Coupling Reactions

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Nitrous Oxide as a Hydrogen Acceptor for the Dehydrogenative Coupling of Alcohols

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Abstract: *The oxidation of alcohols with N_2O as the hydrogen acceptor was achieved with low catalyst loadings of a rhodium complex that features a cooperative bis(olefin)amido ligand under mild conditions. Two different methods enable the formation of either the corresponding carboxylic acid or the ester. N_2 and water are the only by-products. Mechanistic studies supported by DFT calculations suggest that the oxygen atom of N_2O is transferred to the metal center by insertion into the Rh–H bond of a rhodium amino hydride species, generating a rhodium hydroxy complex as a key intermediate.*

Nitrous oxide (N_2O) is an industrial waste product[1] that massively depletes ozone[2] and has a greenhouse gas effect that is 300 times higher than that of CO_2.[2b] Its transformation into less harmful chemicals is therefore of great interest and particularly attractive when useful/value-added products are generated at the same time. N_2O is thermodynamically unstable ($\Delta H_f = +82\ \mathrm{kJ\,mol^{-1}}$) but kinetically inert.[3] Heterogeneous catalysts can decompose N_2O into nitrogen and oxygen[1b,4] or enable the oxidation of hydrocarbons under harsh conditions.[1c,5]

The use of oxygen as an oxygenating agent is often difficult to control, and it forms explosive mixtures with a wide range of organic reagents and solvents.[6] N_2O would be an attractive alternative but has been considered to be rather unreactive and a poor ligand[7a] although the formation of metal oxo species has been established.[7] In rare cases, cleavage of the N–N bond occurs.[8] The insertion of the oxygen atom of N_2O into a metal–carbon[9] or a metal–hydride bond,[10] yielding alkoxy, aryloxy, or hydroxy complexes, has been reported. Under homogeneous conditions, only few metal complexes catalyze reactions that employ N_2O as the oxygenation reagent.[11]

Rhodium(I) amido bis(olefin) complexes are efficient transfer hydrogenation catalysts[12b] and catalyze dehydrogenative coupling (DHC) reactions between primary alcohols and water, methanol, ammonia, or amines.[12c] Mixtures of aldehydes and primary amines or ammonia are also converted into amides with excellent efficiency while the formation of imines is avoided.[12d] Metal–ligand cooperativity between the rhodium center and the amido moiety is responsible for the high activity of these catalysts. A serious drawback of these reactions is the use of hydrogen acceptors.[12b,d] Milstein and others have developed remarkably efficient homogeneously catalyzed DHC reactions without acceptors.[13] However, these transformations require elevated temperatures, and the search for catalytic systems that enable the use of inexpensive hydrogen acceptors that allow for an easy work-up of the reaction mixtures remains attractive. Unactivated olefins can be used as hydrogen acceptors in the presence of palladium nanoparticles supported on silica as a co-catalyst.[14a] Oxygen from the air can also serve as a hydrogen acceptor in the dehydrogenative coupling of primary alcohols with water.[14b] However, in this case, an oxygen acceptor is necessary as only one oxygen atom is transferred to the substrate molecule. Herein, we report our results on using N_2O as a convenient hydrogen acceptor for the efficient dehydrogenative coupling (DHC) of alcohols under mild conditions.

Benzyl alcohol was fully converted into its coupling product benzyl benzoate in the presence of 1 mol% of [Rh(TMIY)(trop$_2$NH)][OTf] (**1**;[14b] TMIY = 1,3,4,5-tetramethylimidazole-2-ylidene, OTf = trifluoromethanesulfonate; Scheme 1), N_2O as the hydrogen acceptor, and activated 4 Å molecular sieves. The optimized conditions for the formation of esters are referred to as anhydrous "conditions 1". During optimization (see the Supporting Information), we observed that 1) other Rh^{I} complexes are not as efficient as complex **1** (see below), 2) the yield of the reaction was sensitive to the solvent mixture, and 3) the amount of molecular sieves had a great influence on the yield. The absence of molecular sieves and the use of non-activated sieves or other Lewis acids, such as SiO_2, Al_2O_3, TiO_2, $ZnCl_2$, or anhydrous $CeCl_3$, led to low conversions. When either the catalyst loading was reduced to 0.5 mol% or the substrate loading doubled under otherwise identical conditions 1, the conversion dropped below 50%. These results suggest that a precise amount of activated molecular sieves as a water trapping agent is needed (1.2 g per mmol of substrate).

