

Nickel-Catalyzed Stereodivergent Synthesis of *E*- and *Z*-Alkenes by Hydrogenation of Alkynes

Kathiravan Murugesan^{+, [a]}, Charles Beromeo Bheeter^{+, [b]}, Pim R. Linnebank,^[b]
Anke Spannenberg,^[a] Joost N. H. Reek,^{*, [b]} Rajenahally V. Jagadeesh,^{*, [a]} and Matthias Beller^{*, [a]}

A convenient protocol for stereodivergent hydrogenation of alkynes to *E*- and *Z*-alkenes by using nickel catalysts was developed. Simple Ni(NO₃)₂·6H₂O as a catalyst precursor formed active nanoparticles, which were effective for the semihydrogenation of several alkynes with high selectivity for the *Z*-alkene (*Z*/*E* > 99:1). Upon addition of specific multidentate ligands (triphos, tetraphos), the resulting molecular catalysts were highly selective for the *E*-alkene products (*E*/*Z* > 99:1). Mechanistic

studies revealed that the *Z*-alkene-selective catalyst was heterogeneous whereas the *E*-alkene-selective catalyst was homogeneous. In the latter case, the alkyne was first hydrogenated to a *Z*-alkene, which was subsequently isomerized to the *E*-alkene. This proposal was supported by density functional theory calculations. This synthetic methodology was shown to be generally applicable in >40 examples and scalable to multi-gram-scale experiments.

Introduction

C=C double bonds represent one of the most valuable functional groups in organic chemistry.^[1] Therefore, the development of protocols to selectively obtain *Z*- or *E*-alkenes continues to be important because the absolute stereochemistry of the molecule is crucial for its physical properties.^[1a-d, 2] As an example, stilbenes have been used as parts of molecular motors, showing significant differences in their photochemistry depending on the *E*- and *Z*-configuration.^[3] The most common synthetic pathway to obtain *Z*-alkenes is by semihydrogenation of alkynes with Lindlar's catalyst, which is based on expensive palladium doped with toxic lead salts.^[4] *E*-alkene synthesis from alkynes is more difficult, and the most commonly practiced method is Birch-type reduction^[5] with Na/NH₃ as a stoichiometric reducing reagent. Both approaches suffer from low functional-group tolerance. Because of these drawbacks, there is a continuing interest in more general alternative catalyst systems.^[1c, d] The majority of investigations have focused on noble

metals such as Pd,^[6] Ru,^[7] Rh,^[8] Au,^[9] and Ir.^[10] In addition, non-noble metal catalysts based on Ni,^[11] Co,^[12] Fe,^[13] Cu,^[14] and Mn^[15] have also been reported. Most of these catalysts promote the selective formation of *Z*-alkenes. In case of hydrogenations, overreduction to form the corresponding alkane is a common pathway that lowers the chemoselectivity.

Interestingly, a limited number of homogeneous systems are known to transform alkynes to either *E*- or *Z*-alkenes, which often results in a mixture of isomers.^[6g, h, 7h, i, 11d, g, 16, 17] In this regard, Liu and co-workers^[12d] recently reported a ligand-controlled protocol for the stereodivergent synthesis of both *Z*- and *E*-alkenes with cobalt catalysts by applying NH₃BH₃ as a reducing agent. Earlier, Kusy and Grela reported a similar strategy by using different Ru-olefin complexes to semihydrogenate alkynes with NaH and HCOOH as reductants.^[7b] Furthermore, Richmond and Moran have developed Ni-based catalysts with stoichiometric amounts of zinc and formic acid as reductant.^[11d] All of these semireduction methods make use of stoichiometric amounts of reducing agents, which generates waste. In addition to these protocols, Ru,^[7g] Pd,^[6f] and Ir^[10b] catalysts have been reported for the synthesis of *Z*- and *E*-alkenes through transfer hydrogenation. Regarding the reductant, the use of molecular hydrogen offers significant advantages because it is inexpensive and allows for 100% atom-efficient transformations. However, so far, only Rh^[8] and borane-based^[16c] catalysts have been used for stereodivergent synthesis of both *E*- and *Z*-alkenes.

Nickel catalysts are commonly used for hydrogenations of a wide range of unsaturated compounds in the chemical industry and academic laboratories.^[18] As a result, we anticipated that defined nickel complexes should also be active in alkyne hydrogenation. However, preventing overreduction to the corresponding alkanes could be challenging.^[19] Herein, we describe the first protocols for stereodivergent Ni-catalyzed semi-

[a] K. Murugesan,⁺ Dr. A. Spannenberg, Dr. R. V. Jagadeesh, Prof. Dr. M. Beller
Leibniz-Institut für Katalyse e.V. an der Universität Rostock
Albert-Einstein-Str. 29a, 18059 Rostock (Germany)
E-mail: Jagadeesh.Rajenahally@katalysis.de
Matthias.Beller@katalysis.de

[b] Dr. C. B. Bheeter,⁺ P. R. Linnebank, Prof. Dr. J. N. H. Reek
Van't Hoff Institute for Molecular Sciences
University of Amsterdam
Science Park 904, 1098 XH, Amsterdam (The Netherlands)
E-mail: J.N.H.Reek@uva.nl

[†] These authors contributed equally to this work.

