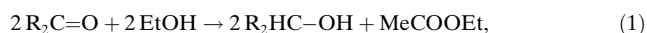


Ethanol as Hydrogen Donor: Highly Efficient Transfer Hydrogenations with Rhodium(I) Amides**

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Homogeneously catalyzed transfer hydrogenation has become a powerful tool in synthetic chemistry, and a wide range of unsaturated substrates can be employed in this reaction.^[1] Impressive activities (turnover frequencies TOF > $1 \times 10^6 \text{ h}^{-1}$)^[2] and selectivities have been reached. Ruthenium(II) arene complexes and rhodium(III) cyclopentadienyl complexes in combination with 2-propanol or formic acid/triethylamine mixtures as hydrogen donors are among the most popular catalytic systems.^[3] Ethanol is a renewable resource and has spurred considerable interest as an alternative to fossil fuels and as a potential feedstock for the chemical industry.^[4] Although reduced organometallic complexes are often prepared by reacting a complex with the metal in a higher oxidation state with ethanol (for example, $\text{Rh}^{\text{III}} \rightarrow \text{Rh}^{\text{I}}$ or $\text{Ru}^{\text{III}} \rightarrow \text{Ru}^{\text{II}}$), ethanol has not been investigated systematically as a hydrogen source in transfer hydrogenation.^[5] This may be due to the fact that ethanol frequently poisons the catalyst by forming stable and inactive carbonyl complexes^[6] and that under basic conditions, aldol condensation products are easily formed with acetaldehyde.

We reported that the d⁸ Rh^I diolefin amide $[\text{Rh}(\text{trop}_2\text{N})(\text{PPh}_3)]$ (**2a**) is an active catalyst for ketone and imine hydrogenation with H_2 ($\text{trop}_2\text{N} = \text{bis}(5\text{-H-dibenzo-[a,d]cyclohepten-5-yl)amide}$).^[7] We report herein that such Rh^I amide complexes are very efficient catalysts for the reaction in Equation (1).



In this reaction, ethanol serves as hydrogen donor and is converted to acetic acid ethyl ester (ethyl acetate).^[8] The reaction in Equation (1) is practically irreversible and for many substrates exothermic by about 10 kcal mol^{-1} . Consequently, it should be possible to perform the transfer hydrogenation (TH) in neat ethanol at high substrate concentrations.

The complexes $[\text{Rh}(\text{trop}_2\text{NH})(\text{PPh}_3)]^+ \text{OTf}^-$ (**1a**), $[\text{Rh}(\text{trop}_2\text{NH})(\text{PPh}_3)]^+ \text{BAR}_4^-$ (**1b**), and $[\text{Rh}(\text{trop}_2\text{NH})(\text{P}(\text{O}^i\text{Pr})_3)]^+ \text{OTf}^-$ (**1c**) were prepared in high yield according

to a reported synthesis protocol ($\text{Ar}^{\text{F}} = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$, $\text{OTf} = \text{CF}_3\text{SO}_3^-$).^[7] The structures of **1a** and **1c** were determined by X-ray diffraction (Figure 1).^[9] The cations in both complex

