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PAPER

Nitrosobenzene as a hydrogen acceptor in rhodium catalysed dehydrogenation reactions of alcohols: synthesis of aldehydes and azoxybenzenes†

Samuel P. Annen and Hansjörg Grützmacher*

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Acids, esters and amides have to date been the only isolated products from the dehydrogenation of primary alcohols with [Rh(trop$_2$N)(L)] (trop = 5-*H*-dibenzo[*a*,*d*]cyclohepten-5yl) type complexes. With the reported method the available product family is finally to aldehydes. Using nitrosobenzene as a hydrogen acceptor the aldehydes could be isolated in up to 96% yield with substrate to catalyst ratios of up to 1000. Nitrosobenzene was found to be reductively coupled to azoxybenzene under the reaction conditions. Several symmetrically substituted azoxybenzene derivatives could be isolated in generally high yields after 2 to 4 h reaction time using a low catalyst loading.

Introduction

We reported the very efficient transfer hydrogenation catalyst[1] [Rh(trop$_2$N)(PPh$_3$)] **1** (trop = 5-*H*-dibenzo[*a*,*d*]cyclohepten-5yl) to also catalyse the dehydrogenative coupling reactions (DHC's) of primary alcohols with water, methanol and amines yielding the corresponding acids, methyl esters and amides.[2] This reaction requires the use of a hydrogen acceptor such as cyclohexanone or methyl methacrylate (MMA) in excess which lowers the atom efficiency of this reaction. Therefore we focused our research on alternative hydrogen acceptors. By exchanging the triphenylphosphane ligand with the carbene ligand 1,3,4,5-tetramethylimidazole-2-ylidene, oxygen from air[3] and nitrous oxide[4] could be used successfully as hydrogen acceptors. Under these conditions, primary alcohols were cleanly converted to the corresponding acids or esters under aqueous or anhydrous conditions, respectively. The modified *N*-heterocyclic carbene (NHC) complex [Rh(trop$_2$N)(NHC)] is less active than the phosphane catalyst and a higher catalyst loading is necessary to achieve complete conversion. But the catalytic system is very robust and can be used in several subsequent runs without significant loss of activity and fairly high turnover numbers can be achieved. Computations[2] suggest that the catalytic dehydrogenative coupling of a primary alcohol, R–CH$_2$–OH, with HX (X = OH, OMe, NHR′) in the presence of a hydrogen acceptor A proceeds step wise according to:

$$\text{R–CH}_2\text{–OH} + \mathbf{A} \rightarrow \text{R–CH=O} + \mathbf{A}\text{H}_2 \qquad (1)$$

Department of Chemistry and Applied Biosciences ETH Zürich, Laboratory of Inorganic Chemistry, Wolfgang Pauli Str. 10, CH-8093 Zürich, Switzerland. E-mail: gruetzmacher@inorg.chem.ethz.ch

† Dedicated to Professor David Cole-Hamilton on the occasion of his retirement and for his outstanding contribution to transition metal catalysis.

$$\text{R–CH=O} + \text{HX} + \mathbf{A} \rightarrow \text{RC(=O)X} + \mathbf{A}\text{H}_2 \qquad (2)$$

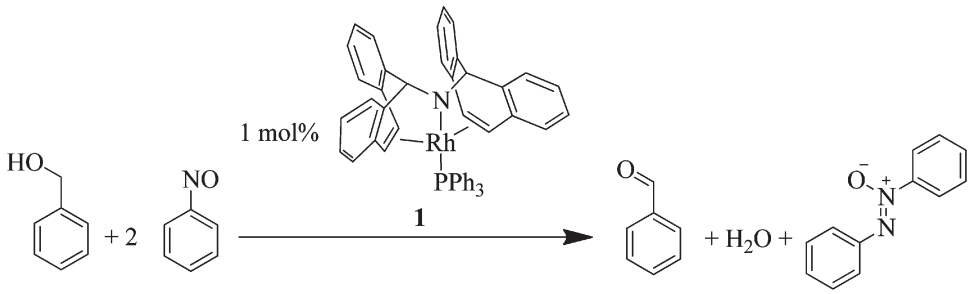
If this scheme is correct, aldehydes must be intermediates which are formed in an alcohol dehydrogenation reaction promoted by **1**. In an attempt to find (a) reaction conditions which allow the isolation of aldehydes as reaction products of a catalytic dehydrogenation reaction and (b) to extend the range of possible hydrogen acceptors, we studied the reaction of primary alcohols with nitrosobenzene.

Nitrosobenzene is a versatile reagent which undergoes a large variety of reactions.[5] Among them, specifically reactions with metal complexes[6] and its facile reduction by many reagents,[5a] such as diborane and trialkylborane,[7] hydrazine derivatives,[8] NADH, NADPH[9] and metal hydride[10] as well as its facile hydrogenation[11] make it a promising candidate as an alternative hydrogen acceptor.

Results and discussion

Preliminary experiments were performed using 1 mol% of the deep green and air-sensitive Rh^{I} amido bis olefin complex [Rh(trop$_2$N)(PPh$_3$)] **1**, benzyl alcohol and 1.5 equiv. of nitrosobenzene. Almost 75% of benzyl alcohol were converted to benzaldehyde whereas the nitrosobenzene was fully converted to azoxybenzene as confirmed by GC-MS. Azoxybenzene, Ph–N=N(O)–Ph, cannot be used as a hydrogen acceptor and its conversion to form azobenzene, Ph–N=N–Ph, and water failed. On the other hand if 2.1 equiv. of nitrosobenzene were used, benzyl alcohol was fully converted to benzaldehyde.

Samples of this reaction were taken after different reaction times and analysed by GC. It was found that per equivalent of formed benzaldehyde, two equivalents of nitrosobenzene were consumed giving one equivalent of azoxybenzene as a final product (Scheme 1).



Scheme 1 Rhodium catalysed dehydrogenation of benzyl alcohol to benzaldehyde using nitrosobenzene as a hydrogen acceptor.

In order to simplify the reaction conditions, we used the cationic air-stable orange complex [Rh(trop$_2$NH)(PPh$_3$)]OTf **2** as a catalyst precursor which together with K_2CO_3 completely converted benzyl alcohol to the aldehyde. Here K_2CO_3 acts as a heterogeneous base and converts **2** into the active catalyst **1** [eqn (3); see also Scheme 2 below]:

$$[\mathrm{Rh}\ (\mathrm{trop_2NH})(\mathrm{PPh_3})]\mathrm{OTf}\ (\mathbf{2}) + \mathrm{K_2CO_3} \rightarrow [\mathrm{Rh}(\mathrm{trop_2N})(\mathrm{PPh_3})]\ (\mathbf{1}) + \mathrm{KOTf} + \mathrm{KHCO_3} \quad (3)$$

In the next step, we tested this catalytic system with other alcohols as substrates and lower catalyst loadings (0.1 mol%) (Table 1).

The catalytic protocol worked best when applied to benzyl alcohol and benzyl alcohol derivatives with electron donating substituents. With low catalyst loading these substrates were smoothly converted in high yields to the corresponding benzaldehyde derivatives. 4-(Methylthio)phenyl methanol (entry 5) needed a higher catalyst loading but could also be quantitatively converted to 4-methylthiobenzaldehyde. Likely the thioether function competes with the substrate in binding to the metal catalyst thereby reducing its activity.

Also allylic alcohol derivatives, like furfuryl alcohol (entry 7), geraniol (entry 10), and the secondary alcohol 1-phenyl ethanol (entry 12) could be converted to the corresponding aldehydes in acceptable to high yields although a higher catalyst loading was needed.

