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Catalytic Generation and Chemoselective Transfer of Nucleophilic Hydrides from Dihydrogen

Felix Pape, Lea T. Brechmann, and Johannes F. Teichert*

Abstract: Copper(I)/N-heterocyclic carbene (NHC) complexes enable the catalytic generation of nucleophilic hydrides from dihydrogen (H₂) and their subsequent transfer to allylic chlorides. The highly chemoselective catalyst displays no concomitant hydrogenation reactivity, as the terminal double bond formed in the hydride transfer remains intact. Switching to deuterium gas (D₂) allows for regioselective monodeuteration with excellent isotope incorporation.

The catalytic generation of nucleophilic hydrides from dihydrogen (H₂) would offer an atom economic^[1] replacement of commonly used complex hydrides such as aluminum- and borohydrides or hydrosilanes, which are all producing a stoichiometric amount of undesired waste.^[2] In order to offer a fully catalytic alternative based on dihydrogen, both the H₂ activation as well as an (ideally) chemoselective downstream hydride transfer must be rendered feasible by the catalyst.

Many transition metal complexes are excellent catalysts for H₂ activation, but their tendency for catalytic hydrogenation (for example of alkenes) prevails (Scheme 1a).^[3] Nucleophilic displacement of leaving groups such as alkyl halides by hydrides generated from H₂ is mostly an unwanted side-reaction that can be suppressed in some cases.^[4] On the other hand, heterogeneous catalysts (with Pd/C being the prime example) generate nucleophilic hydrides from H₂, (as witnessed in hydrodehalogenations^[5] or cleavage of benzyl ethers^[6]). However, also with these catalysts, hydrogenation of alkenes is the prime reaction pathway, hampering a potential hydride transfer in the presence of alkenes (Scheme 1b). In order to effect a chemoselective hydride generation from H₂ and subsequent transfer to an electrophile, a catalyst allowing for H₂ activation that does not display hydrogenative reactivity towards alkenes, which are common functional groups in synthetic building blocks, is required. To the best of our knowledge, in homogeneous catalysis, no such catalyst has been disclosed.^[7]

We herein report a copper(I)/NHC complex which realizes a catalytic hydride transfer from H_2 to allylic chlorides without effecting a catalytic alkene hydrogenation, leaving the terminal double bond thus generated intact (Scheme 1, bottom). Our strategy relies on heterolytic cleavage of the H–H bond by an in situ generated Cu–O bond.^[8] The use of NHC ligands is key to suppress reactivity towards alkenes.^[9–11] We chose allylic halides as highly reactive and therefore challenging model substrates to probe the chemoselectivity of the catalyst.^[7,12]

Initial optimization of the hydride generation and subsequent hydride transfer employing H_2 identified allylic chlorides such as

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Scheme 1. Activation of H_2 , alkene hydrogenation vs. hydride transfer (TM = transition metal, Hal = halogen leaving group).

cinnamyl chloride (2) as optimal substrates (Scheme 2).[13,14] We found that copper(I) halide complexes based upon electron-rich NHC ligands such as $1^{[15]}$ gave the best results in terms of $S_N 2^{2}$ vs. S_N2 regioselectivity (3/4), in combination with sodium tertbutoxide to generate the key Cu-O-bond for H₂ activation.^[8] Employment of strongly donating ligands also suppressed undesired dechlorinated dimers (5).^[16,17] To this end, Z-cinnamyl chloride (Z-2) was fully converted with high preference for the S_N2' product **3**. Notably, no hydrogenation to propylbenzene was observed, underscoring the chemoselectivity of the copper(I) catalyst. We found that the configuration of the allylic double bond has a profound influence on the regioselectivity, as Econfigured allylic chloride E-2 delivered a nearly 1:1 mixture of the regioisomers 3 and 4. Our current hypothesis is that the different double bond configurations lead to a switch in the mechanism.[13,18]



Scheme 2. Hydride/deuteride transfer to cinnamyl chloride (2). Conversion and γ/α ratios determined by GC analysis.

