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Domino Rhodium/Palladium-Catalyzed Dehydrogenation Reactions of Alcohols to Acids by Hydrogen Transfer to Inactivated Alkenes

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Abstract: The combination of the d^8 Rh^I diolefin amide [Rh(trop₂N)(PPh₃)] (trop₂N = bis(5-*H*-dibenzo-

[a,d]cyclohepten-5-yl)amide) and a palladium heterogeneous catalyst results in the formation of a superior catalyst system for the dehydrogenative coupling of alcohols. The overall process represents a mild and direct method for the synthesis of aromatic and heteroaromatic carboxylic acids for which inactivated olefins can be used

Introduction

The catalytic hydrogenation of alkenes, undoubtedly one of the most relevant reactions in organic chemistry, is usually carried out with molecular hydrogen.^[1] Homogeneous catalysts have demonstrated high activity and have extended the scope of catalytic hydrogenation for highly selective transformations.^[2] However, many catalytic hydrogenations are still accomplished by using heterogeneous catalysts and Pd is the preferred industrial catalyst. Despite the mature stage of hydrogenation technologies, studying alternative less explored catalytic systems is still of fundamental importance. We previously reported an example in which the combination of the complex [Rh(cod)(sulfos)] (cod=cycloocta-1,5diene; sulfos= $^{-}O_{3}S(C_{6}H_{4})CH_{2}C(CH_{2}PPh_{2})_{3}$) and supported

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as hydrogen acceptors. Allyl alcohols are also applicable to this coupling reaction and provide the corresponding saturated aliphatic carboxylic acids. This transformation has been found to be very efficient in the presence of silica-supported palladium nanoparti-

Keywords: alkenes • heterogeneous catalysis • hydrogen transfer • nanoparticles • palladium cles. The dehydrogenation of benzyl alcohol by the rhodium amide, [Rh]N, follows the well established mechanism of metal-ligand bifunctional catalysis. The resulting amino hydride complex, [RhH]NH, transfers a H₂ molecule to the Pd nanoparticles, which, in turn, deliver hydrogen to the inactivated alkene. Thus a domino catalytic reaction is developed which promotes the reaction $R-CH_2-OH+NaOH+$ 2 alkene $\rightarrow R-COONa+2$ alkane.

Pd metal nanoparticles (Pd⁰/SiO₂) form a unique stable entity that speed up the overall hydrogenation of benzene to cyclohexane.^[3]

In comparison with the catalytic reduction using hydrogen gas, transfer hydrogenations that employ hydrogen donors present some advantages, principally that the inherent hazards associated with the use of hydrogen gas, such as flammability, containment, and high pressures are avoided. Metal-promoted hydrogen transfer from small organic molecules has been extensively investigated in the reduction of activated unsaturated compounds.^[4] Comparatively little attention has been paid to the transition-metal catalyzed transfer hydrogenation of alkenes and alkynes. In their early pioneering work, Braude and Linstead reduced a range of olefins and alkynes in a catalytic transfer hydrogenation reaction using a heterogeneous palladium catalyst under relatively mild conditions and cyclohexene as the hydrogen donor, which was converted to benzene.^[5] Few more examples were reported in which cyclic ethers were utilized as hydrogen transfer agents.^[6] Nolan and co-workers reported an iridium complex that reduces alkenes in excellent yield using 2-propanol as hydrogen donor.^[7] Recently Crabtree described triazole-derived iridium(I) carbene complexes capable of promoting the transfer hydrogenation of inactivated olefins in 2-propanol.^[8]



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However, the selective oxidation of alcohols by using simple olefins as hydrogen acceptors (HA) has rarely been reported. Jensen et al., used a PCP "pincer" complex for the dehydrogenation of alcohols and an electron-rich alkene as the hydrogen acceptor, albeit under rather forcing conditions.^[9]

Clean and high-yield methods have been established for ruthenium-assisted dehydrogenative coupling (DHC) reactions of alcohols to esters and aldehydes to acids in the presence of benzalacetone^[10a] or primary alcohols to methyl esters by using crotononitrile as the hydrogen acceptor.^[10b] Furthermore, acceptorless alcohol dehydrogenative coupling reactions initially developed by Shvo and Saito^[11] and more recently by Milstein and co-workers are currently of great interest. Here, Ru pyridine-based "dearomatized" pincer complexes promote the DHC between primary alcohols and primary amines or a second alcohol molecule to carbonic acids derivatives without a hydrogen acceptor.^[12]