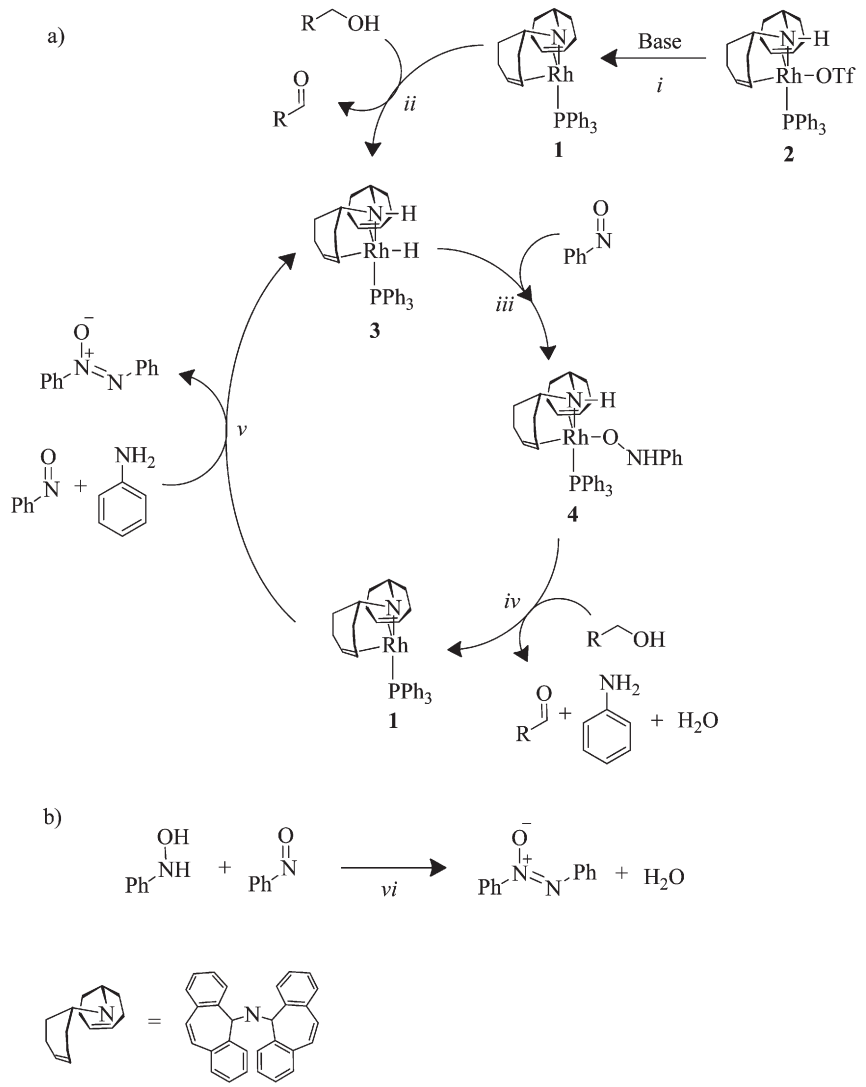
On the other hand, benzyl alcohol substrates with an electron withdrawing group in the aromatic ring were converted to the corresponding aldehydes in rather low yields (about 20%). The conversion of aliphatic alcohols is very low and even with catalyst loading up to 5 mol% only 5% conversion of 1-octanol to octanal was reached. In the reaction mixture, 95% of the non-converted educt were detected while ^{31}P NMR spectra indicated decomposition of the catalyst (see also discussion below). As shown in the last entry in Table 1, also secondary alcohols are catalytically converted to the corresponding ketones. This reaction was not investigated any further at this point.

This is the first time that we observe the clean formation of aldehydes as products when primary alcohols are reacted with [Rh(trop$_2$N)(L)] as dehydrogenation catalysts. So far the aldehyde, assumed to be the primary intermediate of the dehydrogenation reaction, was irreversibly coupled with water, alcohols or amines to the corresponding acids, esters or amides.[2–4] The only exception we observed was with the electron rich alcohol 4-(hydroxymethyl)-2-methoxyphenol (entry 8) which was also converted to the aldehyde under the previously applied reaction conditions with cyclohexanone or MMA as a hydrogen acceptor.[2–4] In this case, likely the aromatic hydroxyl group is deprotonated and the corresponding phenolate lowers the electrophilicity of the carbonyl atom of the aldehyde group in the *para*-position to such an extent that the conversion to the hemiacetal followed by a second dehydrogenation to the carboxylic acid derivative does not take place.

We turned our attention to the formation of azoxybenzene which is the other product in the catalytic reaction discussed above. Azoxyarenes bearing alkyl- or alkoxy-substituents in the *p*,*p*′-position exhibit interesting properties as liquid crystals.[12–16] This type of compound is usually prepared by oxidation of anilines with hydrogen peroxide under harsh conditions.[17,18] If different substituents on the phenyl ring are required they can be prepared by the condensation of the corresponding *N*-arylhydroxylamines and nitrosoarenes.[19] A series of *p*-substituted nitrosobenzenes were synthesized and reacted in an ethanol–THF mixture as a solvent using 0.1 mol% of the catalyst precursor [Rh(trop$_2$NH)(PPh$_3$)]OTf **2**. Under these conditions, ethanol which is present in a large excess serves as a hydrogen donor and is converted to acetaldehyde. Whereas THF was added to improve the solubility of the nitrosobenzene derivatives.

As shown in Table 2 the azoxybenzene derivatives were formed in high yields (>90%) after a reaction time of 2–4 h. The only exception is the 4-methyl ester substituted nitrosobenzene derivative (entry 7) which was converted in moderate yield (about 70%) to the corresponding azoxybenzene compound.

It may seem inconsistent that the reductive coupling reaction of nitrosoarenes to symmetric azoxyarenes using ethanol as a reductant (hydrogen donor) proceeds especially smoothly, whilst alkyl alcohols are inefficiently converted to the corresponding aldehydes (see the poor conversion of 1-octanol to octanal in Table 1, entry 9). Note however that the coupling of the nitroso derivatives proceeds in the presence of a large excess of ethanol which acts as a co-solvent in this catalytic system. Indeed, when 1-octanol was employed in excess as a hydrogen donor (5 equiv. with respect to nitrosobenzene) with a 0.5 mol% catalyst loading, nitrosobenzene is completely converted to azoxybenzene (Table 2, entry 2). As explanation for this observation we assume that in the presence of larger amounts of alcohol the equilibrium (4) lies far to the side of the Rh(I) hydride complex **3** which is not decomposed to catalytically inactive species (*vide infra*).



Scheme 2 (a) Proposed catalytic cycle for the dehydrogenation of alcohols and formation of azoxybenzene based on individually performed reaction steps *i*–*v*. (b) It cannot be excluded that azoxybenzene is also produced by a simple non-catalysed condensation reaction between *N*-phenyl hydroxylamine and nitrosobenzene.

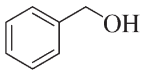
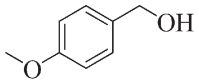
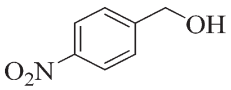
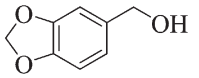
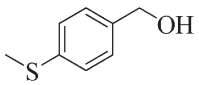
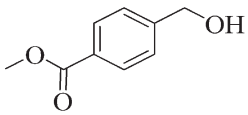
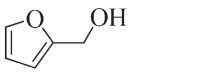
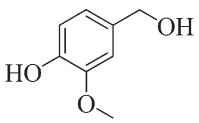
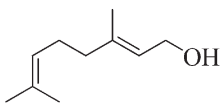
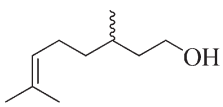
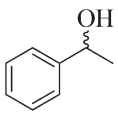
$$[Rh(trop_2N)(PPh_3)]\ (\mathbf{1}) + RCH_2OH \rightleftarrows [Rh(H)(trop_2NH(PPh_3)]\ (\mathbf{3}) + RCHO \quad (4)$$

The amido complex [Rh(trop$_2$N)(PPh$_3$)] (**1**), however, is sensitive and addition of nitrosobenzene leads to irreversible decomposition and deactivation of the catalyst *via* phosphane oxidation. Also the product azoxybenzene reacts with the amide [Rh(trop$_2$N)(PPh$_3$)] (**1**). A new penta-coordinated complex [Rh(trop$_2$N)(*eq*-PPh$_3$)(*ax*-PhN═N(O)Ph)] is formed instantaneously in which the triphenylphosphane ligand occupies the equatorial position (indicated by the low frequency of the ^{31}P resonance $\delta = 7.9$ ppm and a small $^1J(^{103}Rh^{31}P) = 118.8$ Hz) and azoxybenzene an axial position in a trigonal bipyramidal structure. We could not isolate this complex in pure form and determine its structure in detail but the gross structural features are clearly indicated by NMR studies. Note that the adduct between **1** and azoxybenzene can be used as a catalyst precursor which suggests that binding of azoxybenzene is reversible. When this sample was left at room temperature for sometime, the oxygen atom from azoxybenzene is transferred to the phosphane ligand forming triphenylphosphane oxide, azobenzene and further products which we did not identify. Consequently, the concentration of free Rh(I) amide should be as small as possible in order to produce a sustainable catalytic system which can be achieved with high alcohol concentrations. Under these conditions, the amide **1** is rapidly converted to the amino hydride complex **3** which is part of the catalytic cycle.

To demonstrate this, a number of separate stoichiometric experiments were performed which are summarized in Scheme 2, steps *iii*–*v*.

