

Homogeneous Catalysis

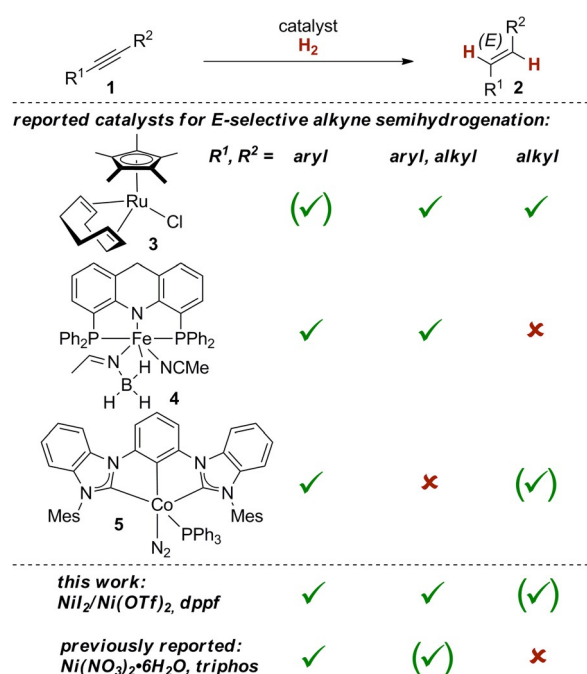
A Simple Nickel Catalyst Enabling an *E*-Selective Alkyne Semihydrogenation**Niklas O. Thiel⁺, Benyapa Kaewmee⁺, Trung Tran Ngoc, and Johannes F. Teichert^{*[a]}

Abstract: Stereoselective alkyne semihydrogenations are attractive approaches to alkenes, which are key building blocks for synthesis. With regards to the most atom-economic reducing agent dihydrogen (H₂), only few catalysts for the challenging *E*-selective alkyne semihydrogenation have been disclosed, each with a unique substrate scope profile.

Here, we show that a commercially available nickel catalyst facilitates the *E*-selective alkyne semihydrogenation of a wide variety of substituted internal alkynes. This results in a simple and broadly applicable overall protocol to stereoselectively access *E*-alkenes employing H₂, which could serve as a general method for synthesis.

Introduction

The stereoselective preparation of alkenes is of prime importance in synthetic chemistry, because the resulting *E*- or *Z*-configuration determines the stereochemical outcome for a variety of commonly employed downstream functionalization reactions (e.g. halogenations, epoxidations).^[1] Catalytic alkyne semihydrogenations based on dihydrogen (H₂) arguably represent the most atom economic approach to alkenes.^[2–4] Hinging on the mechanistic imperative of a *syn*-hydrometallation,^[5,6] many *Z*-selective alkyne semihydrogenations have been developed;^[2] the Lindlar catalyst^[7] arguably being the most prominent. On the other hand, only a few reports about the more challenging transition metal-catalyzed *E*-selective alkyne semihydrogenation have been disclosed.^[8–11] Although for the related *E*-selective alkyne semireductions other—stoichiometric, and therefore undesirable in terms of waste generation—reducing agents have been reported^[3] (such as reduction under Birch-type conditions),^[12] only a handful catalysts for the direct *E*-selective alkyne semihydrogenation with H₂ (1→2, Scheme 1) have been reported: The ruthenium(II) complex 3 is functional group tolerant and gives high *E*-selectivity.^[4,8] However, for



Scheme 1. Approaches to *E*-selective alkyne semihydrogenations with transition metal catalysts.

diaryl alkynes, longer reaction times are required, which led to a significant amount of over-reduction to the corresponding alkane. Emanating from this, catalysts based on first-row transition metals (attractive due to the availability of the metal precursors)^[13] have also been investigated for *E*-selective alkyne semihydrogenation: In this vein, pincer complexes of iron(II) (4)^[9] and cobalt(I) (5)^[10] based on sophisticated, not commercially available ligand frameworks were reported for *E*-selective alkyne semihydrogenations (Scheme 1). These catalysts have been mainly successful for diaryl-substituted alkynes. During the course of the present study, also a nickel-based catalyst has been reported,^[11] which shares the same limitation in sub-

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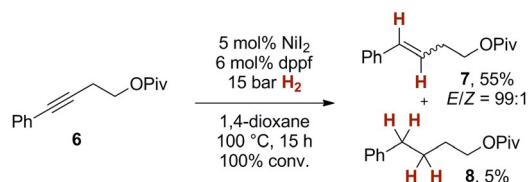
strate scope. However, given that the various catalysts are complementary in the alkyne classes tolerated, there is a clear need for a common, generally applicable protocol.