We reported recently, that the dehydrogenative coupling of primary alcohols can be efficiently catalyzed at room temperature with a Rh^I amide complex (Figure 1), using ke-



Figure 1. The structure of $[Rh(trop_2N)(PPh_3)]$. Plots of the DFT calculations of the HOMO and LUMO.

tones and α,β -unsaturated esters as hydrogen acceptors.^[13] These results encouraged us to design a new catalytic system for an economic process in which a simple olefin is employed as hydrogen acceptor in a DHC reaction under mild conditions. This procedure may offer significant advantages with respect to costs and in the work-up procedure in which the hydrogenated by-product, a (volatile) alkane is easily separated from a polar carbonic acid derivative. Here, we propose a domino catalytic system in which a Rh^I amide serves as the homogeneous catalyst for the dehydrogenation of primary alcohols and heterogeneously suspended metal particles serve as H₂ acceptors and as catalysts for the hydrogenation of inactivated olefins. To the best of our knowledge, such a type of catalytic system, specifically the transfer of hydrogen from a homogeneous transfer hydrogenation catalyst to a heterogeneous hydrogenation catalyst has not been previously investigated.

Results and Discussion

During the course of our study of catalytic systems for hydrogenation^[14] and hydrogen transfer processes,^[15,16] we described the synthesis, from the precursor [Rh(trop₂NH)-(PPh₃)] **1**, of the rhodium(I)/diolefin amido complex [Rh-(trop₂N)(PPh₃)] (trop₂N=bis(5-*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)amide) **2**. This tetra-coordinated Rh¹ amido complex **2** adopts a saw-horse-type structure that is a trigonal bipyramid with one missing corner in the equatorial plane. This structure is created by the combination of two π -acceptor olefinic binding sites in the equatorial positions and an amido and phosphane σ -donor group each placed mutually *trans* in the axial positions.

We believe that this type of structure is essential to promote bond-cleavage reactions via energetically low transition states. The HOMO corresponds to the anti-bonding combination of a filled d-orbital at the metal center with the filled *p*-type orbital at the adjacent N center ("lone-pair") and is polarized to the open face of the complex. Consequently, the HOMO undergoes a symmetry allowed interaction with the σ^* -orbital of the H–H bond (Figure 1), which is readily cleaved across the Rh–N bond even at low temperatures.^[15]

This reaction is reversible but the liberation of H_2 from the hydrogenated complex, the amino hydride **3**, is too endothermic and slow at ambient temperature to allow efficient dehydrogenation reactions. Complex **2** catalyzes the direct hydrogenation of ketones and imines (Scheme 1) and also very efficiently the transfer hydrogenation of ketones and activated olefins using ethanol as hydrogen source which is irreversibly converted to ethylacetate.^[14]



Scheme 1. Catalytic hydrogenation of imines and ketones by $[Rh-(trop_2N)(PPh_3)]$.

In a related process, we studied the possibility of using this system as catalyst for the DHC of primary alcohols with water, methanol, or amines to furnish carboxylic acids, methyl esters, or amides, respectively. A high reaction rate and catalytic turn over is achieved under mild reaction conditions (room temperature) using cyclohexanone or alternatively, methylmethacrylate (MMA) as hydrogen acceptors. The Scheme 2 shows representatively some results for the



Scheme 2. Transfer hydrogenation with various unsaturated systems as hydrogen acceptors (HA).

transfer hydrogenation of benzyl alcohol with different hydrogen acceptors. Treatment of a primary alcohol with cyclohexanone or acetone with 0.1 mol% or less of the precatalyst **1** and NaOH at room temperature for 4 h gives the corresponding carboxylic acid with excellent yield. The reaction was found to be influenced by the strength of the base used. When a weaker inorganic base (like NaHCO₃) or an amine was used, poor conversions are obtained. Furthermore, when we treat benzyl alcohol in water using an inactivated alkene as hydrogen acceptor under otherwise identical conditions, no conversion is observed and the starting alcohol is quantitatively recovered.

