Selective Manganese-Catalyzed Semihydrogenation of Alkynes with *in-situ* Generated H_2 from KBH_4 and Methanol

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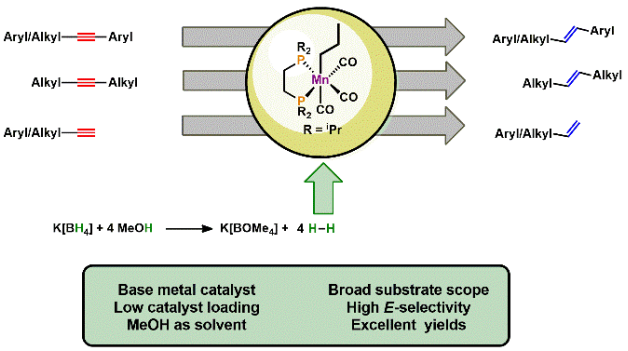
ABSTRACT: The selective semihydrogenation of alkynes with the Mn(I) alkyl catalyst *fac*-[Mn(dippe)(CO)$_3$(CH$_2$CH$_2$CH$_3$)] (dippe = 1,2-bis(di-*iso*-propylphosphino)ethane) as pre-catalyst is described. Hydrogen gas required for the hydrogenation is generated *in situ* upon alcoholysis of KBH_4 with methanol. A series of aryl-aryl, aryl-alkyl, alkyl-alkyl and terminal alkynes were readily hydrogenated to yield *E*-alkenes in good to excellent isolated yields. The reaction proceeds at 90°C with catalyst loadings of 0.5 -2 mol%. The implemented protocol tolerates a variety of electron donating and electron withdrawing functional groups including halides, phenols, nitriles, unprotected amines and heterocycles. The reaction can be upscaled to the gram scale. Mechanistic investigations including deuterium labelling studies and DFT calculations were undertaken to provide a reasonable reaction mechanism showing that initially formed *Z*-isomer undergoes fast isomerization to afford the thermodynamically more stable *E*-isomer.



INTRODUCTION

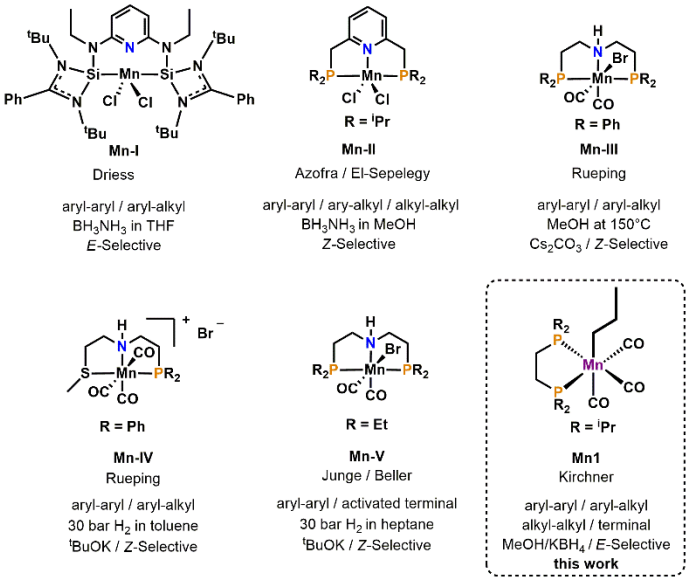
The selective semihydrogenation of alkynes plays a crucial role in bulk industry, fine chemistry and chemical research.[1] Examples of relevant applications are found in the hydrocarbon refinery for petrol industry,[1c, 1e, 2] the commercial synthetic routes for Resveratrol or Vitamin A.[1a] Thus far, traditional systems for the selective formation of *Z*-, *E*- or terminal alkenes consist of Pd/C,[3] Lindlar catalyst,[4] Birch reduction,[5] Raney-Nickel[6] or Wilkinson catalyst.[7] Due to limitations regarding selectivity, activity, amount of produced waste or catalyst price, the study and improvement of these protocols has attracted numerous research groups in academia and industry.[1a, 1b, 8] Thus, high activity and excellent selectivity-tailoring is being achieved by combining fine-tuned ligands with noble metals such as Ru,[9] Rh,[10] Pd[11] and Ir.[12] During the last decade, the concerns in regard to Green chemistry principles have been grown rapidly[13] and the development of catalysts based on earth-abundant metals for organic transformations has become of very important.[14] In recent years, several reports on selective alkyne semihydrogenations using catalysts based on Cr,[15] Mn,[16] Fe,[17] Co,[18] Ni,[19] Cu[20] are described.