Herein, we show that a simple and commercially available nickel catalyst consisting of a Ni^{II} salt and 1,1'-bis(diphenylphosphino)ferrocene (dppf) can be employed for highly *E*-stereoselective alkyne semihydrogenations encompassing a wide variety of substitution patterns, offering a complementary approach to the established Ru-based catalysts.^[8,14]

Results and Discussion

During the course of our studies aiming at the (complementary) *Z*-selective alkyne semihydrogenation,^[15] we identified that trace metal impurities based on transition metals led to an unexpected *E*-selectivity. To assess the performance of the catalyst, we first optimized a model reaction (Scheme 2) before studying the substrate scope and functional-group tolerance, and analyzed the possible mechanism.

To probe the performance of nickel catalysts in *E*-selective alkyne semihydrogenation we studied the conversion of homopropargylic pivaloyl ester **6** (Scheme 2). Under optimized conditions,^[16] we found that catalytic amounts of nickel(II) iodide and dppf (5 and 6 mol%, respectively) gave the corresponding styrene derivative **7** with high stereoselectivity (*E/Z*=99:1) at 15 bar H₂ in 1,4-dioxane at 100 °C (55% yield of isolated material). Along with the desired products, we detected 5% of the over-reduced alkane **8** as well as negligible amounts of alkene isomers (< 1%). This suggests that the catalyst has a high preference for the hydrogenation of alkynes over the competing reaction with alkenes.

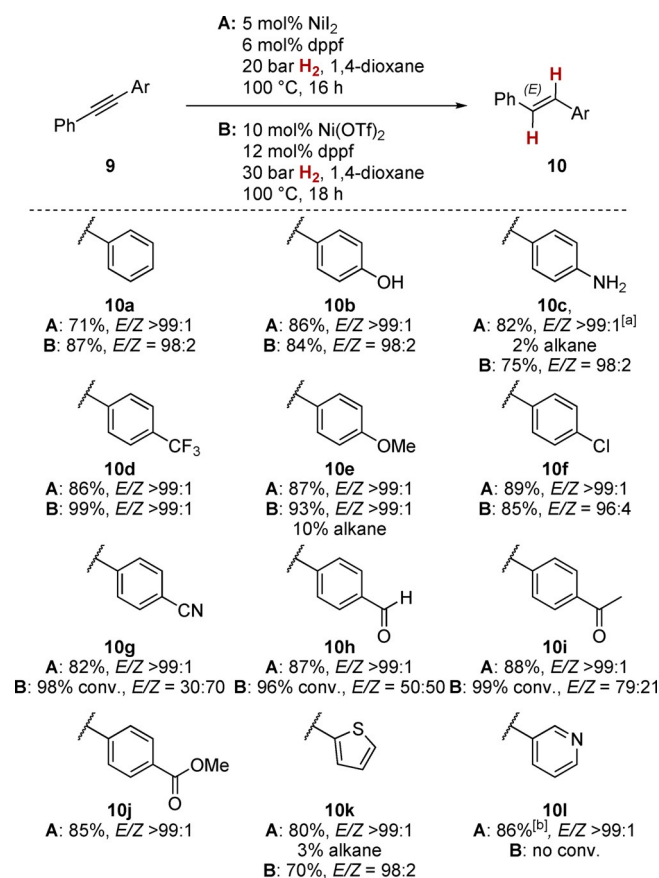


Scheme 2. *E*-selective alkyne semihydrogenation with a nickel(II) complex.

To optimize the catalyst, we investigated various counterions to nickel and found that these are key for high reactivity, because no or little conversion was found with related nickel(II) chloride or bromide complexes.^[16] Best results were obtained with either nickel(II) iodide or nickel(II) triflate. In our hands, wide bite-angle bisphosphine ligands ensured high *E*-selectivity along with little over-reduction.^[16] Elevated pressure of H₂ was needed, because utilizable turnover was only detected at 10 bar H₂ pressure or higher. We also established that—unlike the pivaloyl ester in **6**—under similar reaction conditions, the related benzyl ether was partially cleaved,^[17] which was an early indication for the intermediacy of nickel hydride complexes.^[18]

To explore the substrate scope and functional-group tolerance under optimized conditions with both nickel sources

(conditions **A** and **B**), we investigated the reaction of diaryl alkynes **9** to the corresponding *E*-alkenes **10** (Scheme 3). We had established in preliminary investigations that when nickel(II) triflate was employed, higher catalyst loadings and higher pressure of H₂ (10 mol% Ni(OTf)₂, 30 bar H₂) were necessary.