To achieve the dehydrogenative coupling reaction by using inactivated cheap alkenes as hydrogen acceptors, we have investigated several co-catalysts, which, on one hand, accepts the hydrogen from the primarily formed amino hydride complex [Rh(eq-H)(trop₂NH)(PPh₃)] (**3**) to regenerate the amide **2**. On the other hand, the hydrogen loaded co-catalyst must be able to hydrogenate inactivated olefins to the corresponding hydrocarbons under the used reaction conditions (basic aqueous media) and show no tendency to be deactivated (via decarbonylation reactions of the alcohols, for example). A screening of some established heterogeneous and homogeneous hydrogenation catalysts for the DHC of benzyl alcohol with water to benzoic acid using 1hexene as a hydrogen acceptor is shown in Table 1.

Excellent conversion to the acid is observed when Pd/ SiO₂ is used as co-catalyst (entries 1 and 2, Table 1). Even with small amounts (1.5 wt%) of nanodeposits of Pd on SiO₂ (for preparation and analysis of Pd⁰/SiO₂ see the Supporting Information) excellent results are obtained. Other catalysts that are commercially available or find industrial use and contain Pd or Pt on other polar supports (zeolite or alumina) were less efficient (entries 3–5, Table 1). Remarka-

bly, Pd on an apolar support, that is charcoal, is little active despite the rather high metal content. In a blind experiment we verified that none of these heterogenous catalysts alone are efficient promoters of the DHC. In addition we also demonstrated that there is no reaction in absence of [Rh-(trop₂NH)(PPh₃)]OTf, showing FULL PAPER

(trop ₂ N)(PPh ₃)]. Screening of the co-catalyst. ^[a]		
Entry	Cooperative catalyst	Conversion [%] ^[b]
1	Pd/SiO ₂ (9.8 wt %)	quantitative
2	Pd/SiO_2 (1.5 wt%)	quantitative
3	Pd on zeolite (0.5 wt%)	44
4	Pt on zeolite (0.5 wt%)	41
5	Pt on alumina (5 wt%)	71
6	Pd/C (10 wt %)	16
7	Pd/C (5 wt %)	19
8	[Pd ₂ (dba) ₃]-CHCl ₃ ^[c]	37
9	Na ₂ [PdCl ₄]	64
10	PdCl ₂	68
11	PdCl ₂ /SnCl ₂	48
12	$[Ir(tropp^{Ph})_2]PF_6$	31
13	[RuCl ₂ (PPh ₃) ₃]	43

1-hexene under organic/aqueous biphasic conditions catalyzed by [Rh-

[a] Reaction conditions: aqueous mixture containing BnOH (1.37 mmol), 1-hexene (13.7 mmol), NaOH (1.6 mmol), co-catalyst (0.0137 mmol) and [Rh(trop₂NH)(PPh₃)]OTf (0.00137 mmol). [b] Conversion of BnOH to PhCO₂Na measured by ¹H NMR spectroscopy. [c] dba = dibenzylidene-acetone.

that the combination of both catalyst is essential for the process (domino catalysis).

We subsequently studied the DHC of benzyl alcohol with water and hydrogenation of 1-hexene by using a combination of rhodium amino hydride complex 3 to other well established homogeneous transition metal hydrogenation catalysts. An analysis of some of the most significant homogeneous catalytic palladium systems in hydrogenation, such as [Pd₂(dba)₃], PdCl₂, PdCl₂/SnCl₂ and Na₂(PdCl₄) turn out to be reasonably efficient (entries 8–10, , Table 1, Scheme 3). Some time ago we reported iridium(I) complexes containing (5H-dibenzo[a,d]cyclohepten-5-yl)phosphanes (tropp^{Ph}) as rigid, concave-shaped, mixed phosphane-olefin ligands. These complexes show rather high activity in the hydrogenation of imines [turnover frequency (TOF) of $>6000 \text{ h}^{-1}$].^[17] On the other hand, no or very-low activity was found in transfer hydrogenations. The complex $[Ir(tropp^{Ph})_2]PF_6$ was tested here and showed moderate conversions (entry 12, Table 1) in the dehydrogenative process. Finally [RuCl₂-(PPh₃)₃], a very active hydrogenation catalyst, was also found to be active in the DHC reactions, albeit less efficiently (entry 13, Table 1).