As manganese is concerned, the use of pincer-type ligands and bifunctional catalysis[21] is crucial in the field of semi-(transfer)hydrogenation of alkynes (Scheme 1, **MnI** – **MnV**). However, high selectivity towards *E*-alkenes and the conversion of alkyl-alkyl substituted alkynes or terminal alkynes with high functional group tolerance remains

challenging.[1a] In addition, alcohols are potential coordinating ligands towards organometallic complexes which may have limited the use of more environmentally friendly and potentially bio-accessible alcohols as media for non-precious metal based systems. Therefore, reports of selective semihydrogenations of alkynes are rare.[16b, 18d, 19d, 20a]

We have recently reported on the application of the Mn(I) alkyl complex *fac*-[Mn(dippe)(CO)$_3$(CH$_2$CH$_2$CH$_3$)] (dippe = 1,2-bis(di-*iso*-propylphosphino)ethane) (**Mn1**) as pre-catalysts for the hydrogenation of ketones,[22] nitriles[23] and alkenes,[24] CO_2,[25] the boration and diboration of alkenes and alkynes,[26] the dehydrogenative silylation of alkenes[27] and the dimerization and cross coupling of terminal alkynes.[28] Inspired by these results we wondered if **Mn1** is also active in the semihydrogenation of alkynes. Herein, we report on the use of **Mn1** as pre-catalysts for the *E*-selective semihydrogenation of internal alkynes and the conversion of terminal alkynes in MeOH as solvent in the presence of KBH_4. We take advantage of the fact that the BH_4^- anion undergoes fast alcoholysis to generate *in situ* hydrogen gas[29] which is required for the hydrogenation of alkynes without the need of high-pressure equipment such as autoclaves.

Scheme 1. Overview of Manganese-based Catalysts for the Semihydrogenation Alkynes.



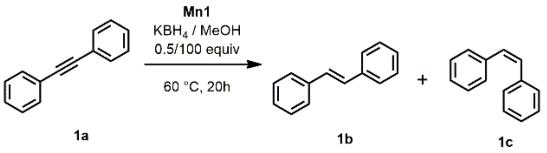
RESULTS AND DISCUSSION

In order to establish the best reaction conditions for the semi-hydrogenation of alkynes, diphenyl acetylene (**1a**) was chosen as model substrate in combination with MeOH and KBH_4 as hydrogen source. When **1a** was treated with 1 mol % of **Mn1** at 60°C with MeOH and 0.5 equiv of KBH_4, *E*-stilbene (**1b**) was obtained in 99% isolated yield (Table 1, entry 1). Only traces of *Z*-stilbene (**1c**) were observed and over-hydrogenation did not take place. Encouraged by this finding, temperature, catalyst loading and H_2 sources were screened (Table 1). With catalyst loadings of 1.0 and 0.5 mol% an almost quantitative formation of **1b** was achieved (Table 1, entries 1 and 2). Further lowering of the catalyst-loading to 0.3 and 0.1mol% resulted in 73 and 1 % yield, respectively (Table 1, entries 3-4). Decreasing the reaction temperature from 60 °C to 45 °C and 35 °C afforded **1b** in 97 and 90% yield (Table 1, entries 5-6). The performance of MeOH was compared to EtOH and *i*PrOH leading to lower yields (Table 1, entries 7-8). It is worth mentioning that the typical by-products from dehydrogenation of EtOH and *i*PrOH such as AcOEt and acetone were not observed and, thus, a transfer hydrogenation process can be ruled out. Instead, the corresponding signals of $[B(OMe)_4]^-$ as a result of alcoholysis of KBH_4 with MeOH were detected by ^{11}B NMR spectroscopy (see SI, Figures S4 and 5).[29] For comparison, when the reaction was performed in the presence of H_2 (30 bar) in MeOH and toluene, respectively, *E*-stilbene (**1b**) was obtained in 13 and 99 % yields (Table 1, entries 9 and 10). Accordingly, *in-situ* formation of H_2 from alcoholysis of the BH_4^- anion plays the key role in this

