Ruthenium-Catalyzed Transfer Hydrogenation of Imines by Propan-2-ol in Benzene

Joseph S. M. Samec and Jan-E. Bäckvall*[a]

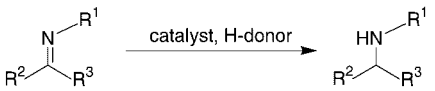
Abstract: Transfer hydrogenation of a variety of different imines to the corresponding amines by propan-2-ol in benzene catalyzed by $[Ru_2(CO)_4(\mu\text{-}H)(C_4Ph_4COHOCC_4Ph_4)]$ (**1**) has been studied. The reaction is highly efficient with turnover frequencies of over 800 per hour, and the product amines were obtained in excellent yields. A remarkable concentration dependence of propan-2-ol was observed when the reaction was run in benzene as cosolvent. An optimum was obtained at 24 equivalents of propan-2-ol to imine, and further increase of the propan-2-ol led to a dramatic decrease in rate. Also the use of polar cosolvents with 24 equivalents of propan-2-ol gave a low rate. It was found that ketimines react faster than aldimines and that electron-donating substituents on the imine increase the rate of the catalytic transfer hydrogenation. Electron-withdrawing substituents decreased the rate. An isomerization was observed with imines having an α-hydrogen at the N-alkyl substituent, which is in accordance with a mechanism involving a ruthenium–amine intermediate. It was demonstrated that the ruthenium–amine complex from α-methylbenzylamine, corresponding to the postulated intermediate, can replace **1** as catalyst in the transfer hydrogenation of imines. A primary deuterium isotope effect of $k_{CH/CD} = 2.7 \pm 0.25$ was observed when 2-deuterio-propan-2-ol was used in place of propan-2-ol in the transfer hydrogenation of *N*-phenyl-(1-phenylethylidene)amine.

Keywords: homogeneous catalysis · hydrogen transfer · imines · reaction mechanisms

Introduction

Transfer hydrogenation of polar functional groups has significantly contributed to the recent growth in organic synthesis.[1] The reaction is recommended for its simplicity since no hydrogen gas is required. When propan-2-ol is used as hydrogen donor, the only side product formed is acetone, which is easily removed by distillation during workup. While the transfer hydrogenation reaction of ketones[1, 2, 3] has been widely explored during the last two decades the corresponding reaction of imines[1, 4, 5] has been less studied (Scheme 1).

The latter transformation is of importance for the synthesis of pharmaceuticals and agrochemicals and therefore further studies on transfer hydrogenation of imines seemed highly desirable. After our group reported the transfer hydrogenation of imines using $[RuCl_2(PPh_3)_3]$, propan-2-ol, and K_2CO_3 as base nearly a decade ago[4c] Noyori et al. reported the first asymmetric transfer hydrogenation of imines by formic acid using a chiral ruthenium catalyst with excellent yields and enantioselectivities.[5a] More recently, Baker and Mao reported transfer hydrogenation of imines by formic acid using chiral Noyori ligands on a rhodium catalyst.[5b] No asymmetric transfer hydrogenation of imines by propan-2-ol has so far been reported.



Scheme 1. The transfer hydrogenation of imines.

Transfer hydrogenation with propan-2-ol is operationally very simple since the latter can be used as solvent or cosolvent. Furthermore, propan-2-ol is a solvent that does not affect the pH and therefore it is preferred over formic acid as hydrogen donor. The lack of efficient procedures for transfer hydrogenation of imines by propan-2-ol motivated further studies of this reaction.

We have recently been involved in the use of catalyst **1** in hydrogen transfer reactions.[6] Catalyst **1** promoted efficient Oppenauer-type oxidation of alcohols[6a,b] and it was also used as an efficient racemization catalyst in enzymatic dynamic kinetic resolution of alcohols.[6c,d] Dimeric catalyst **1** is also known to efficiently disproportionate aldehydes to esters.[7] In solution, catalyst **1** dissociates into species **2** and **3**,[7] where the former can hydrogenate and the latter can dehydrogenate (Scheme 2). Casey et. al[4a] recently studied the stoichiometric hydrogenation of carbonyls and imines by the 18 e^- species **2**,

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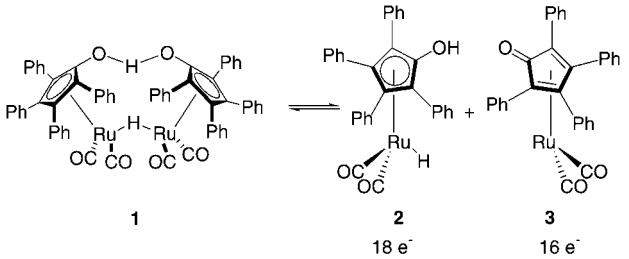
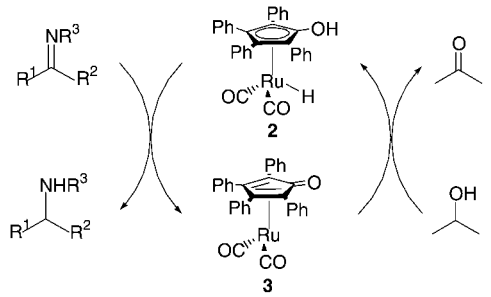


Scheme 2. The dissociation of the dimeric catalyst precursor.

formed from dimeric **1**. From results on kinetic isotope effects for the reaction of benzaldehyde, a concerted mechanism for the addition of the two hydrogens (C–OH and Ru–H; see Scheme 2) of **2** to carbonyls was proposed.

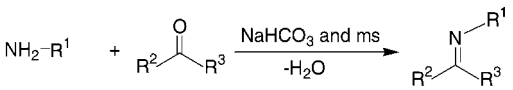
In the present work we have studied the catalytic transfer hydrogenation of imines by employing ruthenium catalyst **1**. Species **2** hydrogenates the imine to the desired amine, and species **3** dehydrogenates the propan-2-ol to acetone. In this process complexes **2** and **3** are interconverted (Scheme 3).[7] A remarkable concentration dependence of propan-2-ol was observed, and a highly efficient transfer hydrogenation was obtained by using 24 equivalents of propan-2-ol (to imine) in benzene. A mechanism involving a ruthenium–amine intermediate is proposed.



Scheme 3.

Results and Discussion

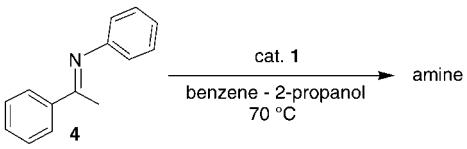
Synthesis of starting materials: The imines were prepared from the corresponding ketone and the appropriate amine. The reaction was carried out in the presence of molecular sieves with $NaHCO_3$ as base [Eq. (1)]. The reactions proceed smoothly and in most cases the imines were isolated in good yields.