To demonstrate the interplay between $[Rh(trop_2NH)-(PPh_3)]OTf$ and the silica-supported palladium nanoparticles (Pd/SiO_2) , some experiments using stoichiometric ratios of



Scheme 3. The palladium catalyzed hydrogen transfer from [Rh(eq-H)(trop₂NH)(PPh₃)] to 1-hexene.

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the reagents were performed (Scheme 3) and followed by ³¹P NMR spectroscopy (for experimental details see the Supporting Information). When a green solution of [Rh-(trop₂N)(PPh₃)] (**3**) in [D₈]THF was treated with one equivalent of BnOH, the solution immediately turned yellow. A NMR spectrum showed the presence of [Rh(eq-H)-(trop₂NH)(PPh₃)] exclusively. Subsequently, this solution was divided in two samples. In one of them, only alkene was added and in the second, Pd/SiO₂ and 1-hexene were added. During a time period of 6 h, the ³¹P NMR spectrum of the first sample showed no conversion and only the signal of the starting material [Rh(eq-H)(trop₂NH)(PPh₃)] was observed. The second sample to which Pd/SiO₂ was added turned back to a greenish color and the ³¹P NMR spectrum showed clearly the formation of [Rh(trop₂N)(PPh₃)] (**2**).

On the basis of these findings as well as the results of the experiments summarized in Table 1, we conclude that the enhanced activity in the DHC of primary alcohols to esters or with aqueous NaOH to carbonic acids with 1-hexene as simple olefin and hydrogen acceptor (HA) is indeed owed to the synergy of the Rh^I-Pd⁰/SiO₂ system as is shown in a simplified manner in Scheme 4.



Scheme 4. A representation of the catalytic cycle in the dehydrogenative coupling (DHC) of primary hydroxyl compounds with water.

In an attempt to generalize this transformation, Pd/SiO_2 was selected for further experiments with several alkenes. Table 2 summarizes the results with mono and diolefins. Not unexpected, we find a dependency on the efficiency of the system on the degree of substitution at the olefinic C=C double bond. Higher degree of substitution leads to lower activities.

We investigated also the scope of this rhodium-palladiumdomino catalysis and used a variety of differently substituted aromatic and heteroaromatic alcohols in the conversion to the corresponding acids. These results are summarized in Table 3. High effective transformations were obtained with benzylic alcohols with electron-donating (entries 1–3, Table 3) or -withdrawing substituents (entry 4, Table 3). In

Table 2. Evaluation of various alkenes as hydrogen acceptors in DHC of ${\rm BnOH.}^{[\rm a]}$

Entry	Alkene (<i>n</i> equiv)	Conversion [%] ^[b]
1	cyclohexene (10)	90
2	1,3-cyclohexadiene (5)	95
2	1-heptene (10)	quantitative
3	1-hexene (10)	quantitative ^[c]
4	1-hexene (5)	93
5	cis-stilbene (5)	27
6	styrene (5)	43
7	2-methyl-3-buten-2-ol (5)	58
8	ethylvinyl ether (5)	31
9	isoprene (5)	39

[a] Reaction conditions: aqueous mixture containing BnOH (1.37 mmol), alkene, NaOH (1.6 mmol), Pd/SiO₂ (0.0137 mmol) and [Rh(trop₂NH)-(PPh₃)]OTf (0.00137 mmol) was stirred for 12 h at room temperature. [b] Conversion of BnOH in PhCO₂Na determined by ¹H NMR analysis of the reaction mixture. [c] It is possible to reduce the catalyst loading to 0.01 mol% of rhodium catalyst with only a slight loss in conversion (determined by NMR spectroscopy).

comparison with other transfer hydrogenation methods, no hydro-dehalogenated product was observed throughout the reaction period with bromobenzyl alcohol as starting material.^[18] Significantly, heteroaromatic substrates as the furan-3methanol, which becomes readily available from biomass,^[19] are also tolerated in the DHC under our reaction conditions and are converted in substantial amounts (>80%, entry 5, Table 3). Allylic substrates required shorter reaction times to reach complete conversion, but the reactions give substantial amounts of side products. This is exemplified by the transformation of cinnamyl alcohol (entry 6, Table 3), that afforded cinnamic acid with moderate yield (50%) along with phenylpropionic acid (28%) and 3-phenylpropanol (13%) as further isolated products. Indeed, the C=C double bond in β-methallyl alcohol served as intra-molecular hydrogen acceptor and the product of DHC and simultaneous C=C double bond hydrogenation, isobutyric acid, is obtained in 50% yield along with 40% of isobutylalcohol (entry 7, Table 3).