hydrogenation. Addition of water resulted in no significant change in conversion and selectivity (Table 1, entry 11). In the absence of catalyst, no reaction takes place (Table 1, entry 12).

GC monitoring of the reaction revealed full consumption of **1a** within 3 h (a kinetic profile is provided in the SI, Figure S1). Upon reaction progress, **1c** was detected as intermediate (ca 10%) which rapidly isomerizes to the corresponding *E*-alkene (**1b**). There was no evidence of overreduction to afford the corresponding alkane after 20 h.

Table 1. Optimization Reactions for the Semihydrogenation of **1a**.[a]



Entry	**Mn1** (mol%)	Solvent	Yield (%)	*E*/*Z*
1	1	MeOH	99[b]	99:1
2	0.5	MeOH	99[b]	99:1
3	0.3	MeOH	73	90:10
4	0.1	MeOH	1	66:33
5[c]	0.5	MeOH	97	99:1
6[d]	0.5	MeOH	90	97:3
7[c]	0.5	EtOH	5	60:40
8[c]	0.5	*i*PrOH	29	86:14
9[e]	0.5	MeOH	13	92:8
10[e]	0.5	toluene	99	99:1
11[f]	0.5	MeOH	99	98:2
12	-	MeOH	-	-

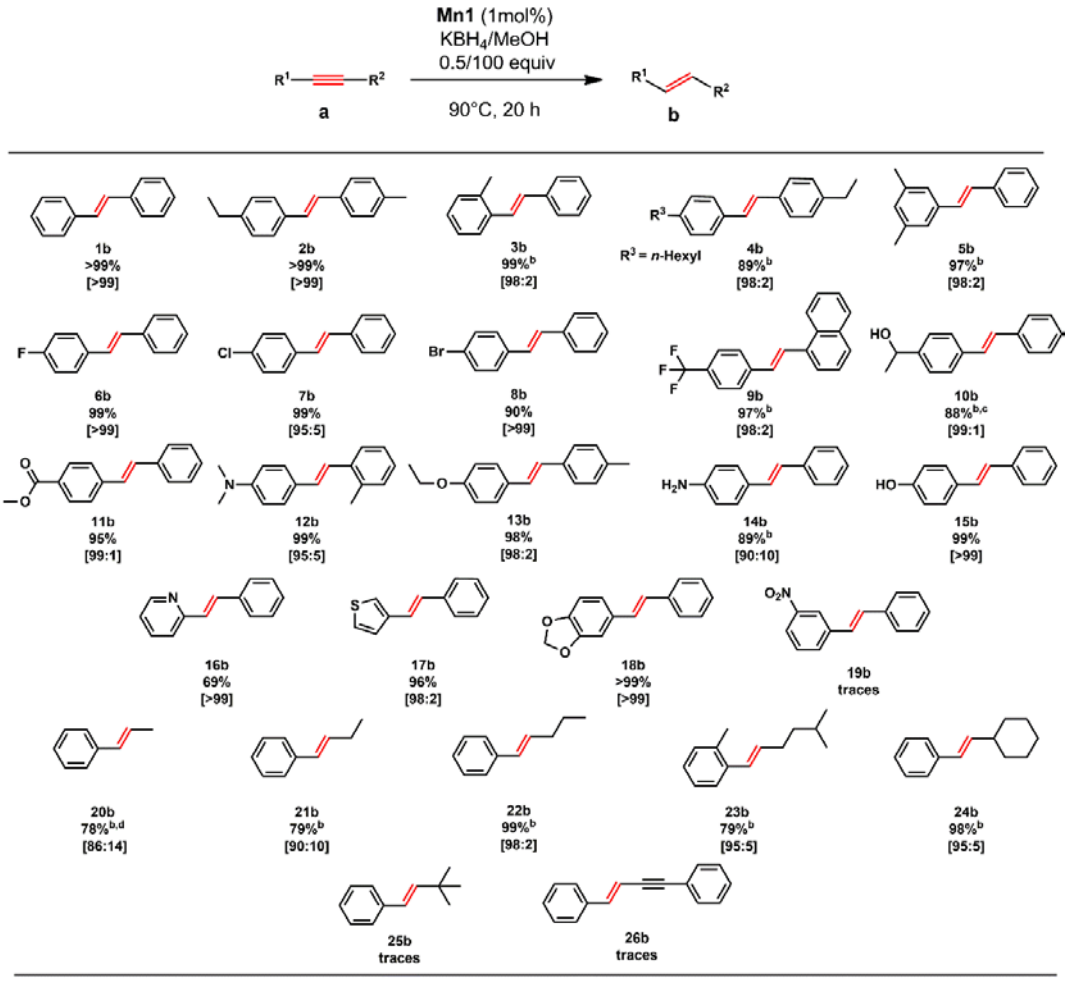
[a]Reaction conditions: diphenyl acetylene (**1a**) (0.9 mmol, 1 equiv), KBH_4 (0.5 equiv), MeOH (3.7 mL, 100 equiv), 60 °C, 20 h, yields determined by by GC-MS using dodecane as internal standard. [b]Isolated yields. [c]45 °C. [d]35 °C. [e]H_2 (30 bar) in the absence of KBH_4. [f]Addition of H_2O (200µL).

Encouraged by the high activity of the semihydrogenation of **1a**, a series of aryl-aryl substituted alkynes were investigated as substrates (Table 2). It turned out that in order to achieve high yields and good *E*/*Z* rations, for substrates other than **1a** the catalyst loadings had to be increased from 0.5 to 1 or 2 mol% in the case of terminal alkynes (*vide infra*). Likewise, when the reactions were performed at 90 °C significantly higher yields and *E*/*Z* ratios could be achieved.