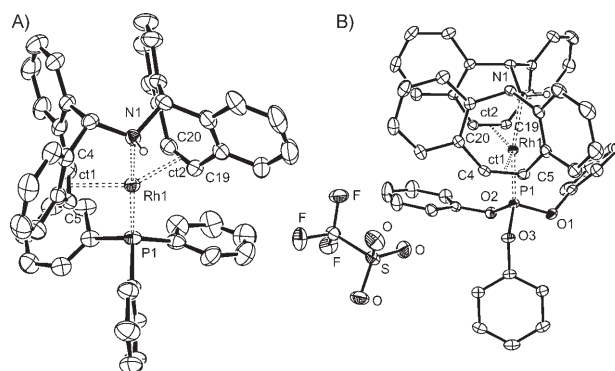


Figure 1. A) Ortep plot (ellipsoids set at 30% probability) of the structure of **1**. The BAR_4^- anion and carbon-bound hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh1-N1 2.155(2), Rh1-P1 2.279(1), Rh1-ct2 2.079(8), Rh1-C5 2.193(3), Rh1-C4 2.191(2), Rh1-C19 2.195(4), Rh1-C20 2.189(4), C4=C5 1.406(4), C19=C20 1.389(4); N1-Rh1-P1 173.1(2), ct1-Rh1-ct2 144.7(4). B) Ortep plot (ellipsoids set at 30% probability) of the structure of **2**. Carbon-bound hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh1-N1 2.147(1), Rh1-P1 2.203(1), Rh1-ct 1 2.074(4), Rh1-ct2 2.133(5), Rh1-C4 2.180(2), Rh1-C5 2.201(2), Rh1-C19 2.241(1), Rh1-C20 2.247(2), C4=C5 1.412(2), C19=C20 1.396(2); N1-Rh1-P1 170.1(4), ct1-Rh1-ct2 145.5(5).

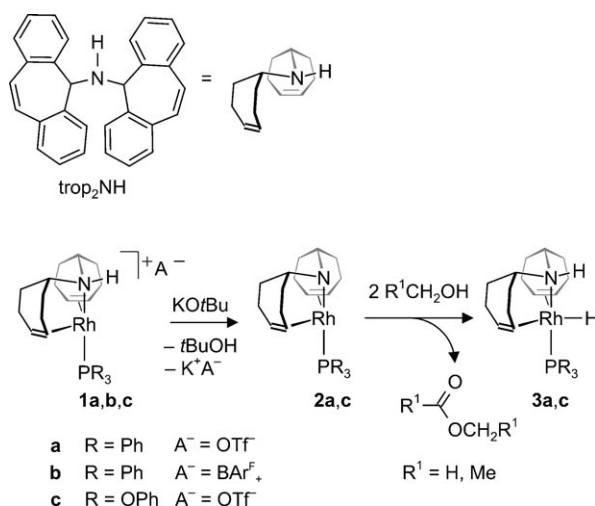
salts adopt saw-horse structures with N-Rh-P angles of about 172° and ct-Rh-ct angles of about 145° (where ct is the center of the coordinated C=C bond). There are no close contacts between the cations and anions.^[10] The NH functional groups in the $[\text{Rh}(\text{trop}_2\text{NH})(\text{PR}_3)]^+$ cations in **1a-c** are sufficiently acidic^[11] to be quantitatively deprotonated by KOtBu or $\text{Li}[\text{N}(\text{SiMe}_3)_2]$ to give the neutral amides $[\text{Rh}(\text{trop}_2\text{N})(\text{PR}_3)]$ (Scheme 1; **2a**: R = Ph, **2c**: R = OPh). These react with two equivalents of methanol or ethanol in stoichiometric reactions to give quantitatively the hydrides $[\text{RhH}(\text{trop}_2\text{NH})(\text{PR}_3)]$ (**3a,c**) and formic methyl ester (HCOOMe) or ethyl acetate (MeCOOEt). The structures of a related amide **2** and amino hydride **3** are known from our previous investigations (with $\text{PR}_3 = \text{PPh}_2\text{tol}$).^[7] and a comparison between **1**, **2**, and **3** shows that there is little change in the corresponding bond lengths and angles (see the Supporting Information).

The rhodium amide complexes **2a,c** are direct catalysts in the reactions described below. But because of their sensitivity, it is more convenient to use the easily storable amino complexes **1a-c** as catalyst precursors in combination with a small amount of base (KOtBu or a suspension of potassium

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Scheme 1. Synthesis of amino olefin complexes **1a–c**, the corresponding amido complexes **2a,c** and their reaction with methanol or ethanol to give the amino hydride complexes **3a,c**.