Remarkably, aliphatic alcohols like ethanol or 1-octanol (not included in Table 1) are not converted in the domino Rh-Pd/SiO₂ catalyzed DHC process using an alkene as hydrogen acceptor. However, the presence of such an alcohol does not prevent the transformation of a benzylic hydroxyl function. This is exemplified by an experiment in which a 1:1 mixture of benzyl alcohol and 1,2-propanediol is coupled with NaOH/H₂O using 1-hexene as HA. In this reaction the aliphatic diol was recovered unchanged (entries 8 and 9, Table 3), whereas the benzylic alcohol was converted to benzoic acid in 71% yield (entry 9, Table 3). Finally, the conversion of polyhydroxyaromatic compounds was investigated. The best results so far we could obtain for the formation of the monoacids from the corresponding benzenedimethanol compounds are given in entries 10 and 11 (isolated yields are given). In these reactions, we used THF as co-solvent, which led to about 50% conversion while 50% of the starting material is recovered. Note, that no protecting groups Table 3. DHC of various alcohols with 1-hexene as HA, catalyzed by $[Rh(trop_2NH)(PPh_3)]OTf$ and $Pd/SiO_2.^{[a]}$



[a] The reaction of the alcohol (1.37 mmol) was carried out in H₂O (1.6 mL) in the presence of [Rh(trop₂NH)(PPh₃)]OTf (0.00137 mmol), Pd/SiO₂ (0.0137 mmol), NaOH (1.6 mmol) and 1-hexene (13.7 mmol) for 12 h at room temperature. [b] Isolated yield, unless otherwise specified. [c] 3% of ArCHO was detected. [d] Phenylpropionic acid (28%) and 3-phenylpropanol (13%) isolated as side products. [e] The reaction was performed without an external hydrogen acceptor. [f] Referred to the conversion of benzyl alcohol, complete recovery of 1,2-propanediol. [g] The reactions were carried out under standard conditions with a mixture of THF/H₂O (2:1).

are needed and the mono-acids are formed with >98% selectivity.

Conclusion

A new catalytic system for the dehydrogenative coupling (DHC) of primary alcohols with NaOH/H₂O has been developed. Use of inactivated alkenes as hydrogen acceptors is now possible with this new methodology. High reactivity is observed upon addition of supported nanoparticles of Pd/

SiO₂ as co-catalyst. Transfer of hydrogen from the homogeneous Rh amino hydride complex [Rh(eq-H)(trop₂NH)- (PPh_3)] (3) to the heterogeneously suspended SiO₂-supported palladium nanoparticles has been demonstrated. The detailed mechanism by which this transfer occurs, remains obscure and needs further detailed studies concerning the interaction of the molecular Rh hydride complex and Pd particles. Most remarkably, although the purely homogeneously catalyzed DHC reaction using the amide [Rh(trop₂N)-(PPh₃)] (2) and ketones or activated olefins as hydrogen acceptors (HA) does not allow to discriminate between aliphatic and benzylic hydroxyl functions, the domino Rh^I-Pd/ SiO₂ catalyzed system with simple olefins as HA does. This may become important when single primary hydroxyl functions are to be converted to functionalized carboxylic acid derivatives in more complex reaction mixtures, as they are obtained from biomass.