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hydrogenation of alkynes. Both *E*- and *Z*-alkenes can be formed with excellent selectivity by using convenient nickel precursors in the presence or absence of phosphine ligands.

Results and Discussion

Synthesis of *E*-alkenes

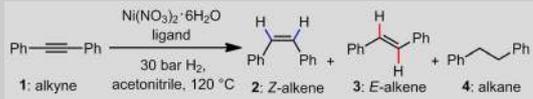
At the start of our investigations we were interested in the influence of phosphine ligands on the (chemo)selectivity of Ni-catalyzed alkyne hydrogenations. The reaction of diphenylacetylene with molecular hydrogen was used as a benchmark system. To identify suitable Ni-catalysts, we tested several commercially available phosphines including privileged mono-, bi-, tri-, and tetradentate ligands in the presence of nickel nitrate.

Surprisingly, in all cases the reaction selectively afforded stilbenes, and only trace amounts of the corresponding alkane reduction products were observed. Interestingly, as shown in Table 1, simple monodentate arylphosphines (**L1**–**L3**) provided *Z*-alkenes with 99:1 selectivity (entries 1–3). Applying bisphosphine ligands gave mixtures of *E*- and *Z*-products (entries 4–7). Gratifyingly, the application of some tri- and tetradentate phosphines (**L8**–**L10**) predominantly afforded *E*-stilbenes. More specifically, in the presence of bis(2-diphenylphosphinoethyl)phenyl-phosphine (linear triphos, **L9**) and tris[2(diphenylphosphino)ethyl]phosphine (**L10**), full conversion of diphenylacetylene and excellent selectivity for the *E*-alkene product (*E/Z* selectivity >99%, entries 9 and 10) was achieved with the nickel catalyst.

These results were in line with the nickel–triphos system with over-stoichiometric amounts of reducing agents (Zn + HCOOH) reported by Richmond and Moran.^[11d] To investigate this *E*-selective hydrogenation in more detail, the influence of the solvent was investigated with the Ni(NO₃)₂·6H₂O/triphos (**L9**) system. If the reaction was performed in acetonitrile or isopropyl alcohol, very high (>99%) selectivity for the *E*-alkene was obtained, whereas the reactions in other solvents resulted in mixtures of the *E*- and the *Z*-product (Table S2 in the Supporting Information).

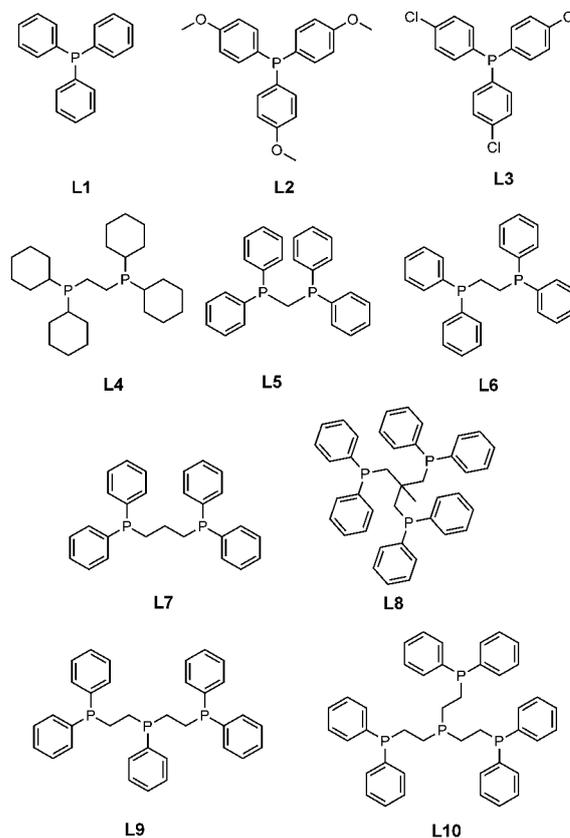
With a convenient system [Ni(NO₃)₂·6H₂O/**L9**] in hand, we explored the substrate scope for this in situ-generated catalyst. Alkynes containing electron-donating or -withdrawing groups were selectively converted to obtain *E*-selective olefins in up to 98% yield (Scheme 1, products **5**–**22**). Functional groups such as hydroxy groups, heterocycles, halide, silyl, and boronic ester groups were well tolerated (products **8**–**11** and **13**–**18**). Even substrates with substituents that could be easily reduced, such as nitriles and ketones, were converted with excellent chemo-selectivity, leaving the functional groups untouched (products **12**, **18**, and **22**). To demonstrate the scalability of the Ni–triphos system, semihydrogenation reactions of four substrates were performed at 1–10 g scale (Scheme 2). Similar yields and selectivities were obtained in all cases. Notably, the catalyst loading was decreased in gram-scale reactions: at 1 g scale, 3 mol% nickel catalyst was used (6 mol% ligand), whereas at a 10 g scale only 2 mol% nickel was applied.