First, the hydride complex **3** was reacted with one equivalent of nitrosobenzene (Scheme 2, step *iii*). In a fast reaction, a new complex **4** was formed which precipitated from the reaction mixture and was isolated by filtration. The same complex **4** was also obtained by the reaction of the amide complex **1** with *N*-phenyl hydroxylamine. Based on NMR studies, **4** is identified

Table 1 Isolated yields for various alcohols dehydrogenated by [Rh(trop$_2$NH)(PPh$_3$)]OTf (**2**) and base using nitrosobenzene as a hydrogen acceptor

Entry	Alcohol	*S*/*C*	Yield[a]
1		1000	91%
2		1000	96%
3		200	23%
4		1000	93%
5		200	97%
6		200	37%
7		200	52%
8		1000	93%
9		200	5%[b]
10		200	97%
11		200	11%[b]
12		200	61%[c]

[a] Conditions for *S*/*C* = 1000: 2.50 mmol alcohol, 5.12 mmol nitrosobenzene, 2.5 μmol [Rh(trop$_2$NH)(PPh$_3$)]OTf (**2**), 0.125 mmol K_2CO_3, 5 mL THF, RT, stirred overnight; conditions for *S*/*C* = 200: 1.25 mmol alcohol, 2.56 mmol nitrosobenzene, 6.0 μmol **2**, 60 μmol K_2CO_3, 2.5 mL THF, RT, stirred overnight. [b] Conversion determined by GC as given by the ratio of aldehyde to not reacted alcohol. [c] *t*-BuOK was used as a base instead of K_2CO_3.

Table 2 Results of the transfer hydrogenative coupling of nitrosobenzene derivatives to symmetric azoxyarene

Entry	*p*-Substituent	Yield[a]
1	H	97%
2	H	99.7%[b]
3	Me	95%
4	OMe	92%
5	F	98%
6	Cl	93%[c]
7	CO_2Me	69%[c]

[a] Conditions: 2.19 mmol substrate, 2.2 μmol [Rh(trop$_2$NH)(PPh$_3$)]OTf (**2**), 0.11 mmol K_2CO_3, 2 mL ethanol, 1 mL THF, RT, 2 h reaction time. [b] 1-Octanol as a hydrogen donor; conditions: 0.48 mmol nitrosobenzene, 2.4 μmol **2**, 0.38 mL 1-octanol, 0.12 mmol K_2CO_3, 2 mL THF, RT, 2 h reaction time, conversion determined by GC. [c] 4 h reaction time.

as the penta-coordinated [Rh(ONHPh)(trop$_2$NH)(PPh$_3$)]. The signal of the ^{103}Rh-NMR differs less than 30 ppm compared to the known hydroxo complex [Rh(OH)(trop$_2$NH)(PPh$_3$)],[20] thus indicating a similar coordination sphere for **4** with an oxygen donor as a fifth ligand in the equatorial position and the phosphane in the axial position of a trigonal bipyramid (indicated by a high frequency shifted ^{31}P resonance δ = 43.1 ppm and a larger $^1J(^{103}Rh^{31}P)$ = 135 Hz). In the ^{1}H-NMR two distinct signals (8.20 ppm and 8.35 ppm) for the *ortho*-protons of the phenyl group from *N*-phenyl hydroxylamine were found indicating that the rotation of the phenyl ring is frozen on the NMR time scale. The ^{13}C-NMR confirmed this finding and six distinct signals (122.8, 125.9, 129.1, 129.2, 130.0 and 132.0 ppm) for the same phenyl ring are observed. These results indicate that the amino hydride complex **3** transfers hydrogen to nitrosobenzene indeed to give *N*-phenyl hydroxylamine and the amide complex **1**. Subsequently, the hydroxyl amine adds across the Rh–N bond of **1** to give **4**.

The hydroxylamine complex **4** reacts with excess of a primary alcohol to the amine hydride complex **3** and aniline which was unequivocally identified.[21] This reaction (Scheme 2, step *iv*) is relatively slow and requires several minutes. Remarkably in the presence of the amide complex **1**, aniline reacts rapidly with nitrosobenzene to azoxybenzene (Scheme 2, step *v*). To our knowledge, this is the first time azoxybenzene instead of azobenzene is produced from aniline and nitrosobenzene.

In Scheme 2, we combined these individual reactions to propose a catalytic cycle which is also consistent with earlier findings and computations for transfer hydrogenations[1] promoted by [Rh(trop$_2$N)(L)] complexes as catalysts. In the first step (*i*), the catalyst precursor **2** is deprotonated to the catalytically active amido complex [Rh(trop$_2$N)(PPh$_3$)] (**1**) which in step (*ii*) dehydrogenates the alcohol to the aldehyde compound forming the amine hydride complex **3** (which was isolated and fully characterised including an X-ray diffraction study).[1–3,22] The hydride complex **3** transfers hydrogen to nitrosobenzene in step (*iii*) to give *N*-phenyl hydroxylamine which immediately reacts with the Rh(I) amide [Rh(trop$_2$N)(PPh$_3$)] to [Rh(ONHPh)(trop$_2$NH)(PPh$_3$)] **4**. In step (*iv*), **4** reacts slowly with alcohol to aniline, aldehyde, and water. Finally in step (*v*), aniline reacts with nitrosobenzene in the presence of Rh(I) amide **1** in a fast reaction to azoxybenzene; **1** is converted to the amino hydride complex **3**. Because we could detect free *N*-phenyl hydroxylamine in reactions under catalytic conditions, we do not exclude that azoxybenzene is partly formed in a non-metal catalysed condensation reaction (*vi*).

The formation of aldehydes and the absence of carboxylates as dehydrogenative coupling products between aldehydes and water[2,20] can be explained as follows: (a) water formed in reactions (*iv*) and eventually (*vi*) is present in very small amounts only and moreover captured by heterogeneously suspended

K_2CO_3. (b) The equilibrium concentration of the Rh(I) amide complex is always very low because it is intercepted by alcohol or *N*-phenyl hydroxylamine to give **3** or **4**, respectively. This prevents water addition across the Rh–N bond in amide **1** to give the hydroxyl complex [Rh(OH)(trop$_2$NH)(PPh$_3$)] which is the active species to convert aldehydes to the corresponding semiacetals and then further to carboxylates.[20] Indeed, even when 10 equiv. of water are added to a mixture of benzyl alcohol and nitrosobenzene, benzaldehyde remains the main product while benzoate is formed in about 30% only. (c) Note that under the reaction conditions, aniline is not dehydrogenatively coupled with aldehydes to amides as previously observed for primary alkyl amines[1–3] but is irreversibly and rapidly converted to azoxybenzene.

Conclusion

A catalytic system could be successfully developed which allows the efficient dehydrogenation of activated alcohols to the corresponding aldehydes using a Rh(I) amido olefin complex as a catalyst (0.1 mol%) and nitrosobenzene as a hydrogen acceptor. Although not all steps involved in this reaction are fully understood, a simplified mechanism for the formation of aldehydes can be proposed while the formation of carboxylic acid derivatives is suppressed. As such, this reaction complements the previously reported protocols with [Rh(trop$_2$N)(L)] catalysts leading exactly to these products, that is carboxylic acids, esters and amides.[2–4] The findings reported here imply that also in these reactions aldehydes are formed as primary intermediates [see eqn (4)] which are subsequently dehydrogenatively coupled to a carboxylic acid derivative in an irreversible reaction. In the reactions we report here, a nitrosoarene as a hydrogen acceptor is first converted to an *N*-arylhydroxylamine. Under the catalytic conditions, this reacts further with a molecule of alcohol to give an aniline derivative and aldehyde. The exact mechanism of this reaction is not known yet. With ethanol as a cheap and readily available "reductant" (hydrogen donor), this catalytic reaction can be used to prepare azoxyarenes in very good yields. Such a catalytic dehydrogenative coupling reaction under the formation of N–N bonds is to our knowledge a new reaction and as such might be useful for the preparation of functionalized azoxyarenes under very mild conditions or inspires further catalysed coupling reactions. Future work will focus also on more robust – phosphane-free – catalysts – ideally with cheap non-noble metals – which shall allow the efficient conversion of also alkyl alcohols to the corresponding alkyl aldehydes and/or the syntheses of unsymmetrical azoxyarenes.

Experimental section

General comments

All experiments were performed under an inert atmosphere of Ar using standard Schlenk and vacuum-line techniques or in a Braun glove box. Glassware was flame dried under high vacuum or dried at 120 °C overnight prior to use. All reagents were used as received from commercial suppliers unless otherwise stated. Solvents were distilled under argon from sodium–benzophenone (THF) and sodium/diethyl phthalate (ethanol) and stored over 3 Å molecular sieves. Deuterated solvents were purchased from *Eurisotop*, degassed and distilled from the proper drying agent, and stored over 3 Å molecular sieves.

