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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]

Abstract: A convenient protocol for stereodivergent hydrogenation of alkynes to E-alkenes and Z-alkenes using nickel catalysts is reported. Simple $Ni(NO_3)_2 \cdot 6H_2O$ as a catalyst precursor forms active nanoparticles, which are 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 are highly selective for the E-alkene products (E:Z>99:1). Mechanistic studies reveal that the Z-alkene selective catalyst is heterogeneous and the E-alkene selective catalyst is homogeneous in nature. In the latter case, the alkyne first gets hydrogenated to a Z-alkene, which is subsequently isomerized to the E-alkene. This proposal is supported by density functional theory (DFT) calculations. This synthetic methodology is shown to be generally applicable in >40 examples and scalable to multi-gram experiments.

Introduction

C-C double bonds represent one of the most valuable functional groups in organic chemistry.[1a-e] Hence, the development of protocols to obtain Z- or E-alkenes selectively continues to be important because the absolute stereochemistry of the molecule is crucial for its physical properties.[1a-d], [2a-c] As an example stilbenes were used as part of molecular motors, showing significant differences in their photochemistry depending on the E- and Z-configuration.[3a-d] The most common synthetic pathway to obtain Z-alkenes is by semihydrogenation of alkynes using 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] using Na/NH_3 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 focused on noble metals such as Pd,[6a-h] Ru,[7a-h] Rh,[8a-b] Au,[9a-b] and Ir[10a-b]. In addition, non-noble metal catalysts based on Ni,[11a-h] Co,[12a-d] Fe,[13a-f] Cu,[14a-c] Mn [15a-b] have also been reported. Most of these catalysts promote the selective formation of Z-alkenes. In case of hydrogenations, over-reduction 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-olefins, which often resulted in the mixtures of isomers.[6g-h],[7h-i],[11g],[16a-c],[11d],[17] In this regard, recently Liu et al.,[12d] reported a ligand controlled protocol for the stereodivergent synthesis of both Z- and E-alkenes using cobalt catalysts applying NH_3-BH_3 as a reducing agent. Earlier on, Grela and co-workers reported a similar strategy using different Ru-olefin complexes to semihydrogenate alkynes using NaH and HCOOH as reductants.[7b] Further, Moran et al. have developed Ni-based catalysts using stoichiometric amounts of zinc and formic acid as reductant.[11d] All of these semi-reduction 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 using transfer hydrogenations. 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.[18a-f] As a result, we anticipated defined nickel complexes should be active in alkyne hydrogenation, too. However, preventing over-reduction to the corresponding alkanes could be challenging.[19a-d] Herein, we describe the first protocols for stereodivergent Ni-catalyzed semihydrogenation of alkynes. Using convenient nickel precursors in the presence or absence of phosphine ligands both E- and Z- alkenes can be formed with excellent selectivity.

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. As a benchmark system, the reaction of diphenylacetylene with molecular hydrogen was used. 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 gave stilbenes selectively and only trace amounts of reduction to the corresponding alkane was observed. Interestingly, as shown in Table 1 simple monodentate arylphosphines (L1-L3) provided Z-alkenes with 99:1 selectivity (Table 1, entries 1-3). Applying bisphosphine ligands gave mixtures of E- and Z-products (Table 1, entries 4-7). Gratifyingly, the application of some tri- and tetradentate phosphines (**L8-L10**) led predominantly to E-stilbene.

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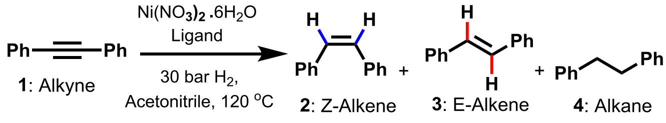
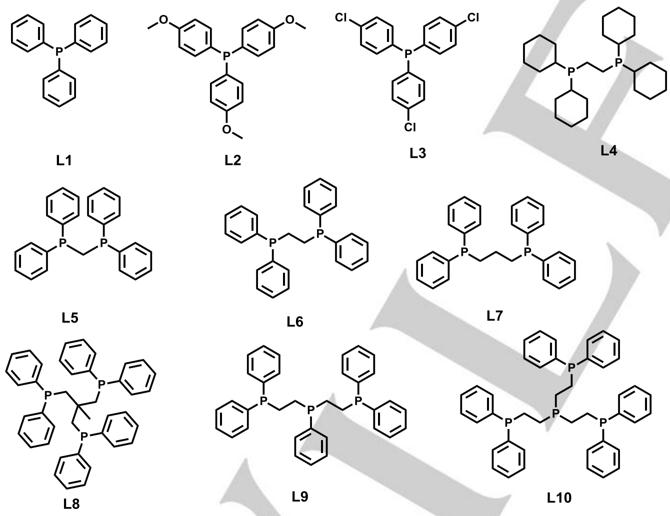
Supporting information for this article is given via a link at the end of the document.

