Catalytic Chemo and Stereoselective Semi-Hydrogenation of Alkynes to E-Alkenes Using the Combination of Pd catalyst and ZnI 2

Radhouan Maazaoui, Raoudha Abderrahim, Fabrice Chemla, Franck Ferreira,
Alejandro Perez-Luna, Olivier Jackowski

► To cite this version:

Radhouan Maazaoui, Raoudha Abderrahim, Fabrice Chemla, Franck Ferreira, Alejandro Perez-Luna, et al.. Catalytic Chemo and Stereoselective Semi-Hydrogenation of Alkynes to E-Alkenes Using the Combination of Pd catalyst and ZnI 2. Organic Letters, 2018, 20 (23), pp.7544-7549. 10.1021/acs.orglett.8b03295 . hal-02297535

HAL Id: hal-02297535

<https://hal.sorbonne-universite.fr/hal-02297535>

Submitted on 26 Sep 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Catalytic Chemo and Stereoselective Semi-Hydrogenation of Alkynes to *E*-Alkenes Using the Combination of Pd catalyst and ZnI₂

Radhouan Maazaoui,^{†,§} Raoudha Abderrahim,[†] Fabrice Chemla,[§] Franck Ferreira,[§] Alejandro Perez-Luna,[§] Olivier Jackowski*,[§]

[§] Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire, IPCM, F-75252 Paris Cedex 05, France.

[†] Université de Carthage, Faculté des Sciences de Bizerte, Laboratoire de Synthèse Hétérocyclique, 7021 Jarzouna. Bizerte, Tunisia.

Supporting Information Placeholder

ABSTRACT: An efficient *E*-selective semihydrogenation of internal alkynes was developed under low dihydrogen pressure and low reaction temperature from commercially available reagents: Cl₂Pd(PPh₃)₂, Zn⁰ and ZnI₂. Kinetic studies and control experiments underline the significant role of ZnI₂ in this process under H₂ atmosphere, establishing that the transformation involves *syn*-hydrogenation followed by isomerization. This simple and easy-to-handle system provides a route to *E*-alkenes under mild conditions.

The semi-hydrogenation of alkynes to alkenes is a remarkable transformation of paramount importance in synthetic fine chemistry.¹ While reduction with *Z*-selectivity is readily achieved through catalytic hydrogenation under H₂ atmosphere with heterogeneous catalysts such as Lindlar's catalyst,² obtaining *E*-selectivity requires Birch-type conditions³ which often lack functional-group compatibility (Scheme 1a). To overcome this constraint, hydrosilylation / desilylation strategies and related *trans*-hydrometallations have been developed (scheme 1b) although stoichiometric waste is produced.⁴ In the same vein, catalytic *E*-selective semi-hydrogenations of alkynes using hydrogen-transfer chemistry or molecular hydrogen have been also explored.⁵ Yet, this transformation remains challenging because most transition metal-catalyzed semi-hydrogenations of C–C triple bonds occur through *cis*-selective processes and *E*-alkenes are only obtained upon isomerization of the initially formed *Z*-alkenes. In such a situation, the over-reduction of the alkene is a major limitation. Hydrogen transfer semi-reductions of alkynes have been completed using chromium reagents⁶ or transition-metal catalysts such as Ir,⁷ Ni,⁸ Co,⁹ Ru¹⁰ and Pd¹¹ (scheme 1c). The use of molecular H₂ has been also reported employing different catalytic systems (Scheme 1d). While the metal-free HB(C₆F₅)₂/pentafluorostyrene system required high temperatures and pressures of H₂ (140 °C and 50 bar),¹² Co-,¹³ Fe-¹⁴ and Ru-catalysts¹⁵ were disclosed to achieve *trans*-selective alkyne semi-hydrogenations under lower temperatures and pressures of H₂ (below 90 °C and below 10 bar).