(1)

Transfer hydrogenation of imines

Effect of solvent: Transfer hydrogenations are usually carried out in a mixture of triethylamine and formic acid or in propan-2-ol without any additional solvent.[1a, 8] Since Casey et al. observed a dramatic solvent effect in the stoichiometric reaction of **2** with benzaldehyde (toluene 50 times faster than THF)[4a] it was of interest to study the effect of an added cosolvent in the transfer hydrogenation of imines by propan-2-ol. A preliminary screening indicated that benzene was an efficient cosolvent. To find the optimal ratio between propan-2-ol and cosolvent we studied the rate of transfer hydrogenation of **4**, with **1** as catalyst, as a function of the concentration of propan-2-ol in benzene [Eq. (2), Figure 1].



(2)

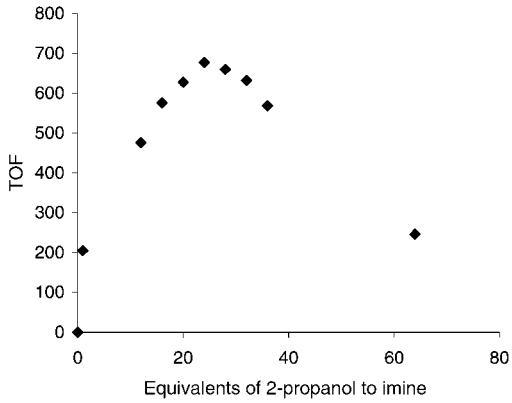


Figure 1. Transfer hydrogenation of **4** according to Equation (2).

Surprisingly, the results show that there is a maximum of the rate, measured as in terms of the initial turnover frequency (TOF), at about 24 equivalents of propan-2-ol (Figure 1), which corresponds to a benzene:propan-2-ol ratio of 1.7:1. The concentration dependence is most likely due to two effects: at low concentrations of propan-2-ol there is a large increase in rate with an increased concentration. This effect levels out at higher concentrations of propan-2-ol and the negative solvent effect by propan-2-ol compared to benzene will dominate, leading to a lower rate.[9]

The effect of propan-2-ol encouraged us to screen different solvents using the optimal concentration of propan-2-ol, that is, 24 equivalents. The initial TOF as well as the conversion to amine after 90 min was measured. Toluene gave almost the same rate as benzene and both of these solvents gave full conversion to amine within 90 min (Table 1, entries 5 and 6). Using more polar systems, such as THF,[4a, 7] *tert*-butanol, or propan-2-ol decreased the TOF and did not give full conversions after 90 min. For *tert*-butyl alcohol and THF this may be explained by a coordination of the solvent to **3**, which has been previously suggested by Shvo and Menashe in hydrogen transfer to aldehydes.[7] However, for propan-2-ol this should not lead to a rate deceleration since propan-2-ol is expected to coordinate to the ruthenium center prior to dehydrogenation.

Casey et al. have previously reported the effect of water using **2** in the transfer hydrogenation of benzaldehyde.[4a] Therefore, we screened the influence of water on the catalytic activity. We observed a rate acceleration upon addition of

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Table 1. The screening of different solvents.[a]

Entry	Solvent	TOF[b]	% Conversion[c]
1	THF	140	72
2	*tert*-butyl alcohol	190	97
3	propan-2-ol	250	97
4	cyclohexane	440	100
5	toluene	650	100
6	benzene	700	100

[a] These reactions were performed by using the catalyst **1** (1 μmol, 0.33 %) stirred for 8 min in the solvents above (0.95 mL) at 70 °C. The imine **4** (0.6 mmol) dissolved in propan-2-ol (0.55 mL, 7.2 mmol, 24 equiv) pre-heated at 73 °C was then added. The reactions were monitored by ^{1}H NMR spectroscopy. [b] The TOF was measured during the first 10 min (mol substrate × conversion after 10 min × mol catalyst^{-1} × time^{-1} (h)). The TOF based on Ru will be half of the values given. [c] Conversion after 90 min.

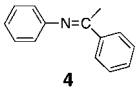
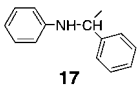
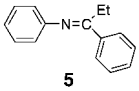
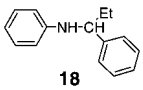
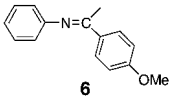
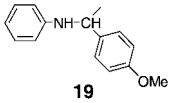
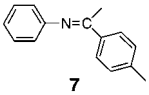
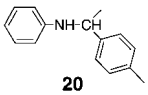
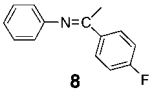
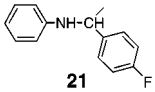
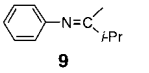
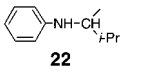
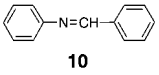
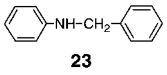
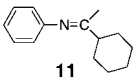
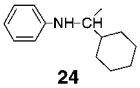
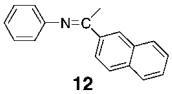
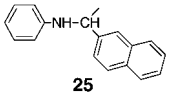
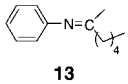
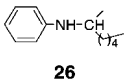
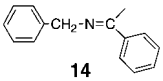
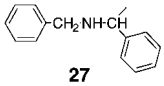
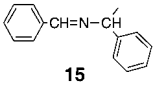
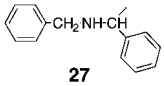
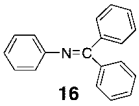
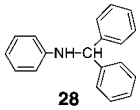
small amounts of water (20 % rate acceleration with 0.8 % of water). Above 1 % of water content the results are inconsistent and difficult to interpret.

Catalytic procedure and substituent effects: The optimized conditions from above with 24 equivalents of wet propan-2-ol in benzene (i.e. propan-2-ol:benzene:H_2O = 1:1.7:0.02) were employed for the transfer hydrogenation of various imines. In most cases the reaction proceeds within a few hours at 70 °C by using 0.3–1 mol % of catalyst, to give excellent yields (93–98 %). For example, imines **4**–**7** (Table 2, entries 1–4) undergo transfer hydrogenation by propan-2-ol within 0.75–1.5 h by employing 0.3 mol % of **1** to give 95–97 % of the corresponding amine.

Some variations of the substrates were made to elucidate the mechanism of the reaction. Our model substrate was *N*-phenyl-(1-phenylethylidene)amine **4**, which is a ketimine. In our report from 1992[4c] one of the conclusions was that aldimines react faster than ketimines, which has been confirmed by Yamagishi et al.[10] This is also the normal order of reactivity for reduction of imines with hydride reagents.[11] However, with catalyst **1** the results indicate the reversed reactivity (Table 2, entries 1 and 7), that is ketimines react faster than aldimines. This order of reactivity is unusual and in contrast to that for hydrogenation of imines.[9a] Placing an ethyl group instead of a methyl group on the imine-carbon atom further increased the rate (Table 2, entry 2). To examine if this was an electronic effect the phenyl ring was substituted with electron-donating and electron-withdrawing groups in the *para* position. Both *p*-methoxy and *p*-methyl groups increased the rate (Table 2, entries 3 and 4, respectively) whereas a *p*-fluoro substituent decreased the rate (Table 2, entry 5). A more quantitative comparison of the electronic properties of the substrates is given in Table 3 in which the rate is measured as the initial TOF after 10 min.