Table 1. Ligand effects in the semihydrogenation of diphenyl acetylene to obtain stilbenes



Entry	Metal precursor	Ligand	Conv. (%)	Yield **2 & 3** (%)	Select-ivity (E: Z)	Yield **4** (%)
1[a]	$Ni(NO_3)_2{\cdot}6H_2O$	**L1**	98	95	1:99	2
2[a]	$Ni(NO_3)_2{\cdot}6H_2O$	**L2**	90	88	1:99	1
3[a]	$Ni(NO_3)_2{\cdot}6H_2O$	**L3**	97	94	1: 99	2
4[a]	$Ni(NO_3)_2{\cdot}6H_2O$	**L4**	>99	96	5:95	2
5[a]	$Ni(NO_3)_2{\cdot}6H_2O$	**L5**	80	78	10:90	1
6[a]	$Ni(NO_3)_2{\cdot}6H_2O$	**L6**	>99	97	40:60	1
7[a]	$Ni(NO_3)_2{\cdot}6H_2O$	**L7**	>99	96	50:50	1
8[a]	$Ni(NO_3)_2{\cdot}6H_2O$	**L8**	>99	98	65:35	-
9[a]	$Ni(NO_3)_2{\cdot}6H_2O$	**L9**	>99	98	>99:1	-
10[a]	$Ni(NO_3)_2{\cdot}6H_2O$	**L10**	>99	98	>99:1	-

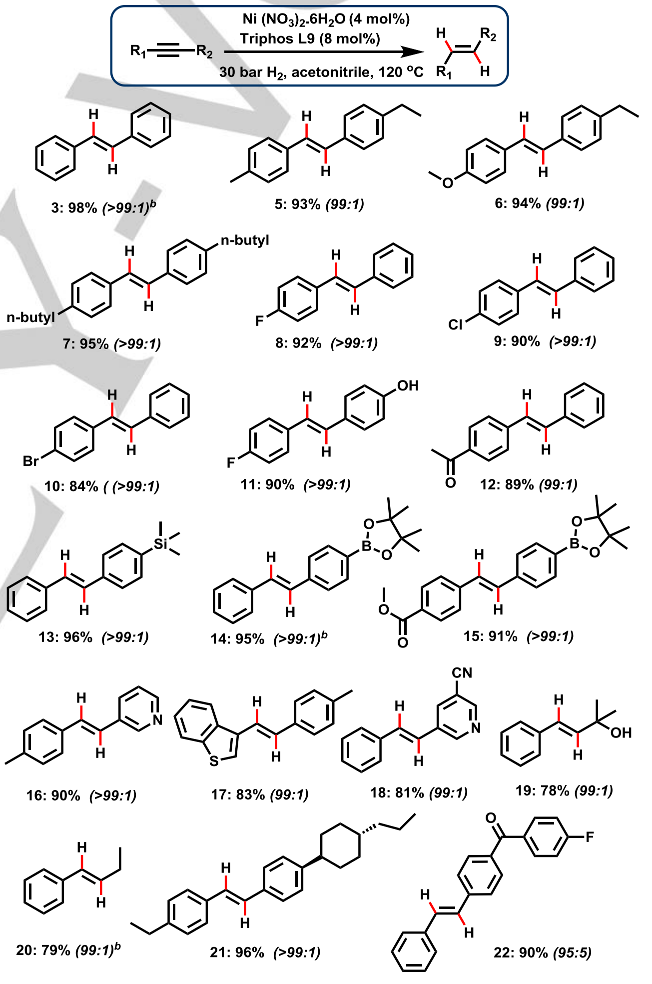


Reaction conditions: [a]0.5 mmol diphenylacetylene, 4 mol% $Ni(NO_3)_2{\cdot}6H_2O$, 8 mol% ligand, 30 bar H_2, 2 mL acetonitrile, 120°C, 15 h, yields were determined by GC using n-hexadecane as standard. E:Z isomeric ratios were determined by GC-MS and NMR.