Standard chemicals were purchased from *ABCR*, *Acros*, *Fluka*, and *Sigma-Aldrich*; $RhCl_3$ was provided by *STREM*. Argon and helium gas were purchased from *PanGas*. Argon was further purified with an *MBraun* 100 HP gas-purification system. Chemicals used for catalysis were distilled if possible otherwise used as received. The following organic and metal–organic compounds were synthesized according to known literature procedures: *p*-substituted nitrosobenzene derivates,[22] [RhCl(trop$_2$NH)(PPh$_3$)],[23] [Rh(trop$_2$NH)(PPh$_3$)]OTf[23] and [Rh(trop$_2$N)(PPh$_3$)].[23]

Solution NMR spectra were recorded on Bruker Avance 500, 400, 300, 250 and 200 spectrometers. The chemical shifts (δ) are measured according to IUPAC[24] and expressed in ppm relative to TMS, $CFCl_3$ and [Rh(acac)$_3$] for ^{1}H, ^{2}H and ^{13}C, ^{19}F, and ^{103}Rh, respectively. Coupling constants J are given in Hz as absolute values. Where a first order analysis is appropriate, the multiplicity of the signals is indicated as s, d, t, q, or m for singlets, doublets, triplets, quartets, or multiplets. The abbreviation br. is given for broadened signals. Aromatic units are indicated as H^{ar} or C^{ar} when not noted otherwise. Quaternary ^{13}C are indicated as C^{quat}. The olefinic protons and ^{13}C atoms are indicated as H^{olef} and C^{olef}, respectively.

Melting points were determined with a Büchi melting-point apparatus and are not corrected. Samples were prepared in open glass capillaries.

IR and Raman spectra were measured on a Perkin-Elmer Spectrum 2000 FTIR-Raman spectrometer using ATR-techniques. Absorption bands are described as follows: s strong; m medium; w weak.

Gas chromatography was performed on a Hewlett Packard HP 6890 Series GC System using the following temperature programs: column: Hewlett-Packard HP-5 phenyl methyl siloxane (30 m × 0.32 mm × 0.25 μm); temperature program: 1 min 80 °C then 4 °C min^{-1} to 180 °C; H_2 pressure: 0.05 MPa. Hydrogen was used as a carrier gas provided from a Messer SL 9100 hydrogen generator.

GC-MS analysis was done with a Trace GC Ultra and a Polaris Q device both from Thermo Finnigan. Columns: Zebron ZB-5MS 5% phenyl-arylene 95% dimethylpolysiloxane (30 m × 0.25 mm × 0.25 μm). Ion source: EI. Mass analyser: ion trap.

Dehydrogenation of alcohols with nitrosobenzene as hydrogen acceptor

Benzaldehyde. To a solution of benzyl alcohol (0.26 mL, 270 mg, 2.50 mmol, 1 equiv.) and nitrosobenzene (549 mg, 5.12 mmol, 2.05 equiv.) in THF (5 mL) were added [Rh(trop$_2$NH)(PPh$_3$)]OTF (**2**) (2.3 mg, 2.5 μmol, 0.001 equiv.) and K_2CO_3 (17.3 mg, 125 μmol, 0.05 equiv.). The resulting mixture was stirred overnight at room temperature then all volatiles were removed under high vacuum at 100 °C and collected in a cooling trap. The trapped chemicals proved to be THF and benzaldehyde. The latter was obtained by removing the THF under reduced pressure. Yield: 242 mg, 91%. ^{1}H-NMR (500.23 MHz,

$CDCl_3$, 25 °C): δ = 7.55 (dd, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 7.7 Hz, 2H, C*H*^{ar}), 7.65 (tt, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, C*H*^{ar}), 7.90 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.2 Hz, 2H, C*H*^{ar}), 10.04 (s, 1H, C*H*O); $^{13}C\{^1H\}$-NMR (125.78 MHz, $CDCl_3$, 25 °C): δ = 129.4 (s, 2C, *C*H^{ar}), 130.1 (s, 2C, *C*H^{ar}), 134.9 (s, 1C, *C*H^{ar}), 136.8 (s, 1C, *C*^{quat}), 192.8 (s, 1C, *C*HO).

4-Methoxybenzaldehyde. To a solution of (4-methoxyphenyl)-methanol (0.31 mL, 345 mg, 2.50 mmol, 1 equiv.) and nitrosobenzene (549 mg, 5.12 mmol, 2.05 equiv.) in THF (5 mL) were added [Rh(trop$_2$NH)(PPh$_3$)]OTF (**2**) (2.3 mg, 2.5 μmol, 0.001 equiv.) and K_2CO_3 (17.3 mg, 125 μmol, 0.05 equiv.). The resulting mixture was stirred overnight at room temperature then the solvent was removed under reduced pressure and the residue purified by column chromatography (petrol ether 30 : 50 : ethyl acetate 10 : 1). Yield: 326 mg, 96%. ^{1}H-NMR (300.13 MHz, $CDCl_3$, 25 °C): δ = 3.90 (s, 3H, OC*H*$_3$), 7.01 (d, $^3J_{HH}$ = 8.8 Hz, 2H, C*H*^{ar}), 7.85 (d, $^3J_{HH}$ = 8.8 Hz, 2H, C*H*^{ar}), 9.89 (s, 1H, C*H*O); $^{13}C\{^1H\}$-NMR (75.48 MHz, $CDCl_3$, 25 °C): δ = 55.6 (s, 1C, OCH_3), 114.3 (s, 2C, *C*H^{ar}), 130.0 (s, 1C, *C*^{quat}), 132.0 (s, 2C, *C*H^{ar}), 164.6 (s, 1C, *C*^{quat}), 190.8 (s, 1C, *C*HO).

4-Nitrobenzaldehyde. To a solution of (4-nitrophenyl)-methanol (183 mg, 1.25 mmol, 1 equiv.) and nitrosobenzene (262 mg, 2.56 mmol, 2.05 equiv.) in THF (2.5 mL) were added [Rh(trop$_2$NH)(PPh$_3$)]OTF (**2**) (5.5 mg, 6.0 μmol, 0.005 equiv.) and K_2CO_3 (8.2 mg, 60 μmol, 0.05 equiv.). The resulting mixture was stirred overnight at room temperature then the solvent was removed under reduced pressure and the residue purified by column chromatography (petrol ether 30 : 50 : ethyl acetate 30 : 1). Yield: 41 mg, 23%. ^{1}H-NMR (500.23 MHz, $CDCl_3$, 25 °C): δ = 8.10 (d, $^3J_{HH}$ = 8.7 Hz, 2H, C*H*^{ar}), 8.43 (d, $^3J_{HH}$ = 8.7 Hz, 2H, C*H*^{ar}), 10.19 (s, 1H, C*H*O); $^{13}C\{^1H\}$-NMR (125.78 MHz, $CDCl_3$, 25 °C): δ = 124.7 (s, 2C, *C*H^{ar}), 130.9 (s, 2C, *C*H^{ar}), 140.5 (s, 1C, *C*^{quat}), 151.0 (s, 1C, *C*^{quat}), 190.7 (s, 1 C, *C*HO).

3,4-(Methylenedioxy)-benzaldehyde. To a solution of piperonyl alcohol (380 mg, 2.50 mmol, 1 equiv.) and nitrosobenzene (549 mg, 5.12 mmol, 2.05 equiv.) in THF (5 mL) were added [Rh(trop$_2$NH)(PPh$_3$)]OTF (**2**) (2.3 mg, 2.5 μmol, 0.001 equiv.) and K_2CO_3 (17.3 mg, 125 μmol, 0.05 equiv.). The resulting mixture was stirred overnight at room temperature then the solvent was removed under reduced pressure and the residue purified by column chromatography (petrol ether 30 : 50 : ethyl acetate 10 : 1). Yield: 348 mg, 93%. ^{1}H-NMR (300.13 MHz, $CDCl_3$, 25 °C): δ = 6.07 (s, 2H, CH_2), 6.93 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C*H*^{ar}), 7.33 (d, $^4J_{HH}$ = 1.4 Hz, 1H, C*H*^{ar}), 7.41 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, C*H*^{ar}), 9.81 (s, 1H, C*H*O); $^{13}C\{^1H\}$-NMR (75.48 MHz, $CDCl_3$, 25 °C): δ = 102.1 (s, 1C, *C*H$_2$), 106.9 (s, 1C, *C*H^{ar}), 108.3 (s, 1C, *C*H^{ar}), 128.6 (s, 1C, *C*H^{ar}), 131.9 (s, 1C, *C*^{quat}), 148.7 (s, 1C, *C*^{quat}), 153.1 (s, 1C, *C*^{quat}), 190.3 (s, 1C, *C*HO).