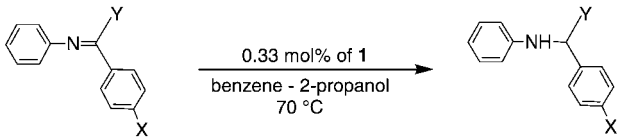
It is expected that an electron-rich imine would coordinate better to ruthenium. The increased reaction rate observed with electron-donating groups on the imine may therefore reflect that coordination of imine to ruthenium comes into the rate expression. This would also account for the increased reactivity of ketimines versus aldimines in which the methyl and even more the ethyl group on the ketimine are better electron donors than the aldimine-hydrogen atom. The faster relative rate for electron-rich imines is also consistent with the concerted mechanism,[4a] in which proton transfer from **2** to the imine is crucial for promoting hydride transfer to ruthenium. Substituting the phenyl group by a naphthyl group (Table 2, entry 9) decreased the reaction rate. This is also consistent with the discussion above in which the naphthyl group is more electron-withdrawing than the phenyl group thus creating an electron-poor imine. Substituting the aniline component with a benzyl group (Table 2 entries 11 and 12)

Table 2. The transfer hydrogenation of different imines to the corresponding amine.

Entry	Imine	Amine	C:S ratio	Time [min][a]	Yield[b]
1	 **4**	 **17**	1:330	90	97
2	 **5**	 **18**	1:330	60	95
3	 **6**	 **19**	1:330	45	97
4	 **7**	 **20**	1:330	45	96
5	 **8**	 **21**	1:100	480	95
6	 **9**	 **22**	1:330	240	94
7	 **10**	 **23**	1:330	300	98
8	 **11**	 **24**	1:200	360	97
9	 **12**	 **25**	1:200	240	98
10	 **13**	 **26**	1:200	360	94
11	 **14**	 **27**	1:200	360	94
12	 **15**	 **27**	1:100	240	93
13	 **16**	 **28**	1:100	240	94[c]

[a] The reactions were carried out using imine (1.0 mmol), benzene (3.15 mL), propan-2-ol (24 mmol, 1.85 mL) and catalyst **1** (0.003–0.01 mmol) at 70 °C. Full conversion was measured by ^{1}H NMR spectroscopy. [b] Yield of isolated product. [c] In this case yield was determined by GC.

Table 3. Influence of electronic properties of the substrate.[a]

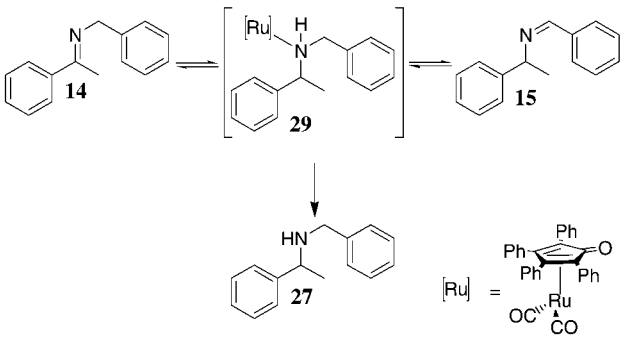


Imine	X	Y	TOF[b]
6	MeO	Me	840
7	Me	Me	800
5	H	Et	730
4	H	Me	700
10	H	H	300
8	F	Me	120[c]

[a] The reactions were run using imine (0.3 mmol), benzene (0.95 mL), and propan-2-ol (7.2 mmol, 0.55 mL) with 0.3 mol% of **1** at 70 °C. [b] TOF was measured after 10 min by ^{1}H NMR spectroscopy and based on catalyst **1**. The TOF based on Ru will be half of the values given. [c] 1 mol% of **1** was used.

decreased the rate. This effect may be due to the observed isomerization between **14** and **15** (vide infra). The catalyst **1** is even effective in catalyzing the transfer hydrogenation of imine **16**. Substituting the aromatic group with an aliphatic group decreased the rate (Table 2, entries 6, 8, and 10). The lower rate for these imines may be due to the fact that the aliphatic groups are less efficient in stabilizing a carbonium ion at the imine-carbon atom.

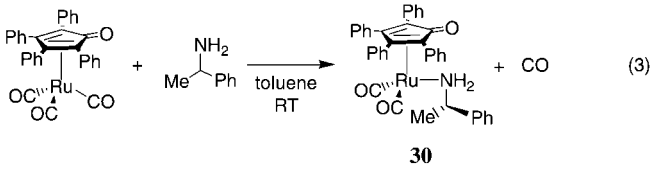
Isomerization: In the transfer hydrogenation of **14** (and **15**) with **1** as catalyst, we observed an isomerization of **14** to **15** (Table 2, entries 11 and 12). The imine **15** appears to be more stable than **14**. When starting from **14** there is a fast conversion to **27** with concomitant isomerization to **15**. The latter imine reacts slower in transfer hydrogenation. When starting from **15** the conversion to **27** is slower and the isomerization to **14** occurs at a much lower rate than that of isomerization of **14** to**15** (Scheme 4). This isomerization is likely to proceed through a ruthenium–amine intermediate.[12]



Scheme 4. The isomerization of imine **14** and **15**.

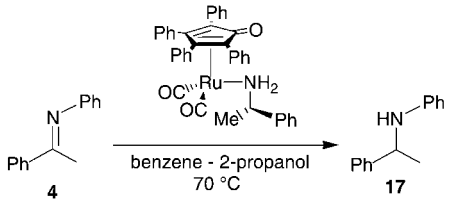
Ruthenium–amine complexes as catalysts: Attempts to isolate a ruthenium–amine intermediate such as **29** from the reaction mixture or to observe it by NMR spectroscopy during the reaction have so far been unsuccessful. Another approach to investigate if the transfer hydrogenation of imines proceeds via a ruthenium–amine intermediate would be to prepare a ruthenium amine complex and test it as catalyst.[13] Attempts to synthesize the ruthenium complex with amines **17** or **27** by employing the procedure described for primary amines[12] were unsuccessful. When raising the temperature to 100 °C using amine **27** we observed the formation of imines **14** and **15**. This suggests that a ruthenium–amine complex is formed but that it easily undergoes β-elimination.

Amine complexes with primary amines, analogous to **29** have been previously reported.[12] To get more information concerning possible intermediate amine complexes we therefore synthesized the primary amine complex **30** from 1-phenylethylamime [Eq. (3)]. It was found that the amine complex



(3)

30 worked as a catalyst for the transfer hydrogenation of **4** with propan-2-ol to give amine **17** (Scheme 5). The reaction rate was lower (40% conversion after 90 min using 1 mol% of **29** compared to 100% conversion after 90 min using 0.3 mol% of **1**), which is likely due to the slower β-elimination form the primary amine.[14]



Scheme 5.

Deuterium isotope effect: The deuterium isotope effect for the catalytic hydrogen transfer reaction of imine **4** was measured by the use of 2-deuteriopropan-2-ol. The initial rate was measured (between 200 and 600 s) for both the deuterated and the nondeuterated propan-2-ol in the transfer hydrogenation of imine **4** to amine **17**. The initial rate using nondeuterated propan-2-ol was $k_{obs} = (6.6 \pm 0.4) \times 10^{-8}\,mol\,s^{-1}$ and for the 2-deuteriopropan-2-ol was $k_{obs} = (2.4 \pm 0.3) \times 10^{-8}\,mol\,s^{-1}$. The deuterium isotope effect of the reaction was therefore $k_{H/D} = (2.7 \pm 0.25)$.