Under these conditions, *ortho*-, *meta*- and *para*-alkyl substituted alkynes gave full conversion to *E*-stilbenes with excellent selectivity (Table 2, **1b-5b**). In the case of 1-methyl-2-(phenylethynyl)benzene (**3a**)and 1-ethyl-4-((4-hexylphenyl)ethynyl)benzene (**4a**) the catalyst loading had to be increased to 2 mol% to afford the desired *E*-alkenes in high isolated yields of 99 and 89%, respectively (Table 2, **3b** and **4b**). At 60°C with a catalyst loading of 1 mol %, the yields of **3b** and **4b** were only 17 and 51 %, respectively. Moreover, F-, Cl-, and Br-substituted substrates were tolerated yielding corresponding *E*-products in high yields (Table 2, **6b-9b**). Notably, the ester functionality remained unaltered under the given reaction conditions yielding desired product with 95% yield (Table 2, **11b**). The ketone substituted substrate **10a** yielded *E*-1-(4-styrylphenyl)ethane-1-ol (**10b**) with 88% yield (Table 2, **10b**). Substrates bearing strong electron-withdrawing groups such as CF_3 and COOMe underwent up to 5% over hydrogenation (Table 2, **9b** and **11b**). More challenging substrates containing electron-donating groups such as OEt and NMe_2 were also successfully reduced to corresponding *E*-alkenes with 98 and 99% yields and excellent *E*-selectivity (Table 2, **12b** and **13b**). Furthermore, unprotected phenol- and aniline-substituted alkynes (**14a**, **15a**) were obtained in 89 and 99% isolated yield (Table 2, **14b** and **15b**). In the case of 2-