4-(Methylthio)benzaldehyde. To a solution of 4-(methylthio)-phenyl methanol (193 mg, 1.25 mmol, 1 equiv.) and nitrosobenzene (262 mg, 2.56 mmol, 2.05 equiv.) in THF (2.5 mL) were added [Rh(trop$_2$NH)(PPh$_3$)]OTF (**2**) (5.5 mg, 6.0 μmol, 0.005 equiv.) and K_2CO_3 (8.2 mg, 60 μmol, 0.05 equiv.). The resulting mixture was stirred overnight at room temperature then the solvent was removed under reduced pressure and the residue purified by column chromatography (petrol ether 30 : 50 : ethyl acetate 10 : 1). Yield: 183 mg, 97%. ^{1}H-NMR (300.13 MHz, $CDCl_3$, 25 °C): δ = 2.54 (s, 3H, SC*H*$_3$), 7.33 (d, $^3J_{HH}$ = 8.4 Hz, 2H, C*H*^{ar}), 7.78 (d, $^3J_{HH}$ = 8.4 Hz, 2H, C*H*^{ar}), 9.93 (s, 1H, C*H*O); $^{13}C\{^1H\}$-NMR (75.48 MHz, $CDCl_3$, 25 °C): δ = 14.7 (s, 1C, SCH_3), 125.2 (s, 2C, *C*H^{ar}), 130.0 (s, 2C, *C*H^{ar}), 133.0 (s, 1C, *C*^{quat}), 147.9 (s, 1C, *C*^{quat}), 191.2 (s, 1C, *C*HO).

4-Methoxycarbonylbenzaldehyde. To a solution of methyl 4-(hydroxymethyl)benzoate (208 mg, 1.25 mmol, 1 equiv.) and nitrosobenzene (262 mg, 2.56 mmol, 2.05 equiv.) in THF (2.5 mL) were added [Rh(trop$_2$NH)(PPh$_3$)]OTF (**2**) (5.5 mg, 6.0 μmol, 0.005 equiv.) and K_2CO_3 (8.2 mg, 60 μmol, 0.05 equiv.). The resulting mixture was stirred overnight at room temperature then the solvent was removed under reduced pressure and the residue purified by column chromatography (petrol ether 30 : 50 : ethyl acetate 9 : 1). Yield: 76 mg, 37%. ^{1}H-NMR (500.23 MHz, $CDCl_3$, 25 °C): δ = 3.99 (s, 3H, CO_2CH_3), 7.98 (d, $^3J_{HH}$ = 8.5 Hz, 2H, C*H*^{ar}), 8.22 (d, $^3J_{HH}$ = 8.5 Hz, 2H, C*H*^{ar}), 10.13 (s, 1H, C*H*O); $^{13}C\{^1H\}$-NMR (125.78 MHz, $CDCl_3$, 25 °C): δ = 53.0 (s, 1C, CO_2CH_3), 129.9 (s, 2C, *C*H^{ar}), 130.6 (s, 2C, *C*H^{ar}), 135.5 (s, 1C, *C*^{quat}), 139.6 (s, 1C, *C*^{quat}), 166.5 (s, 1C, *C*O_2CH$_3$), 192.0 (s, 1C, *C*HO).

2-Furan-carboxaldehyde. To a solution of furan-2-ylmethanol (0.11 mL, 123 mg, 1.25 mmol, 1 equiv.) and nitrosobenzene (262 mg, 2.56 mmol, 2.05 equiv.) in THF (2.5 mL) were added [Rh(trop$_2$NH)(PPh$_3$)]OTF (**2**) (5.5 mg, 6.0 μmol, 0.005 equiv.) and K_2CO_3 (8.2 mg, 60 μmol, 0.05 equiv.). The resulting mixture was stirred overnight at room temperature then the solvent was removed under reduced pressure and the residue purified by column chromatography (petrol ether 30 : 50 : ethyl acetate 30 : 1). Yield: 63 mg, 52%. ^{1}H-NMR (300.13 MHz, $CDCl_3$, 25 °C): δ = 6.61 (dd, $^3J_{HH}$ = 3.6 Hz, $^3J_{HH}$ = 1.7 Hz, 1H, C*H*), 7.26 (dd, $^3J_{HH}$ = 3.64, $^4J_{HH}$ = 0.8 Hz, 1H, C*H*), 7.70 (m, 1H, C*H*), 9.67 (s, 1H, C*H*O); $^{13}C\{^1H\}$-NMR (125.78 MHz, $CDCl_3$, 25 °C): δ = 112.6 (s, 1C, *C*H), 120.9 (s, 1C, *C*H), 148.0 (s, 1C, *C*H), 153.0 (s, 1C, *C*^{quat}), 177.9 (s, 1C, *C*HO).

4-Hydroxy-3-methoxybenzaldehyde. To a solution of 4-(hydroxymethyl)-2-methoxyphenol (385 mg, 2.50 mmol, 1 equiv.) and nitrosobenzene (549 mg, 5.12 mmol, 2.05 equiv.) in THF (5 mL) were added [Rh(trop$_2$NH)(PPh$_3$)]OTF (**2**) (2.3 mg, 2.5 μmol, 0.001 equiv.) and K_2CO_3 (17.3 mg, 125 μmol, 0.05 equiv.). The resulting mixture was stirred overnight at room temperature then all volatiles were removed under reduced pressure. The residue was dissolved in aqueous NaOH (5%) and extracted 2 times with small portions of Et_2O. The aqueous phase was acidified with HCl and extracted 3 times with small portions of Et_2O. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated. Yield: 353 mg, 93%. ^{1}H-NMR (500.23 MHz, $CDCl_3$, 25 °C): δ = 3.97 (s, 3H, OC*H*$_3$), 6.50 (s, br, 1H, O*H*), 7.06 (d, $^3J_{HH}$ = 8.5 Hz, 1H, C*H*^{ar}), 7.44–7.45 (m, 2H, C*H*^{ar}), 9.84 (s, 1H, C*H*O); $^{13}C\{^1H\}$-NMR (125.78 MHz, $CDCl_3$, 25 °C): δ = 56.5 (s, 1C, OCH_3), 109.3 (s, 1C, *C*H^{ar}), 114.9 (s, 1C, *C*H^{ar}), 127.9 (s, 1C, *C*H^{ar}), 130.2 (s, 1C, *C*^{quat}), 147.6 (s, 1C, *C*^{quat}), 152.2 (s, 1C, *C*^{quat}), 191.4 (s, 1C, *C*HO).

Octanal. To a solution of 1-octanol (0.20 mL, 162 mg, 1.25 mmol, 1 equiv.) and nitrosobenzene (262 mg, 2.56 mmol, 2.05 equiv.) in THF (2.5 mL) were added [Rh(trop$_2$NH)(PPh$_3$)]-OTF (**2**) (5.5 mg, 6.0 µmol, 0.005 equiv.) and K_2CO_3 (8.2 mg, 60 µmol, 0.05 equiv.). The resulting mixture was stirred overnight at room temperature then analysed by GC. Conversion: 5%.

Geranial. To a solution of geraniol (0.22 mL, 193 mg, 1.25 mmol, 1 equiv.) and nitrosobenzene (262 mg, 2.56 mmol, 2.05 equiv.) in THF (2.5 mL) were added [Rh(trop$_2$NH)(PPh$_3$)]-OTF (**2**) (5.5 mg, 6.0 µmol, 0.005 equiv.) and K_2CO_3 (8.2 mg, 60 µmol, 0.05 equiv.). The resulting mixture was stirred overnight at room temperature then the solvent was removed under reduced pressure and the residue purified by column chromatography (petrol ether 30 : 50 : ethyl acetate 30 : 1). Yield: 184 mg, 97%. ^{1}H-NMR (500.23 MHz, $CDCl_3$, 25 °C): δ = 1.62 (s, 3H, CH_3), 1.69 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 2.20–2.25 (m, 4H, CH_2), 5.08 (t, $^3J_{HH}$ = 6.7 Hz, 1H, CH^{olef}), 5.89 (d, $^3J_{HH}$ = 8.0 Hz, 1H, CH^{olef}), 10.00 (d, $^3J_{HH}$ = 8.0 Hz, 1H, CHO); ^{13}C{^{1}H}-NMR (125.78 MHz, $CDCl_3$, 25 °C): δ = 18.0 (s, 1C, CH$_3$), 18.1 (s, 1C, CH$_3$), 26.0 (s, 1C, CH$_3$), 26.1 (s, 1C, CH$_2$), 41.0 (s, 1C, CH$_2$), 123.0 (s, 1C, CH^{olef}), 127.8 (s, 1C, CH^{olef}), 133.3 (s, 1C, C^{olef}), 164.2 (s, 1C, C^{olef}), 191.7 (s, 1C, CHO).