Table 1. Ligand effects in the semihydrogenation of diphenyl acetylene to obtain stilbenes.^[a]



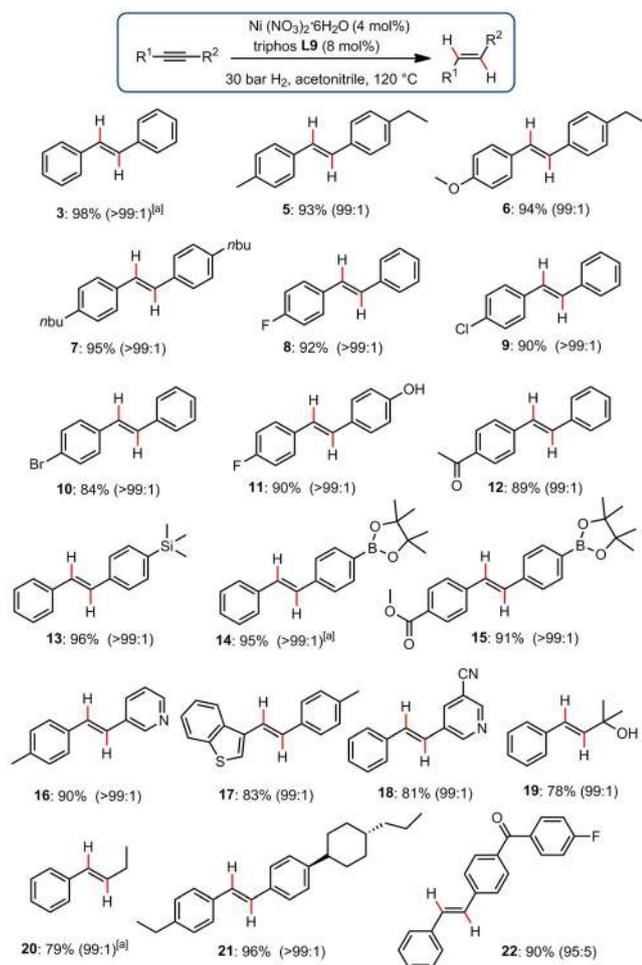
Entry	Ligand	Conv. [%]	Yield 2 + 3 [%]	Selectivity (<i>E/Z</i>)	Yield 4 [%]
1	L1	98	95	1:99	2
2	L2	90	88	1:99	1
3	L3	97	94	1:99	2
4	L4	>99	96	5:95	2
5	L5	80	78	10:90	1
6	L6	>99	97	40:60	1
7	L7	>99	96	50:50	1
8	L8	>99	98	65:35	–
9	L9	>99	98	>99:1	–
10	L10	>99	98	>99:1	–

Reaction conditions: [a] diphenylacetylene (0.5 mmol), Ni(NO₃)₂·6H₂O (4 mol%), ligand (8 mol%), 30 bar H₂, acetonitrile (2 mL), 120 °C, 15 h. Yields were determined by GC with *n*-hexadecane as standard. *E/Z* isomeric ratios were determined by GC–MS and NMR spectroscopy.

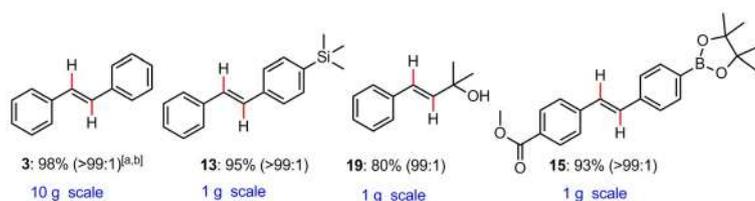


Synthesis of *Z*-alkenes

Next, we turned our interest to the selective synthesis of *Z*-stilbene by using Ni(NO₃)₂·6H₂O in the presence of monodentate arylphosphines. Interestingly, similar reactivity and selectivity



Scheme 1. Ligand-controlled Ni-catalyzed synthesis of *E*-alkenes. Reaction conditions: alkyne (0.5 mmol), Ni(NO₃)₂·6H₂O (4 mol%), triphos (8 mol%), 30 bar H₂, acetonitrile (2 mL), 120 °C, 15 h, isolated yields. [a] GC yields with *n*-hexadecane as standard. Values in parentheses refer to *E/Z* isomeric ratio determined by GC–MS and NMR spectroscopy.