While these results showed the feasibility of using H_2 as a hydride source in a catalytic hydride transfer reaction, one additional advantage of the current approach is that upon

switching to deuterium gas (D₂), selective monodeuteration in the allylic position could be achieved, which leads to valuable deuterated products. Selective isotope labeling is a key technology for drug discovery^[19] as well as the elucidation of reaction mechanisms^[20] or biosynthetic pathways.^[21] In this vein, we could show that a catalytic method for regio- and chemoselective monodeuteration employing D₂ is viable (Scheme 2). When cinnamyl chloride (*Z*-2) was subjected to the allylic reduction conditions with D₂, we found that the conversion dropped to 68% (indicating a kinetic isotope effect) with improved regioselectivity (**3**-d₁/**4**-d₁ = 95:4), and excellent isotope incorporation (>95% D of **3**-d₁).^[22]

For the ensuing investigation of the substrate scope with D₂ at 90 bar pressure,^[17] the reaction time was set at 48 h to ensure full conversion of the starting materials. Notably, in all cases, the deuterium incorporation in the γ position of the terminal alkenes was excellent (≥96% D) and no alkene hydrogenation was observed, highlighting the chemoselectivity of the catalyst employed. Arvl substituted allvlic chlorides 6a-f generally showed high reactivity, and consequently, a reaction temperature of 10 °C was maintained for this substrate class (Scheme 3). Biphenyl and napththyl substituted monodeuterated terminal alkenes 7a and 7c were obtained in good vields (72%) and 69%, respectively) and with very good regioselectivity of 91:9. favoring the γ products 7.^[23] This method was also amenable to higher substituted allylic chlorides 6d-6f.[24] Of particular note is the catalytic deuteride transfer to diaryl allylic chloride 6e. As electrophiles with two aryl groups are rarely viable substrates for transition metal-catalyzed allylic substitutions,^[25] the isolation of diphenylpropene 7e with a respectable regioselectivity of 75:25 favoring the γ substitution product marks a strong point of the catalyst.



Scheme 3. Chemoselective deuteride transfer to aryl allylic chlorides. γ/α ratios determined by ¹H NMR or GC analysis. D incorporation determined by quant. ¹H NMR or by mass spectrometry. [a] 9% D incorporation in the α position. [b] 8 mol% 1 were used. [c] Reaction was run with 10 mol% 1 and 2.4 equiv NaOtBu. [d] 5% D incorporation in the α position. [e] Reaction was run at 40 °C. [f] Product is volatile.

The formation of cyclopropane derivative **7f** with a good 90:10 regioselectivity (γ/α) delivers an important indication that the catalytic hydride transfer does not involve a carbon based radical intermediate. Therefore, at this stage, a polar mechanism

with hydride formation through a heterolytic H–H bond cleavage by the intermediately formed Cu–O-bond^[8,13] followed by coppercatalyzed hydride transfer is assumed.

Generally, alkyl substituted allylic chlorides 9a-I gave excellent results in terms of regioselectivity with slightly elevated reaction temperature (40 °C, Scheme 4). A benzyl as well as a silyl ether (10b, 10c) and a tosylate (10d, as potential additional leaving group) remained intact. The former is of particular note with respect to chemoselectivity, as many transition metal catalysts are known to cleave benzyl ethers under hydrogenative conditions.^[6] Similarly good results were obtained with aryl chloride 10e and aryl bromide 10f, for which no or little deuterodehalogenation (7% for 10f) were observed. In the context of more complex molecular architectures, estrone and pregnenolone derivatives 9i and 9j could be monodeuterated. Whereas the methoxy-substituent of 9i seems to interfere with the regioselectivity of the catalyst ($\gamma/\alpha = 46:54$) most probably through coordination, 10j could be obtained with excellent regioselectivity and good yield (76%, γ/α >95:5). The deuteride transfer from D₂ can also be applied to the corresponding higher substituted allylic chlorides 9k and 9l, indicating little steric interference with the catalyst. Finally, catalytic monodeuteration of farnesyl chloride (91)[26] giving the corresponding terminal alkene 101 displays the potential applicability of the present process for the selective labelling of biologically relevant terpenoid molecules.



Scheme 4. Chemoselective deuteride transfer to alkyl allylic chlorides. γ/α ratios determined by ¹H NMR or GC analysis. D incorporation determined by quant. ¹H NMR or by mass spectrometry. [a] 7% Deuterodehalogenation detected. [b] The product was obtained as a mixture of *tert*-butyl and methyl ester (5:1). [c] 10 mol% **1** were used.