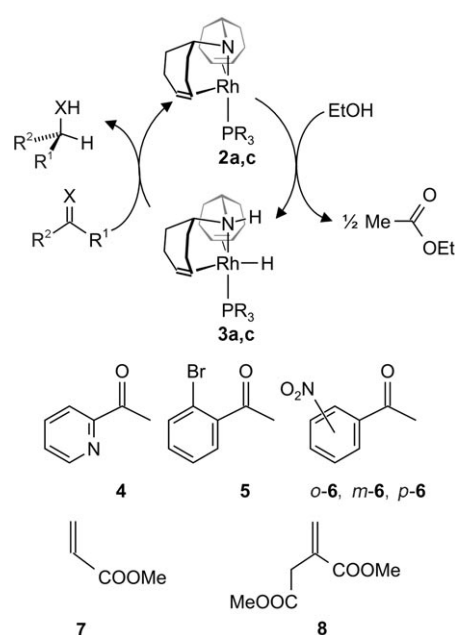
carbonate). No catalytic turnover was observed with **1a–c** in the absence of base. The anion (OTf⁻, BAR₄^{F-}) of the precatalyst has no influence on the catalyst activity. Methanol is not an efficient hydrogen donor in catalytic TH, and only a few catalytic cycles were observed. However, the efficiency with ethanol is excellent (Table 1, entries 1–3).^[1,2] 2-Propanol can be used as hydrogen donor but is less efficient and requires more dilute conditions to obtain comparable conversions (Table 1, entries 11, 12).

Table 1: Transfer hydrogenations with complexes **1a–c** as catalyst precursors or amide **2a** as catalyst. In all cases, greater than 98% conversion was achieved.

Entry	Substrate	S/C	TOF ₅₀ [h ⁻¹]
1	acetone ^[a]	100 000	500 000
2	cyclohexanone ^[a]	100 000	750 000
3	acetophenone ^[a]	100 000	600 000
4	2-acetylpyridine (4) ^[b]	100 000	300 000
5	2-bromoacetophenone (5) ^[b]	5000	5000
6	2-nitroacetophenone (<i>o</i> - 6) ^[b]	5000	5000
7	3-nitroacetophenone (<i>m</i> - 6) ^[b]	10 000	5000
8	4-nitroacetophenone (<i>p</i> - 6) ^[b]	20 000	25 000
9	acrylic acid methyl ester (7) ^[c]	10 000	300 000
10	itaconic acid dimethyl ester (8) ^[c]	10 000	90 000
11	cyclohexanone ^[d]	100 000	150 000
12	acetophenone ^[d]	10 000	100 000

[a] **1a** or **1b**, 1 mol% KOtBu, substrate 2 M in EtOH, room temperature. [b] **1c**, 1 mol% K₂CO₃, Substrate 2 M in EtOH, 40°C. [c] **2a**, substrate 2 M in EtOH, room temperature. [d] **1a**, 1 mol% KOtBu, substrate 0.5 M in *i*PrOH.

The performance of **2a,c** is impressively demonstrated when acetone, the byproduct in classical transfer hydrogenation with 2-propanol as hydrogen donor, is quantitatively converted to 2-propanol in the reaction Me₂C=O + 2 EtOH → Me₂CH–OH + MeCO(OEt) (Table 1, entry 1; see also Scheme 2). The computed reaction enthalpy for this reaction is ΔH_r = –14 kcal mol⁻¹. Under the given conditions, this

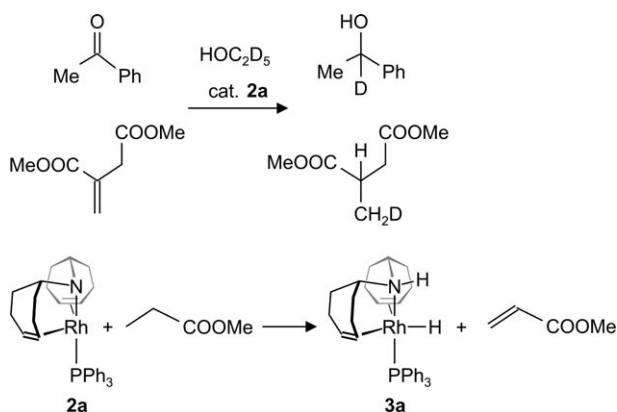


Scheme 2. Simplified catalytic transfer hydrogenation cycle by which substrates **4–8** are quantitatively converted into the corresponding alcohols with catalysts **2a,c**.