Mechanistic considerations: Two different mechanisms have been proposed for the transfer hydrogenation of aldehydes and ketones with **1** as catalyst.[4a, 7] In the first mechanism proposed by Shvo and Menashe[7] the carbonyl compound is coordinated to ruthenium in **2** followed by migratory insertion. This mechanism was supported by the isolation of the corresponding amine complex.[12] The second mechanism, proposed recently by Casey et al.,[4a] involves a concerted addition of the hydride and the acidic proton from catalyst **2** to the carbonyl compound without prior coordination of the

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latter. This mechanism was supported by the fact that selective deuteration of the hydroxy and the hydride positions of **2** gave individual isotope effects in agreement with the combined isotope effect observed by deuteration of **2** in both positions.

It is expected that an electron-rich imine would coordinate better to ruthenium. The increased reaction rate observed with electron-rich imines is consistent with a coordination of the imine to ruthenium. In the concerted mechanism proposed by Casey et al.[4a] the protonation would be expected to be faster with an electron-rich imine. However, the hydride addition should be slower with an electron-rich imine and therefore the effect is expected to cancel to some extent in the concerted mechanism.

In the transfer hydrogenation of **14** (and **15**) with **1** as catalyst, we observed an isomerization between **14** and **15** (Table 2, entries 11 and 12). This shows that the transfer hydrogenation is reversible, that is the catalyst **1** can β-eliminate a ruthenium–amine intermediate leading to the formation of the imine. This resembles the mechanism proposed for transfer hydrogenation of carbonyls[1, 15] involving coordination of the substrate to the catalyst and migratory insertion. Isomerization between **14** and **15** has also been observed by Brune et al.[4e] with the Wilkinson catalyst and more recently by Yamagishi et al.[4b] with the active catalyst $[RuH_2(PPh_3)_4]$.[16] The transfer hydrogenation of imine **4** using ruthenium amine complex **30** instead of **1** as catalyst (Scheme 5) also supports that the reaction proceeds via a ruthenium amine intermediate.

Conclusion

The transfer hydrogenation of imines using catalyst **1** and propan-2-ol shows an interesting solvent effect, where polar solvents decrease the rate. Less polar solvents with 24 equivalents of propan-2-ol to imine showed a higher rate and the best solvent system (of those studied) was benzene (benzene/propan-2-ol = 1.7:1). The substrate itself had a significant influence on the process. Ketimines react faster than aldimines. Electron-donating groups increase the rate while electron-withdrawing groups decrease the rate. An isomerization was observed between **14** and **15**, suggesting that the process is reversible proceeding through a ruthenium–amine intermediate. Involvement of a ruthenium–amine intermediate is supported by the fact that the isolated ruthenium–amine complex **30** acts as a catalyst in transfer hydrogenation of imines.

Experimental Section

General methods: ^{1}H (400 or 300 MHz) and ^{13}C (100 or 75 MHz) spectra were recorded on a Varian Mercury spectrometer. Chemical shifts (δ) are reported in ppm, using residual solvent as internal standard, and coupling constants (J) are given in Hz. IR spectra were obtained by using a Perkin-Elmer 1600 FT-IR instrument, and the samples were examined as $CDCl_3$ solutions on NaBr plates. Only the strongest/structurally most important peaks (cm^{-1}) are listed. Elemental analyses were performed by Analytische Laboratorien, Lindlar, Germany. Merck silica gel 60 (240–400 mesh) was used for flash chromatography. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. All reactions were performed under a dry argon atmosphere in oven-dried (140 °C) glassware. Distillations were conducted in a Büchi Glass oven B-580.

$[Ru_2(CO)_4(\mu\text{-}H)(C_4Ph_4COHOCC_4Ph_4)]$ (1): The title compound was synthesized according to the literature.[17]

General procedure for the synthesis of imines: *N*-phenyl-(1-phenylethylidene)amine (4): In a typical experiment $NaHCO_3$ (4.2 g, 50 mmol), aniline (0.91 mL, 10 mmol), acetophenone (1.17 mL, 10 mmol), activated molecular sieves (7 g; 4 Å), and benzene (4 mL) were added to a Schlenk-tube and the mixture was exposed to an argon atmosphere and heated to reflux overnight. The reaction mixture was filtered through Celite, the Celite washed with CH_2Cl_2, the filtrate was collected, and the solvents were evaporated in vacuo. The starting material was removed by distillation (120 °C, 1 mbar) and the product was subsequently distilled (160 °C, 1 mbar). Yield (1.52 g, 78 %) of yellow crystals. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.95–8.00 (m, 2H), 7.41–7.49 (m, 3H), 7.32–7.39 (m, 2H), 7.06–7.12 (m, 1H), 6.77–6.83 (m, 2H), 2.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 165.6, 151.9, 139.7 130.8, 129.2, 128.6, 127.4, 123.4, 119.6, 17.6; IR ($CDCl_3$): $\tilde{\nu}$ = 3058, 3027,1638, 1593, 1482, 1447, 1288, 1214 cm^{-1}; elemental analysis calcd (%) for $C_{14}H_{13}N$ (195.3): C 86.12, H 6.71, N 7.17; found: C 85.96, H 6.63, N 7.30.

***N*-Phenyl-(1-phenylpropylidene)amine (5)**: Prepared according to the general procedure. Yield (1.59 g, 76 %) of yellow crystals as a 10:1 mixture of geometric isomers. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): major isomer: δ = 7.91–7.95 (m, 2H), 7.43–7.48 (m, 3H), 7.31–7.37 (m, 2H), 7.04–7.11 (m, 1H), 6.77–6.81 (m, 2H), 2.66 (q, J = 7.7 Hz, 2H), 1.08 (t, J = 7.7 Hz, 3H); minor isomer: δ = 2.80 (q, J = 7.4 Hz, 2H), 1.23 (t, J = 7.4 Hz, 3H), aromatic resonances are obscured by the major isomer; ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 170.9, 151.8, 138.2, 130.5, 129.1, 128.7, 127.8, 123.2, 119.3, 23.7, 13.1. According to the ^{1}H NMR spectrum there was 4 % of the corresponding enamine in the product mixture. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.34 (s, 1H), 5.59 (q, J = 7.0 Hz, 1H), 1.79 (d, J = 7.0 Hz, 3H), aromatic resonances are obscured by the major isomer; IR ($CDCl_3$): $\tilde{\nu}$ = 3058, 3027, 2977, 1633, 1593, 1485, 1210 cm^{-1}; elemental analysis calcd (%) for $C_{15}H_{15}N$ (209.3): C 85.67, H 7.19, N 7.14; found: C 85.83, H 7.26, N 6.56.