Citronellal. To a solution of citronellol (0.23 mL, 196 mg, 1.25 mmol, 1 equiv.) and nitrosobenzene (262 mg, 2.56 mmol, 2.05 equiv.) in THF (2.5 mL) were added [Rh(trop$_2$NH)(PPh$_3$)]-OTF (**2**) (5.5 mg, 6.0 µmol, 0.005 equiv.) and K_2CO_3 (8.2 mg, 60 µmol, 0.05 equiv.). The resulting mixture was stirred overnight at room temperature then analyzed by GC. Conversion: 11%.

Acetophenone. To a solution of 1-phenylethanol (0.15 mL, 153 mg, 1.25 mmol, 1 equiv.) and nitrosobenzene (262 mg, 2.56 mmol, 2.05 equiv.) in THF (2.5 mL) were added [Rh(trop$_2$NH)(PPh$_3$)]OTF (**2**) (5.5 mg, 6.0 µmol, 0.005 equiv.) and *t*-BuOK (6.8 mg, 60 µmol, 0.05 equiv.). The resulting mixture was stirred overnight at room temperature then the solvent was removed under reduced pressure and the residue purified by column chromatography (petrol ether 30 : 50 : ethyl acetate 50 : 1, then 10 : 1). Yield: 92 mg, 61%. ^{1}H-NMR (300.13 MHz, $CDCl_3$, 25 °C): δ = 2.61 (s, 3H, CH_3), 7.44–7.50 (m, 2H, CH^{ar}), 7.57 (tt, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, CH^{ar}), 7.95–7.99 (m, 2H, CH^{ar}); ^{13}C{^{1}H}-NMR (125.78 MHz, $CDCl_3$, 25 °C): δ = 26.6 (s, 1C, CH$_3$), 128.3 (s, 2C, CH^{ar}), 128.6 (s, 2C, CH^{ar}), 133.1 (s, 1C, CH^{ar}), 137.2 (s, 1C, C^{quat}), 198.1 (s, 1C, CO).

General procedure for the reductive coupling of nitrosobenzenes to azoxybenzenes

To a solution of a nitrosobenzene derivative (2.19 mmol, 1 equiv.) and [Rh(trop$_2$NH)(PPh$_3$)]OTF (**2**) (2.0 mg, 2.2 µmol, 0.001 equiv.) in ethanol (2 mL) and THF (1 mL) was added K_2CO_3 (15 mg, 0.11 mmol, 0.05 equiv.). The resulting mixture was stirred for 2 h then all volatiles were removed and the residue was purified by column chromatography.

Azoxybenzene. From nitrosobenzene. Yield: 224 mg, 97%. ^{1}H-NMR (300.13 MHz, $CDCl_3$, 25 °C): δ = 7.39–7.44 (m, 1H, CH^{ar}), 7.49–7.59 (m, 5H, CH^{ar}), 8.20 (dd, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 1.2 Hz, 2H, CH^{ar}), 8.34 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.5 Hz, 2H, CH^{ar}); ^{13}C{^{1}H}-NMR (75.48 MHz, $CDCl_3$, 25 °C): δ = 122.4 (s, 2C, CH^{ar}), 125.5 (s, 2C, CH^{ar}), 128.7 (s, 2C, CH^{ar}), 128.8 (s, 2C, CH^{ar}), 129.6 (s, 1C, CH^{ar}), 131.6 (s, 1C, CH^{ar}), 144.1 (s, 1C, C^{quat}), 148.4 (s, 1C, C^{quat}).

4,4′-Dimethyl-azoxybenzene. From 1-methyl-4-nitrosobenzene. Yield: 240 mg, 95%. ^{1}H-NMR (500.23 MHz, $CDCl_3$, 25 °C): δ = 2.45 (s, 3H, CH_3), 2.48 (s, 3H, CH_3), 7.31–7.33 (m, 4H, CH^{ar}), 8.15 (d, $^3J_{HH}$ = 8.5 Hz, 2H, CH^{ar}), 8.22 (d, $^3J_{HH}$ = 8.5 Hz, 2H, CH^{ar}); ^{13}C{^{1}H}-NMR (125.78 MHz, $CDCl_3$, 25 °C): δ = 21.7 (s, 1C, CH$_3$), 21.9 (s, 1C, CH$_3$), 122.6 (s, 2C, CH^{ar}), 126.1 (s, 2C, CH^{ar}), 129.7 (s, 4C, CH^{ar}), 140.4 (s, 1C, C^{quat}), 142.3 (s, 2C, C^{quat}), 146.7 (s, 1C, C^{quat}).

4,4′-Dimethoxyazoxybenzene. From 1-methoxy-4-nitrosobenzene. Yield: 260 mg, 92%. ^{1}H-NMR (500.23 MHz, $CDCl_3$, 25 °C): δ = 3.91 (s, 3H, CH_3), 3.91 (s, 3H, CH_3), 6.99 (d, $^3J_{HH}$ = 9.3 Hz, 2H, CH^{ar}), 7.01 (d, $^3J_{HH}$ = 9.3 Hz, 2H, CH^{ar}), 8.28 (d, $^3J_{HH}$ = 9.2 Hz, 1H, CH^{ar}), 8.31 (d, $^3J_{HH}$ = 9.2 Hz, 1H, CH^{ar}); ^{13}C{^{1}H}-NMR δ = (125.78 MHz, $CDCl_3$, 25 °C): δ = 55.9 (s, 1C, CH$_3$), 56.1 (s, 1C, CH$_3$), 114.0 (s, 2C, CH^{ar}), 114.2 (s, 2C, CH^{ar}), 124.2 (s, 2C, CH^{ar}), 128.2 (s, 2C, CH^{ar}), 138.5 (s, 1C, C^{quat}), 142.2 (s, 1C, C^{quat}), 160.6 (s, 1C, C^{quat}), 162.3 (s, 1C, C^{quat}).

4,4′-Difluoroazoxybenzene. From 4-fluoro-nitrosobenzene. Yield: 248 mg, 98%. ^{1}H-NMR (300.13 MHz, $CDCl_3$, 25 °C): δ = 7.14–7.24 (m, 4H, CH^{ar}), 8.24–8.37 (m, 4H, CH^{ar}); ^{13}C{^{1}H}-NMR (75.48 MHz, $CDCl_3$, 25 °C): δ = 115.5 (d, $^2J_{CF}$ = 3.5 Hz, 2C, CH^{ar}), 115.8 (d, $^2J_{CF}$ = 4.4 Hz, 2C, CH^{ar}), 124.5 (d, $^3J_{CF}$ = 9.3 Hz, 2C, CH^{ar}), 128.0 (d, $^3J_{CF}$ = 8.5 Hz, 2C, CH^{ar}), 140.3 (d, $^4J_{CF}$ = 3.2 Hz, 1C, C^{quat}), 144.3 (br, 1C, C^{quat}), 162.6 (d, $^1J_{CF}$ = 252.5 Hz, 1C, C^{quat}), 164.5 (d, $^1J_{CF}$ = 252.9 Hz, 1C, C^{quat}). ^{19}F-NMR (188.31 MHz, $CDCl_3$, 25 °C): δ = −108.62 to −108.48 (m, 1F), −108.06 to −107.92 (m, 1F).

4,4′-Dichloro-azoxybenzene. To a solution of 4-chloro-nitrosobenzene (310 mg, 2.19 mmol, 1 equiv.) and [Rh(trop$_2$NH)-(PPh$_3$)]OTF (**2**) (2.0 mg, 2.2 µmol, 0.001 equiv.) in ethanol (6 mL) and THF (6 mL) was added K_2CO_3 (15 mg, 110 µmol, 0.05 equiv.). The resulting mixture was stirred for 4 h then all volatiles were removed and the residue was purified by column chromatography. Yield: 273 mg, 93%. ^{1}H-NMR (300.13 MHz, $CDCl_3$, 25 °C): δ = 7.46 (d, $^3J_{HH}$ = 9.3 Hz, 2H, CH^{ar}), 7.50 (d, $^3J_{HH}$ = 9.3 Hz, 2H, CH^{ar}), 8.17 (d, $^3J_{HH}$ = 8.9 Hz, 2H, CH^{ar}), 8.27 (d, $^3J_{HH}$ = 8.9 Hz, 2H, CH^{ar}); ^{13}C{^{1}H}-NMR (75.48 MHz, $CDCl_3$, 25 °C): δ = 123.7 (s, 2C, CH^{ar}), 127.1 (s, 2C, CH^{ar}), 129.0 (s, 2C, CH^{ar}), 129.0 (s, 2C, CH^{ar}), 135.3 (s, 1C, C^{quat}), 138.1 (s, 1C, C^{quat}), 142.2 (s, 1C, C^{quat}), 146.6 (s, 1C, C^{quat}).