Scheme 1. Selective Semihydrogenation of Alkynes to *E*-Alkenes

Atmospheric pressure of H₂ can be also used. Dinuclear Ir-complexes¹⁶ and an Ag-Ru bimetallic complex¹⁷ were described to be efficient under 1 atm of H₂. Recently, propargylic alcohol derivatives can be transformed to *E*-allylic alco-

hols with Ru-catalyst^{15b} and a ruthenium hydride catalyst was reported to require only 10 equivalents of H₂.¹⁸ Finally, the heterogeneous combination of Pd₃Pb/SiO₂ and RhSb/SiO₂ was related to achieve *trans*-semi-reductions under 1 atm of H₂ at 25 °C.¹⁹

Our interest in semi-hydrogenation was instigated by the observation that zinc salts tamed the catalyst activity in the catalytic hydrogenation of alkenes.²⁰ We thus speculated that catalytic systems modified with zinc salt additives could allow for the partial hydrogenation of alkynes to alkenes with a subsequent *Z*-to-*E* isomerization. Herein we report the development of such a catalytic system competent for the semi-hydrogenation of internal alkynes to *E*-alkenes (Scheme 1).

We initiated our study by investigating the partial hydrogenation of diphenylacetylene **1** as model substrate (Table 1). First, a control experiment was carried out with Pd(PPh₃)₄ in the absence of zinc additive: full conversion was observed but a mixture of alkane, *Z*- and *E*-alkenes was obtained (entry 1). By contrast, adding MeZnI to the system (entry 2) allowed for ~50% conversion with an encouraging *E/Z* ratio (5:1). In this transformation, the isomerization step without alkane formation is favored thanks to organozinc reagents. We then considered using Cl₂Pd(PPh₃)₂ as precatalyst and its *in situ*

reduction by MeZnI. A noticeably improvement was observed: *E/Z* ratio reached 64:1 while keeping alkane formation at 10% (entry 3). On the other hand, when the reaction was conducted with Me₂Zn as reducing agent (0.2 equivalent), 1,2-diphenylethane **3** was the only product (entry 4). However, the desired catalytic semi-hydrogenation was obtained upon addition of 2 equivalents of ZnI₂ to the previous system: an excellent *E*-selectivity and a low proportion of **3** were obtained (entry 5). Zn metal was then used as reducing agent. *E*-stilbene **2** was delivered in 86% yield with limited alkane formation (entry 6). We also screened different solvents under these conditions but no better results were obtained (entries 7-9). Then, the influence of the counterion of the zinc salt was investigated. The use of anions such as Cl⁻ and Br⁻ was not selective (entries 10 and 11), while softer donor anions provided good *E*-selectivities (entries 6 and 12). However, alkane proportion was dramatically increased with the use of Zn(OTf)₂ (entry 12). Metal salts with other main-group cations were also considered. Replacing ZnI₂ by LiI or MgI₂ or AlI₃ diminished *E*-selectivity and/or conversion (entries 13-15). Definitively, ZnI₂ emerged as the salt of choice to combine reactivity (full conversion) and selectivity (excellent *E*-stereoselectivity and low amounts of alkane).

Table 1. *E*-Selective Semi-Hydrogenation of Alkynes: Optimization of Reaction Conditions^a