***N*-Phenyl-[1-(4-methoxyphenyl)ethylidene]amine (6)**: Prepared according to the general procedure. Yield (1.8 g, 79 %) of white crystals. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.95 (d, J = 9.0 Hz, 2H), 7.31–7.37 (m, 2H), 7.04–7.09 (m, 1H), 6.94 (d, J = 9.0 Hz, 2H), 6.77–6.80 (m, 2H); 3.87 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 164.7, 161.8, 152.1, 132.5, 129.1, 129.1, 123.2, 119.8, 113.8, 55.6, 17.4; IR ($CDCl_3$): $\tilde{\nu}$ = 3058, 2971, 1636, 1604 1364 cm^{-1}; elemental analysis calcd (%) for $C_{15}H_{15}NO$ (225.1): C 79.97, H 6.71, N 6.22; found: C 79.81. H 6.95, N 6.40.

***N*-Phenyl-[1-(4-methylphenyl)ethylidene]amine (7)**: Prepared according to the general procedure. Yield (1.1 g, 35 %) of yellow crystals. Spectral data were in accordance with those previously reported.[18]

***N*-Phenyl-[1-(4-fluorophenyl)ethylidene]amine (8)**: Prepared according to the general procedure. Yield (1.61 g, 76 %) of white-yellow crystals. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.96–8.00 (m, 2H), 7.33–7.37 (m, 2H), 7.07–7.14 (m, 3H), 6.78–6.80 (m, 2H), 2.22 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 164.5 (d, $J_{C,F}$ = 251 Hz), 164.4, 151.7 135.9, 129.5 (d, $J_{C,F}$ = 8.6 Hz), 129.2, 123.6, 119.6, 115.5 (d, $J_{C,F}$ = 21.5 Hz), 17.5; IR ($CDCl_3$): $\tilde{\nu}$ = 3065, 3049, 1636, 1591, 1507, 1486, 1221, 1164 cm^{-1}.

***N*-Phenyl-(1,2-dimethylpropylidene)amine (9)**: Prepared according to the general procedure. Yield (0.63 g, 39 %) of a brown oil as a 7:1: mixture of geometric isomers. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): major isomer: δ = 7.25–7.30 (m, 2H), 7.00–7.04 (m, 1H), 6.66–6.68 (m, 2H), 2.62 (heptet, J = 7.0, 1H), 1.73 (s, 3H), 1.20 (d, J = 7.0 Hz, 6H); minor isomer: δ = 2.69–2.76 (m, 1H), 2.07 (s, 3H), 1.03 (d, J = 7.0 Hz, 6H), aromatic resonances are obscured by those of the major isomer. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): major isomer: δ = 176.3, 152.0, 129.0, 123.0, 119.5, 39.4, 20.1, 17.2; minor isomer: δ = 129.0, 122.9, 119.4, 31.9, 20.3; IR ($CDCl_3$): $\tilde{\nu}$ = 3060, 2966, 1661, 1594, 1484 cm^{-1}.

***N*-Phenyl-(1-phenylmethylidene)amine (10)**: Prepared according to the general procedure. Yield (3.6 g, 99 %) of white crystals. Spectral data were in accordance with those previously reported.[19]

***N*-Phenyl-[1-(cyclohexyl)ethylidene]amine (11)**: Prepared according to the general procedure. Yield (3.1 g, 77%) of a yellow oil as an 11:1 mixture of geometric isomers. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): major isomer: $\delta = 7.25-7.30$ (m, 2H), 6.99–7.04 (m, 1H), 6.65–6.69 (m, 2H), 1.86–1.98 (m, 4H), 1.73 (s, 3H), 1.33–1.72 (m, 7H); minor isomer: $\delta =$ 2.24–2.29 (m, 4H), 2.09 (s, 3H), All other resonances are obscured by those of the major isomer. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta =$ 175.7, 152.0, 129.0, 122.9, 119.5, 49.6, 30.4, 26.3, 26.3, 17.8; IR ($CDCl_3$): $\tilde{\nu} =$ 3019, 2929, 2952, 1659, 1595, 1484, 1448, 1166 cm^{-1}.

***N*-Phenyl-[1-(2-naphthyl)ethylidene]amine (12)**: Prepared according to the general procedure. Yield (2.0 g, 80%) of yellow crystals. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 8.35$ (s, 1H), 8.23 (m, 1H), 7.86–7.96 (m, 3H), 7.50–7.58 (m, 2H), 7.35–7.41 (m, 2H), 7.11 (m, 1H), 6.85 (m, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 165.5$, 152.0, 137.1, 134.6, 133.1, 129.2, 129.1, 128.2, 127.9, 127.8, 127.4, 126.6, 124.4, 123.5, 119.6, 17.6; IR ($CDCl_3$): $\tilde{\nu} = 3430$, 1626, 1483, 1446, 1369 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{15}N$ (245.3): C 88.13, H 6.61, N 5.71; found: C 87.96, H 6.43 N 5.90.

***N*-Phenyl-(1-methylhexylidene)amine (13)**: Prepared according to the general procedure. Yield (1.55 g, 80%) of a yellow oil as a 3:1: mixture of geometric isomers. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): major isomer: $\delta = 7.25-7.30$ (m, 2H), 7.00–7.04 (m, 1H), 6.67–6.70 (m, 2H), 2.38–2.42 (m, 2H), 1.77 (s, 3H), 1.66–1.69 (m, 2H), 1.35–1.40 (m, 4H) 0.91–0.94 (m, 3H); minor isomer: 2.15 (s, 3H), 2.09–2.13 (m, 2H), 1.44–1.51 (m, 2H), 1.14–1.24 (m, 4H), 0.83 (t, $J = 7.0$, 3H), aromatic resonances are obscured by those of the major isomer. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): major isomer: $\delta = 172.4$, 151.8, 129.5, 123.1, 119.7, 41.9, 31.8, 26.3, 22.7, 19.6, 14.2; minor isomer: 129.0, 123.0, 115.3, 34.2, 31.7, 26.8, 26.1, 22.4, 14.0; IR ($CDCl_3$): $\tilde{\nu} = 3310$, 2955, 2929, 1662, 1595, 1484, 1365, 1242 cm^{-1}.

***N*-benzyl-(1-phenylethylidene)amine (14)**: Prepared according to the general procedure. Yield (2.5 g, 60%) of white crystals as a 14:1: mixture of geometric isomers. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): major isomer: $\delta = 7.88-7.90$ (m, 2H), 7.27–7.46 (m, 9H), 4.46 (s, 2H), 2.35 (s, 3H); minor isomer: $\delta = 4.44$ (s, 2H), 2.40 (s, 3H), aromatic resonances are obscured by those of the major isomer. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 166.2$, 141.3, 140.8, 129.8, 128.6, 128.5, 127.9, 127.0, 126.8, 55.9, 16.1; IR ($CDCl_3$): $\tilde{\nu} = 3084$, 3026, 1633, 1494, 1446, 1280 cm^{-1}.