4,4′-Azoxybenzoic acid dimethyl ester. To a solution of methyl 4-nitrosobenzoate (190 mg, 1.15 mmol, 1 equiv.) and [Rh(trop$_2$NH)(PPh$_3$)]OTF (**2**) (1.1 mg, 1.2 µmol, 0.001 equiv.) in ethanol (4 mL) and THF (4 mL) was added K_2CO_3 (8.0 mg, 58 µmol, 0.05 equiv.). The resulting mixture was stirred for 4 h then all volatiles were removed and the residue was purified by column chromatography. Yield: 124 mg, 69%. ^{1}H-NMR

(250.13 MHz, $CDCl_3$, 25 °C): δ = 1H, 3.97 (s, 3H, CH_3), 3.99 (s, 3H, CH_3), 8.18–8.19 (m, 4H, CH^{ar}), 8.21–8.23 (m, 2H, CH^{ar}), 8.39–8.42 (m, 2H, CH^{ar}); $^{13}C\{^1H\}$-NMR (62.90 MHz, $CDCl_3$, 25 °C): δ = 52.3 (s, 1C, CH_3), 52.6 (s, 1C, CH_3), 122.6 (s, 2C, CH^{ar}), 125.3 (s, 2C, CH^{ar}), 130.2 (s, 2C, CH^{ar}), 130.4 (s, 2C, CH^{ar}), 130.7 (s, 1C, C^{quat}), 133.3 (s, 1C, C^{quat}), 147.0 (s, 1C, C^{quat}), 150.9 (s, 1C, C^{quat}), 165.7 (s, 1C, CO_2Me), 166.2 (s, 1C, CO_2Me).

Complex synthesis

[Rh(trop$_2$NH)(PPh$_3$)(PhNHO)] (4). To a solution of [Rh(trop$_2$N)(PPh$_3$)] (**1**) (42 mg, 55 μmol, 1 equiv.) in THF (1 mL) was added *N*-phenyl hydroxylamine (6.3 mg, 58 μmol, 1.05 equiv.). After 15 min the orange precipitate was filtered off, washed with a small portion of Et_2O (2 mL) and dried under high vacuum. Yield: 38 mg, 79%.

Alternative procedure. Hydrogen gas was bubbled through a solution of [Rh(trop$_2$N)(PPh$_3$)] (**1**) (84 mg, 0.11 mmol, 1 equiv.) in THF (1 mL) until the colour of the solution changed from deep green to yellow and the ^{31}P-NMR confirmed complete reaction to the hydride complex [RhH(trop$_2$NH)(PPh$_3$)] (**3**). To this solution nitrosobenzene (11.8 mg, 0.11 μmol, 1 equiv.) was added and after 15 min the precipitate was filtered off, washed with a small portion of Et_2O (2 mL) and dried under high vacuum. Yield: 59 mg, 61%. M.p.: 170–175 °C (decomposition); ^{1}H-NMR (500.23 MHz, $CDCl_3$, 298 K): δ = 4.59 (d, J = 6.4 Hz, 1H, NH^{trop}), 4.67 (d, J = 8.7 Hz, 2H, CH^{benzyl}), 4.80 (d, J = 9.2 Hz, 2H, CH^{olef}), 4.87 (d, J = 9.4 Hz, 2H, CH^{olef}), 6.64 (d, J = 7.3 Hz, 2H, C$H^{ar,\ trop}$), 6.75 (t, J = 7.33 Hz, 2H, C$H^{ar,\ trop}$), 6.77 (d, J = 8.3 Hz, 2H, C$H^{ar,\ trop}$), 6.83 (t, J = 7.1 Hz, 2H, C$H^{ar,\ trop}$), 7.07–7.10 (m, 2H, C$H^{ar,\ trop}$), 7.16 (d, J = 7.3 Hz, 2H, C$H^{ar,\ trop}$), 7.19–7.21 (m, 4H, C$H^{ar,\ trop}$), 7.56 (m, 13H, C$H^{ar,\ phosphane}$, C$H^{ar,\ PhNHO}$, NH^{PhNHO}), 8.02 (br, 6H, C$H^{ar,\ phosphane}$), 8.20 (d, J = 7.6 Hz, 1H, C$H^{ar,\ PhNHO}$), 8.35 (d, J = 8.0 Hz, 1H, C$H^{ar,\ PhNHO}$); $^{13}C\{^1H\}$-NMR (125.78 MHz, $CDCl_3$, 298 K): δ = 67.4 (d, J = 12.0 Hz, 2C, CH^{olef}), 69.7 (d, J = 7.4 Hz, 2C, CH^{olef}), 73.0 (s, 2C, CH^{benzyl}), 122.8 (s, 1C, $CH^{ar,\ PhNHO}$), 125.5 (s, 2C, $CH^{ar,\ trop}$), 125.9 (m, 3C, $CH^{ar,\ trop}$, $CH^{ar,\ PhNHO}$), 125.9 (s, 2C, $CH^{ar,\ trop}$), 127.4 (s, 2C, $CH^{ar,\ trop}$), 127.7 (s, 2C, $CH^{ar,\ trop}$), 128.5 (s, 2C, $CH^{ar,\ trop}$), 128.6 (s, 2C, $CH^{ar,\ trop}$), 128.7 (d, J = 9.6 Hz, 6C, $CH^{ar,\ phosphane}$), 129.1 (s, 1C, $CH^{ar,\ PhNHO}$), 129.2 (s, 1C, $CH^{ar,\ PhNHO}$), 129.5 (s, 2C, $CH^{ar,\ trop}$), 129.6 (s, 2C, $CH^{ar,\ trop}$), 130.0 (s, 1C, $CH^{ar,\ PhNHO}$), 130.9 (s, 3C, $CH^{ar,\ phosphane}$), 131.1 (d, $^1J_{PC}$ = 45.6 Hz, 3C, $C^{quat,\ phosphane}$), 132.0 (s, 1C, $C^{quat,\ PhNHO}$), 134.6 (s, 2C, $C^{quat,\ trop}$), 134.7 (s, 2C, $C^{quat,\ trop}$), 135.1 (d, J = 8.9 Hz, 6C, $CH^{ar,\ phosphane}$) 136.4 (s, 2C, $C^{quat,\ trop}$), 139.8 (s, 2C, $C^{quat,\ trop}$); $^{31}P\{^1H\}$-NMR (202.50 MHz, $CDCl_3$, 298 K) δ = 43.1 (d, $^1J_{RhP}$ = 135.0 Hz); ^{1}H, ^{103}Rh-NMR (15.81 MHz, $CDCl_3$, 298 K): δ = −7147 (d, $^1J_{PRh}$ = 135.0 Hz); ATR IR (ν in cm^{-1}): 3147 (w), 3044 (w), 2848 (w), 1719 (w), 1636 (w), 159 (w), 1474 (m), 1435 (m), 1403 (w), 1341 (w), 1297 (w), 1258 (w), 1223 (w), 1186 (w), 1157 (w), 1114 (w), 1092 (m), 1064 (w), 1042 (w), 1024 (w), 998 (w), 984 (m), 936 (w), 887 (w), 879 (w), 856 (w), 840 (w), 825 (w), 801 (w), 742 (s), 714 (w), 699 (s) 683 (s), 618 (m).

