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Regioselective Hydrosilylation of Epoxides Catalysed by Nickel(II) Hydrido Complexes

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Bench-stable nickel fluoride complexes bearing NNN pincer ligands have been employed as precursors for the regioselective hydrosilylation of epoxides at room temperature. A nickel hydride assisted epoxide opening is followed by the cleavage of the newly formed nickel oxygen bond by σ -bond metathesis with a silane.

Hydrosilylation of alkenes, alkynes, aldehydes, or ketones is typically carried out with platinum group catalysts, especially complexes of Ru,¹ Rh,² or Ir.³ Costs, toxicity and low abundance recently has led to the development of catalyst systems based on 3d metals such as iron,⁴ cobalt,⁵ or nickel.⁶

Nickel hydrido complexes are key intermediates in a variety of chemical transformations.⁷ They are either generated in situ in stoichiometric reaction sequences of catalytic cycles or may be synthesized by substitution of another anionic ligand as in the cleavage of a nickel-X bond (X = F, OR) by a silane.⁷ This transformation is a key step in the nickel-catalysed hydrosilylation of aldehydes or ketones,^{6c,6e,6g-i,8} while nickel hydride catalysts have also been employed for the hydrosilylation of olefins in recent years.^{6a,6b,6d,6f,9} There have been very few reports of transition metal-catalysed hydrosilylations of epoxides with concomitant ring opening.¹⁰



Scheme 1 Synthesis of (PdmBox)nickel hydrido complexes 2a and 2b.

Although there are some examples for catalytic and stoichiometric activations of epoxides with nickel compounds¹¹, there is no report of a catalytic hydrosilylation. In this communication, we present the first nickel-based catalyst for a regioselective hydrosilylation of epoxides.

We recently reported a new type of NNN pincer ligands

2,5-bis(2-oxazolinyldimethylmethyl)pyrroles (PdmBox) which stabilize Ni-H species¹² as compared to previous studies employing the non-methylated PmBOX pincer in which the Ni hydride underwent bimolecular transformation to T-shaped Ni⁽¹⁾ complexes.¹³ The latter gave rise to characteristic radical reactivity. The new PdmBox nickel pincer complexes were found to react readily with PhSiH₃ or Ph₂SiH₂ to generate nickel hydrido complexes **2a** and **2b** from fluoridonickel(II) precursors **1a** and **1b** (Scheme 1) which are bench-stable in the solid state and can be prepared on a multi-gram scale (for structural details see ESI).¹²

Upon treatment of a solution of hydrido complex **2a** with an equimolar amount of styrene oxide or of 2,2diphenyloxirane at room temperature, the exclusive formation of the anti Markovnikov insertion products **3a** and **4a** occured (Scheme 2). Complex **3a** was also prepared independently by salt metathesis of [(PdmBox)NiCl] with PhCH₂CH₂ONa (ESI), both synthetic routes giving rise to the same reaction product.



Scheme 2 Synthesis of nickel alkoxido complexes 3a and 3b.

The molecular structure of **3a** was determined by single crystal X-ray structure analysis of **3a** Ph(CH₂)₂OH (Figure 1), confirming the pincer-type coordination of the spectator ligand and the occupation of the fourth coordination site by the alkoxide ligand resulting from the epoxide insertion into the Ni-H bond. The helical twist [\angle _{helix} = 29.6(1)°] between the coordination plane of the d⁸-Ni(II) and the plane of the pyrrole ring results from the structural flexibility of the ligand backbone, which allows the donor functions to adapt to the size of the central metal atom. The greater trans influence of the hydrido ligand in **2a**¹² compared to the alkoxido ligand in **3a** is reflected in the Ni-N(2) bond lengths [**2a**: 1.910(2); **3a**: 1.865(3) Å].

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Figure 1 Molecular structure of **3a**. One molecule of $Ph(CH_2)_2OH$, hydrogen bonded to O3 and Hydrogen atoms are omitted for clarity; thermal ellipsoids displayed at 50% probability. Selected bond lengths [Å] and angles [°]: **3a** Ni-O(3) 1.862(2); Ni-N(1) 1.887(3), Ni-N(2) 1.865(3), Ni-N(3) 1.874(2), O(3)-Ni-N(1) 90.29(11); O(3)-Ni-N(2) 177.85(12); O(3)-Ni-N(3) 91.00(11); N(2)-Ni-N(1) 90.08(12).

To regenerate the hydride **2a** from the alkoxide resulting from the insertion, complex **3a** was reacted with various hydrosilanes. PhSiH₃ and Ph₂SiH₂ were identified as good silyl transfer reagents, leading to complete regeneration of **2a** and release of the silyl ether products within a few minutes (Scheme 3). Other silanes such as Et₃SiH, (EtO)₃SiH and poly(methylhydrosiloxane) (PMHS) regenerated hydride **2a** only in poor yields. They required elevated temperatures, or were found to be completely unreactive (for an overview of the silane screening see ESI).