Experimental Section

General: All syntheses and catalyses were performed under an atmosphere of argon using standard Schlenk techniques. Cyclohexanone was distilled from calcium hydride and acetone from CaSO4. Alkenes and alcohols employed for the synthesis of acids were distilled prior to use. The catalysts from Table 1 (entries 3-11 and 13) were used as obtained from the commercial supplier. [Ir(tropp^{Ph})₂]PF₆ was synthesized according to the reported method.^[17] ¹H NMR spectra were recorded at 400, 300, or 250 MHz and chemical shifts were referenced to the residual solvent peak. 13C NMR spectra are proton decoupled and were recorded at 75.5 MHz; chemical shifts were referenced to the solvent. ³¹P NMR spectra were recorded at 162.0, 121.5 or 101.3 MHz; chemical shifts were referenced to an external standard of H₃PO₄. Coupling constants J are given in Hertz [Hz] as absolute values, unless specifically stated. The data is being reported as: s=singlet, d=doublet, t=triplet, q=quadruplet, m=multiplet or unresolved, br=broad signal, coupling constant(s) in Hz, integration, interpretation. Melting points were determined by using a Büchi melting point apparatus and are reported uncorrected. Mass spectrometry (LCMS) was carried out by the ETH Zurich Mass Spectrometry Facility.

Preparation of silica-supported palladium nanoparticles: The Davicat (Grace) silica employed in this work was a high-surface-area hydrophilic mesoporous non-ordered material. The support was finely milled, washed with 1 M HNO₃ and, subsequently, with distilled water to neutrality. The material was dried overnight in an oven at 100 °C. Porosity and surface area were determined by nitrogen adsorption. Nitrogen adsorption/desorption isotherms at liquid nitrogen temperature were measured by using a Micromeritics ASAP 2010 instrument. All silica samples were degassed at 300 °C. Average pore radius (9.70 nm) and specific pore volume (1.43 cm³g) were calculated according to the Barret–Joyner–Halenda (BJH) theory. The specific surface area (295 m²g) was obtained using the Brunauer–Emmett–Teller (BET) equation.

Usually, 1 g batches (Pd content ranging from 1.5 to 10 wt %), were prepared from PdCl₂/SiO₂ by the following treatment: 1) calcination at 500 °C for 1 h in an O₂ flow (40 mLmin⁻¹) at a heating rate of 10 °Cmin⁻¹, followed by cooling in argon flow (40 mLmin⁻¹) to room temperature; 2) reduction at 300 °C for 1 h in a H₂ flow (40 mLmin⁻¹) at a heating rate of 10 °Cmin⁻¹ followed by cooling in argon flow (40 mLmin⁻¹) at a heating rate of 10 °Cmin⁻¹ followed by cooling in argon flow (40 mLmin⁻¹) at a heating rate of 10 °Cmin⁻¹ followed by cooling in argon flow (40 mLmin⁻¹) to room temperature. PdCl₂/SiO₂ (1.96–9.24 wt % Pd) was prepared by impregnation of 5 g of silica with a solution of PdCl₂ (167–910 mg) in de-ionized water (50–250 mL) and 36 % HCl (2–10 mL). The suspension was maintained under stirring for 4 h and then the solvent was removed by evaporation under reduced pressure. After the solid resi-

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due was removed by means of a small amount of water, it was quickly dried and kept under vacuum overnight.

General procedure for the catalyzed dehydrogenative coupling of alcohols to acids: A mixture of alcohol (1 equiv, 1.37 mmol), water (66 equiv, 90 mmol, 1.6 mL), sodium hydroxide (1.2 equiv, 1.6 mmol, 64 mg), and alkene are combined in a Schlenk-flask under argon atmosphere. The biphasic mixture is degassed by purging with argon for 10 min. prior the addition of [Rh(trop₂NH)(PPh₃)]OTf (0.001 equiv, 0.00137 mmol, 1 mg) and Pd/SiO₂ 10 wt% (0.01 equiv, 0.0137 mmol Pd, 14.6 mg) under a stream of argon. After 12 h at RT (reaction followed by NMR spectroscopy) water is added (20 mL), and the mixture is extracted with diethyl ether (2×20 mL). The aqueous phase is then acidified with 10% HC1 and extracted with ethyl acetate (4×25 mL).The combined extracts were washed with brine (25 mL), dried over Na₂SO₄, and evaporated under reduced pressure, affording the pure acid after purification.