(phenylethynyl)pyridine (**16a**) a mixture *E*/*Z* isomers in a 34:66 ratio was detected. Prolonging the reaction time from 20 to 25 h resulted in an increased *E*/*Z* ratio of 78:22 and **16b** was isolated in 69% yield (Table 2, **16b**). Other heterocycles containing sulphur or oxygen (**17a** and **18a**) where readily converted into the corresponding *E*-alkenes in 96 and 99 % isolated yield (Table 2, **17b** and **18b**). Only traces of product were obtained in the presence of a NO_2 group (Table 2, **19b**). The practical applicability of the system was demonstrated upon up-scaling giving *E*-stilbene in >99% yield on a gram scale (Table 2, **1b**).

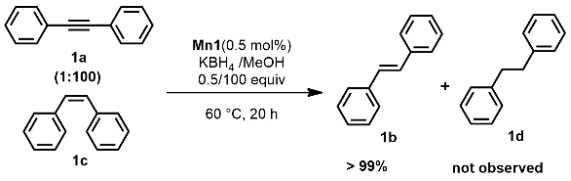
Table 2. Mn1 catalyzed semihydrogenation of aryl-aryl alkynes and aryl-alkyl alkynes[a]



[a]Reaction conditions: alkyne (0.9 mmol, 1 equiv), **Mn1** (1mol%), KBH_4 (0.5 equiv), MeOH (3.7 mL, 100 equiv), 90°C, 20 h, isolated yields. Value in the brackets corresponds to the *E*/*Z* ratio determined by ^{1}H-NMR spectroscopy. [b]**Mn1** (2 mol%). [c]Substrate: *(E)*-1-(4-styrylphenyl)ethanone (**10a**), KBH_4 (1 equiv). [d]Yield determined by GC-MS using dodecane as internal standard.

In the next step, aryl-alkyl substituted alkynes were investigated. These substrates tend to be more challenging in selective semihydrogenation due to over reduction and isomerization. Under the given reaction conditions non-activated aryl-alkyl alkynes bearing several alkyl group substituents afforded corresponding *E*-styrene derivatives in good to excellent yields (Table 2, **20b-24b**). For instance, **20a** gave the desired alkene with a *E*/*Z* ratio of 86:14 in 78% yield together with only 3 % over-hydrogenated product (Table 2, **20b**). In the case of the sterically hindered 1-*t*butyl-2-phenylacetylene (**25a**) as well as the conjugated diyne **26a** only traces of product were detected (Table 2, **25b**, **26b**).

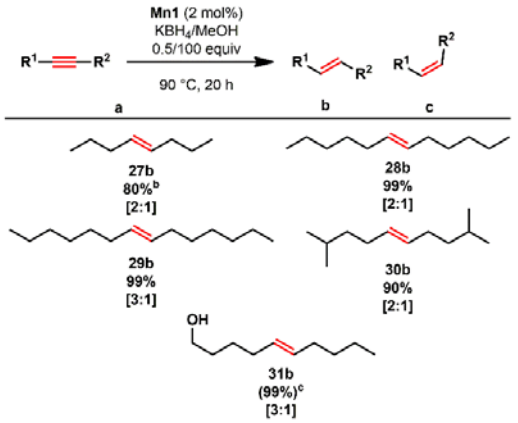
Scheme 2. Selective Hydrogenation of 1a and Isomerization of *Z*-Stilbene (1c) to *E*-Stilbene (1b) Catalyzed by Mn1.