Scheme 3 Cleavage of nickel alkoxides by silanes.

Having established the protocol of stoichiometric epoxide insertion and hydride regeneration, we set out to investigate the catalytic activity of hydrido complex **2a** in the catalytic hydrosilylation of styrene oxide. Using PhSiH₃ as reducing agent, hydrido complex **2a** catalysed the hydrosilylation of styrene oxide. The reaction was complete within 16 h at room temperature with catalyst loadings of 5 mol% on a 1 mmol scale (Scheme 4). After alkaline cleavage of the silyl ether, the "anti-Markovnikov" alcohol could be isolated in good yield. Both NMR data and GCMS analysis of the reaction mixture and of the crude products after alkaline hydrolysis give no evidence of the formation of the other possible regioisomer.



Upon monitoring the catalytic transformation by ¹H NMR, the nickel hydrido complex **2a** was identified as the resting state during the entire reaction while the presence of nickel alkoxido species was not observed (ESI). A control experiment in the absence of the nickel hydride **2a** showed no significant conversion, even at 80 °C for 5 days. Furthermore the mercury test had no influence on the outcome of the reaction, rendering colloidal nickel as active catalyst unlikely. Finally, we also probed the presence of radicals during the reaction by addition of radical traps: Neither triphenylmethane nor 9,10-

dihydroanthracene had a significant impact on the reactivity observed. DOI: 10.1039/C7CC01655G

Table 1 Substrate scope of nickel-catalysed hydrosilylation of styrene oxide derivatives.



Entry	Substrate	Product	conditions	(NMR Yield) ^b
1	C C	ОН	rt, 16 h	2a 94 (95) 2b 91 (95)
2	°	ОН	rt, 16 h	2a 93 (95) 2b 90 (95)
3	Ph	Ph	rt, 16 h	2a 95 (95) 2b 90 (95)
4		ОН	rt, 16 h	2a 95 (95) 2b 95 (95)
5	F C C C C C C C C C C C C C C C C C C C	F	rt, 16 h	2a 74 (95)
6	CI CI	CI	rt, 36 h	2a 64 (70)
7	Br	Br	rt, 16 h	2a 37 (40) 2b 32 (38)
8	F ₃ C	F ₃ C OH	rt, 24 h	2a 89 (95) 2b 89 (95)
9	Aco	НО	rt, 24 h	2a 55º (95) 2b 45º (95)
10	C C C C	ОН	rt, 16 h	2a 90 (95) 2b 95 (95)
11		ОН	rt, 16 h	2a 95 (95) 2b 90 (95)
12		ОН	rt, 72 h	2a 80 (85)
13	cis or trans	OH	50 °C, 24 h	2a 80, rac. ^d 2b 70, rac. ^d

^aAlcohol after workup determined by ¹H-NMR using 1,4-dimethoxybenzene as internal standard. ^bNMR yield of the corresponding silylprotected alcohol of the crude reaction NMR using 1,4-dimethoxybenzene as internal standard. ^cK₂CO₃/MeOH was used for workup. ^ddetermined by chiral HPLC.

The scope of the catalytic system was investigated using 5 mol% of nickel fluoride complex **1a** or **1b** as precatalysts to generate the catalytically active hydrido species **2a** or **2b** in situ in the presence of a excess of PhSiH₃ (Scheme 1). The

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reaction products were isolated as alcohols following basic hydrolysis of the silyl ethers. After a reaction time of 16 to 36 h at room temperature, complete conversion of substituted styrene oxide derivatives (Table 1, entries 1–5; 8-11) was observed. In those cases, the formation of the corresponding silyl-protected alcohol was observed in high yields. The differing electronic nature of each substrate had no influence on the regioselectivity.

Notably, halide substitution on the aromatic system was at least in part tolerated (entries 6 and 7). Nevertheless, hydrodehalogenation was observed as a slow side reaction yielding the catalytically inactive nickel chloride or bromide species. Although the *p*-acetoxy-derivative in entry 9 was converted to the corresponding silyl ether in high yield, the low isolated yields are due to the basic work up which led to partial ester hydrolysis. In contrast to the other substrates, cisor trans-stilbene oxide required elevated temperatures (50 °C) react and, after workup, yielded racemic 1,2to diphenylethanol. Finally, we were able quantitatively to convert 4 mmol (500 mg) of styrene oxide with very low catalyst loading (1 mol%) in four hours under solvent-free version conditions. Solvent free conditions were also found to be possible for solid epoxides as substrates using a ball mill¹⁴ (for details see ESI). We have found that only aryl-substituted epoxides, can be converted to an acceptable degree under catalytic conditions. The use of aliphatic epoxides leads to no reaction at room temperature and raising the reaction temperature led to the partial decomposition of the catalytically active nickel hydride species, resulting in very low conversions for alkyl-substituted epoxides (< 5%).