Scheme 2. Practical utility of a Ni–triphos system for synthesis of *E*-alkenes. Reaction conditions: alkyne (1 g), Ni(NO₃)₂·6H₂O (3 mol%), triphos (6 mol%), 30 bar H₂, acetonitrile (12 mL), 120 °C, 15 h, isolated yields, *E/Z* ratio was determined by GC–MS and NMR spectroscopy. [a] GC yields with *n*-hexadecane as standard. [b] alkyne (10 g), Ni(NO₃)₂·6H₂O (2 mol%), triphos (4 mol%), 30 bar H₂, acetonitrile (120 mL), 120 °C, 15 h, GC yields. Values in parentheses refer to *E/Z* isomeric ratio determined by GC–MS and NMR spectroscopy.

(93% *Z*-stilbene with >99% selectivity) was observed in the absence of phosphines (Table 2, entry 1). Therefore, we evaluated different nickel(II) salts for the benchmark hydrogenation. As shown in Table 2, NiCl₂, NiBr₂, and Ni(OAc)₂ did not show any activity (entries 2–4).

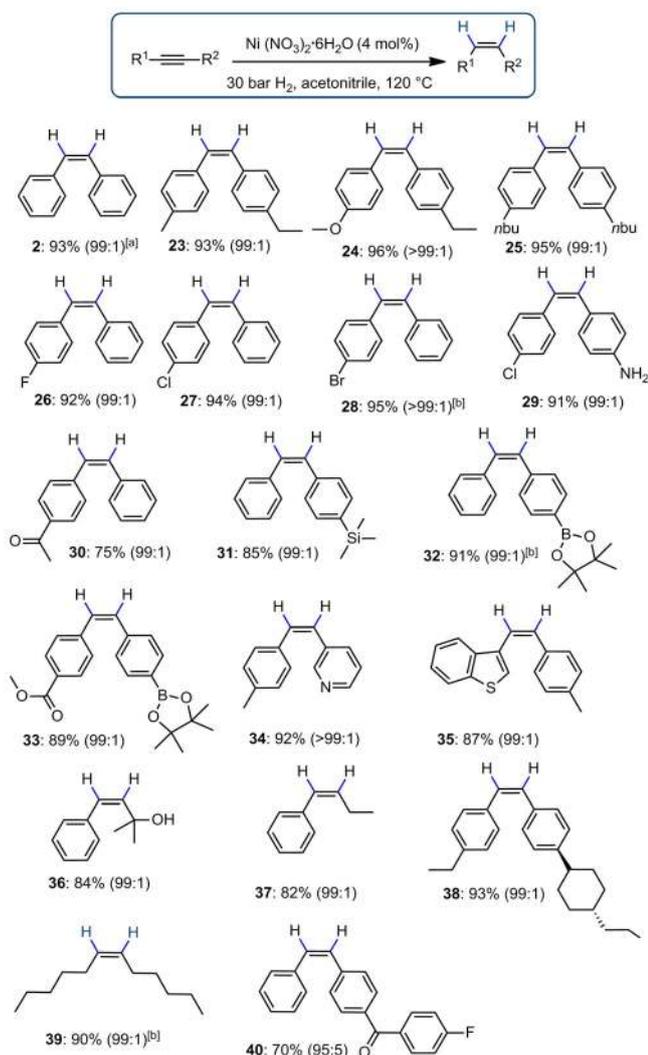
Table 2. Hydrogenation of diphenylacetylene using different metal salts.^[a]

Entry	Metal precursor	Conv. [%]	Yield of alkene [%]	Selectivity (<i>Z/E</i>)	Yield of alkane [%]
1	Ni(NO ₃) ₂ ·6H ₂ O	99	93	99:1	6
2	NiBr ₂ ·xH ₂ O	–	–	–	–
3	NiCl ₂ ·DME	–	–	–	–
4	Ni(OAc) ₂ ·4H ₂ O	–	–	–	–
5	Ni(OTf) ₂	65	59	99:1	5
6	Ni(acac) ₂	50	45	99:1	4
7	Co(NO ₃) ₂ ·6H ₂ O	–	–	–	–
8	Fe(NO ₃) ₃ ·9H ₂ O	–	–	–	–
9	Mn(NO ₃) ₂ ·4H ₂ O	–	–	–	–
10 ^[b]	Ni(NO ₃) ₂ ·6H ₂ O	99	93	99:1	6
11 ^[c]	Ni(NO ₃) ₂ ·6H ₂ O	99	93	99:1	6
12 ^[d]	Ni(NO ₃) ₂ ·6H ₂ O	70	65	99:1	5