<div style="text-align: center;"> </div>						
entry	catalyst	solvent	additive (equiv)	1 (%)	2 (%) (<i>E/Z</i>)	3 (%)
1	Pd(PPh ₃) ₄	THF	-	0	63 (1.3/1)	37
2	Pd(PPh ₃) ₄	THF	MeZnI (2)	54	46 (5/1)	0
3	Cl ₂ Pd(PPh ₃) ₂	THF	MeZnI (2)	9	81 (64/1)	10
4	Cl ₂ Pd(PPh ₃) ₂	THF	Me ₂ Zn (0.2)	1	0	99
5	Cl ₂ Pd(PPh ₃) ₂	THF	Me ₂ Zn (0.2) + ZnI ₂ (2)	4	83 (61/1)	13
6	Cl ₂ Pd(PPh ₃) ₂	THF	Zn ⁰ (3) + ZnI ₂ (2)	2	86 (<i>E</i>)	12
7	Cl ₂ Pd(PPh ₃) ₂	Et ₂ O	Zn ⁰ (3) + ZnI ₂ (2)	88	12 (5/1)	0
8	Cl ₂ Pd(PPh ₃) ₂	CH ₃ CN	Zn ⁰ (3) + ZnI ₂ (2)	75	25 (2/1)	0
9	Cl ₂ Pd(PPh ₃) ₂	DMF	Zn ⁰ (3) + ZnI ₂ (2)	21	75 (1.1/1)	4
10	Cl ₂ Pd(PPh ₃) ₂	THF	Zn ⁰ (3) + ZnCl ₂ (2)	42	55 (1/3)	3
11	Cl ₂ Pd(PPh ₃) ₂	THF	Zn ⁰ (3) + ZnBr ₂ (2)	2	85 (1/3.5)	13
12	Cl ₂ Pd(PPh ₃) ₂	THF	Zn ⁰ (3) + Zn(OTf) ₂ (2)	0	62 (11.5/1)	38
13	Cl ₂ Pd(PPh ₃) ₂	THF	Zn ⁰ (3) + LiI (2)	2	98 (2/1)	0
14	Cl ₂ Pd(PPh ₃) ₂	THF	Zn ⁰ (3) + MgI ₂ (2)	82	18 (1/11)	0
15	Cl ₂ Pd(PPh ₃) ₂	THF	Zn ⁰ (3) + AlI ₃ (2)	63	33 (1.5/1)	4
16	Cl ₂ Pd(P ^{<i>n</i>} Bu) ₃) ₂	THF	Zn ⁰ (3) + ZnI ₂ (2)	95	5 (nd)	0
17	Cl ₂ Pd(PO ^{<i>i</i>} Pr) ₃) ₂	THF	Zn ⁰ (3) + ZnI ₂ (2)	55	44 (20/1)	1
18	Cl ₂ Pd(dppp)	THF	Zn ⁰ (3) + ZnI ₂ (2)	79	21 (4/1)	0
19	Cl ₂ Pd(xantphos)	THF	Zn ⁰ (3) + ZnI ₂ (2)	95	5 (nd)	0
20	Pd-PEPPSI- ^{<i>i</i>} Pr	THF	Zn ⁰ (3) + ZnI ₂ (2)	94	6 (nd)	0
21 ^b	Cl ₂ Pd(PPh ₃) ₂	THF	Zn ⁰ (3) + ZnI ₂ (1)	0	96 (<i>E</i>)	4

^a Product distribution was determined by ¹H NMR analysis. ^b Reaction time was 8 h.

Scheme 2. *E*-Selective Semi-Hydrogenation of Alkynes: Scope and Limitations.

^a Product distribution was determined by ¹H NMR analysis.

Finally, we investigated the influence of the palladium ligand, but the results obtained with the simplest PPh₃ ligand were not improved. Indeed, a moderate conversion (44%) with a good *E*-selectivity was obtained with a less electron-donating ligand (entry 17), while the uses of more electron-donating or bidentate ligands were detrimental. (entries 16, 18 and 19). With Pd complex bearing a NHC ligand, only 6% conversion of alkyne was observed (entry 20). Conditions were fully optimized by diminishing the amount of ZnI₂ to 1 equivalent (lower amounts offered erratic results) and setting the reaction time to 8 h (alkane formation was limited to 4%) (entry 21).

Then we considered the semi-hydrogenation of a range of substrates bearing a variety of functional groups to examine if the alkene formation could be sensitive to the electron density of the C–C triple bond. For some cases, the reactions had to be stopped before full conversion to prevent significant alkane formation (Scheme 2). Non-symmetrical diphenylacetylenes having one ring substituted with one electron-donating group proceeded with excellent *E*/alkane ratios (**2b–2e**). The transformation was compatible with chloride substitution as alkene **2f** was obtained in a good yield with an acceptable *E*/alkane ratio (90:10). Non-symmetrical diphenylacetylenes having one ring substituted with one electron-withdrawing group also proceeded in excellent yields and *E*/alkane ratios (**2g–2i**). Formation of CF₃-substituted stilbene **2j** required 72 h of