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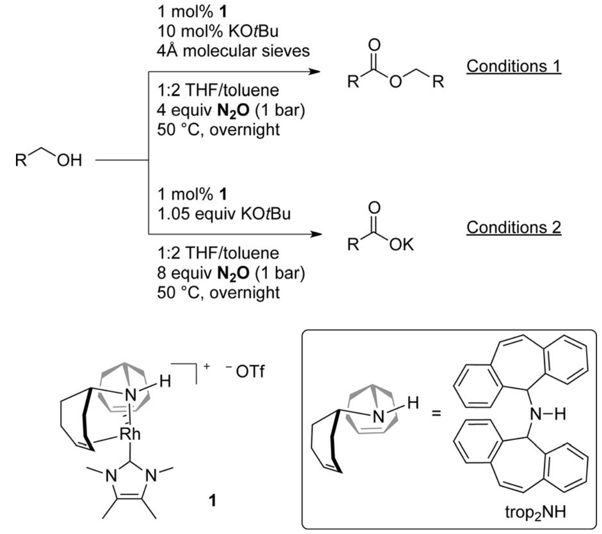
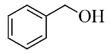
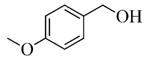
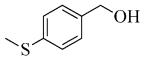
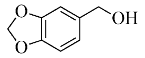
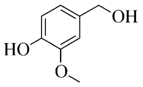
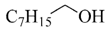
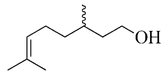
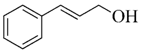
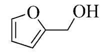
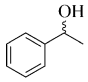


Scheme 1. The two optimized procedures for the formation of esters (conditions 1, top) and carboxylates (conditions 2, bottom) from primary alcohols by dehydrogenative coupling reactions with N_2O as the hydrogen acceptor.

Furthermore, these results indicate that **1** may be an efficient catalyst for the conversion of alcohols into carboxylates in the presence of water and base and N_2O as the hydrogen acceptor. This is indeed the case. Attempts to optimize the reaction led to the following observations: 1) Large amounts of base are disadvantageous, and 1.05 equivalents of KO*t*Bu are optimal, and 2) an excess of N_2O (ca. 8 equiv) is needed to convert benzyl alcohol into benzoic acid in high yield (for details see the Supporting Information). These conditions are referred to as "conditions 2". Under both conditions 1 and 2, N_2 was detected within the reaction vessel by GC-MS analysis. No conversion was observed in the absence of N_2O.

A variety of primary alcohols were converted into either their esters (conditions 1) or carboxylates (conditions 2; see Table 1). Benzyl alcohols were converted into their benzoic acid derivatives in very good to excellent yields (entries 1–4). No poisoning of the catalyst or oxidation of the sulfur center was observed when 4-(methylthio)phenylmethanol was converted into the corresponding ester or benzoic acid (entry 3). Only the conversion of 4-hydroxy-3-methoxybenzyl alcohol into its ester proceeded with a yield $<60\%$ (entry 5). Aliphatic alcohols were converted into the corresponding esters and acids in high yields (entries 6 and 7), and an unsaturated C=C bond remote from the hydroxy functional group was tolerated. With cinnamyl alcohol as the substrate, product mixtures of the unsaturated and saturated esters or acids were obtained (entry 8). This observation is consistent with our previous finding that activated C=C bonds in conjugation with a carbonyl group, such as in methyl methacrylate, can be used as hydrogen acceptors.[12b] A secondary alcohol such as 1-phenyl ethanol (entry 10) was also cleanly dehydrogenated to acetophenone under conditions 1, but only traces of the ketone were formed with stoichiometric amounts of base (entry 10, conditions 2). No molecular sieves needed to be added to obtain high yields of the ketone because it is the final product.

Table 1: Dehydrogenative coupling reactions of various alcohols with N_2O as the hydrogen acceptor.