Reaction conditions: [a] diphenylacetylene (0.5 mmol), metal salt (10 mol%), 30 bar H₂, acetonitrile (2 mL), 120 °C, 15 h. Yields were determined by GC with *n*-hexadecane standard. *Z/E* isomeric ratios were determined by GC–MS and NMR spectroscopy. [b] 6 mol% catalyst loading. [c] 4 mol% catalyst loading. [d] 2 mol% catalyst loading. DME = ethylene glycol dimethyl ether; acac = acetylacetonate.

After finding that Ni(NO₃)₂·6H₂O was a convenient and inexpensive precatalyst for *Z*-selective semihydrogenation of alkynes, we evaluated its general applicability for different aromatic and aliphatic alkynes (Scheme 3). Gratifyingly, all investigated substrates were converted into the corresponding *Z*-alkenes in up to 96% yield with 99% selectivity (>99% *Z/E*). This simple Ni salt also exhibited excellent chemoselectivity. The generated active catalyst was compatible with halogen substituents (Br, Cl, F), and no significant dehalogenation was observed (products 26–29) even though nickel complexes are generally known to be dehalogenation catalysts.^[20] In addition, alkyne groups were selectively reduced in the presence of other sensitive groups such as silyl, boronic ester, ketone, and ester groups (products 30–33 and 40). Furthermore, heterocyclic and aliphatic alkynes were also semihydrogenated to the respective *Z*-alkenes with excellent yield and stereoselectivity (products 34–35 and 39).

After these successful semihydrogenation reactions of internal alkynes, we evaluated the semihydrogenation of terminal alkynes (Scheme 4). Selective hydrogenation of these substrates is more challenging because terminal alkenes are easier to hydrogenate than internal ones. Nevertheless, all terminal alkynes we studied were converted to the corresponding alkenes with good selectivity (Scheme 4, products 44–50; 45 and 50 have 15 and 17% overhydrogenation product, respectively).

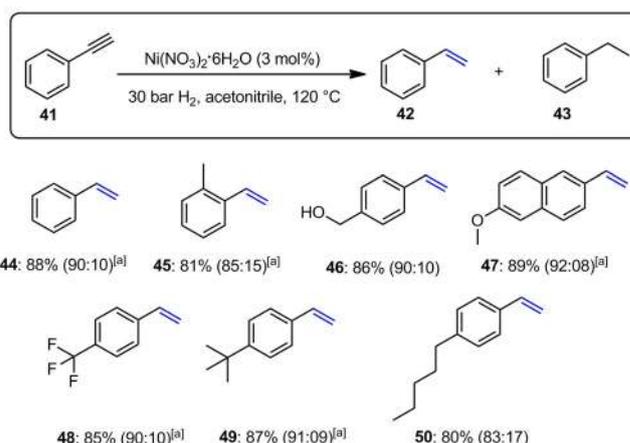


Scheme 3. Substrate scope for the synthesis of *Z*-alkenes. Reaction conditions: alkyne (0.5 mmol), Ni(NO₃)₂·6H₂O (4 mol%), 30 bar H₂, acetonitrile (2 mL), 120 °C, 15 h, isolated yields. [a] GC yields with *n*-hexadecane as standard. [b] 8 mol% Ni(NO₃)₂·6H₂O. Values in parentheses refer to *Z/E* isomer ratio determined by GC-MS and NMR spectroscopy.

Mechanistic studies

To determine if the catalyst was homogeneous or heterogeneous, we performed mercury tests^[12c,d] for both the *Z*- and the *E*-alkene-selective catalyst systems. The ligand-free Ni(NO₃)₂·6H₂O catalyst system showed no conversion in the presence of a drop of Hg under otherwise identical conditions, which indicated that the active catalyst was heterogeneous. This was in line with the work of Bai and co-workers,^[11e] who reported the formation of nickel nanoparticles from nickel salts during the reduction of alkynes to *Z*-alkenes with NaBH₄. In general, semihydrogenation of alkynes gives *Z*-alkenes owing to *syn*-addition of adsorbed hydrogen on the surface of a heterogeneous catalyst.^[4]

In contrast, the Ni-triphos (L9) catalyst system showed no change in catalytic activity in the presence of Hg and still produced the *E*-alkene with similar high selectivity, demonstrating that under these conditions the active species was homogene-