Scheme 3. Nickel-catalyzed semihydrogenation of diaryl alkynes. [a] Pre-formed NiI₂/dppf complex^[20] had to be used. [b] Conditions: 10 mol% NiI₂, 12 mol% dppf, 40 bar H₂, 100 °C, 24 h.

With nickel(II) iodide (conditions **A**), we found that the reactive functional groups of phenol and aniline derivatives **10b** and **10c**, respectively, did not interfere with the catalyst because these products gave similarly good results in terms of yield and stereoselectivity as the unfunctionalized stilbene **10a** (*E/Z*>99:1, 71–86% yield). For aniline **9c** to be successfully converted, the nickel(II)/dppf complex had to be pre-formed, because the presence of the aniline inhibited the formation of the active catalyst.^[19,20] Both electron-poor and electron-rich tolane derivatives bearing trifluoromethyl, methoxy, chloro, and nitrile substituents **10d–10g** were all converted with equally good results in terms of yields and stereoselectivity (>82% yield, *E/Z*>99:1). Noteworthy, with chlorostyrene **10f**, no dehalogenation^[21] was observed under the reaction conditions. A variety of carbonyl and carboxyl functional groups were not affected by the present catalytic protocol, as can be seen from the successful formation of products **10h–10j**, in which aldehydes, ketones, and carboxylic esters are present.

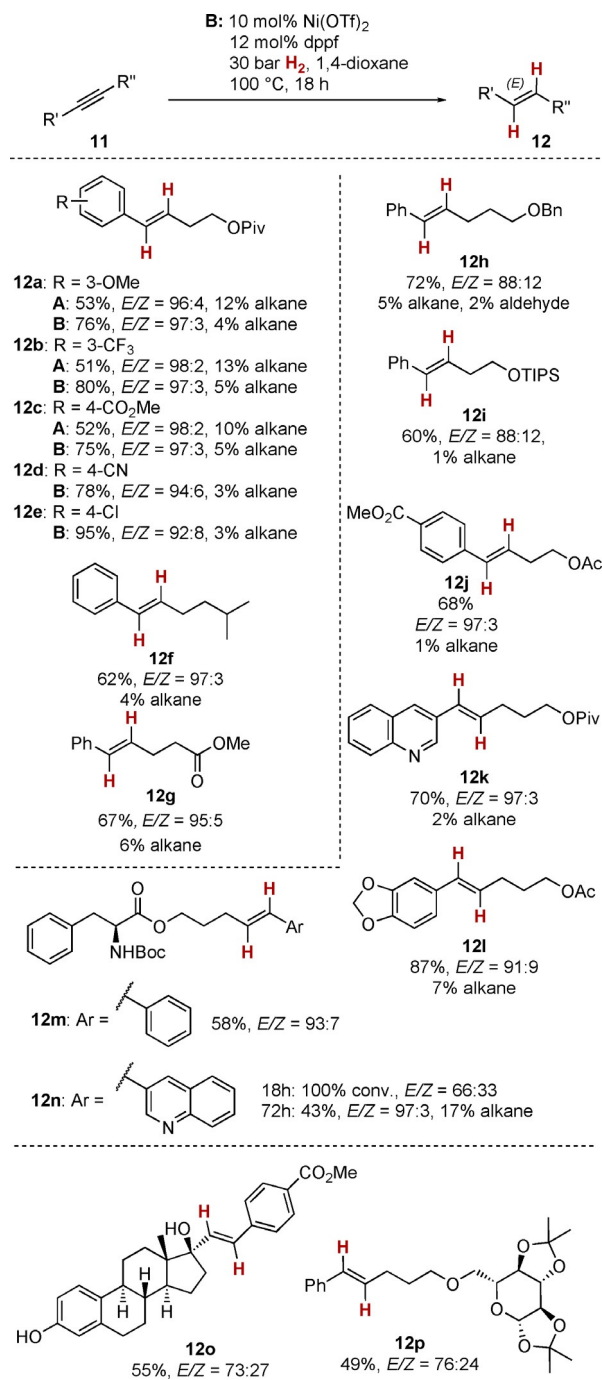
The successful turnover of aldehyde **10h** is noteworthy, as in previous studies, the related nickel-catalyzed alkyne semireductions (with H₂^[11] or other reducing agents than H₂)^[14] aldehydes (and ketones) were not shown to be tolerated, underscoring the considerably milder conditions when employing H₂ as terminal reductant. In terms of functional-group tolerance, these results thus match or outplay the results with diaryl alkynes with the abovementioned catalysts **3–5** reported in literature.^[8–11]

Finally, we turned our attention to heterocyclic systems. Thiophene derivative **10k** was isolated in good yield and with excellent stereoselectivity (80%, *E/Z* > 99:1) along with 3% of over-reduced alkane. 3-Pyridine derivative **10l** gave the usual good results with respect to stereoselectivity (*E/Z* > 99:1) and yield (86%), albeit requiring higher catalyst loading (10 mol% NiI₂, 12 mol% dppf) and elevated pressure (40 bar H₂).