[Rh(trop₂NH)(PPh₃)]OTf (1): [RhCl(trop₂NH)(PPh₃)]₂ (for synthesis details of this complex see the Supporting Information of [14a]) (1 equiv, 0.63 mmol, 500 mg) and (1.03 equiv, 0.65 mmol, 166 mg) AgOTf were suspended in DCM (15 mL) and stirred for 12 h. The formed AgCl was removed by filtration over a plug of celite. Addition of n-hexane precipitated the orange product complex. The mother liquor was decanted off and the product dried under vacuum. A second fraction was obtained from the mother liquor upon re-crystallization from DCM/hexane. Yield: 542 mg, 0.6 mmol, 95 %. ¹H NMR (400.1 MHz, CDCl₃) δ = 7.84 (m, 6H, CHar), 7.70-7.55 (m, 9H, CHar), 7.40-7.15 (m, 8H, CHar), 7.00-6.85 (m, 4H, CH^{ar}), 6.85–6.70 (m, 4H, CH^{ar}), 5.66 (dd, ${}^{3}J_{PH}=5.8$ Hz, ${}^{2}J_{RhH}=$ 2.1 Hz, 1 H, N*H*), 5.43 (ddd, ${}^{3}J_{HH} = 9.3$ Hz, ${}^{2}J_{RhH} = 3.3$ Hz, ${}^{3}J_{PH} = 2.8$ Hz, 2H, CH^{olefin}), 4.94 (ddd, ${}^{3}J_{HH} = 9.3$ Hz, ${}^{3}J_{PH} = 2.7$ Hz, ${}^{2}J_{RhH} = 1.8$ Hz, 2H, CH^{olefin}), 4.91 ppm (d, ${}^{4}J_{\text{PH}}$ = 8.4 Hz, 2H, CH^{benzyl}); 13 C NMR (101.6 MHz, CDCl₃) $\delta = 136.9$ (s, 2 C, C^{quart}), 135.5 (d, ²J_{RhC} = 1.8 Hz, 2 C, C^{quart}), 134.6 (s, 2 C, C^{quart}), 134.6 (s, 2 C, C^{quart}), 134.5 (d, ${}^{2}J_{\text{PC}}$ =9.2 Hz, 6 C, $C\text{H}^{\text{ar}}$), 131.0 (d, ${}^{4}J_{PC} = 2.3$ Hz, 3 C, CH^{ar}), 129.6 (s, 2 C, CH^{ar}), 129.5 (s, 2 C, CH^{ar}), 129.0 (d, ${}^{1}J_{PC}$ =46.4 Hz, 3 C, C^{quart}), 128.7 (d, ${}^{3}J_{PC}$ =10.1 Hz, 6 C, CHar), 128.5 (s, 2 C, CHar), 128.2 (s, 2 C, CHar), 127.5 (s, 2 C, CHar), 127.2 (s, 2 C, CH^{ar}), 126.4 (s, 2 C, CH^{ar}), 126.4 (s, 2 C, CH^{ar}), 119.8 (q, ${}^{1}J_{FC} =$ 321.1 Hz, C, CF₃), 74.2 (d, ${}^{1}J_{RhC}$ =13.3 Hz, 2 C, CH^{olefin}), 74.0 (d, ${}^{1}J_{RhC}$ = 6.9 Hz, 2 C, CH^{olefin}), 72.7 ppm (d, ³J_{PC}=1.4 Hz, 2 C, CH^{benzyl}); ³¹P NMR $(162.0 \text{ MHz}, \text{CDCl}_3) \delta = 40.6 \text{ ppm} (d, {}^1J_{\text{RhP}} = 137.7 \text{ Hz}).$

