (*S*,*S*)-**1** (Ts = *p*-toluenesulfonyl, see Scheme 1).[3] The kinetic resolution in acetone occurs with the general sense of Equation (a). Thus, when a 2 M solution of racemic 1-phenylethanol (**2a**) in acetone containing (*S*,*S*)-**1b** (substrate/catalyst molar ratio (S/C) = 500) was left at 28 °C for 30 h, a 97:3 mixture of (*R*)- and (*S*)-**2a** (94% *ee*) was recovered in 51% yield in addition to the acetophenone product in 49% yield. The use of (*S*,*S*)-**1**, which has a unique 16-electron configuration, is a key reason for the success when the reaction is conducted under nearly neutral conditions. Although treatment of the HCl adduct of **1**, which has an 18-electron configuration,[2] with KOH generates the catalytically active species (*S*,*S*)-**1** in situ,[1a, 2, 3] excess base



Scheme 1. Un = unsaturated group.



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