Scheme 4. Selective hydrogenation of terminal alkynes by Ni(NO₃)₂·6H₂O. Reaction conditions: alkyne (0.5 mmol), Ni(NO₃)₂·6H₂O (3 mol%), 30 bar H₂, acetonitrile (2 mL), 120 °C, 15 h, isolated yields along with alkene/alkane ratio. [a] GC yields with *n*-hexadecane as standard.

ous. To understand this active catalyst in more detail, we synthesized a Ni-triphos complex in quantitative yield (Section S6 in the Supporting Information). Crystals suitable for single-crystal XRD were grown by recrystallization in ethanol. Analysis of the solid-state structure showed that the complex was pentacoordinated and all the three phosphorous atoms were coordinated to the nickel center (Figure 1). The ³¹P{¹H} NMR spectrum of this complex in CDCl₃ solution (Figure S4 in the Supporting Information) displayed a doublet at $\delta_p = 48$ ppm and a triplet at $\delta_p = 110$ ppm, in line with a tridentate coordination to nickel in solution.

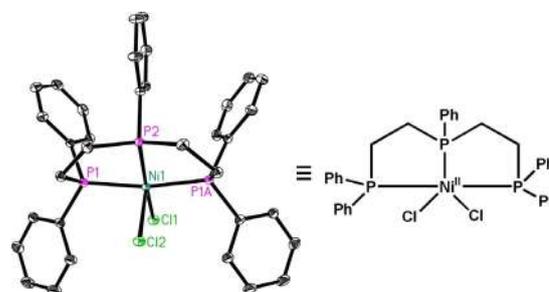


Figure 1. Molecular structure of complex **A** obtained by X-ray analysis. Displacement ellipsoids drawn at the 30% probability level. Hydrogen atoms omitted for clarity.

To investigate if the Ni complex **A** was active in the isomerization reaction, we added *Z*-stilbene to Ni complex **A** (6 mol%) at 120 °C under 30 bar H₂. In this experiment, *Z*-stilbene was completely isomerized to *E*-stilbene within 15 h (Table 3, entries 1 and 2). Remarkably, not even traces of alkane were observed under these conditions. Surprisingly, the same experiment without H₂ gave 20% of *E*-stilbene, and isomerization was not observed without the addition of catalyst (entries 3 and 4). Interestingly, cobalt catalysts that have been used for *E*-selective alkyne semihydrogenation reactions have shown

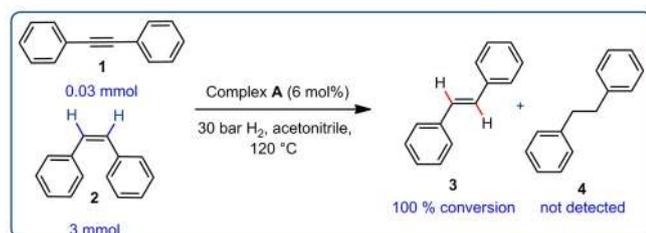
Table 3. Isomerization of *Z*- to *E*-stilbene.^[a]



Entry	Amount of substrate [mmol]	H ₂ pressure [bar]	Selectivity (Z/E)	Yield of 3 [%]
1	0.5	30	0:100	> 99
2	5	30	0:100	> 99
3	0.5	0	80:20	20
4 ^[b]	0.5	30	100:0	0

Reaction conditions: [a] *Z*-stilbene (0.5 mmol), complex **A** (6 mol%), 30 bar H₂, acetonitrile (2 mL), 120 °C, 15 h, GC yields with *n*-hexadecane as standard. [b] Without catalyst.

similar isomerization behavior.^[12d] In another control experiment, a mixture of diphenyl acetylene and *Z*-stilbene (1:100) was hydrogenated to mimic the reaction conditions under which most of the alkyne has been converted but no isomerization has taken place yet. Under standard experimental conditions with complex **A**, 100% *E*-stilbene was formed, and no overhydrogenated product was detected (Scheme 5). All these observations were in line with a mechanism in which the alkyne is first converted to the *Z*-alkene, which is subsequently isomerized to the *E*-alkene by a homogeneous nickel complex.



Scheme 5. Hydrogenation of a diphenylacetylene/*Z*-stilbene mixture with complex **A**. Reaction conditions: alkyne (0.03 mmol), alkene (3 mmol), complex **A** (6 mol%) or Ni(NO₃)₂·6H₂O (4 mol%), triphos (8 mol%), 30 bar H₂, acetonitrile (2 mL), 120 °C, 15 h, isolated yields. GC yields with *n*-hexadecane as standard.