It has to be mentioned that the removal of alkyne impurities in the presence of olefins *via* alkyne semi-hydrogenation is of interest for industrial purposes since it benefits the subsequent polymerizations of some light hydrocarbon fractions from steam cracking.[2] Due to the high selectivity of the introduced protocol, we investigated the potential applicability of this system for the purification of olefins. Accordingly, treating a mixture of **1a** and **1c** (1:100) with **Mn1** (0.5 mol%) in the presence of KBH_4 in MeOH resulted in full conversion of the mixture to *E*-stilbene (**1b**) without formation of over-hydrogenated product **1d** (Scheme 2).

Alkyl-alkyl substituted alkynes tend to be a challenging class of substrates in the field of semihydrogenation. Selective semihydrogenation of these substrates using manganese catalyst is rare and so far limited to dodecyne (**28a**) in up to 67% yield.[16d, 16e] Interestingly, **Mn1** was proven to be highly active also for the transformation of alkyl-alkyl substrates alkenes with moderate selectivity as depicted in Table 3. Over-hydrogenation was observed for some substrates. For instance, 4-octyne (**27a**) yielded 80% yield of desired product with an *E*/*Z* ratio of 2:1 ratio together with 20% of over-hydrogenated product (Table 3, **27b**). On the other hand, alkynes with longer aliphatic chains proved to be more successful and 6-dodecyne (**28a**), 7-tetradecyne (**29a**) and 2,9-dimethyl-5-decyne (**30a**) were fully converted to corresponding alkenes with 90 to 99% yields (Table 3, **28b-30b**). The two isomers of 5-decenol (**31b**) are known to be hormones of the Peach Twig Borer and the Lepidoptera, respectively, and can be encountered in different industrial formulations of pesticides and fragrances.[30] Interestingly, the presence of a primary alcohol in the corresponding precursor **31a** was tolerated and quantitatively transformed into the corresponding alkene **31b** with 99% isolated yield and a 3:1 *E*/*Z* ratio (Table 3, **31b**). Notably, double bond migration was not observed in any case.

Table 3. Mn1 catalyzed semihydrogenation of alkyl-alkyl alkynes[a]

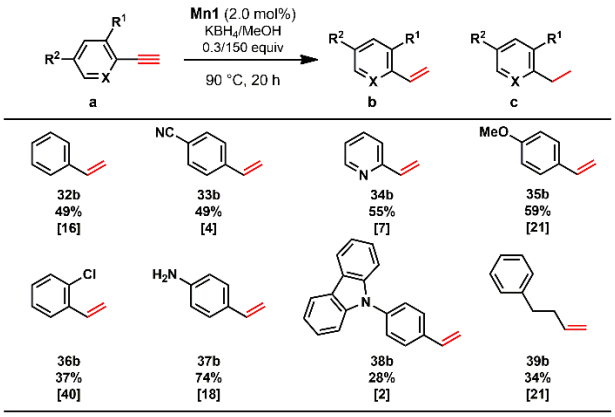


[a]Reaction conditions: alkyne (0.9 mmol, 1 equiv), **Mn1** (2 mol%), KBH_4 (0.5 equiv), MeOH (3.7 mL, 100 equiv), 90°C, 20 h, isolated yields. Values in the brackets correspond to the *E*/*Z* ratio determined by ^{1}H NMR spectroscopy. [b]Yield determined by GC-MS using dodecane as intenal standard. [c]**Mn1** (1 mol%).

Terminal alkynes display another challenging class of substrates in semihydrogenation due to over hydrogenation yielding alkanes as well as dimerization to afford 1,3-enynes.[28] However, it was possible to achieve 49% yield of styrene (Table 4, **32b**) upon increasing the catalyst loading to 2 mol%. Under the optimized reaction conditions, heterosubstituted phenylacetylenes were fully hydrogenated albeit with moderate selectivity (Table 4).