[Rh(trop$_2$N)(*eq*-PPh$_3$)(*ax*-PhN═N(O)Ph)]. To a solution of [RhCl(PPh$_3$)(trop$_2$NH)] (100 mg, 0.125 mmol, 1 equiv.) in THF (2 mL) and toluene (1 mL) was added *t*-BuOK (14 mg, 0.125 mmol, 1 equiv.). The reaction mixture was stirred for 30 min then all volatiles were removed under reduced pressure. Toluene (1 mL) was added to the residue and removed again under reduced pressure. The residue was dissolved in THF and filtrated, then azoxybenzene (26 mg, 0.132 mmol, 1.05 equiv.) was added. The resulting solution was stirred overnight then the solvent was removed under reduced pressure. Yield: 101 mg, 84%. M.p.: 74–76 °C (decomposition); ^{1}H-NMR (400.13 MHz, [D$_8$]THF, 273 K): δ = 0.86 (s, 1H, NH), 4.06 (s, 2H, CH^{benzyl}), 4.80 (dd, J = 9.2 Hz, J = 5.0 Hz, 2H, CH^{olefin}), 4.92 (t, J = 7.4 Hz, 2H, CH^{olefin}), 5.49 (t, J = 7.60 Hz, 2H, CH^{ar}), 6.42 (d, J = 7.5 Hz, 2H, CH^{ar}), 6.56 (d, J = 7.3 Hz, 2H, CH^{ar}), 6.67–6.73 (m, 4H, CH^{ar}), 6.75–6.81 (m, 4H, CH^{ar}), 6.86 (t, J = 7.4 Hz, 2H, CH^{ar}), 6.94 (t, J = 7.3 Hz, 2H, CH^{ar}), 7.05 (d, J = 7.6 Hz, 2H, CH^{ar}), 7.15 (t, J = 7.3 Hz, 1H, CH^{ar}), 7.30–7.37 (m, 6H, CH^{ar}), 7.45 (t, J = 7.4 Hz, 1H, CH^{ar}), 7.53 (t, J = 7.7 Hz, 3H, CH^{ar}), 7.59–7.65 (m, 2H, CH^{ar}), 8.28 (d, J = 7.9 Hz, 2H, CH^{ar}), 8.33–8.39 (m, 6H, CH^{ar}); $^{13}C\{^1H\}$-NMR (100.61 MHz, [D$_8$]THF, 273 K): δ = 67.6–67.7 (m, 1C, CH^{olefin}), 70.0 (dd, J = 17.6 Hz, J = 10.3 Hz, 2C, CH^{olefin}), 71.0 (s, 2C, CH^{benzyl}), 122.4 (s, 2C, CH^{ar}), 123.7 (d, J = 1.6 Hz, 2C, CH^{ar}), 124.1 (s, 2C, CH^{ar}), 125.9 (s, 2C, CH^{ar}), 126.6 (s, 2C, CH^{ar}), 127.7 (d, J = 4.3 Hz, 2C, CH^{ar}), 127.9–128.0 (m, 8C, CH^{ar}), 128.5 (s, 2C, CH^{ar}), 128.5–128.7 (m, 3C, CH^{ar}), 128.9 (s, 2C, CH^{ar}), 129.1–129.2 (m, 4C, CH^{ar}), 129.2 (s, 2C, CH^{ar}), 130.0 (s, 1C, CH^{ar}), 131.4 (d, J = 8.7 Hz, 2C, CH^{ar}), 131.8 (d, J = 2.5 Hz, 1C, $C^{quat,\ azoxybenzene}$), 132.0 (s, 1C, CH^{ar}), 132.2 (d, $^1J_{PC}$ = 9.4 Hz, 1C, $C^{quat,\ phosphane}$), 133.6 (d, J = 10.5 Hz, 4C, CH^{ar}), 133.9 (d, J = 2.1 Hz, 2C, $C^{quat,\ trop}$), 136.2 (s, 2C, $C^{quat,\ trop}$), 137.5 (d, J = 4.6 Hz, 2C, $C^{quat,\ trop}$), 138.0 (d, $^1J_{PC}$ = 24.7 Hz, $C^{quat,\ phosphine}$), 142.0 (d, J = 4.1 Hz, 2C, $C^{quat,\ trop}$), 144.5 (s, 1C, $C^{quat,\ azoxybenzene}$); $^{31}P\{^1H\}$-NMR (161.98 MHz, [D$_8$]THF, 273 K) δ = 7.9 (d, $^1J_{RhP}$ = 118.8 Hz); ^{1}H, ^{103}Rh-NMR (15.81 MHz, [D$_8$]THF, 273 K): δ = −6508 (d, $^1J_{PRh}$ = 118.8 Hz); ATR IR (ν in cm^{-1}): 3199 (w), 3039 (w), 2953 (w), 1598 (w), 1569 (w), 1472 (m), 1435 (m), 1413 (w), 1396 (w), 1324 (w), 1300 (w), 1258 (w), 1216 (w), 1188 (w), 1159 (w), 1119 (w), 1088 (w), 1069 (m), 1025 (m), 999 (w), 971 (w), 925 (w), 906 (w), 859 (w), 810 (m), 763 (m), 745 (s), 698 (s), 684 (s), 618 (w).

Miscellaneous reactions

To a solution of [Rh(trop$_2$N)(PPh$_3$)] (**1**) (10 mg, 13 μmol, 1 equiv.) in THF (0.5 mL) was added nitrosobenzene (14 mg, 0.13 mmol, 10 equiv.). The solution turned dark red. $^{31}P\{^1H\}$-NMR (202.50 MHz, [H$_8$]THF, 298 K) δ = 25.7 (s, $OPPh_3$).

[RhH(trop$_2$NH)(PPh$_3$)] (**3**) was generated *in situ* by reacting a solution of [Rh(trop$_2$N)(PPh$_3$)] (**1**) (10 mg, 13 μmol, 1 equiv.) in THF (0.5 mL) with hydrogen gas. To this solution nitrosobenzene (2.1 mg, 20 μmol, 1.5 equiv.) was added. After a short reaction time (less than 10 s) the solution turned dark yellow and a precipitate formed. $^{31}P\{^1H\}$-NMR (101.25 MHz, [H$_8$]THF, 298 K) δ = 24.6 (s, $OPPh_3$), 39.9 (d, $^1J_{RhP}$ = 134.9, **4**).

A suspension of [Rh(trop$_2$NH)(PPh$_3$)(PhNHO)] (**4**) (5.0 mg, 5.7 μmol) in THF (0.5 mL) was treated overnight with hydrogen

gas. The hydride complex **3** and aniline were found by ^{31}P-NMR and GC-MS analysis respectively.

A suspension of [Rh(trop$_2$NH)(PPh$_3$)(PhNHO)] (**4**) (5.0 mg, 5.7 μmol, 1 equiv.) in THF (0.5 mL) was treated overnight with benzyl alcohol (10 μL, 10 mg, 96 μmol, 17 equiv.). The hydride complex **3**, aniline and *N*-benzylideneaniline were found by ^{31}P-NMR and GC-MS analysis respectively.

To a solution of [Rh(trop$_2$N)(PPh$_3$)] (**1**) (44 mg, 58 μmol, 1 equiv.) and aniline (21 μL, 22 mg, 0.23 mmol, 5 equiv.) in THF (2 mL) was added nitrosobenzene (25 mg, 0.23 mmol, 5 equiv.). The reaction mixture was stirred for 10 min then analysed. ^{31}P{^{1}H}-NMR (101.25 MHz, [H$_8$]THF, 298 K) δ = 21.2 (s, OPPh$_3$), 38.4 (d, $^1J_{RhP}$ = 134.7, **4**). Analysis by GC-MS showed beside unreacted starting material the formation of azoxybenzene and azobenzene in approximately 50 : 1 ratio.

To a solution of [Rh(trop$_2$NH)(PPh$_3$)(PhNHO)] (**4**) (2.0 mg, 2.3 μmol, 1 equiv.) in THF (1.5 mL) was added benzaldehyde (23 μL, 24 mg, 0.23 mmol, 100 equiv.). Even after 90 min of stirring no reaction was observed.

To a solution of benzyl alcohol (26 μL, 27 mg, 0.25 mmol, 1 equiv.) and nitrosobenzene (55 mg, 0.51 mmol, 2.05 equiv.) in THF (1 mL) were added [Rh(trop$_2$NH)(PPh$_3$)]OTF **2** (2.3 mg, 2.5 μmol, 0.01 equiv.) and K_2CO_3 (3.5 mg, 25 μmol, 0.01 equiv.). The resulting mixture was stirred overnight at room temperature then analysed by NMR. ^{31}P{^{1}H}-NMR (202.5 MHz, [H$_8$]THF, 298 K) δ = 25.6 (s, OPPh$_3$).

A solution of [Rh(trop$_2$N)(*eq*-PPh$_3$)(*ax*-PhN═NOPh)] (10 mg, 10 μmol) in THF (0.5 mL) was left for 2 days at room temperature, the complex was partially decomposed to triphenyl phosphane oxide (confirmed by ^{31}P NMR), azobenzene (confirmed by GC-MS) and other not identified products.

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