reaction proceeds with TOF₅₀ = 500 000 h⁻¹ at room temperature. The further results listed in Table 1 show that the catalysts **2a,c** tolerate a variety of functional groups and are not deactivated by nitrogen donors (Table 1, entry 4). Notably, with the triphenylphosphite complex **1c** as catalyst precursor, *ortho*-bromoacetophenone (Table 1, entry 5) and the nitroacetophenones *o*/*m*/*p*-**6** (Table 1, entries 6–8) are converted with high activity under mild conditions (40°C, 1 mol% K₂CO₃).^[12] No reduction of the nitro moiety was observed, and no aldol-type condensations were detected, despite the high C–H acidity. The high efficiency with which electron-poor olefins such as acrylic acid methyl ester (**7**) or itaconic acid dimethyl ester (**8**) are cleanly converted at substrate/catalyst (S/C) ratios of 10 000 under base-free conditions is also remarkable (Table 1, entries 9 and 10). Less-activated or electron-rich olefins such as styrene or 3,4-dihydro-2*H*-pyrane are not hydrogenated.

Addition of a large excess of triphenylphosphine (100 equiv relative to **2a**) had no influence on the catalyst's activity. This finding supports our assumption that **2a** is the catalyst and not a species formed from **2a** by PPh₃ dissociation. The TH of acetophenone in [D₅]ethanol resulted in complete deuteration of the 1-position in the product 1-phenylethanol (Scheme 3). When itaconic acid dimethyl ester **7** was transfer hydrogenated with [D₅]ethanol, deuterium was incorporated exclusively in the β-position of methylsuccinic acid dimethyl ester. Furthermore, the amide **2a** cleanly dehydrogenates propionic acid methyl ester to give acrylic acid methyl ester **8** and the hydride **3a**.^[14] These findings suggest a Noyori-type mechanism for the transfer hydrogenation of activated C=C double bonds.^[13c]

The observation that the formation of ethyl acetate is efficiently promoted by the isolated amide **2a** in the absence



Scheme 3. Selective deuterium incorporation into acetophenone and itaconic acid dimethyl ester and dehydrogenation of propionic acid methyl ester promoted by **2a**.

of any additional external base prompted us to investigate this process by DFT calculations (B3PW91/BS211B3PW91/BS1; for computational details see the Supporting Information). The mechanism is divided into two parts, which are displayed in Figure 2. Step 1 shows the reaction of the model complex $[\text{Rh}(\text{cht}_2\text{N})(\text{PH}_3)]$ (**2'**) with ethanol, leading to adducts **A**, **B**, or **C** (cht = cycloheptatrienyl). Adduct **A**, in which ethanol is merely H-bonded to the Rh amide nitrogen atom, is slightly more stable than **B** and **C**, in which the oxygen center also interacts with the Rh atom. Adducts **A** and **B** are interconverted by inversion at the oxygen center and are in rapid equilibrium. Adduct **C**, best described as an ethoxide complex, is almost isoenergetic to **B**, and the activation barrier $E_a(\text{B,C})$ via **TS1** is very low ($2.9 \text{ kcal mol}^{-1}$). Adduct **A** lies on the reaction coordinate that leads to the formation of the primary oxidation product acetaldehyde. We find that the O–H bond of the coordinated ethanol molecule is cleaved first via **TS2a**, leading to intermediate **D**; subsequently, the α -CH