***N*-(1-phenylethyl)benzylidenamine (15)**: Prepared according to the general procedure. Yield (3.1 g, 98.7%) of colorless oil. Spectral data were in accordance with those previously reported.[20]

***N*-phenyl-(diphenylmethylidene)amine (16)**: Prepared according to the general procedure. Yield (3.0 g, 58%) of yellow crystals. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.73-7.77$ (m, 2H), 7.37–7.50 (m, 3H), 7.24–7.27 (m, 3H), 7.10–7.17 (m, 4H), 6.89–6.94 (m, 1H), 6.70–6.74 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 130.9$, 129.7, 129.5, 128.7, 128.6, 128.3, 128.0, 123.3, 121.1; IR ($CDCl_3$): $\tilde{\nu} = 3058$, 3027, 1638, 1593, 1482, 1447, 1289, 1214 cm^{-1}; elemental analysis calcd (%) for $C_{19}H_{15}N$ (257.3): C 88.68, H 5.88, N 5.44; found: C 88.80, H 5.89, N 5.34.

Screening the influence of propan-2-ol: In these reactions imine **4** (58.6 mg, 0.3 mmol), catalyst (0.98 mg, 0.9 μmol, 0.33%), and benzene were added to a reaction flask. The reaction flask was heated at 70 °C for 5 min. The equivalents of propan-2-ol were varied (1–64 equivalents), preheated, and added to the reaction flask. The total volume was held constant at 1.5 mL. The reactions were analyzed by ^{1}H NMR spectroscopy after 10 min. TOF was measured after 10 min (mol substrate*conversion after 10 min*mol catalyst^{-1}*time^{-1} (h)).

Screening solvents: The catalyst (1 mg, 0.9 μmol, 0.33%) was dissolved in the solvents (0.95 mL) reported in Table 1 and stirred for 8 min at 70 °C. A solution of imine **4** (58.6 mg, 0.3 mmol) dissolved in propan-2-ol (0.55 mL, 7.2 mmol) heated at 73 °C for 5 min was added to the catalyst dissolved in the solvent. The reaction was monitored by ^{1}H NMR spectroscopy.

Transfer hydrogenation of imines: *N*-phenyl-1-phenylethylamine (17): In a typical experiment the imine **4** (0.195 g, 1.0 mmol) catalyst **1** (3.26 mg, 3.0 μmol), benzene (3.15 mL), and propan-2-ol (1.84 mL, 24.0 mmol) were added to a 10 mL round-bottomed flask. After 90 min the solvents were evaporated in vacuo. The product was distilled (220 °C, 1 mbar) to afford amine **17** (191 mg; 97%). Spectral data were in accordance with those previously reported.[21]

***N*-phenyl-1-phenylpropylamine (18)**: The general procedure was followed by using imine **5** (0.209 g, 1.0 mmol) and catalyst **1** (3.26 mg, 3.0 μmol). The product was distilled (220° C, 1 mbar) to afford 0.2 g (97%) of amine **18**. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.30-7.37$ (m, 4H), 7.21–7.25 (m, 1H), 7.07–7.11 (m, 2H), 6.62–6.66 (m, 1H), 6.51–6.54 (m, 2H), 4.24 (t, $J = 6.8$ Hz, 1H), 4.07 (bs, 1H), 1.85 (m, 2H), 0.97 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 147.7$, 144.1, 129.2, 128.7, 127.0, 126.7, 117.3, 113.4, 59.9, 31.8, 11.0; IR ($CDCl_3$): $\tilde{\nu} = 3412$, 3052, 2965, 1603, 1505, 1317 cm^{-1}; elemental analysis calcd (%) for $C_{15}H_{17}N$ (211.3): C 85.26, H 8.11, N 6.63; found C 85.12, H 7.99, N 6.48.

***N*-phenyl-1-(4-methoxyphenyl)ethylamine (19)**: The general procedure was followed by using imine **6** (0.222 g, 1.0 mmol) and catalyst **1** (3.26 mg, 3.0 μmol). The product was purified by distillation (250° C, 1 mbar) to afford amine **19** (0.22 g; 98%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 77.27-7.29$ (m, 2H), 7.07–7.11 (m, 2H), 6.84–6.87 (m, 2H), 6.62–6.66 (m, 1H), 6.50–6.53 (m, 2H), 4.45 (q, $J = 6$ Hz, 1H), 3.98 (bs, 1H), 3.78 (s, 3H), 1.49 (d, $J = 6$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta =$ 158.7, 147.5, 137.4, 129.3, 127.1, 117.3, 114.2, 113.5, 55.4, 53.0, 25.2; IR ($CDCl_3$): $\tilde{\nu} = 3407$, 3051, 2963, 1603, 1509, 1244 cm^{-1}.

***N*-phenyl-1-(4-methylphenyl)ethylamine (20)**: The general procedure was followed by using imine **7** (0.209 g, 1.0 mmol) and catalyst **1** (3.26 mg, 3.0 μmol). The product was purified by distillation (220 °C, 1 mbar) to afford amine **20** (0.20 g (96%)). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.24-7.27$ (m, 2H), 7.07–7.13 (m, 4H), 6.61–6.66 (m, 1H), 6.50–6.53 (m, 2H), 4.46 (q, $J = 6.6$ Hz, 1H), 3.99 (bs, 1H), 2.32 (s, 3H), 1.50 (d, $J =$ 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 147.6$, 142.4, 136.6, 129.5, 129.3, 125.9, 117.3, 113.5, 53.3, 25.2, 21.2; IR ($CDCl_3$): $\tilde{\nu} = 3410$, 3052, 2967, 1603, 1504, 1318 cm^{-1}; elemental analysis calcd (%) for $C_{15}H_{17}N$ (211.3): C 85.26, H 8.11, N 6.63; found: C 85.11, H 8.09, N 6.67.

***N*-phenyl-1-(4-fluorophenyl)ethylamine (21)**: The general procedure was followed by using imine **8** (0.213 g, 1.0 mmol) and catalyst **1** (10.85 mg, 10.0 μmol). The product was purified by distillation (220 °C, 1 mbar) to afford amine **20** (0.202 g; 95%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.32-7.37$ (m, 2H), 7.08–7.14 (m, 2H), 6.98–7.09 (m, 2H), 6.65–6.70 (m, 1H), 6.48–6.53 (m, 2H), 4.48 (q, $J = 6.6$ Hz, 1H), 4.01 (bs, 1H), 1.51 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 162.0$ (d, $J_{C,F} = 244$), 147.3, 141.1, 129.4, 127.5 (d, $J_{C,F} = 7.6$ Hz), 117.7, 115.65 (d, $J_{C,F} =$ 21.4 Hz), 113.6, 53.1, 25.41; IR ($CDCl_3$): $\tilde{\nu} = 3410$, 3051, 2968, 1603, 1507, 1318, 1220 cm^{-1}.

***N*-phenyl-(3-methyl-2-butyl)amine (22)**: The general procedure was followed by using imine **9** (0.156 g, 0.97 mmol) and catalyst **1** (3.26 mg, 3.0 μmol). The product was purified by distillation (200 °C, 1 mbar) to afford amine **22** (0.147 g; 90%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.15-7.19$ (m, 2H), 6.58–6.68 (m, 3H) 3.48 (bs, 1H), 3.36 (m, 1H), 1.85 (m, 1H), 1.11 (d, $J = 7.3$ Hz, 3H), 0.98 (d, $J = 7.1$ Hz, 3H), 0.92 (d, $J =$ 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 148.0$, 129.4, 116.8, 113.2, 53.6, 32.4, 19.4, 17.7, 16.8; IR ($CDCl_3$): $\tilde{\nu} = 3407$, 3052, 2961, 1602, 1505, 1320 cm^{-1}; elemental analysis calcd (%) for $C_{11}H_{17}N$ (163.2): C 80.93, H 10.50. N 8.58; found: C 80.96, H 10.42, N 8.75.