More specifically, in the presence of bis(2-diphenylphosphinoethyl)phenyl-phosphine (linear triphos)(**L9**) and tris[2(diphenylphosphino) ethyl]phosphine (**L10**) the nickel catalyst gave full conversion of diphenylacetylene and excellent selectivity for the E-alkene product (E:Z selectivity >99%, Table 1, entries 9-10).

These results are in line with the nickel-triphos system using over-stoichiometric amounts of reducing agents (Zn+HCOOH) reported by Moran and co-workers.[11d] To investigate this E-selective hydrogenation in more detail, the influence of the solvent was investigated with the $Ni(NO_3)_2{\cdot}6H_2O$/ triphos (L9) system. When 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).

Scheme 1. Ligand controlled Ni-catalyzed synthesis of E-alkenes

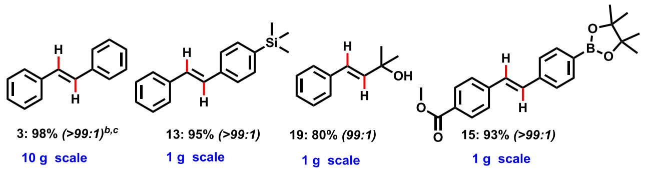


Reaction conditions: [a]0.5 mmol alkyne, 4 mol% $Ni(NO_3)_2{\cdot}6H_2O$, 8 mol% bis(2-diphenylphosphinoethyl)phenylphosphine (triphos), 30 bar H_2, 2 mL acetonitrile, 120 °C, 15 h, isolated yields. [b]GC yields using n-hexadecane as standard. Values in parenthesis refer to E: Z isomeric ratio determined by GC-MS and NMR

Having a convenient system ($Ni(NO_3)_2{\cdot}6H_2O$/bis(2-diphenyl-phosphinoethyl) phenylphosphine **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%

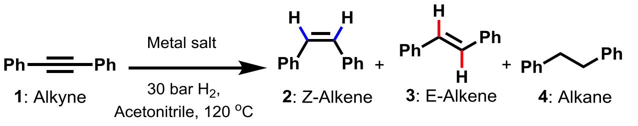
yield (Scheme 1, products 5-22). Functional groups such as hydroxy, heterocycles, halide, silyl, and boronic ester are well tolerated (Scheme 1, products 8-11, and 13-18).

Scheme 2. Practical utility of Ni-triphos system for synthesis of E-alkenes



Reaction conditions: ^{a}1 g alkyne, 3 mol% $Ni(NO_3)_2.6H_2O$, 6 mol% triphos, 30 bar H_2, 12 mL acetonitrile, 120 °C, 15 h, isolated yields, E:Z ratio was detected by GC-MS and NMR. ^{b}GC yields using n-hexadecane as standard. ^{c}10 g alkyne, 2 mol% $Ni(NO_3)_2.6H_2O$, 4 mol% triphos, 30 bar H_2, 120 mL acetonitrile, 120 °C, 15 h, GC yields. Values in parenthesis refer to E : Z isomeric ratio determined by GC-MS and NMR.

Table 2. Hydrogenation of diphenylacetylene using different metal salts



Entry	Metal precursor	Conv. (%)	Yield of alkene (%)	Selec-tivity (Z: E)	Yield of alkane (%)
1^a	$Ni(NO_3)_2{\cdot}6H_2O$	99	93	99:1	6
2^a	$NiBr_2{\cdot}XH_2O$	-	-	-	-
3^a	$NiCl_2{\cdot}DME$	-	-	-	-
4^a	$Ni(OAc)_2.4H_2O$	-	-	-	-
5^a	$Ni(OTf)_2$	65	59	99:1	5
6^a	$Ni(acac)_2$	50	45	99:1	4
7^a	$Co(NO_3)_2{\cdot}6H_2O$	-	-	-	-
8^a	$Fe(NO_3)_3{\cdot}9H_2O$	-	-	-	-
9^a	$Mn(NO_3)_2{\cdot}4H_2O$	-	-	-	-
10^b	$Ni(NO_3)_2{\cdot}6H_2O$	99	93	99:1	6
11^c	$Ni(NO_3)_2{\cdot}6H_2O$	99	93	99:1	6
12^d	$Ni(NO_3)_2{\cdot}6H_2O$	70	65	99:1	5