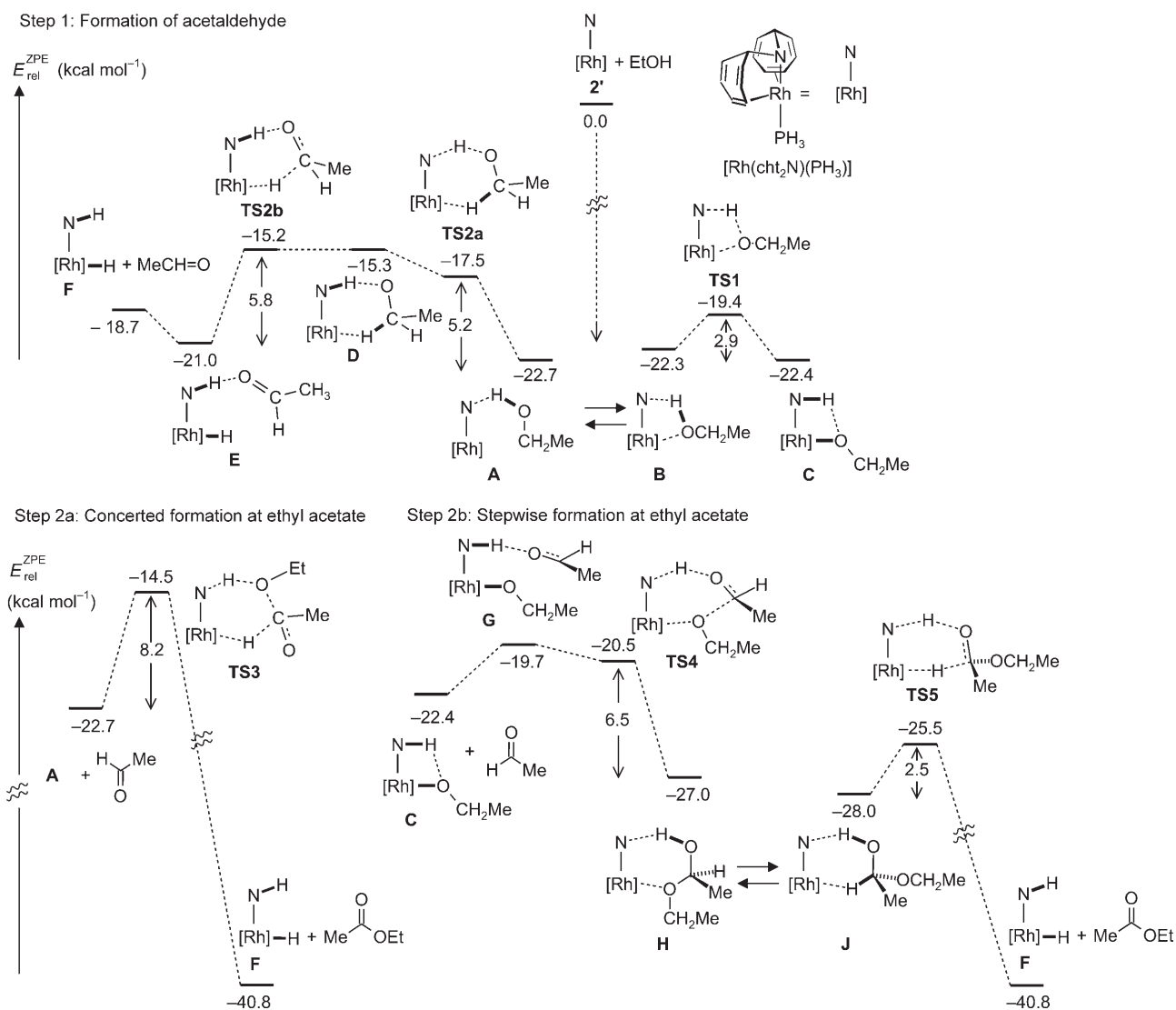


Figure 2. Formation of acetaldehyde (step 1) and ethyl acetate (step 2a or 2b) catalyzed by rhodium amide $[\text{Rh}(\text{cht}_2\text{N})(\text{PH}_3)]$ (**2'**) according to DFT calculations.

bond is broken via **TS2b**. However, **TS2a** is lower in energy than the intermediate **D**, and at this point we simply note that the potential surface is very flat in this region of the reaction. The maximal calculated barrier on the way from **A** to the acetaldehyde adduct **E** is given by $E^{\text{ZPE}}(\text{TS2b}) - E^{\text{ZPE}}(\text{A}) = 7.5 \text{ kcal mol}^{-1}$.