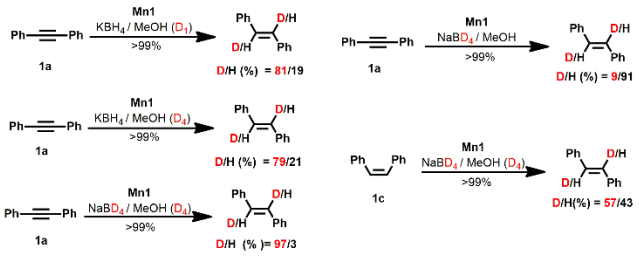
Mechanistic studies were carried out to gain insights in the reaction mechanism (Scheme 3). Upon addition of PPh_3 only traces of *E*/*Z*-stilbene were obtained. This is attributed to coordination of PPh_3 to the manganese center blocking a vacant side of the catalyst. This again indicates that an inner-sphere mechanism is operating in this system. Furthermore, deuterium labelling experiments were performed. If **1a** was treated with KBH_4 in MeOH-d_1, a deuterium content of 81% was observed in *E*-stilbene. This amount of deuterium incorporation did not change significantly when MeOH-d_4 was used instead. As expected, up to 97% deuterium content was incorporated when **1a** was treated with $NaBD_4$ in MeOH-d_4. In contrast, only a negligible amount of merely 9% deuterium was incorporated when $NaBD_4$ was used in combination with MeOH. When *Z*-stilbene (**1c**) was treated with $NaBD_4$ in MeOH-d_4 only a deuterium content of 57% was observed in the isomerized product. These observations clearly show that the acidic proton of MeOH is almost exclusively incorporated into the substrate presumably via fast proton exchange with hydride intermediates shown the catalytic cycle (*vide infra*).[31]

Table 4. Mn1 catalyzed semihydrogenation of terminal alkynes[a]



[a]Reaction conditions: alkyne (0.4 mmol, 1 equiv), **Mn1** (2 mol%), KBH_4 (0.3 equiv), MeOH (3.5 mL, 150 equiv), 90°C, 20 h, yield corresponds to alkene (**b**), values in brackets correspond to yield of saturated alkane (**c**) as determined GC-MS using dodecane as internal standard.

Scheme 3. Deuterium Labelling Studies for the *E*-Selective Semihydrogenation of 1a and the Isomerization of 1c Catalyzed by Mn1.



A plausible catalytic cycle based on experimental data and DFT calculations (PBE0/(SDD,6-31G**))[32] with diphenylacetylene (**1a**) as model substrate could be established. The resulting free energy profiles are represented in Figures 1 and 2 while Scheme 4 depicts the simplified catalytic cycle (only key intermediates are shown).

The activation of **Mn1** by dihydrogen has been reported recently.[24] Substitution of the weakly-bonded *n*-butanal by **1a** leads to formation of the hydride species **A** featuring an η^2-bound acetylene ligand (free energy values are referred to this complex). Insertion of the acetylene into the Mn-H bond affords the coordinatively unsaturated vinyl complex **B** which is stabilized by an agostic C-H bond. This process is exergonic by -23.8 kcal/mol with a very small barrier of 0.6 kcal/mol. Addition of dihydrogen leads via the van der Waals adduct **C** to the formation of intermediate **D**. This step is endergonic by 9.9 kcal/mol with an overall barrier of 18.6 kcal/mol being the highest

of the entire cycle. Heterolytic cleavage of dihydrogen results in the formation of the hydride complex **E** featuring a C-H bound *Z*-stilbene in an exergonic step (ΔG = -9.4 kcal/mol) with a negligible barrier of 1.8 kcal/mol. The reaction proceeds with reorientation of the olefin from the C-H σ-complex in **E** to the π-coordinated complex in **H**. This process proceeds via intermediates **F** and **G** which are equivalent van der Waals pairs of the *Z*-stilbene and the metallic fragment. It involves olefin dissociation, clockwise rotation of the olefin by about 90° and re-coordination of the olefin. The overall process has a negligible barrier of 1.2 kcal/mol and is favorable with ΔG = -7.1 kcal/mol, reflecting the stronger coordination of the η^2-olefin in **H** compared to the C-H σ-bound olefin in complex **E**.