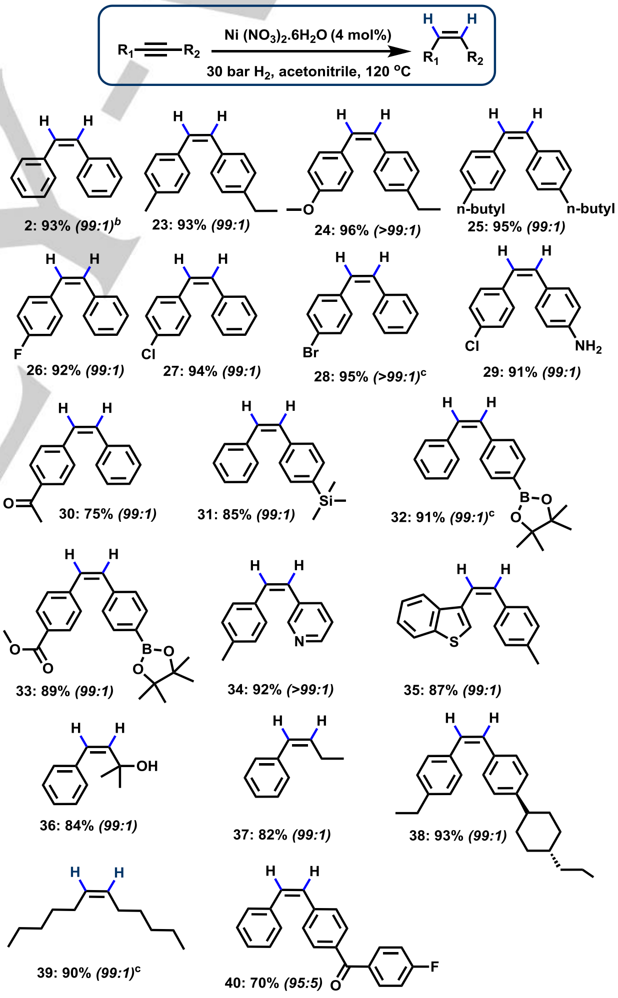
Reaction conditions: ^{a}0.5 mmol of diphenylacetylene, 10 mol% of metal salt, 30 bar H_2, 2 mL acetonitrile, 120°C, 15 h, yields were determined by GC using n-hexadecane standard. ^{b} 6 mol% catalyst loading. ^{c} 4 mol% catalyst loading ^{d} 2 mol% catalyst loading. Z:E isomeric ratio were determined by GC-MS and NMR

Even substrates with substituents that are reduced easily, such as nitrile and ketone, were converted with excellent chemoselectivity leaving the functional groups untouched (Scheme 1, products 12, 18, and 22). To demonstrate the scalability of the Ni-triphos system, semi-hydrogenation of 4 substrates were performed at 1-10 g scales (Scheme 2). In all these cases similar yields and selectivities were obtained. Noteworthy, the catalyst loading was decreased in gram scale reactions; at 1 g scale 3 mol% of nickel catalyst was used (6 mol % of ligand) and at 10 g scale only 2 mol% of nickel was applied.

Synthesis of Z- Alkenes

Next, we turned our interest to the selective synthesis of Z-stilbene using $Ni(NO_3)_2{\cdot}6H_2O$ in the presence of monodentate arylphosphines. Interestingly, similar reactivity and selectivity (93% of Z-stilbene with >99% selectivity) was observed in the absence of phosphines (Table 2, entry 1). Thus, we evaluated different nickel (II) salts for the benchmark hydrogenation. As shown in Table 2, $NiCl_2$, $NiBr_2$ and $Ni(OAc)_2$ did not show any activity (Table 2, entries 2-4).