Therefore, we propose the following mechanism for the formation of *E*-alkenes, which consists of two cycles that both start with a Ni^{II} monohydride species (Figure 2). Initially, the Ni-hydride species inserts into the alkyne, and the *Z*-alkene is formed after subsequent hydrogenolysis. In the second cycle, the molecular Ni–H complex inserts into the formed *Z*-alkene, leading to a nickel alkyl species. A similar insertion has been reported for alkene hydrogenation with nickel(II) phosphine-based systems.^[18b] In contrast to such hydrogenations, the triphos-ligated complex undergoes bond rotation and β-hydride elimination to yield the *E*-alkene.

To validate the proposed mechanism, DFT calculations were conducted (see the Supporting Information for details, Figure S10).^[21] All energy values are given in kcal mol⁻¹. A tricoor-

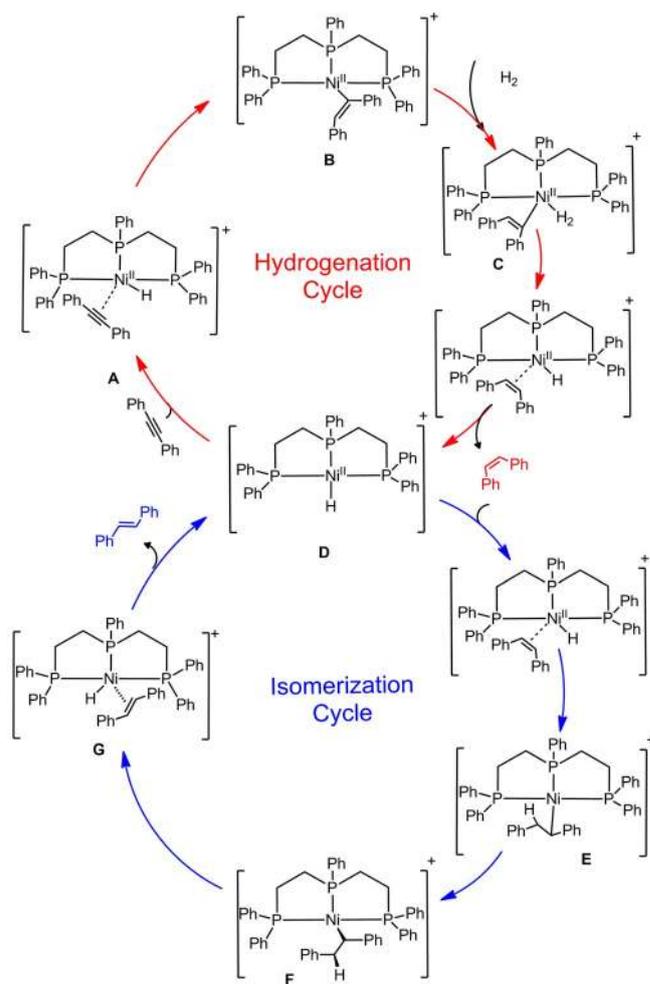


Figure 2. Proposed mechanism for the *E*-selective nickel-catalyzed hydrogenation of alkynes.

ordinated Ni^{II} hydride was used as the common intermediate for both cycles (Figures 3 and 4). The benchmark substrate diphenyl acetylene was used for the calculations. Insertion of the nickel monohydride into the alkyne moiety (**II**) has a low energy barrier, leading to intermediate **III**. Coordination of hydrogen to the nickel moiety (**IV**) is slightly uphill, and after the hydrogenolysis step (**V**), the *Z*-alkene is formed, and the nickel hydride species (**VI**) is regenerated. No transition state that directly forms the *Z*-alkene from hydrogenolysis was found because this would involve rotation around a double bond. For the isomerization cycle (Figure 4), the *Z*-stilbene coordinates to the nickel hydride, which subsequently inserts into the double bond (**VII**) to form intermediate **VIII**. The alkyl species is able to freely rotate around its axis, and the *E*-alkene (**X**) is formed via a β-hydride elimination transition state (**IX**). The barriers of isomerization are low, which explains the high chemoselectivity for the *E*-alkene obtained by using this system. Additionally, we computed hydrogen coordination to the nickel alkyl species (**XI**) and subsequent hydrogenolysis (**XII**) towards the alkane product (**XIII**) (Figure 5). The barrier for hydrogenation was almost 6 kcal mol⁻¹ higher compared with that of the β-hydride elimination leading to the *E*-product, which is in line