Dissociation of acetaldehyde from **E** to give the amino hydride **F** is slightly endothermic. Overall, the dehydrogenation of ethanol by the rhodium amide follows the well-established mechanism of metal–ligand bifunctional catalysis.^[5a,13] Possible routes for the formation of ethyl acetate are shown in steps 2a and 2b (Figure 2). In step 2a, a concerted reaction is shown, which starts with the ethanol adduct **A**, to which acetaldehyde (from step 1) is added. In a single step via the transition state **TS3**, simultaneous nucleophilic attack of the acetaldehyde carbonyl group by the oxygen atom of the coordinated ethanol molecule and concerted transfer of the OH and CH hydrogen atoms gives the rhodium amino hydride **F** and ethyl acetate. The calculated activation barrier for this process is low ($8.2 \text{ kcal mol}^{-1}$). A second route is shown in step 2b. The ethoxide complex **C** reacts with acetaldehyde to give the adduct **G** which immediately rearranges via **TS4** (which is slightly lower in energy than **G** indicating again a flat potential surface in this region; see discussion for **D** and **TS2a** above) to give the hemiacetal complex **H**. The latter may easily rearrange into the reactive conformation **J**. A concerted hydrogen transfer from the OH and α -CH groups via the very low-lying transition state **TS5** results in the exothermic formation of ethyl acetate and the rhodium amino hydride complex **F**. The latter transfers hydrogen to the substrate to give the hydrogenated product under regeneration of catalyst **2'** (see the Supporting Information for the reaction profile calculated for acetone as substrate).

In summary, the rhodium amides **2a,c** with a saw-horse structure are highly efficient catalysts for the transfer hydrogenation of ketones and activated olefins using ethanol as hydrogen donor, which is irreversibly converted to ethyl acetate. The reactions can be performed at high substrate concentrations in neat ethanol at room temperature. Although we do not exclude that the hemiacetal MeHC(OH)(OEt) is formed classically in a non-metal-assisted reaction (and enters the catalytic cycle via **H** or **J**; see step 2b in Figure 2), results from DFT calculations show that its formation may be also a metal-catalyzed reaction. Note that according to the calculations only very low activation barriers (less than 10 kcal mol^{-1}) are encountered along the reaction path, which explains the high catalytic activity.

Experimental Section

A description of all experiments and detailed listing of spectroscopic data is given in the Supporting Information. All experiments were performed under argon.

1b: Compound **1a** (103 mg, 0.113 mmol) and NaBARF₄ (100 mg, 0.11 mmol) were dissolved in CH₂Cl₂ (10 mL). The solution was stirred for 2 h. The formed NaOTf was removed by filtration over celite. CH₂Cl₂ was removed under reduced pressure; the product was washed with pentane and dried under vacuum. Yield: 165 mg, 0.10 mmol, 90%. Crystals suitable for X-ray diffraction could be

obtained from CHCl₃/*n*-hexane. M.p.: 205 °C (decomp). ¹H NMR (500.1 MHz, CDCl₃): δ = 3.61 (dd, ³J_{PH} = 5.7 Hz, ²J_{RhH} = 2.2 Hz, 1H, NH), 4.91 (ddd, ³J_{HH} = 8.2 Hz, ³J_{PH} = 2.5 Hz, ²J_{RhH} = 0.2 Hz, 2H, CH_{olefin}), 5.25 (dd, ³J_{RhH} = 1.4 Hz, ⁴J_{PH} = 7.3 Hz, 2H, CH_{benzyl}), 6.40 ppm (ddd, ³J_{HH} = 8.9 Hz, ²J_{RhH} = 3.7 Hz, ³J_{PH} = 2.8 Hz, 2H, CH_{olefin}). ¹³C NMR (101.6 MHz, CDCl₃): δ = 81.7 (d, ¹J_{RhC} = 7.3 Hz, 2C, CH_{olefin}), 91.4 ppm (d, ¹J_{RhC} = 12.5 Hz, 2C, CH_{olefin}). ³¹P NMR (162.0 MHz, CDCl₃): δ = 40.3 ppm (d, ¹J_{RhP} = 143.5 Hz). ¹⁰³Rh NMR (12.6 MHz, CDCl₃): δ = 1053.1 ppm (d, ¹J_{RhP} = 144 Hz).