Scheme 3. Substrate scope for the synthesis of Z-alkenes

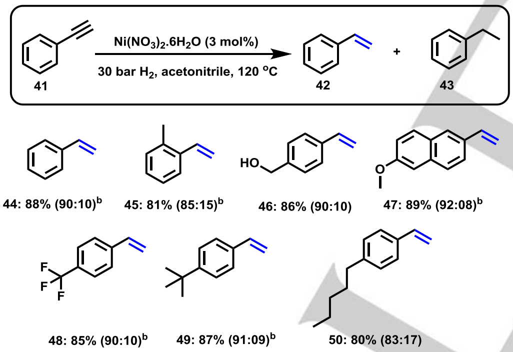


Reaction conditions: ^{a}0.5 mmol alkyne, 4 mol% $Ni(NO_3)_2{\cdot}6H_2O$, 30 bar H_2, 2 mL acetonitrile, 120 °C, 15 h, isolated yields. ^{b}GC yields using n-hexadecane as standard. ^{c} with 8 mol% $Ni(NO_3)_2{\cdot}6H_2O$. Values in parenthesis refer to Z:E isomeric ratio determined by GC-MS and NMR.

After having found that $Ni(NO_3)_2{\cdot}6H_2O$ is a convenient and inexpensive pre-catalyst for Z-selective semihydrogenation of alkynes, we evaluated its general applicability for the different aromatic and aliphatic alkynes (Scheme 3). Gratifyingly, all the investigated substrates were converted into the corresponding Z-alkenes in up to 96% yields with 99% selectivity (>99% Z:E). This simple Ni-salt also exhibits excellent chemoselectivity. Thus, the generated active catalyst is compatible with the halogen substituents (Br, Cl, F) and no significant dehalogenation is observed (Scheme 3, products **26-29**), despite the fact that nickel complexes are generally known to be dehalogenation catalysts.[20a-f] In addition, alkyne groups are selectively reduced in the presence of other sensitive groups such as silyl, boronic esters, ketone and ester (Scheme 3, products **30 – 33** and **40**). Further, heterocyclic and aliphatic alkynes were also semi-hydrogenated to respective Z- alkenes with excellent yield and stereoselectivity (Scheme 3, products **34-35** and **39**).

After these successful semihydrogenations of internal alkynes, we evaluated the semi- hydrogenation of terminal alkynes (Scheme 4). For these substrates the selectivity issue is more challenging as terminal alkenes are easier to hydrogenate compared to the internal ones. Nevertheless, all the terminal alkynes studied, were converted to the corresponding alkenes with good selectivity (Scheme 4, products **44** to **50**) (entries 45 and 50 have 15% and 17% overhydrogenation product respectively).

Scheme 4. Selective hydrogenation of terminal alkynes by $Ni(NO_3)_2{\cdot}6H_2O$



Reaction conditions: [a]0.5 mmol alkyne, 3 mol% $Ni(NO_3)_2{\cdot}6H_2O$, 30 bar H_2, 2 mL acetonitrile, 120 °C, 15 h, isolated yields along with alkene:alkane ratio. [b]GC yields using n-hexadecane as standard.

Mechanistic Studies: To determine if the catalyst is homogeneous or heterogeneous in nature, we performed mercury tests[12c-d] for both the Z- and E-alkene selective catalyst systems. The ligand-free $Ni(NO_3)_2{\cdot}6H_2O$ catalyst system showed no conversion in the presence of a drop of Hg under otherwise identical conditions, showing that the active catalyst is heterogeneous in nature. This is in line with the work of Bai et al.[11e] who reported the formation of nickel nanoparticles from nickel salts during the reduction of alkynes to Z-alkenes using $NaBH_4$. In general, semihydrogenation of alkynes gives Z-olefins due to syn-addition of adsorbed hydrogen on the surface of heterogeneous catalyst.[4]

In contrast, the Ni/triphos (**L9**) catalyst system showed no change in catalytic activity in the presence of Hg, still producing the E-alkene with similar high selectivity, demonstrating that under these conditions the active species is homogeneous in nature. To understand this active catalyst in more detail, we synthesized a Ni-triphos complex in quantitative yield (Supporting Information-S6). Crystals suitable for single crystal X-ray diffraction were grown after recrystallization with ethanol. Analysis of the solid state structure shows that the complex is pentacoordinated and all the three phosphorous atoms are coordinated to the nickel centre (Figure 1). The $^{31}P\{^1H\}$ NMR spectrum of this complex in $CDCl_3$ solution (Figure S4) shows a doublet at δ_P = 48 ppm and a triplet at δ_P = 110 ppm, in line with a tridentate coordination to nickel in solution.