Entry	Alcohol	Ester[a] [%]	Carboxylic acid[b] [%]
1		98	96
2		86[c]	98
3		85[c]	87
4		84[c]	91
5		54[d]	83[d]
6		89	92
7		92	92
8		92[e]	37[f]
9		90	43
10		97[g,h]	6[g]

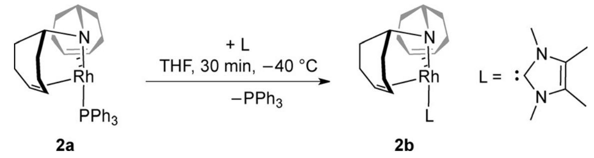
[a] Conditions 1 and 1.25 mmol of the substrate in 5 mL THF/10 mL toluene. [b] Conditions 2 and 0.625 mmol of the substrate in 2.5 mL THF/5 mL toluene, followed by acidic work-up. [c] The corresponding aldehyde side products were formed in yields of 12, 3, and 4% (entries 2, 3, and 4, respectively). [d] The aldehyde vanillin was formed as the only side product. [e] 3-Phenylpropyl cinnamate formed in 7% yield. [f] A 7:3 mixture of 3-phenylpropanoic acid and cinnamic acid was obtained. [g] The corresponding ketone was formed. [h] Conditions 2 and 0.625 mmol of the substrate, 10 mol% KO*t*Bu, 2.5 mL THF/5 mL toluene.

In previous work, the formation of aldehyde intermediates by initial dehydrogenation of the alcohol could not be directly observed.[12b,d] Here, the aldehydes were detected in reactions with electron-rich benzyl alcohols and even isolated as secondary products in up to 12% yield (entries 2–4). With very electron-rich 4-(hydroxymethyl)-2-methoxyphenol, in particular, vanillin was isolated as a secondary product under conditions 1 and 2 (entry 5). With benzyl alcohol, in situ GC analysis of the reaction mixture revealed the formation of benzaldehyde.

Attempts to use the phosphane complex $[Rh(PPh_3)(trop_2NH)][OTf]$ instead of carbene complex **1** resulted in slower conversion of benzyl alcohol, and a 1:10 mixture of benzaldehyde and benzyl benzoate was obtained. Rearrangement to a complex with the PPh_3 ligand in an equatorial position of the trigonal bipyramidal structure was observed; such species are known to be catalytically inactive.[12a–c] Furthermore, triphenylphosphine oxide was detected by ^{31}P NMR spectroscopy, indicating catalyst decomposition. Therefore, the use of the more strongly bound and not readily oxidized NHC moiety as an axial ligand is necessary for efficient catalysis.

We performed stoichiometric experiments to gain insight into the reaction mechanism. The amido phosphane complex

[Rh(PPh$_3$)(trop$_2$N)] (**2a**)[14c] was used to synthesize the amido carbene complex [Rh(TMIY)(trop$_2$N)] (**2b**), which was obtained as green crystals in good yield by ligand exchange (91%, Scheme 2). Compound **2b** was analyzed by single-crystal X-ray diffraction and shown to have a typical butterfly-type structure (Figure 1).[12] The Rh−N(1) bond [2.046(4) Å] is significantly shorter than the Rh−N bond in amino complex **1** [2.131(4) Å], which is consistent with the formation of an amide.



Scheme 2. Formation of the amido carbene rhodium complex **2b**.

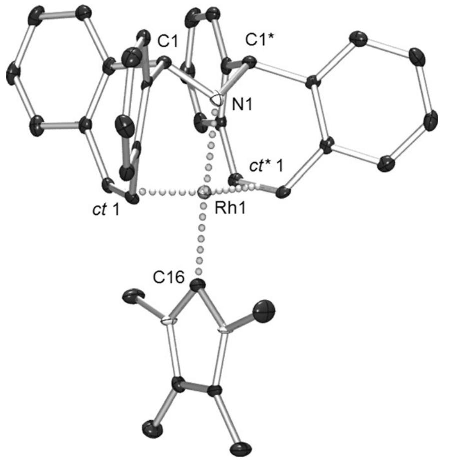
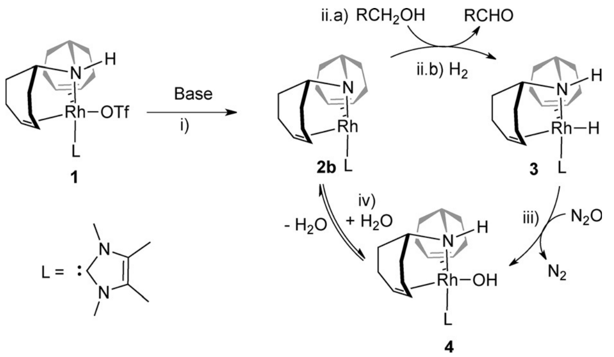


Figure 1. X-ray crystal structure of [Rh(TMIY)(trop$_2$N)] (**2b**). Ellipsoids set at 50% probability. Hydrogen atoms removed for clarity. The crystallographic parameters are given in the Supporting Information.