Comparing the two catalytic protocols (A and B) for diaryl alkynes, it can be noticed that overall conditions A give better results in terms of yield and stereoselectivity. A drastic case in this vein being pyridine **10l**, for which conditions B fail entirely, whereas good results were obtained with conditions A. This indicates that the catalyst derived from nickel(II) triflate is more prone to alteration by coordination of substrates. Therefore, for this substrate class, nickel(II) iodide-based catalysts should be employed.

To demonstrate the broad applicability of the present nickel catalyst, we investigated aryl alkyl alkynes **11** next (Scheme 4). Our initial results (formation of *E*-alkenes **12a–c**) unambiguously indicated that for this substrate class, the protocol relying on nickel(II) triflate (conditions B) were clearly superior in terms of yield and chemoselectivity.

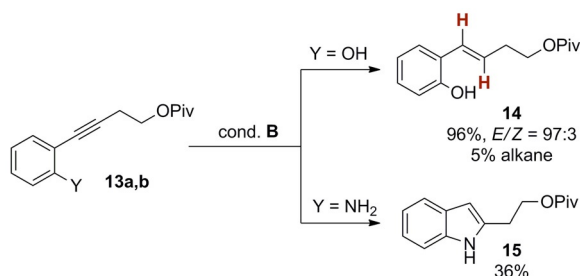
In this vein, a variety of substituted phenylacetylenes bearing electron donating and electron withdrawing groups **11a–e** delivered the corresponding substituted *E*-styrenes **12a–e** with very good *E*-selectivity and little over-reduction to the alkane (*E/Z* ≥ 92:8, ≤ 5% alkane). No reduction of ester (**12c**, see also **12g**) or nitrile (**12d**) groups or dehalogenation (**12e**) was detected. The investigation of potential alcohol protecting groups in **11h–j** established that for a benzyl or silyl ether (**12h** and **12i**), somewhat diminished stereoselectivity was found, whereas the acetate **12j** was formed with the usual high *E*-selectivity (*E/Z* = 97:3). The observation of trace amounts of the terminal aldehyde in the case of **12h** indicates the viability of chain-walking of the alkene by a putative nickel hydride intermediate after ether cleavage.^[18] Heterocyclic substrates **12k** and **12l** were also converted equally well. Furthermore, the presence of a protected amino acid as in phenylalanine derivatives **12m** and **12n** was tolerated by the nickel catalyst. Quinoline **12n** displayed a dependence of the *E*-selectivity on the reaction time. Although a mediocre *E*-selectivity of 66:33 was reached after 18 h reaction time, satisfactory stereoselectivity was achieved after prolonged time (72 h, *E/Z* = 97:3). However, this improved stereoselectivity is accompanied by a drop in yield and an unusual high alkane formation (17%). These data indicate that with extended reaction times, secondary processes leading to over-reduction occur. Furthermore, a possible rapid primary formation of the *Z*-alkene fol-



Scheme 4. Nickel-catalyzed semihydrogenation of aryl alkyl alkynes.

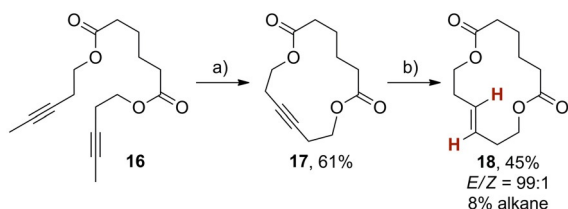
lowed by an isomerization process could be present. Therefore, for sophisticated substrates, one has to balance overall yield and stereoselectivity by choice of reaction time. In addition, for some substrates cyclotrimerization to the corresponding six-fold-substituted benzenes processes occur, which could explain the lower yield (see the Supporting Information for details). Similarly, terminal alkynes do not undergo alkyne semihydrogenation, but instead lead exclusively to cyclotrimerization. In this vein, ethinylestradiol derivative **12o** and glucose derivative **12p** were isolated in acceptable yields after the standard 18 h reaction time. The formation of **12o** indicates that the