reaction time and 20 mol% of Pd catalyst to reach 89% yield and an excellent *E*/alkane selectivity (96:4). Conversely, introducing an electron-donating group (OMe) in *para* position on the other phenyl part to balance the CF₃ electron withdrawing effect led to a suitable yield (69%) and a decent *E*/alkane ratio (85:15) within only 7 h (**2k**). Compound **2l** was obtained in a moderate yield due to its low solubility in THF that needed addition of dichloromethane, but the *E*/alkane selectivity was still excellent. Finally, non-symmetrical heteroaryl derivatives were also good partners as illustrated by the semi-hydrogenation delivering **2m** and **2n**. A slight decrease in the *E/Z* selectivity (93.5:6.5) was observed for compound **2m**, and this was attributed to competitive binding of nitrogen to the catalyst that could thwart the isomerization. Diene **2o** formation required 20 mol % of Pd catalyst to reach 90% conversion with a total *E*-selectivity. Replacing one aryl moiety by an alkyl motif was also tolerated. Over-hydrogenation was almost inexistent (1%) and a good conversion with an excellent *E*-selectivity (97:3) was obtained for alkene **2p**. Slight worst results were observed for the formation of **2q**: *E*-selectivity was lower (*E/Z* ratio 91:9) and alkane formation slightly higher (9%). However, from 7-tetradecyne no alkane was formed but the isomerization step was not efficient enough as a 34:66 *E/Z* ratio was detected for alkene **2r**. The semi-reduction of trimethylsilyl phenylacetylene gave only

10% of the corresponding *E*-vinyl silane. In the reaction medium, it was produced but it was directly transformed to ethyl benzene by Pd-catalyzed desilylation and subsequent hydrogenation of styrene.

To get more information about the transformation, monitoring studies were conducted on the semi-hydrogenation of diphenylacetylene (Figure 1). At the beginning (Figure 1), rapid formation of *Z*-stilbene was observed and reached a maximum after 4 hours of reaction. In the same time, *E*-stilbene was also accumulated and a 1:1:1 mixture of alkyne/*E*/*Z* was observed after 4 h. During the following three hours of reaction, the amount of *E*-stilbene increased steadily to reach 97% whereas both *Z*-stilbene and diphenylacetylene were totally consumed. Thus, the semi-hydrogenation of diphenylacetylene into *E*-stilbene was achieved within 7 h. These studies lend clear evidence that *E*-alkene formation with our new catalytic conditions involving the combination of ZnI_2 and Pd^0 complex is

Figure 1. Monitoring Studies: from Diphenylacetylene toward *E*-Stilbene^a

^a Proportion was determined by GC analysis.

Table 2. Control Experiments: Role of ZnI_2

		substrate	conditions	$\xrightarrow{\text{THF, 25 } ^\circ\text{C, 24 h}}$

				<i>E</i> -2	<i>Z</i> -2	3	
entry	substrate	conditions	conv (%) ^a	<i>E</i> -2 (%) ^a	<i>Z</i> -2 (%) ^a	3 (%) ^a	
1		H ₂ (1 atm), I ₂ Pd(PPh ₃) ₂ (5 mol %), Zn ⁰ (3 equiv)	55	23	22	0	
2		H ₂ (1 atm), Cl ₂ Pd(PPh ₃) ₂ (5 mol %), Zn ⁰ (3 equiv)	5	-	-	-	
3		H ₂ (1 atm), I ₂ Pd(PPh ₃) ₂ (5 mol %), Zn ⁰ (3 equiv), ZnI ₂ (1 equiv)	100	85	1	14	
4		I ₂ Pd(PPh ₃) ₂ (5 mol %), Zn ⁰ (3 equiv.), ZnI ₂ (1 equiv.)	0	-	-	-	
5		H ₂ (1 atm), I ₂ Pd(PPh ₃) ₂ (5 mol %)	100	84	0	16	
		Me ₂ Zn (12 mol %), ZnI ₂ (1 equiv)					
6		H ₂ (1 atm), I ₂ Pd(PPh ₃) ₂ (5 mol%), Me ₂ Zn (12 mol %)	100	0	0	100	
7		H ₂ (1 atm), Zn ⁰ (3 equiv), ZnI ₂ (1 equiv)	18	18	82	0	
8		H ₂ (1 atm), I ₂ Pd(PPh ₃) ₂ (5 mol %), Me ₂ Zn (12 mol %)	100	0	0	100	
9		H ₂ (1 atm), I ₂ Pd(PPh ₃) ₂ (5 mol %), Zn ⁰ (3 equiv), ZnI ₂ (1 equiv)	30	70	0	30	