Amide complex **2b** is the active catalyst and reacts with either primary alcohols (Scheme 3, ii.a) or dihydrogen (ii.b) to generate the amino hydride species **3**.[14b] The reactive Rh−N bond in **2b** also enables the addition of H_2O to form amino hydroxy rhodium complex **4** (iv). As in the corresponding amido phosphane complex [Rh(trop$_2$N)(PPh$_3$)] (**2a**),[14c] this addition is reversible, and under vacuum, complex **4** releases H_2O, thus regenerating **2b**. Exposure of an anhydrous [D$_8$]THF solution of amino hydride **3** to an atmosphere of N_2O generated **2b** and water (Scheme 3, iii). However, complex **4** was quantitatively formed instead of **2b** when an excess of degassed water was present prior to addition of N_2O (Scheme 3, iii; see also the Supporting Information). When **2b** was exposed to a mixture of N_2O/H_2 at 50 °C, N_2 was detected by GC-MS analysis of the reaction atmosphere (see the Supporting Information). This experiment indicates that **2b** efficiently catalyzes the reaction of N_2O and H_2 to H_2O and N_2 ($\Delta_f H^o = -321.85$ kJ mol^{-1}).[3]

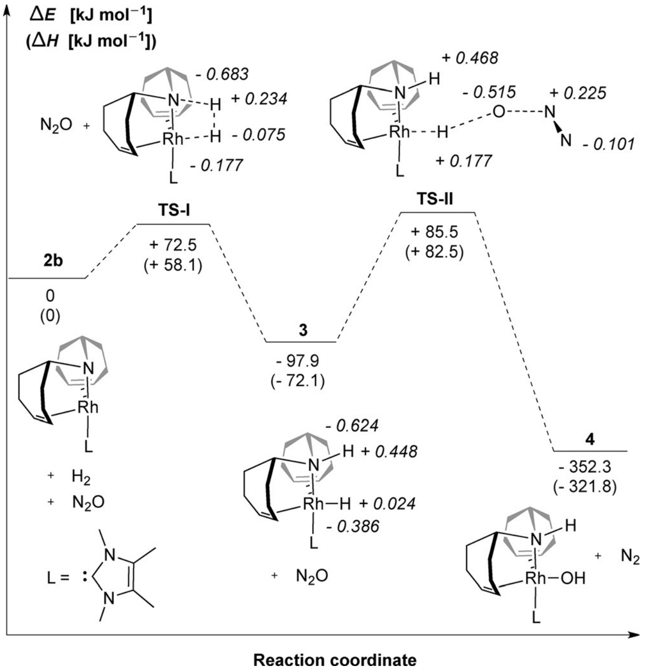
Based on previous investigations,[12,14] we propose the mechanism presented in Scheme 3: i) The active amido complex **2b** is generated by reaction of the stable precatalyst **1** with a Brønsted base. ii) The 16-electron species **2b** enables alcohol dehydrogenation and forms the 18-electron amino hydride complex **3**. iii) N_2O transfers its oxygen atom to the metal center, which results in the formation of amino hydroxy species **4**. iv) In the final step, the active catalyst **2b** is regenerated upon release of H_2O, which is trapped by molecular sieves (conditions 1) or KO*t*Bu (conditions 2).



Scheme 3. Proposed mechanism for the dehydrogenative coupling of alcohols with N_2O as the hydrogen acceptor.