present nickel-catalyzed alkyne semihydrogenation can also be successfully carried out with highly substituted propargylic alcohols. We therefore investigated the reaction of *ortho*-phenol and *ortho*-aniline derivatives **13a** and **13b** to probe a possible disruption of the catalyst by coordination of the functional group to the catalyst (Scheme 5). Although phenol **13a** cleanly delivered the desired styrene derivative **14** with the usual results in terms of yield and stereoselectivity (96%, *E/Z* = 97:3), aniline **13b** led in contrast to indole **15** as the major product. In the latter case, a cyclization occurs with higher rates than the respective alkyne semihydrogenation.^[22]



Scheme 5. Complementary reactions of *ortho*-phenol (**13a**) and *ortho*-aniline (**13b**); alkyne semihydrogenation vs. cyclization.

The nickel-catalyzed alkyne semihydrogenation also was extended to cyclic dialkyl alkynes, for which only few catalysts can facilitate an *E*-selectivity. Therefore, we prepared cyclic bislactone **17** by alkyne ring-closing metathesis from diester **16** employing W(CCM₃)(OCMe₃)₃^[23] as catalyst (Scheme 6). Subsequent nickel-catalyzed semihydrogenation of **17** (under conditions **A**) gave *E*-bislactone **18** with complete control of alkene geometry (*E/Z* > 99:1, 45% yield). The stereoselectivity in this transformation is remarkable. *E*-selective semihydrogenations of cyclic alkynes are highly attractive, because these are accessible through alkyne ring-closing metathesis.^[24] The subsequent transformation to *E*-cycloalkenes is a useful alternative to the challenging *E*-selective olefin ring-closing metathesis.^[25] It has to be noted that noncyclic dialkyl alkynes (thus lacking electronic predisposition through conjugation) lead to significant alkene isomerization and/or cyclotrimerization. Therefore, such compounds are not viable substrates for the present catalytic protocol (see the Supporting Information for details).

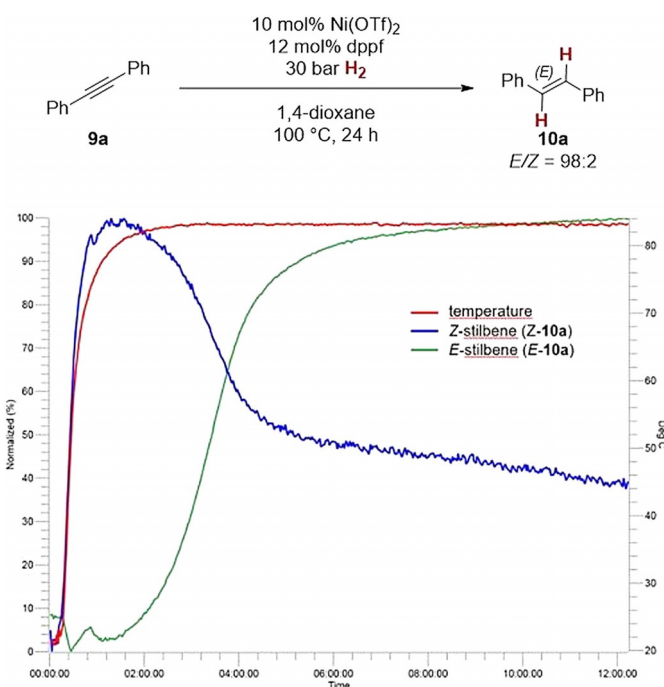


Scheme 6. Ring-closing alkyne metathesis and nickel-catalyzed semihydrogenation of cycloalkyne **17**. Strategy to access cyclic compounds with *E*-configured alkenes. Conditions: a) 3 mol% W(CCM₃)(OCMe₃)₃, 4 Å molecular sieves (MS), toluene, rt, 20 h. b) 5 mol% NiL₂, 6 mol% dppe, 15 bar H₂, 100 °C, 24 h.

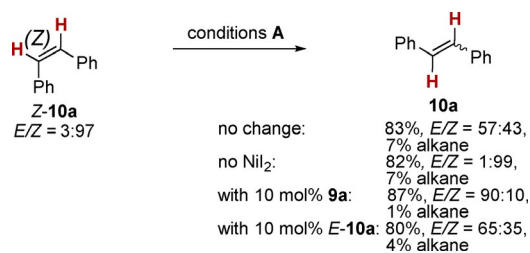
The investigation of the substrate scope led to the conclusion that the commercially available nickel catalyst developed for *E*-selective alkyne semihydrogenation could be widely applied to a variety of substrates, surpassing most of the catalysts previously reported in terms of substrate scope and functional-group tolerance. Especially, the present catalyst marks a convenient complementary approach to the Ru-based catalyst reported earlier,^[8] because diaryl alkynes are prime substrates for the Ni catalyst reported here.