***N*-(phenyl)benzylamine (23)**: The general procedure was followed by using imine **10** (0.181 g, 1.0 mmol) and catalyst **1** (3.26 mg, 3 μmol). The product was purified by distillation (220 °C, 1 mbar) to afford amine **23** (0.198 g; 94%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.28-7.42$ (m, 5H), 7.15–7.23 (m, 2H), 6.70–6.76 (m, 1H), 6.63–6.68 (m, 2H), 4.35 (s, 2H), 4.03 (bs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 148.3$, 139.6, 129.4, 128.8, 127.7, 127.4, 117.8, 113.0, 48.1; IR ($CDCl_3$): $\tilde{\nu} = 3419$, 3052, 3035, 1602, 1506, 1324 cm^{-1}; elemental analysis calcd (%) for $C_{13}H_{13}N$ (183.3): C 85.21, H 7.15, N 7.64; found: C 85.09, H 6.96, N 7.63.

***N*-phenyl-1-cyclohexylethylamine (24)**: The general procedure was followed by using imine **11** (0.201 g, 0.96 mmol) and catalyst **1** (5.5 mg, 5 μmol). The product was purified by distillation (220 °C, 1 mbar) to afford amine **24** (0.190 g; 93%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta =$ 7.13–7.17 (m, 2H), 6.62–6.66 (m, 1H), 6.56–6.58 (m, 2H), 3.48 (bs, 1H), 4.03 (quintet, $J = 6.3$ Hz, 1H), 1.66–1.82 (m, 5H), 1.44–1.47 (m, 1H), 1.02–1.27 (m, 5H), 1.11 (d, $J = 6.3$ Hz, 3H), ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 148.1$, 129.4, 116.7, 113.1, 53.1, 43.2, 30.0, 28.6, 26.8, 26.7, 26.5, 17.6; IR ($CDCl_3$): $\tilde{\nu} = 3407$, 3051, 2924, 2851, 1601, 1506, 1319 cm^{-1}.

***N*-phenyl-1-(2-naphtyl)ethylamine (25)**: The general procedure was followed by using imine **12** (0.24 g, 0.98 mmol) and catalyst **1** (5.5 mg, 5 μmol). The product was purified by distillation (250 °C, 1 mbar) to afford amine **25**

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(0.231 g; 98%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.82-7.86$ (m, 4H), 7.46–7.55 (m, 3H), 7.10–7.14 (m, 2H), 6.58–6.70 (m, 3H), 4.68 (q, $J = 6.6$ Hz, 1H), 4.16 (bs, 1H), 1.62 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 147.5$, 142.9, 133.8, 132.9, 129.3, 128.6, 128.0, 127.8, 126.2, 125.7, 124.6, 124.4, 117.5, 113.6, 53.9, 25.2; IR ($CDCl_3$): $\tilde{\nu} = 3412$, 3052, 2967, 1602, 1505, 1319 cm^{-1}.

***N*-phenyl-1-methylhexylamine (26)**: The general procedure was followed by using imine **13** (0.189 g, 1.0 mmol) and catalyst **1** (5.5 mg, 5.0 μmol). The product was purified by distillation (182 °C, 1 mbar) to afford amine **26** (0.180 g; 94%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.13-7.18$ (m, 2H), 6.64–6.68 (m, 1H), 6.56–6.59 (m, 2H), 3.45 (m, 2H), 1.26–1.58 (m, 9H), 1.17 (d, $J = 6.2$ Hz, 3H),), 0.89 (t, $J = 7.1$ Hz, 3H), ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 147.9$, 129.4, 116.9, 113.2, 48.6, 37.4, 32.1, 26.0, 22.8, 21.0, 14.2; IR ($CDCl_3$): $\tilde{\nu} = 3403$, 3052, 2958, 2929, 1602, 1505, 1319 cm^{-1}; elemental analysis calcd (%) for $C_{13}H_{21}N$ (191.3): C 81.61, H 11.06, N 7.32; found: C 81.49, H 11.15, N 7.36.

***N*-benzyl-1-phenylethylamine (27)**: The general procedure was followed by using imine **14** (0.209 g, 1.0 mmol) and catalyst **1** (5.5 mg, 5 μmol). The product was purified by distillation (250 °C, 1 mbar) to afford amine **27** (0.198 g; 94%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.24-7.38$ (m, 10H), 3.82 (q, $J = 6.6$ Hz, 1H), 3.67, 3.60 (AB, $J = 13.2$ Hz, 2H), 1.57 (bs, 1H), 1.37 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 145.8$, 140.9, 128.7, 128.6, 128.4, 127.2, 127.1, 126.9, 57.7, 51.9, 24.7; IR ($CDCl_3$): $\tilde{\nu} = 3325$, 3025, 2962, 1602, 1584, 1505, 1493, 1452, 1304 cm^{-1}; elemental analysis calcd (%) for $C_{15}H_{17}N$ (211.3): C 85.26, H 8.11, N 6.63; found: C 85.09, H 8.20, N 6.63.

***N*-benzyl-1-phenylethylamine (27)**: The general procedure was followed by using imine **15** (0.209 g, 1.0 mmol) and catalyst **1** (10.85 mg, 10 μmol). The product was purified by distillation (250 °C, 1 mbar) to afford amine **27** (0.198 g; 94%). See above for spectral data.

***N*-phenyl-1-benzhydrylamine (28)**: The imine **16** (77.2 mg, 0.3 mmol), catalyst **1** (3.26 mg, 3 μmol), propan-2-ol (0.55 mL, 7.2 mmol), and benzene (0.95 mL) were stirred at 70 °C. The reaction was monitored by GC, and spectral data for NMR spectroscopy were in accordance with those previously reported.[22]

Dicarbonyl(tetraphenylcyclopentadienone)(phenylethylamine)ruthenium (30): The complex was synthesized according to a literature procedure.[13]

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[1] a) S. Gladiali, G. Mestroni in *Transition Metal Organic Synthesis*, *Vol. 2* (Eds.: M. Beller, C. Bolm,) Wiley-VCH Weinheim, **1998**, p. 97; b) J.-E. Bäckvall, R. L. Chowdhury, U. Karlsson, G.-Z. Wang in *Perspectives in Coordination Chemistry* (Eds.: A. F. Williams, C. Floriani, A. E. Merbach), Verlag Helvetica Chimica Acta, Basel, **1992**, p. 463; c) M. J. Palmer, M. Wills, *Tetrahedron: Asymmetry* **1999**, *10*, 2045.