To further confirm the proposed mechanism, we turned to quantum-chemical calculations. Our group previously reported extensive DFT studies of the mechanism of alcohol dehydrogenation with Rh^I amide species leading to complexes of type **3**.[12b,c] Here, the role of the catalyst was investigated for the simpler model reaction $N_2O+H_2 \rightarrow H_2O+N_2$ (see Scheme 4 and the Supporting Information for a complete discussion). We carried out density functional theory (DFT) calculations employing the PBE0 hybrid functional with a large triple-zeta TZVPP basis set. As found previously for **2a**,[12a] the heterolytic splitting of H_2 across the Rh−N bond of **2b** is exothermic by −98 kJ mol^{-1} (−72 kJ mol^{-1}) and proceeds in a single step with a barrier of +73 kJ mol^{-1} (+58 kJ mol^{-1}) to give the Rh^I amino hydride complex **3** (reported are electronic-energy differences, ΔE, and, in parentheses, enthalpy differences, ΔH, at 323.15 K; see Scheme 4). All attempts to find a stable complex between N_2O and **3** failed. Even for an energetically high-lying conformation of complex **3**, in which the N-heterocyclic carbene ligand is moved between two phenyl rings of the chelating trop$_2$N ligand, an N_2O-bound intermediate was not found. Instead, we were able to locate an activated complex, **TS-II**, as the transition state at +86 kJ mol^{-1} (+83 kJ mol^{-1}) in which the N_2O molecule interacts with the hydride bound to the rhodium center.[15]

An intrinsic reaction coordinate (IRC) calculation confirmed that this transition state connects the two reaction valleys of **3** and **4**. In a strongly exothermic reaction, **TS-II** decomposes to the hydroxide complex **4** and N_2 ($\Delta E = -352$ kJ mol^{-1} and $\Delta H = -322$ kJ mol^{-1}). In this process, the oxygen atom of N_2O is inserted into the Rh−H bond under simultaneous loss of N_2. The release of water from **4** to give amido complex **2b** closes the catalytic cycle and is slightly endothermic by +55 kJ mol^{-1} (+40 kJ mol^{-1}). This finding is in agreement with the experimental observation that water



Scheme 4. PBE0/TZVPP electronic-energy differences (in kJ mol^{-1}) and enthalpy differences at 323.15 K (in parentheses, in kJ mol^{-1}) for H_2 heterolytic addition and the activation and splitting of N_2O at rhodium complex **2b**. NBO charges for the Rh and N atoms and H_2 and N_2O molecules in **TS-I**, **3**, and **TS-II** are given in italics.

needs to be removed either by molecular sieves (conditions 1) or chemically as a coupling product (conditions 2) for efficient catalysis. Thus far, we have deliberately neglected dispersion corrections as we did not model the solvent environment of all structures and therefore would neglect dispersion interactions with solvent molecules. However, we carried out such calculations (see Table S6). The reaction from **2b** to **3** would be favored by about -16 kJ mol^{-1} because of dispersion, and the barrier height to transition state **TS-II** would decrease by about -15 kJ mol^{-1} (see the Supporting Information). Whereas these changes in energy are on the order of 10%, the final exothermic step that produces complex **4** is hardly affected by dispersion corrections ($+6$ kJ mol^{-1}).

In conclusion, a robust rhodium(I) carbene complex with a cooperative bis(olefin)amino/amido ligand catalyzes the dehydrogenation of alcohols with N_2O as the hydrogen acceptor under mild conditions and low catalyst loadings. Calculations indicate that N_2O is activated in the second coordination sphere of the metal center, which is a barely studied phenomenon. As only water and N_2 are formed as by-products, the reaction mixtures can be conveniently worked up. The results given here may also inspire the development of efficient catalytic systems for the decomposition of the greenhouse gas N_2O.

Experimental Section

Computational details: The PBE0 density functional was chosen for DFT calculations because it performs well in benchmark calculations on ligand binding energies.[16] All PBE0[17a] structure optimizations were performed with the program TURBOMOLE Version 6.3.1 with a valence triple-zeta plus polarization TZVPP[17b] basis set. Vibrational analyses and zero-point vibrational energy (ZPVE) corrections were calculated with TURBOMOLE (see the Supporting Information). The initial transition-state search and the NBO analysis were performed using the program Gaussian09[18a] with the B3PW91[18b] functional and a lanl2dz[18c] basis set. The transition-state structures were then further optimized with PBE0/TZVPP and subjected to a frequency calculation in TURBOMOLE. All transition states show only one negative eigenvalue of the Hessian, and the corresponding normal mode corresponds to the reaction coordinate for either the H_2 splitting and addition to the complex or N_2O splitting and addition to the hydride complex, respectively. IRC calculations for both transition states were performed with Gaussian09 to show that the proper reactant valleys are connected.[18] Grimme D3[19] dispersion corrections were considered in PBE0-D3/TZVPP structure optimizations to obtain an estimate for these effects.

Acknowledgements

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