^a Product distribution was determined by ^1H NMR analysis.

achieved through a pathway entailing semi-hydrogenation and subsequent isomerization. Alkane formation was only detected after 6 h of reaction when the amount of *E*-stilbene reached 75%. Furthermore, monitoring studies on isomerization and over-reduction conducted respectively from *Z*-stilbene and *E*-stilbene (see supporting information) suggest that 1,2-diphenylethane **3** arises essentially from the reduction of *E*-stilbene.

Then to understand better the role of ZnI_2 , several experiments were carried out. ^{31}P NMR (162 MHz in CDCl_3) analysis evidenced that the peak for $\text{Cl}_2\text{Pd}(\text{PPh}_3)_2$ shifted from 23.73 ppm to 13.31 ppm on addition of ZnI_2 (see supporting information). By comparison, freshly prepared $\text{I}_2\text{Pd}(\text{PPh}_3)_2$ ²¹ presented a signal at 13.11 ppm. This suggests that chlorine exchange by iodine takes place and delivers $\text{I}_2\text{Pd}(\text{PPh}_3)_2$. This pre-catalyst was then used for other control experiments (Table 2). First, by introducing $\text{I}_2\text{Pd}(\text{PPh}_3)_2$ instead of $\text{Cl}_2\text{Pd}(\text{PPh}_3)_2$ when only Zn^0 was present, 45% conversion was obtained within 24 h but low *E*/*Z* selectivity was observed (entry 1). By contrast only 5% conversion was observed with $\text{Cl}_2\text{Pd}(\text{PPh}_3)_2$ (entry 2). Seemingly, $\text{I}_2\text{Pd}(\text{PPh}_3)_2$ pre-catalyst is more easily reduced and the presence of ZnI_2 allows to regain a high transformation (entry 3). In fact, ZnI_2 appears to be involved at two levels: the Pd^0 generation through $\text{I}_2\text{Pd}(\text{PPh}_3)_2$ formation and the *E*-selective semi-hydrogenation kinetics. As isomerization and over reduction are involved in this catalytic process, specific experiments with *E*- and *Z*-stilbenes were then conducted to acquire more information about these steps. In a first experiment, H_2 atmosphere was removed and no reaction was observed (entry 4). Then two reactions were conducted on *Z*-stilbene under H_2 atmosphere using Me_2Zn as reducing agent. In the presence of ZnI_2 , a mixture of *E*-stilbene and 1,2-diphenylethane **3** was obtained in 84/16 ratio (entry 5) whereas in the absence of ZnI_2 , only compound **3** was obtained (entry 6).

Finally, suppressing the pre-catalyst resulted in a strong drop in the *Z*-stilbene isomerization (entry 7). At last, alkane formation from *E*-stilbene was also investigated and ZnI_2 appears to significantly reduce alkene hydrogenation. (entries 8 vs 9). Overall, the newly developed catalytic *E*-selective semi-hydrogenation of alkynes can be explained through a *syn*-hydrogenation / isomerization pathway. First ZnI_2 interacts with the Pd^{II} pre-catalyst to deliver $\text{I}_2\text{Pd}(\text{PPh}_3)_2$ which is reduced to Pd^0 . It is worthy of mention that ZnI_2 can also dramatically modify the nature of Pd species and, a “cocktail system” of mononuclear Pd and/or clusters and/or nanoparticles could be envisioned in the absence of any further information concerning its specific structure.²² Preliminary studies conducted in the presence of Hg^0 suggest the existence of heterogeneous species in our “cocktail system”.²³ Hence, this “cocktail system” activates H_2 and *Z*-alkene is liberated then rapidly converted to *E*-alkene. The combination of Pd^0 and ZnI_2 is essential to promote isomerization without alkane formation.