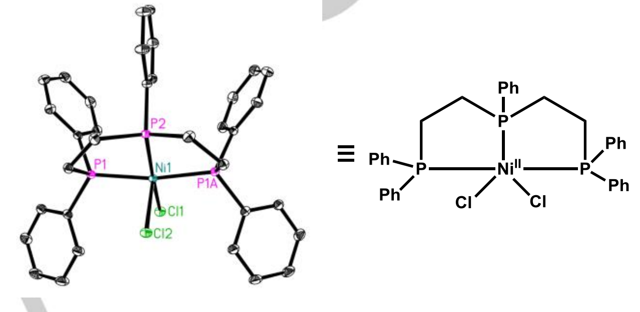
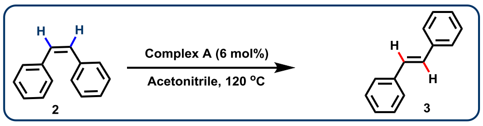


Figure 1. Molecular structure of Complex A obtained by X-ray analysis. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

To investigate if the Ni complex **A** is active in isomerization, we added Z-stilbene to Ni complex A (6 mol %) at 120°C under 30 bar of H_2. In this experiment, Z-stilbene is completely isomerized to E-stilbene within 15 h (Scheme 5, entries 1-2). Remarkably, not even traces of alkane are observed under these conditions.

Scheme 5. Isomerization of Z- to E-stilbene

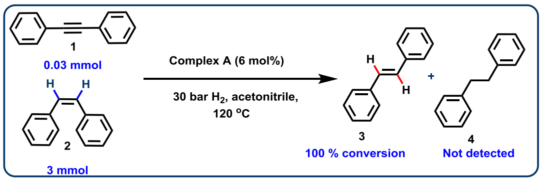


Entry	Substrate (mmol)	H_2 (bar)	Selectivity (Z:E)	Yield of **3**
1	0.5	30	0:100	>99
2	5	30	0:100	>99
3	0.5	0	80:20	20
4[b]	0.5	30	100:0	0

Reaction conditions: [a]0.5 mmol Z-stilbene, 6 mol% complex A, 30 bar H_2, 2 mL acetonitrile, 120 °C, 15 h, GC yields using n-hexadecane as standard. [b]same as a but without catalyst.

Surprisingly, the same experiment without H_2 gave 20% of E-stilbene and without catalyst isomerization was not observed (Scheme 5, entries 3-4).

Scheme 6. Hydrogenation of diphenylacetylene/Z-stilbene mixture using complex A



Reaction conditions: [a]0.03 mmol alkyne and 3 mmol of alkene, complex A 6 mol% or 4 mol% $Ni(NO_3)_2 \cdot 6H_2O$, 8 mol% triphos , 30 bar H_2, 2 mL acetonitrile, 120 °C, 15 h, isolated yields. [b]GC yields using n-hexadecane as standard.

Interestingly, cobalt catalysts which have been used also for E-selective alkyne semihydrogenations showed similar isomerization behavior.[12d] In another control experiment a mixture of diphenyl acetylene and *Z*-stilbene (1:100 ratio) was hydrogenated to mimic reaction conditions in which most of the alkyne has been converted but no isomerization has taken place yet.