We carried out further experiments to shed light on the possible reaction mechanism. First, we obtained kinetic data by following the high-pressure reaction by IR spectroscopy (Scheme 7). The respective traces indicate that a rapid *Z*-selective alkyne semihydrogenation occurs even when the reaction vessel is still warming up (blue curve for *Z*-stilbene, **Z-10a**). Only after the reaction mixture has reached 80 °C after about 90 minutes, the formation of *E*-stilbene **E-10a** is observed (green curve). After about 3 h, the rate of the formation of *E*-**10a** increases until it becomes the major product. The spectroscopic data therefore suggests two mechanisms which are operative: a first *Z*-selective alkyne semihydrogenation and a second *Z*→*E* isomerization process. This type of mechanism has been observed earlier for the other first-row transition metal-based catalysts for *E*-selective alkyne semihydrogenation.^[9–11]

To investigate whether a reaction pathway through preliminary *Z*-selective alkyne semihydrogenation followed by a (necessarily rapid) *Z*→*E*-isomerization sequence involving nickel hydride complexes^[18] is operative, we subjected *Z*-stilbene (**Z-10a**) to the standard semihydrogenation conditions



Scheme 7. Following the nickel-catalyzed alkyne semihydrogenation (conditions **B**) by in situ IR spectroscopy. Horizontal axis: time [h], left vertical axis: normalized percentage, right vertical axis: temperature [°C]. (Trace of **Z-10a** becomes more unclear with larger conversion due to overlap of signals.)

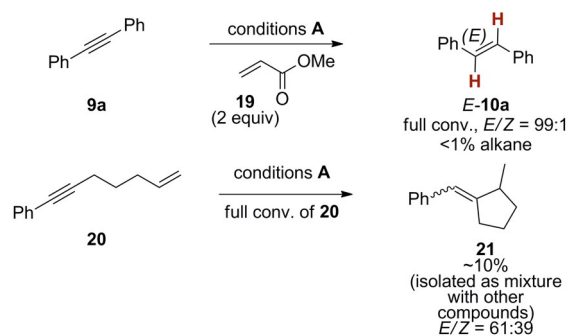


Scheme 8. Experiments probing the reaction mechanism of the alkyne semihydrogenation: *Z/E*-isomerization of stilbene **Z-10a**. Standard conditions **A**: 5 mol% NiI₂, 6 mol% dppf, 20 bar H₂, 1,4-dioxane, 100 °C, 16 h.

(Scheme 8). If an upstream *Z*-selective alkyne semihydrogenation of tolane (**9a**) occurred, **Z-10a** would be a competent reaction intermediate in the formation of **E-10a**. However, we observed only partial isomerization and obtained a 57:43 *E/Z* mixture of **10a** with an unusually high percentage of over-reduction to the alkane (7%, compared with <1% in the semihydrogenation of **9a**, see Scheme 3). Given that in the absence of nickel(II) iodide no change of the *E/Z* ratio of **Z-10a** occurred, a thermal isomerization process was ruled out. A faster isomerization to **E-10a** along with suppressed alkane formation (*E/Z* = 90:10, 1% alkane) was observed when a catalytic amount of tolane (**9a**) was added to the isomerization experiment. Even though these results do not match the values found in the alkyne semihydrogenation, they nevertheless give an indication for an involvement of the alkyne in a putative secondary catalytic *Z*→*E* isomerization process. The effect of adding catalytic amounts of *E*-alkene **E-10a** to the mixture were found to be negligible, underscoring that the presence of an alkyne and not an alkene seems to be key for the reactivity and selectivity. Even though these results demonstrate that *Z*→*E*-isomerization of the alkene products **10** can indeed occur under the standard semihydrogenation conditions, the rate of isomerization is not in agreement with the results of the alkyne semihydrogenation. This data therefore suggests an alternative mechanism which does not involve preliminary *Z*-selective alkyne semihydrogenation followed by *Z*→*E*-isomerization. Alternatively, the nature of the nickel catalyst could be altered by the presence of alkyne and/or alkene, leading to a more sophisticated catalyst.