To further demonstrate mechanistic dichotomy of selective single hydride (deuteride) transfer from H₂ (or D₂) and "classic" hydrogenations, in which two hydrogen atoms are transferred from H₂, a combination of both processes each relying on copper(I)/NHC complexes was carried out (Scheme 5). First, a copper(I)-catalyzed alkyne semihydrogenation with imidazolinium salt 15 as ligand precursor was carried out,^[10a,10c,27] yielding a dideuterated Z-allyl silyl ether (not shown) from propargylic silyl ether 12. After subsequent transformation to allylic chloride Z-13-d₂, the catalytic hydride (deuteride) transfer process gave dideuterated 14-d₂ (from the allylic substitution of Z-13-d₂ with H_2) as well as trideuterated 14-d₃ (both catalytic processes using D₂) with excellent isotope incorporations. Therefore, a combination of hydrogenation and hydride/deuteride transfer process each relying on H₂/D₂ can be used to selectively generate H/D labeling patterns.



Scheme 5. Selective preparation of labelling patterns by combination of alkyne semihydrogenation and allylic hydride/deuteride transfer. Conditions: a) 10 mol% CuCl, 16 mol% **15**, 31 mol% *n*BuLi, 90 bar D₂, THF, 60 °C, 48 h. b) 2 equiv TBAF, THF, rt, 4 h, 68% over two steps. c) 2 equiv LiCl, 2 equiv MsCl, 2 equiv 2,6-lutidine, DMF, 0 °C to rt, 14 h, 75%. d) 5 mol% **1**, 1.2 equiv NaO*t*Bu, 90 bar H₂ or D₂, 1,4-dioxane/C₆H₆ (1:1), 40 °C, 16 h (with H₂) or 48 h (for D₂).

We found that under optimized conditions, internal alkynes are not tolerated due to competing catalytic semihydrogenation.^[10] However, when a competition experiment between an internal alkyne (tolane, 16) and allylic chloride 9c (1:1 ratio) was carried out, we observed the formation of skipped diene 17 (after subsequent deprotection of the silyl ether) as result of a reductive coupling reaction (Scheme 6). This result demonstrates that the hydrocupration of the internal alkyne occurs with faster rate than the transfer of the hydride to the allylic chloride, and that a putative vinylcopper intermediate^[9] acts as a nucleophile for a subsequent allylic substitution in an S_N2' fashion. Again, no overreduction/hydrogenation of skipped diene 17 and/or isomerization was observed, underscoring the chemoselectivity of the present catalyst and its suppressed reactivity towards alkenes.^[28] H₂-mediated reductive coupling reactions are attractive due to their atom economy;^[29] and as can be seen from this result, the present catalytic generation of hydrides from H₂ can not only serve as means of selective hydride transfer, but additionally offers a possible replacement of waste-generating hydride sources in C-C bond forming processes. Especially in relation to the much-researched reductive functionalizations with copper hydride intermediates resting on hydrosilanes,^[30] this is an important improvement for reduced waste generation.



Scheme 6. D2-mediated reductive C-C bond formation.

In summary, we have developed a chemo- and regioselective hydride transfer to allylic chlorides using H₂ as seldomly used and atom economic source of nucleophilic hydrides. This approach allows for the possible replacement of commonly used waste-generating hydride donors based on AI, B or Si compounds. Even though a transition metal is employed for the activation of H₂, the choice of catalyst resting on NHC ligands completely suppresses alkene hydrogenation, leading to a chemoselective overall hydride transfer. The fact that H₂ can easily be switched to D_2 allows for a selective catalytic monodeuteration protocol which delivers useful labelled compounds with potential application in drug analytics and elucidation of (bio)-synthetic reaction mechanisms.

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- [16] The dimerized Wurtz-type products **5** were also formed in the absence of H₂, (with and without added TEMPO). We speculate that a polar copper-catalyzed process not involving H₂ is responsible for the formation of these products, as in the absence of a copper catalyst, neither of the products **3–5** were detected.
- [17] Unfunctionalized allylic chlorides such as **9b** could be fully converted at H₂ pressure as low as 25 bar. At even lower pressures, the conversion and regioselectivity deteriorated and unwanted side-reactions (such as the nucleophilic displacement of the allylic chloride by the *tert*-butoxide anion) were observed. For the substrate scope, high D₂ or H₂ pressure (90 bar) was applied to ensure full conversion of all substrates after 48 h. See the Supporting Information for details.
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- [24] The corresponding *E* isomer of **6d** gave **7d** with the inverse regioselectivity of $\gamma/\alpha = 36:64$ in 45% yield. This results demonstrates that also for the higher substitued allylic chlorides, the double bond geometry has a profound impact on the regioselectivity of the monodeuteration.
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