In conclusion, we have developed a catalytic process for the semi-hydrogenation of internal alkynes with excellent *E*-selectivity. Monitoring studies and control experiments underline the significant role of ZnI_2 in this process, establishing that the transformation involves *syn*-hydrogenation followed by isomerization under H_2 atmosphere. Finally, this simple and easy-to-handle system constitutes a route to *E*-alkenes under mild conditions. Further studies are currently under investigation to determine more precisely the role of ZnI_2 and to elucidate the structure of the active catalytic species

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Experimental data, product characterizations, and spectral data for new compounds (PDF)

AUTHOR INFORMATION

Corresponding Author

* olivier.jackowski@sorbonne-universite.fr

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

We thank to Université de Carthage for financial support (to R. Maazaoui).

REFERENCES

- (a) Crespo-Quesada, M.; Cardenas-Lizana, F.; Dessimoz, A.-L.; Kiwi-Minsker, L. Modern Trends in Catalyst and Process Design for Alkyne Hydrogenations. *ACS Catal.* **2012**, *2*, 1773–1786. (b) Kluwer, A. M.; Elsevier, C. J. Homogeneous Hydrogenation of Alkynes and Dienes. In *Handbook for Homogeneous Hydrogenation*, 1st ed.; de Vries, J. G., Elsevier, C. J., Eds.; Wiley-VCH: Weinheim, Germany, 2007; Vol. 1, 375–413.
- (a) Lindlar, H. Ein neuer Katalysator für selektive Hydrierungen. *Helv. Chim. Acta* **1952**, *35*, 446–450. (b) Lindlar, H.; Dubuis, R. Palladium Catalyst for Partial Reduction of Acetylenes. *Org. Synth.* **1966**, *46*, 89–91.
- Pasto, D. J. Reductions of $\text{C}=\text{C}$ and $\text{C}\equiv\text{C}$ by Noncatalytic Chemical Methods. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, U.K., 1991; Vol. 8, 471–488.
- (a) Trost, B. M.; Ball, Z. T.; Jöge, T. A Chemoselective Reduction of Alkynes to (*E*)-Alkenes. *J. Am. Chem. Soc.* **2002**, *124*, 7922–7923. (b) Interligand Interactions Dictate the Regioselectivity of trans-Hydrometalations and Related Reactions Catalyzed by $[\text{Cp}^*\text{RuCl}]$. Hydrogen Bonding to a Chloride Ligand as a Steering Principle in Catalysis. *J. Am. Chem. Soc.* **2015**, *137*, 5506–55019. (c) Frihed, T. G.; Fürstner, A. Progress in the trans-Reduction and trans-Hydrometalation of Internal Alkynes. Applications to Natural Product Synthesis. *Bull. Chem. Soc. Jpn.* **2016**, *89*, 135–160.
- Kumara Swamy, K. C.; Siva Reddy, A.; Sandeep, K.; Kalayani, A. Advances in Chemoselective and/or Stereoselective SemiHydrogenation of Alkynes. *Tetrahedron Lett.* **2018**, *58*, 419–4269.
- (a) Castro, C. E.; Stephens, R. D. The Reduction of Multiple Bonds by Low-Valent Transition Metal Ions. The Homogeneous Reduction of Acetylenes by Chromous Sulfate. *J. Am. Chem. Soc.* **1964**, *86*, 4358–4363. (b) Smith, A. B., III; Levenberg, P. A.; Suits, J. Z. Reduction of α -Acetylenic Ketones to trans-Enones. *Synthesis* **1986**, 184–189.
- Tani, K.; Iseki, A.; Yamagata, T. Efficient transfer hydrogenation of alkynes and alkenes with methanol catalysed by hydrido(methoxy)iridium(III) complexes. *Chem. Commun.* **1999**, 1821–1822.