1c: [RhCl(trop₂NH){P(OPh)₃}] (150 mg, 0.18 mmol; see the Supporting Information and reference [7]) and AgOTf (47 mg, 1.83 mmol, 1.03 equiv) were dissolved in CH₂Cl₂ (5 mL), and the resulting suspension was stirred for 12 h and subsequently filtered over a plug of celite. CH₂Cl₂ was removed under reduced pressure, and the resulting red solid was recrystallized from acetone/*n*-hexane and dried under vacuum. Yield: 162 mg, 0.169 mmol, 95%. Crystals suitable for X-ray diffraction were obtained by layering a solution of the complex in CH₂Cl₂ with *n*-hexane. M.p.: 233 °C (decomp). ¹H NMR (300.1 MHz, CDCl₃): δ = 5.09 (dd, ³J_{PH} = 7.3 Hz, ²J_{RhH} = 1.0 Hz, 1H, NH), 5.32 (dd, ⁴J_{PH} = 13.0 Hz, ²J_{RhH} = 0.8 Hz, 2H, CH_{benzyl}), 5.55 (dd, ³J_{HH} = 8.6 Hz, ³J_{PH} = 1.2 Hz, 2H, CH_{olefin}), 6.63 ppm (ddd, ³J_{HH} = 8.6 Hz, ²J_{RhH} = 3.8 Hz, ³J_{PH} = 2.9 Hz, 2H, CH_{olefin}). ¹³C NMR (75.5 MHz, CDCl₃): δ = 75.1 (br. s 2C, CH_{olefin}), 79.8 ppm (d, ¹J_{RhC} = 11.7 Hz, 2C, CH_{olefin}). ³¹P NMR (121.5 MHz, CDCl₃): δ = 105.7 ppm (d, ¹J_{RhP} = 227.0 Hz). ¹⁰³Rh NMR (12.6 MHz, CDCl₃): δ = 1131.4 ppm (d, ¹J_{RhP} = 227.0 Hz).

Catalyses: Protocol 1: A solution of **1c** in ethanol (1 mg mL⁻¹, 1.04 mm) was added to a Schlenk tube containing a 2 M solution of the substrate in ethanol. For the solid substrates 3-nitroacetophenone and 4-nitroacetophenone, a 1 M solution in THF/ethanol (1:1) was prepared. The solution was degassed by three freeze-pump-thaw cycles, and 1 mol % solid K₂CO₃ was added under argon. The suspension was warmed to 40 °C and the reaction monitored by NMR spectroscopy. Protocol 2: Compound **2a** in THF (1 mg mL⁻¹, 1.1 mm) was added to a 2 M solution of the substrate in ethanol. The reaction was monitored by GC and NMR spectroscopy. TOF values were determined after 50 % conversion.

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- [14] For the reaction $2' + \text{H}_2 \rightarrow 3'$, $\Delta H_r = -32.6 \text{ kcal mol}^{-1}$ was computed (0 K, gas phase, DFT at B3PW91/BS211B3PW91/BS1 level); the reported hydrogenation enthalpy for acrylic acid is given as $-30.3 \text{ kcal mol}^{-1}$.
- [15] Gaussian03, M. J. Frisch et al., Gaussian, Inc., Wallingford CT, **2004**, full reference given in the Supporting Information.