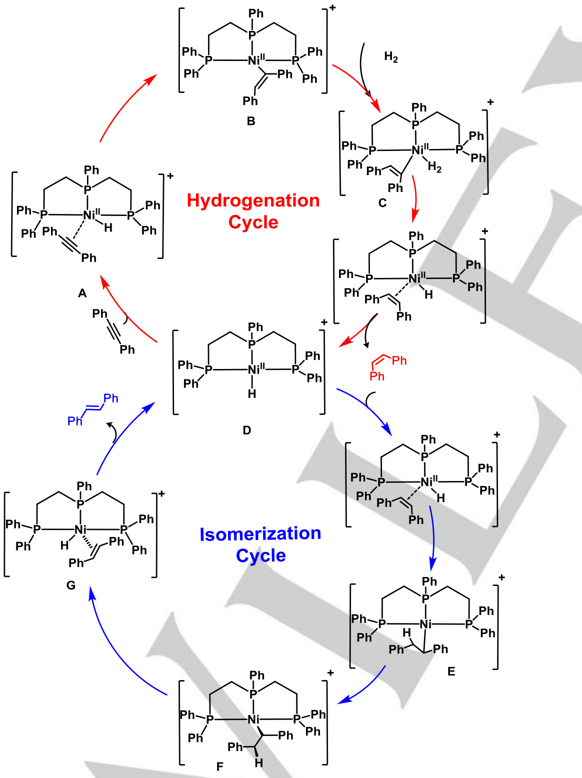


Figure 2. Proposed mechanism for the E-selective nickel-catalyzed hydrogenation of alkynes.

Under standard experimental conditions using complex **A** 100% of E-stilbene was formed and no over hydrogenated product was detected (Scheme 6). All these observations are 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.

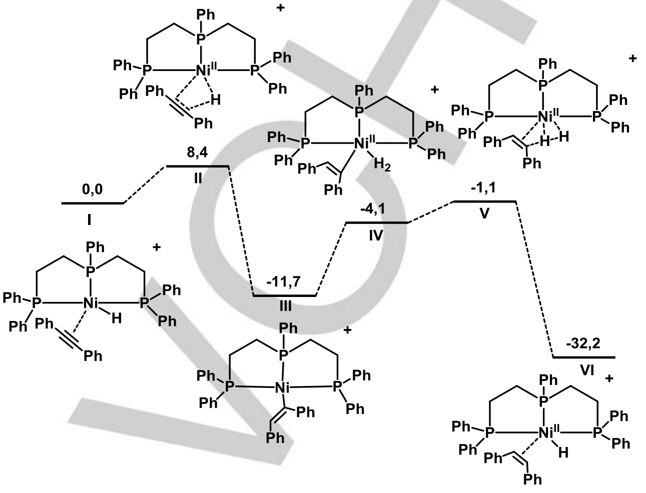


Figure 3. DFT calculations for hydrogenation of diphenylacetylene to Z-stilbene. 1 set at 0,0 kcal mol^{-1}. All energies presented are in kcal mol^{-1}

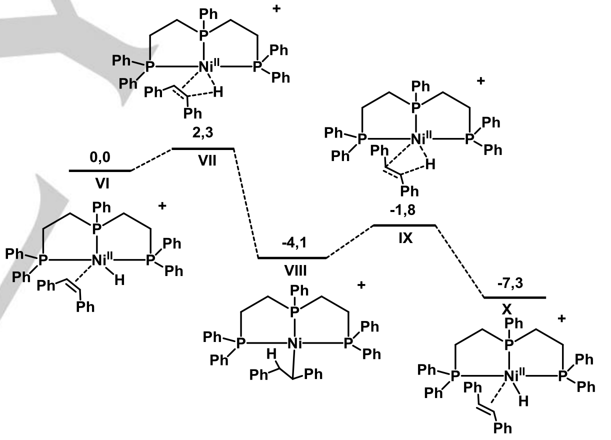


Figure 4. DFT calculations for isomerization of Z-stilbene to E-stilbene. Intermediate 6 was set at 0,0 kcal mol-1. All energies presented are in kcal mol-1

Hence, 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 after subsequent hydrogenolysis the Z-alkene is formed. In the second cycle, the molecular Ni-H complex inserts into the formed Z-alkene leading to a nickel alkyl species. A similar insertion was reported for alkene hydrogenation using nickel(II) phosphine based systems.[18b] Contrary to such hydrogenations, the triphos-ligated complex undergoes bond rotation and ß-hydride elimination to yield the E-alkene.

In order to validate the proposed mechanism, DFT calculations were conducted (see Supporting Information for details, S10) [21a-b]. All energy values are given in kcal mol^{-1}. A tricoordinated Ni(II)-Hydride is used as the common intermediate for both cycles.