[Rh(trop₂N)(PPh₃)] (2): To a suspension of [RhCl(trop₂NH)(PPh₃)] (1 equiv, 0.188 mmol, 150 mg.) in THF (2 mL) was added a solution of potassium tert-butoxide (1 equiv, 0.188 mmol, 21.1 mg) in THF (1 mL). After 30 min. of stirring, toluene (1 mL) was added to the resulting deepgreen solution and the solvents were removed under vacuum. The darkgreen residue was extracted with THF (2×3 mL), filtered over Celite. The clear filtrate was reduced under vacuum to a volume of approximately 1 mL. Dark-green microcrystals of [Rh(trop₂N)(PPh₃)] (110 mg, 0.144 mmol, 77%) grew upon layering of this solution with toluene (1 mL) and hexane (10 mL). ¹H NMR (300 MHz, $[D_8]$ THF): $\delta = 7.63$ (m, 6H), 7.56 (m, 9H), 7.22 (d, ${}^{3}J_{HH}$ =6.7 Hz, 2H), 7.03 (m, 4H), 6.95 (d, ${}^{3}J_{\rm HH}$ =7.0 Hz, 2 H), 6.90 (d, ${}^{3}J_{\rm HH}$ =7.3 Hz, 2 H), 6.79 (d, ${}^{3}J_{\rm HH}$ =7.6 Hz, 2 H), 6.67 (dd, ${}^{3}J_{HH} = 7.2$ Hz, ${}^{3}J_{HH} = 7.2$ Hz, 2 H), 6.57 (dd, ${}^{3}J_{HH} = 7.3$ Hz, ${}^{3}J_{\text{HH}} = 7.3 \text{ Hz}, 2 \text{H}$), 5.62 (ddd, ${}^{3}J_{\text{HH}} = 9.0 \text{ Hz}, {}^{2}J_{\text{RhH}} = 3.3 \text{ Hz}, {}^{3}J_{\text{PH}} = 2.9 \text{ Hz}$, 2H), 4.92 (d, ${}^{4}J_{PH} = 13.5$ Hz, 2H), 4.69 ppm (ddd, ${}^{3}J_{HH} = 9.0$ Hz, ${}^{3}J_{PH} =$ 6.2 Hz, ${}^{2}J_{\text{RhH}}$ =1.2 Hz, 2H); 13 C NMR (75 MHz, [D₈]THF): δ =146.8 (s, 2C), 143.7 (s, 2C), 137.7 (s, 2C), 136.6 (s, 2C), 135.5 (d, ²J_{RhC}=11.0 Hz, 6C), 132.1 (d, ${}^{1}J_{RhP}$ =35.5 Hz, 3C), 131.1 (s, 3C), 129.5 (d, ${}^{3}J_{RhC}$ =8.6 Hz, 6C), 128.7 (s, 2C), 127.9 (s, 2C), 127.3 (s, 2C), 126.4 (s, 2C), 126.4 (s, 2C), 126.3 (s, 2C), 126.0 (s, 2C), 125.8 (s, 2C), 84.5 (d, ${}^{1}J_{RhC}$ =14.7 Hz, 2C), 82.3 (s, 2C), 76.2 ppm (d, ${}^{1}J_{RhC} = 6.7$ Hz, 2C); ${}^{31}P$ NMR (121.5 MHz, $[D_8]$ THF): $\delta = 38.0$ ppm (d, ${}^1J_{RhP} = 125$ Hz).

[Rh(eq-H)(trop₂NH)(PPh₃)] (3): The [Rh(eq-H)(trop₂NH)(PPh₃)] complex was prepared by adding BnOH (12 mg, 0.11 mmol) to a green solution of [Rh(trop₂N)(PPh₃)] (2) (76 mg, 0.1 mmol) in [D₈]THF (1 mL). A yellow solution was obtained immediately in which the hydride is the only observed product. ¹H NMR (300 MHz, [D₈]THF): δ =7.90–6.10 (31H), 5.56 (d, ³J_{PH}=4.9 Hz, 1H), 4.56 (d, ⁴J_{PH}=7.8 Hz, 2H), 3.91 (dd, ³J_{HH}=9.3 Hz, ³J_{HH}=4.7 Hz, 2H), 3.55 (d, ³J_{HH}=9.3 Hz, 2H), -8.15 ppm (dd, ¹J_{RhH}=23.0 Hz, ²J_{PH}=23.0 Hz, 1H); ¹³C NMR (75.5 MHz, [D₈]THF):

δ=144.1–119.9, 72.2 (s, 2C), 60.6 (d, ¹*J*_{RhC}=8.6 Hz, 2C), 57.8 ppm (d, ¹*J*_{RhC}=8.0 Hz, 2C); ³¹P{¹H} NMR (121.5 MHz, [D₈]THF): δ=62.2 ppm (d, ¹*J*_{RhP}=145 Hz).

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