- (a) Barrios-Francisco, R.; Garcia, J. J. Semihydrogenation of Alkynes in the Presence of $\text{Ni}(0)$ Catalyst using Ammonia-borane and Sodium Borohydride as Hydrogen Source. *Applied Catalysis A General* **2010**, *385*, 108–113. (b) Richmond, E.; Moran, J. Ligand Control of *E/Z* Selectivity in Nickel-Catalyzed Transfer Hydrogenative Alkyne Semireduction. *J. Org. Chem.* **2015**, *80*, 6922–6929.
- Fu, S.; Chen, N.; Liu, X.; Shao, Z.; Luo, S.; Liu, Q. Ligand-Controlled Cobalt-Catalyzed Transfer Hydrogenation of Alkynes: Stereodivergent Synthesis of *Z*- and *E*-Alkenes. *J. Am. Chem. Soc.* **2016**, *138*, 8588–8594.
- (a) Li, J.; Hua, R. Stereodivergent Ruthenium-Catalyzed Transfer Semihydrogenation of Diaryl Alkynes. *Chem. Eur. J.* **2011**, *17*, 8462–8465. (b) Schabel, T.; Belger, C.; Plietker, B. A Mild Chemoselective Ru-Catalyzed Reduction of Alkynes, Ketones, and Nitro Compounds. *Org. Lett.* **2013**, *15*, 2858–2861. (c) Musa, S.; Ghosh, A.; Vaccaro, L.; Ackermann, L.; Gelman, D. Efficient *E*-Selective Transfer Semihydrogenation of Alkynes by Means of Ligand-Metal Cooperating Ruthenium Catalyst. *Adv. Synth. Catal.* **2015**, *357*, 2351–2357. (d) Kusy, R.; Grela, K. *E*- and *Z*-Selective Transfer Semihydrogenation of Alkynes Catalyzed by Standard Ruthenium Olefin Metathesis Catalysts. *Org. Lett.* **2016**, *18*, 6196–6199.
- (a) Shirikawa, E.; Otsuka, H.; Hayashi, T. Reduction of Alkynes into 1,2-dideuteroalkenes with Hexamethyldisilane and Deuterium Oxide in the Presence of a Palladium Catalyst. *Chem. Commun.* **2005**, 5885–5886. (b) Luo, F.; Pan, C.; Wang, W.; Ye, Z.; Cheng, J. Palladium-catalyzed Reduction of Alkynes Employing HSiEt_3 : Stereoselective Synthesis of trans- and cis-Alkenes. *Tetrahedron* **2010**, 1399–1403. (c) Shen, R.; Chen, T.; Zhao, Y.; Qiu, R.; Zhou, Y.; Yin, S.; Wang, X.; Goto, M.; Han, L.-B. Facile Regio- and Stereoselective Hydrometalation of Alkynes with a Combination of Carboxylic Acids and Group 10 Transition Metal Complexes: Selective Hydrogenation of Alkynes with Formic Acid. *J. Am. Chem. Soc.* **2011**, *133*, 17037–17044. (d) Zhong, J.-J.; Liu, Q.; Wu, C.-J.; Meng, Q.-Y.; Gao, X.-W.; Li, Z.-J.; Chen, B.; Tung, C.-H.; Wu, L.-Z. Combining Visible Light Catalysis and Transfer Hydrogenation for in situ Efficient and Selective Semihydrogenation of Alkynes under Ambient Conditions. *Chem. Commun.* **2016**, 52, 1800–1803.
- Liu, A.; Hu, L.; Chen, H.; Du, H. An Alkene-Promoted Borane-Catalyzed Highly Stereoselective Hydrogenation of Alkynes to Give *Z*- and *E*-Alkenes. *Chem. Eur. J.* **2015**, *21*, 3495–3501.
- Tokmic, K.; Fout, A. R. Alkyne Semihydrogenation with a Well-Defined Nonclassical Co-H_2 Catalyst: A H_2 Spin on Isomerization and *E*-Selectivity. *J. Am. Chem. Soc.* **2016**, *138*, 13700–13705.
- Srimani, D.; Diskin-posner, Y.; Ben-David, Y.; Milstein, D. Iron Pincer Complex Catalyzed, Environmentally Benign, *E*-Selective Semi-Hydrogenation of Alkynes. *Angew. Chem. Int. Ed.* **2013**, *52*, 14131–14134.
- (a) Radkowski, K.; Sundararaju, B.; Fürstner, A. A Functional-Group-Tolerant Catalytic trans Hydrogenation of Alkynes.