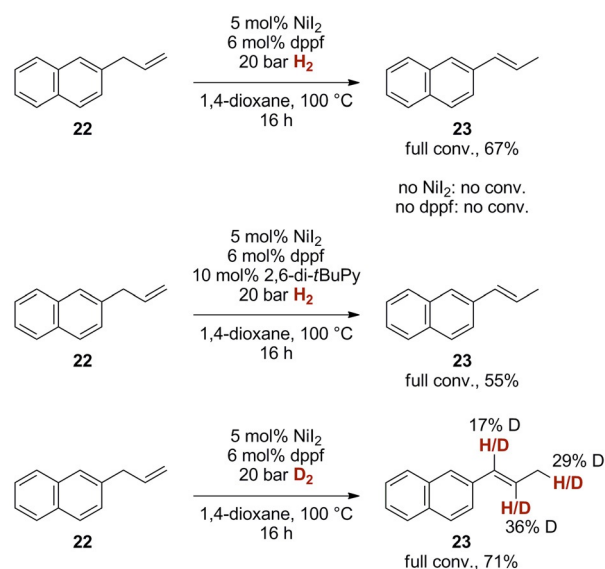
To probe whether a radical mechanism might be operative, methyl acrylate (**19**) was added to the semihydrogenation of **9a** to intercept any radical intermediates (Scheme 9). However, no disruptive effect on the clean and selective formation of **E-10a** was observed. When 1,6-enyne **20** was subjected to the semihydrogenation conditions **A**, full conversion of **20** was observed along with the formation of a mixture of products. Noteworthy is the formation of a small amount of cyclopentane **21** as a mixture of isomers (*E/Z* = 61:39) in these experiments.^[16] The observed cyclization could either be indicative for a radical mechanism, or—more likely—be the result of a cyclization reaction involving a polar carbonickelation mechanism.^[26]

To shed light on possible nickel hydride intermediates present in either of the proposed steps of the catalysis (*Z*-selective



Scheme 9. Experiments probing the reaction mechanism of the alkyne semihydrogenation: trapping/cyclization experiments. Standard conditions **A**: 5 mol% NiI₂, 6 mol% dppf, 20 bar H₂, 1,4-dioxane, 100 °C, 16 h.

alkyne semihydrogenation, *Z*→*E* isomerization), we investigated the isomerization of 2-allylnaphthalene (**22**, Scheme 10) under the reaction conditions **A**. When **22** was subjected to the standard reaction conditions (5 mol% NiI₂, 6 mol% dppf, 20 bar H₂, 1,4-dioxane, 100 °C), we found complete isomerization towards *E*-propenyl-naphthalene **23** (67% yield). This result is an indication for the presence of nickel hydride intermediates, which could facilitate this isomerization through a hydronickelation/β-hydride elimination pathway. It should be noted that in the absence of nickel(II) iodide and also in the absence of dppf, no conversion of **22** was observed, underscoring the crucial role of the ligand for H₂ activation and/or isomerization. To exclude that possibly formed HI could permit a Brønsted acid-catalyzed isomerization,^[27] we carried out the same isomerization (**22**→**23**) in the presence of 10 mol% base (2,6-di-*tert*-butylpyridine). This additive did not hinder the isomerization, indicating the absence of acid-catalyzed processes (Scheme 10, middle). Finally, application of the standard conditions **A** utilizing deuterium gas (D₂) showed a pattern of

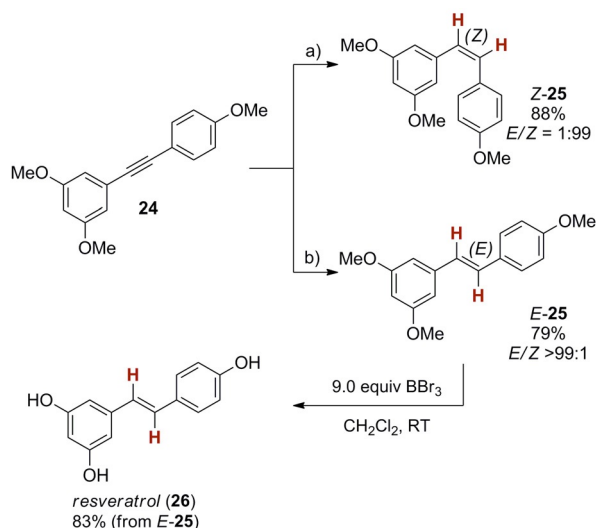


Scheme 10. Isomerization studies. Indication for the presence of nickel hydride intermediates.

partial deuteration at all three side chain carbon atoms (17–36% deuterium incorporation, Scheme 10, bottom). Especially the presence of partial deuterium labelling at the quasi-benzylic position (17% D incorporation) hints towards a re-insertion of a putative nickel deuteride into the alkene already in conjugation to the aromatic ring.