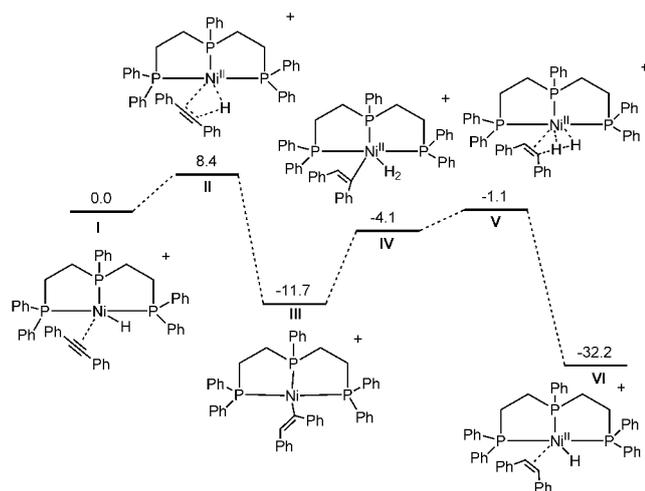


Figure 3. DFT calculations for hydrogenation of diphenylacetylene to *Z*-stilbene. I was set at 0.0 kcal mol⁻¹. All energies presented are in kcal mol⁻¹.

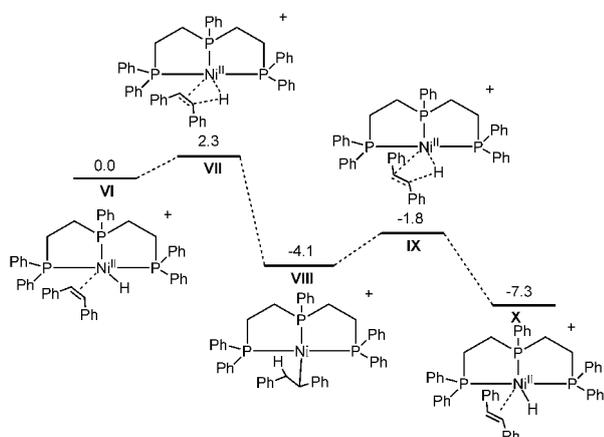


Figure 4. DFT calculations for isomerization of *Z*-stilbene to *E*-stilbene. Intermediate VI was set at 0.0 kcal mol⁻¹. All energies presented are in kcal mol⁻¹.

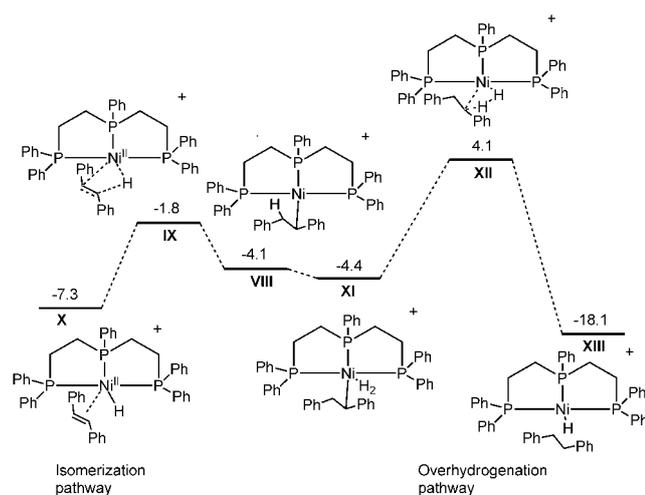


Figure 5. Comparison of the alkene hydrogenation step and β -hydride elimination step towards the *E*-stilbene product. Energies are presented relative to intermediate VI set at 0.0 kcal mol⁻¹. All energies presented are in kcal mol⁻¹.

with the high chemoselectivity because the alkane product was not formed in significant amounts.

Conclusions

The first nickel-based catalysts for stereodivergent semihydrogenation of alkynes with molecular hydrogen is reported, as well as protocols for the preparation of both *E*- and *Z*-alkenes. These products were formed in an atom-efficient manner in high yields with excellent chemo- and stereoselectivity. The *Z*-alkenes were selectively formed when simple Ni(NO₃)₂ was used as a catalyst precursor. The presence of triphos as a tridentate ligand was needed to yield the corresponding *E*-alkenes (> 99:1 selectivity). Mechanistic studies showed that the Ni(NO₃)₂ system is heterogeneous, whereas the *E*-selective Ni-triphos system operates as a homogeneous catalyst. Furthermore, the latter catalyst initially produced the *Z*-alkene, which subsequently isomerized to the *E*-alkene in a separate catalytic cycle. Notably, both nickel nanoparticles and the molecular-defined Ni-triphos catalyst tolerated a broad scope of molecules containing internal and terminal alkynes as well as different substituents and functional groups. Both catalyst systems were compatible with a benchtop set-up and could be applied to multigram-scale reactions.

Experimental Section

Experimental details and spectra can be found in the Supporting Information. CCDC 1869414 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: alkenes · alkynes · hydrogenation · nickel · stereoselectivity

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