Angew. Chem. Int. Ed. **2013**, *52*, 355–360. (b) Guthertz, A.; Leutzsch, M.; Wolf, L. M.; Gupta, P.; Rummelt, S. M.; Goddard, R.; Farès, C.; Thiel, W.; Fürstner, A. Half-Sandwich Ruthenium Carbene Complexes Link trans-Hydrogenation and gem-Hydrogenation of Internal Alkynes. *J. Am. Chem. Soc.* **2018**, *140*, 3156–3169.

16 Higashida, K.; Mashima, K. E-Selective Semi-hydrogenation of Alkynes with Dinuclear Iridium Complexes under Atmospheric Pressure of Hydrogen. *Chem. Lett.* **2016**, *45*, 866–868.

17 Karunananda, M. K.; Mankad, N. P. E-Selective Semi-Hydrogenation of Alkynes by Heterobimetallic Catalysis. *J. Am. Chem. Soc.* **2015**, *137*, 14598–14601.

18 Neumann, K. T.; Klimczyk, S.; Burhardt, M. N.; Bang-Andersen, B.; Skrydstups, T.; Lindhart, A.; T. Direct trans-Selective Ruthenium-Catalyzed Reduction of Alkynes in Two-Chamber Reactors and Continuous Flow. *ACS Catal.* **2016**, *6*, 4710–4714.

19 Furukawa, S.; Komatsu, T. Selective Hydrogenation of Functionalized Alkynes to (E)-Alkenes, Using Ordered Alloys as Catalysts. *ACS Catal.* **2016**, *6*, 2121–2125.

20 Maazaoui, R.; Pin-Nó, M.; Gervais, K.; Abderrahim, R.; Ferreira, F.; Perez-Luna, A.; Chemla, F.; Jackowski, O. Domino Methylenation/Hydrogenation of Aldehydes and Ketones by Combining Matsubara's Reagent and Wilkinson's Catalyst. *Eur. J. Org. Chem.* **2016**, 5732–5737.

21 Vicente, J.; Abad, J.-A.; López-Serrano, J. L.; Jones, P. G.; Najera, C.; Segure, L. B. Synthesis and Reactivity of Ortho-Palladated Arylureas. Synthesis and Catalytic Activity of a C,N,C Pincer Complex. Stoichiometric Syntheses of Some N-Heterocycles. *Organometallics*, **2005**, *24*, 5044–5057.

22 a) Ananikov, V. P.; Baletskaia, I. P. Toward the Ideal Catalyst: From Atomic Centers to a “Cocktail” of Catalysts. *Organometallics*, **2012**, *31*, 1595–1604. b) Eremin, D. B.; Ananikov, V. P. Understanding Active Species in Catalytic Transformations: From Molecular Catalysis to Nanoparticles, Leaching, “Cocktails” of Catalysts and Dynamic Systems. *Coordination Chemistry Reviews*, **2017**, *346*, 2–19.

23 Two experiments were conducted in the presence of Hg⁰ (~ 2 mmol). When mercury was directly added at the beginning to the reaction mixture no conversion was observed after 6h. In a second experiment, reaction was carried out normally within 2 h (conv ~ 40%) and then Hg⁰ was added. No further evolution was observed during the following twenty hours.