[2] a) Y. R. Santosh Laxmi, J.-E. Bäckvall, *Chem. Commun.* **2000**, 611; b) A. Aranyos, G. Csjernyik, K. Szabo, J.-E. Bäckvall, *Chem. Commun.* **1999**, 4, 351; c) G.-Z. Wang, J.-E. Bäckvall, *J. Chem. Soc. Chem. Commun.* **1992**, 337; d) R. L. Chowdhury, J.-E. Bäckvall, *J. Chem. Soc. Chem. Commun*. **1991**, 1063; e) D. E. Linn, J. Halpern, *J. Organomet. Chem.* **1987**, *330*, 155; f) D. E. Linn, J. Halpern, *J. Am. Chem. Soc*. **1987**, *109*, 2969; g) W. A. Fordyce, R. Wilczynski, J. Halpern, *J. Organomet. Chem.* **1985**, *296*, 115; h) T. A. Smith, P. M. Maitlis, J. Imai, *J. Organomet. Chem.* **1985**, *289*, 385; i) T. A. Smith, P. M. Maitlis, *J. Organomet. Chem.* **1984**, 269; j) H. T. Nishiguchi, K. Fukuzumi, *J. Org. Chem.* **1976**, *41*, 665; k) Y. Sassons, J. Blum, *J. Org. Chem.* **1975**, *40*, 887; l) Y. Sassons, G. L. Rempel, *Tetrahedron lett.* **1974**, 4133.

[3] a) D. A. Alonso, P. Brandt, S. J. M. Nordin, P. G. Andersson, *J. Am. Chem. Soc.* **1999**, *121,* 9580; b) T. Sammakia, E. L. Stangeland, *J. Org. Chem.* **1997**, *62,* 6104; c) T. Langer, G. Helmchen, *Tetrahedron Lett.* **1996**, *37*, 1381; d) S. Hashiguchi, A. Fujii, J. Takehera, T. Ikariya, S. Hashiguchi, A. Fujii, J. Takehera, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1995**, *117*, 7562; d) J. P. Genêt, V.Ratovelomanana-Vidal, C. Pinel, *Synlett*, **1993**, 478.

[4] a) C. P. Casey, S. W. Singer, D. R. Powell, R. K. Hayashi, M. Kavana, *J. Am. Chem. Soc.* **2001**, *123*, 1090; b) E. Mizushima, M. Yamaguchi, T. Yamagishi, *Chem. Lett.* **1997**, 237; c) G.-Z. Wang, J.-E. Bäckvall, *J. Chem. Soc. Chem. Commun.* **1992**, 980; d) S. Bhaduri, N. Sapre, K. Sharma, P. G. Jones, G. Carpenter, *J. Chem. Soc. Dalton Trans.* **1990**, 1305; e) H. A. Brune, J. Unsin, R. Hemmer, M. Reichhardt, *J. Organomet. Chem.* **1989**, *369*, 335; f) Y. Watanabe, Y.Tsuji, H. Ige, Y. Ohsugi, T. Ohta, *J. Org. Chem.* **1984**, *49*, 3359; g) F. Martinelli, G. Mestroni, A. Camus, G. Zassinovich, *J. Organomet. Chem.* **1981**, 220, 383; h) R. Grigg, T. R. B. Mitchell, N. Tongpenyai, *Synthesis* **1981**, 442.

[5] a) N. Uematsu, A. Fujii, S. Hashiguchi, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1996**, *118*, 4916; b) J. Mao, D. C. Baker, *Org. Lett*. **1999**, *6*, 841.

[6] a) G.-Z. Wang, U. Andreasson, J.-E. Bäckvall, *Chem. Commun.* **1994**. 1037; b) M. L. S. Almeida, M. Beller, G.-Z. Wang, J.-E. Bäckvall, *Chem. Eur. J.* **1996**, *2*, 1533; c) A. L. E. Larsson, B. A. Persson, J.-E. Bäckvall, *Angew. Chem.* **1997**, *109*, 1256; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1211; d) B. A. Persson, A. L. E. Larsson, M. L. Ray, J.-E. Bäckvall, *J. Am. Chem. Soc.* **1999**, *121*, 1645.

[7] N. Menashe, Y. Shvo, *Organometallics* **1991**, *10*, 3885.

[8] G. Zassinovich, G. Mestroni, S. Gladiali, *Chem. Rev.* **1992**, *92*, 1051.

[9] a) B. R. James, *Catal. Today* **1997**, *37*, 209; b) D. Beaupère, L. Nadjo, R. Uzan, P. Bauer, *J. Mol. Catal*. **1983**, *18*, 73; c) D. Beaupere, L. Nadjo, R. Uzan, P. Bauer, *J. Mol. Catal*. **1982**, *14*, 129.

[10] E. Miizushima, M. Yamaguchi, T. J. Yamagishi, Mol. Catal. A. **1999**, *148*, 69.

[11] K. Harada, in Patai *The Chemistry of the Carbon-Nitrogen Double Bond*, pp. 276–293.

[12] M. Abed, I. Goldberg, Z. Stein, Y. Shvo, *Organometallics* **1988**, *7*, 2054.

[13] Ruthenium–amine complexes have been isolated by Shvo, see refs [12] and [7].

[14] Secondary amines were found to isomerize faster than primary amines: N. Hermanns, unpublished results from these laboratories.

[15] a) O. Blum, D. Milstein, *J. Am. Chem. Soc*. **1995**, *117*, 4582; b) S. Murahashi, T. Naota, Y. Oda, N. Hirai, *Synlett*, **1995**, 733; c) G.-Z. Wang, U. Andreasson, J.-E. Bäckvall, *J. Chem. Soc. Chem. Commun.* **1994**, 1037; d) U. Karlsson, G.-Z. Wang, J.-E. Bäckvall, *J. Org. Chem.* **1994**, *59*, 5850; e) S. Murahashi, T. Naota, *Synthesis,* **1993**, *4*, 433; f) D. Morton, D. J. Cole-Hamilton, *J. Chem. Soc. Chem. Commun.* **1988**, 1154; g) S. Murahashi, T. Naota, K. Ito, Y. Maeda, H. Taki, *J. Org. Chem*. **1987**, *52*, 4319; h) S.-I. Murahashi, T. Naota, N. Nakajima, *Tetrahedron Lett*. **1985**, *7*, 925.

[16] J. E. Bäckvall, *J. Organometal. Chem.*, in press.

[17] F. F. Huerta, Y. R. Santosh Laxmi, J.-E. Bäckvall, *Org. Lett.* **2000**, *3*, 1037.

[18] P. Milart, J. Cioslowski, *Synthesis* **1984**, *4*, 328.

[19] J. R. Hwu, W. N. Tseng, H. V. Patel, F. F. Wong, D.-N. Horng, B. R. Liaw, L. C. Lin, *J. Org. Chem*. **1999**, *64*, 2211.

[20] F. Texier-Boullet, *Synthesis* **1985**, *6/7*, 679–681.

[21] T. Kawakami, T. Sugimoto, I. Shibata, A. Baba, H. Matsuda, N. Sonoda, *J. Org. Chem*. **1995**, *60*, 2677.

[22] A. R. Katritzky, M. Qi, *J. Org. Chem.* **1997** *62*, 4116.

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