The stereocenter of the racemic epoxides is lost during the reaction. However, in order to determine whether our chiral catalyst system is capable of distinguishing the isomers, the reaction was stopped at 50% conversion and the configuration of the unreacted starting material was investigated. No kinetic resolution was observed (i.e. the unreacted epoxide was racemic). In the case of styrene oxide, both enantiomerically pure starting materials are commercially available. The use of the enantiomeric pure compounds had no effect on the results or reaction rates compared to the racemic starting material.

In order to obtain insight into the reaction mechanism, we carried out deuterium labelling experiments. Hydrosilylation of styrene oxide using PhSiD₃ or Ph₂SiD₂ yielded the corresponding silyl ether and after hydrolysis the β -monodeuterated alcohol exclusively [Scheme 5 (a)].

This contrasts with the observation made by Brookhart et al. for a cationic η -1-silane iridium(III) complex that catalysed the regioselective hydrosilylation of epoxides, in which deuteration of the α -position in the resulting alcohol was observed.^{10b} The Lewis acid catalysed ("Meinwald") epoxide rearrangement to aldehydes or ketones is well known.^{15} Followed by hydrosilylation the deuterium incorporation at the α position can be explained. Since the nickel catalyst system is *inactive* for the conversion carbonyl functions, an epoxide isomerization followed by a hydrosilylation step can be excluded.



Scheme 5 Synthesis of β -deuterated alcohols using 1a as a catalyst (a). Competition experiment to determine the kinetic isotopic effect (b). Stoichiometric conversion of Styreneoxide with equivmolar amounts of nickelhydride 2a and deuterosilane (c).

A H/D kinetic isotope effect (KIE) of $k_{\rm H}/k_{\rm D}$ = 1.5 was determined by ¹H and ¹³C NMR employing equal amounts of hydrosilane and deuterosilane in the nickel catalysed hydrosilylation and workup of the product with NaOH/MeOH [Scheme 5 (b)].

The deuterium-labeled silane was found not to undergo H/D exchange with the metal hydride within 24 hours. Therefore, the origin of the hydride in the product could be studied by stoichiometric reaction of styrene oxide, Ph₂SiD₂ and the nickel hydrido complex.^{8a,16} No incorporation of deuterium into the product alcohol was detected by NMR after alkaline hydrolysis while the formation of the nickel deuteride complex occurred concomitantly [Scheme 5 (c)]. The nickel hydride **2a** was thus unambiguously identified as the hydride-transfer reagent and a potential non-hydride mechanism for the catalytic reaction could be excluded.

Furthermore, a kinetic study of the reaction was carried out by ¹⁹F NMR using 4'-fluorostyrene oxide as a substrate under the conditions employed previously for the substrate screening (see Table 1). Notably, the reaction profiles of the conversions displayed no induction periods (ESI), i.e. the nickel hydride, which is initially formed, reacts directly. The reaction kinetics were determined by the initial rate method in which the initial concentrations of either substrate, phenylsilane, or precatalyst **1a** were varied while the other two were kept constant. The initial rate was found to display first-order dependence on substrate concentration and on nickel concentration, but observed to be independent of the concentration of the silane (zeroth order dependence, see Figure 2 and ESI).



From these kinetic data, the following rate law for the nickelcatalysed hydrosilylation on epoxides is derived.

$$\frac{d[P]}{dt} = k \left[\left[(PdmBox)NiF \right] \right] * \left[Styrene \text{ oxide} \right]$$
$$k_{295 K} = 5.75 \pm 0.56 * 10^{-4} \frac{l}{mol * 5}$$

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Based on this first experimental mechanistic study we propose a catalytic cycle for the nickel-catalysed hydrosilylation of epoxides which is similar to a mechanism proposed by Guan *et al.* for the nickel-catalysed hydrosilylation of aldehydes and ketones.^{6h} Initially, the precatalyst **1a** or **1b** is rapidly transformed into the nickel hydride **2a** or **2b** by reaction with the silane. The apparent rate law, the low H/D kinetic isotope effect, as well as the observation of NiH as the resting state suggests that the *rate-limiting step* in this hydrosilylation of epoxides is the insertion of the epoxide into the nickel hydride bond. The resulting alkoxido complex then reacts rapidly with the silane in a σ -bond metathesis to regenerate the nickel hydrido complex and release the silyl ether.



epoxides.

In conclusion, we have developed the first protocol for nickel-catalysed anti-Markovnikov hydrosilylation of epoxides. Such primary alcohols, which are of considerable synthetic value, are usually obtained by hydroboration and subsequent oxidation. We point out that our catalytic system also provides a useful tool for the selective preparation of β -deuterated alcohols, which can be difficult to obtain by alternative catalytic methods.¹⁷

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