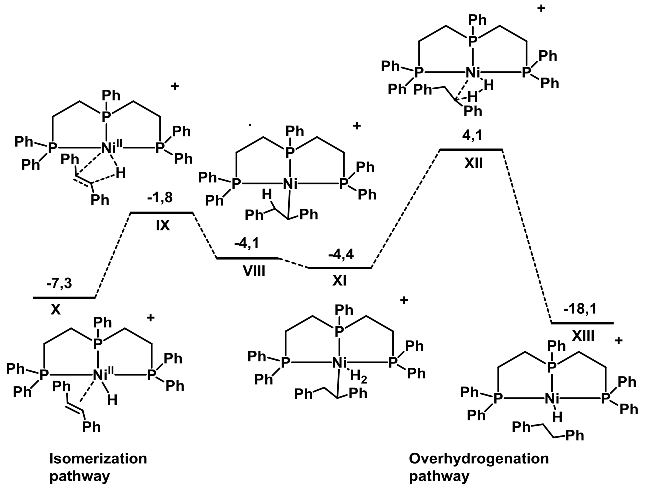


Figure 5. Comparison of the alkene hydrogenation step and ß-hydride elimination step towards the E-stilbene product. Energies presented relative to intermediate 6 set at 0,0 kcal mol-1. All energies presented are in kcal mol-1

Also for the calculations we used the benchmark substrate diphenyl acetylene. 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 was found that directly forms the Z-alkene from hydrogenolysis, as this would involve rotation around a double bond. For the isomerization cycle, 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 rotate freely around its axis and via a β-hydride elimination transition state (**IX**) the E-alkene (**X**) is formed. The barriers of isomerization were low and therefore explain the high chemoselectivity obtained for the E-alkene using this system. Additionally, we computed hydrogen coordination to the nickel alkyl specie (**XI**) and subsequent hydrogenolysis (**XII**) towards the alkane product (**XIII**) (Figure 5). The barrier for hydrogenation is almost 6 kcal/mol higher in energy compared to the β-hydride elimination leading to the E-product, in line with the high chemoselectivity as the alkane product is not formed in significant amounts.

Conclusions

In conclusion, we present the first nickel-based catalysts for stereodivergent semi-hydrogenation of alkynes with molecular hydrogen. Protocols for the preparation of both E- and Z-alkenes are reported, forming these products in an atom-efficient manner in high yields with excellent chemo- and stereoselectivity. The Z-alkenes are selectively formed when simple $Ni(NO_3)_2$ was used as a catalyst precursor. The presence of triphos as tridentate ligand is needed to yield the corresponding E-alkenes (>99:1 selectivity). Mechanistic studies showed that the $Ni(NO_3)_2$ system is heterogeneous in nature, whereas the E-selective Ni-triphos system operates as a homogeneous catalyst. Furthermore, it was shown that the latter catalyst initially produces the Z-alkene, which subsequently isomerizes to the E-alkene in a separate catalytic cycle. Notably, both nickel nanoparticles and the molecular-defined Ni-triphos catalyst tolerate a broad scope of internal and terminal alkynes bearing different substituent and functional groups. Both these catalyst systems are compatible with benchtop set up and can be applied to multi gram 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.

Acknowledgements

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Keywords: Nickel catalysis. alkyne semihydrogenation. Stereoselectivity. molecular hydrogen.

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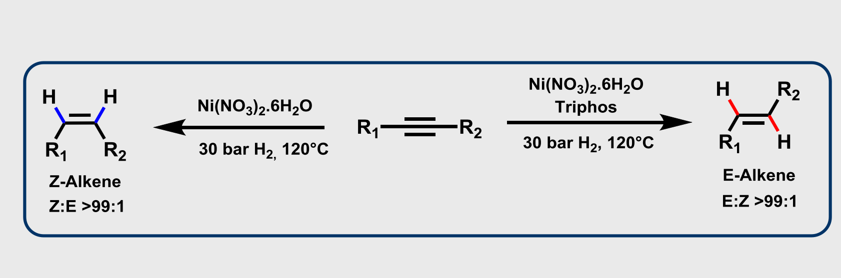

Kathiravan Murugesan, Charles Beromeo Bheeter, Pim R. Linnebank, Anke Spannenberg, Joost N. H. Reek, Rajenahally V. Jagadeesh*, and Matthias Beller**

Page No. – Page No.

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