The mechanistic investigations for the present nickel-catalyzed alkyne semihydrogenation thus suggest a mechanism similar to the *E*-selective alkyne semihydrogenation with earlier reported Fe, Co, and Ni complexes (Scheme 1),^[9–11] namely a primary *Z*-selective alkene formation followed by an efficient *Z*→*E*-isomerization by hydronickelation and β-hydride elimination. From the results of the isomerization experiments, the involvement of nickel hydride intermediates is highly probable. However, given that the presence of alkynes for an efficient *Z*→*E*-isomerization is important, the exact structure of the catalyst is not known at present.

To demonstrate the applicability of the nickel catalyst, we carried out a stereoselective synthesis of a naturally occurring compound, resveratrol (**26**, Scheme 11). The synthesis emanates from internal alkyne **24**, which is the key precursor for the alkyne semihydrogenation. To highlight the orthogonal stereoselectivity of the nickel catalyst to “classic” hydrometalation chemistry, we first carried out a *Z*-selective copper(I)-catalyzed alkyne semihydrogenation with [IPrCuOH] as catalyst.^[15b] In this manner, *Z*-**25** was obtained with excellent stereoselectivity (*E/Z* = 1:99, 88% yield). In contrast, the nickel catalyst gave the opposite isomer *E*-**25** in 79% yield (*E/Z* > 99:1). The latter was demethylated^[28] to give resveratrol (**26**) in 83% yield.



Scheme 11. Complementary stereoselective alkyne semihydrogenations and synthesis of resveratrol (**26**). a) 5 mol% [IPrCuOH], 100 bar H₂, THF, 60 °C. b) 5 mol% Ni₂, 6 mol% dppe, 1,4-dioxane, 20 bar H₂, 100 °C.

Conclusions

Stereoselective alkyne semihydrogenations with H₂ are among the most efficient access to alkenes. Only few catalysts are available which offer high *E*-selectivity in this process. Further-

more, these catalysts have been shown to be limited in their substrate scope, with either aryl or alkyl substituents not tolerated. Here, we presented a simple and commercially available nickel catalyst which sustains many of the abovementioned substitution patterns, thus offering a practical approach to *E*-selective alkyne semihydrogenation. Next to a broad substrate scope, mechanistic investigations have been carried out which indicate a two-step overall process of primary *Z*-selective alkyne semihydrogenation and subsequent *Z*→*E* isomerization, with the involvement of nickel hydride intermediates. Our study therefore puts forward a broadly applicable catalyst with a simple protocol for the catalytic and atom-economic access of *E*-alkenes from internal alkynes. These results have implications for synthetic chemistry because the catalyst presented here is widely applicable.

Experimental Section

E-Selective alkyne semihydrogenation, general procedure

Typical reactions were carried out on a 0.26 mmol scale. A glass vial was charged with Ni₂ (5 mol%), and dppe (6 mol%) or Ni(OTf)₂ (10 mol%) and dppe (12 mol%), the corresponding substrate (if solid, 1.0 equiv), a magnetic stirrer and a septum. The charged vial was evacuated and repressurized with N₂ gas using a Schlenk line. Then, the corresponding amount of solvent (7.7 mL mmol⁻¹ substrate) was added. Substrates (1.0 equiv) which are liquid at room temperature were added dropwise using a syringe after the solvent was added. After addition of all components the reactions were stirred at room temperature for 2 min. The autoclave was purged with N₂ (1 × 1 bar, 3 × 10 bar) before the reaction vessels were placed in an autoclave under a counterflow of N₂. Afterwards the autoclave was purged with N₂ (3 × 10 bar) and H₂ (3 × 10 bar) before the appropriate H₂ pressure was applied (pressure is given as initial pressure before heating). The heating block was preheated to the temperature given before the autoclave was placed inside. After the reported reaction time the autoclave was allowed to cool to room temperature and H₂ was released. The autoclave was purged with N₂ (3 × 10 bar) before the reaction vessels were taken out. The reaction mixture was concentrated under reduced pressure, diluted with CH₂Cl₂ and filtered through a small plug of silica (Ø: 2 cm, 2 mL, CH₂Cl₂ as eluent), and all volatiles were removed under reduced pressure. Reactions were subsequently analyzed either by GC and/or ¹H NMR. The crude mixture was then subjected to purification as indicated with the appropriate substrates.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: alkynes · catalysis · hydrogenation · nickel · stereoselectivity

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