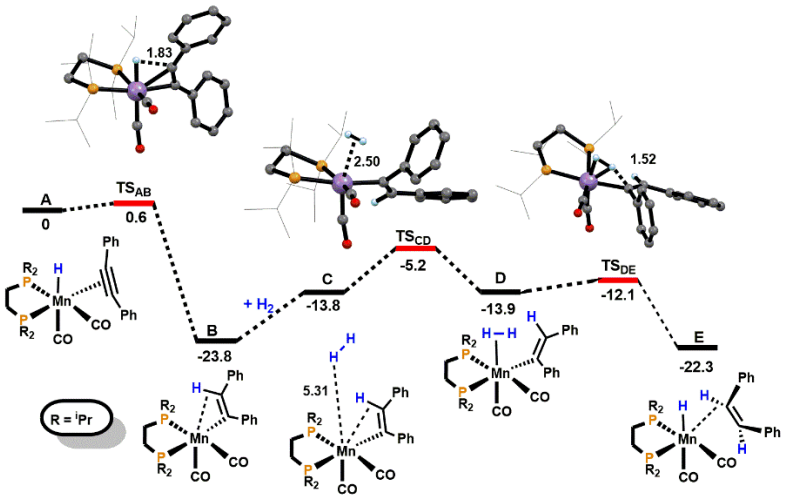


Figure 1. Free Energy Profile Calculated at the PBE0/(SDD,6-31G**) Level for the Semihydrogenation of Phenylacetylene. Free Energies (kcal/mol) are Referred to [Mn(dippe)(CO)$_2$(H)(η^2-PhC≡CPh)] (**A**).

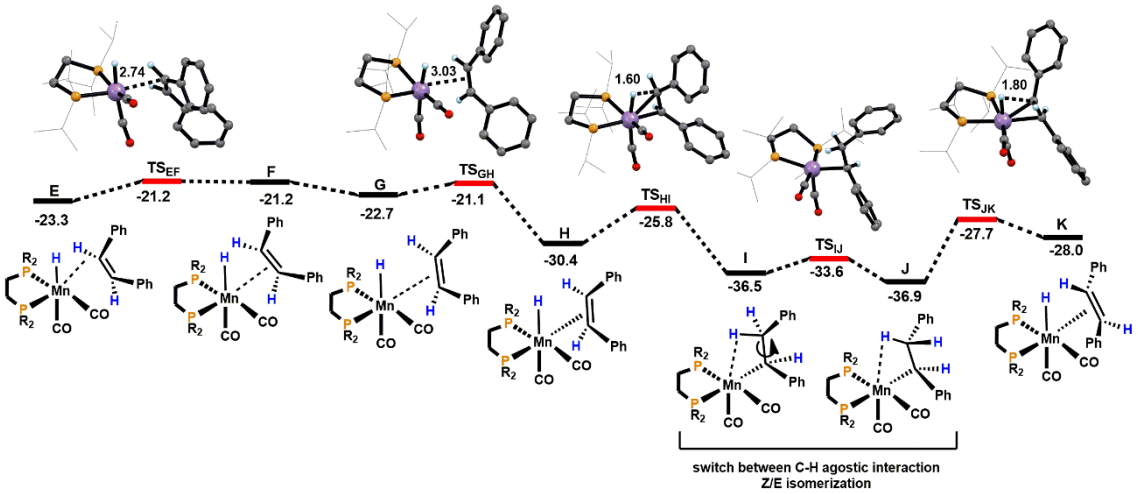
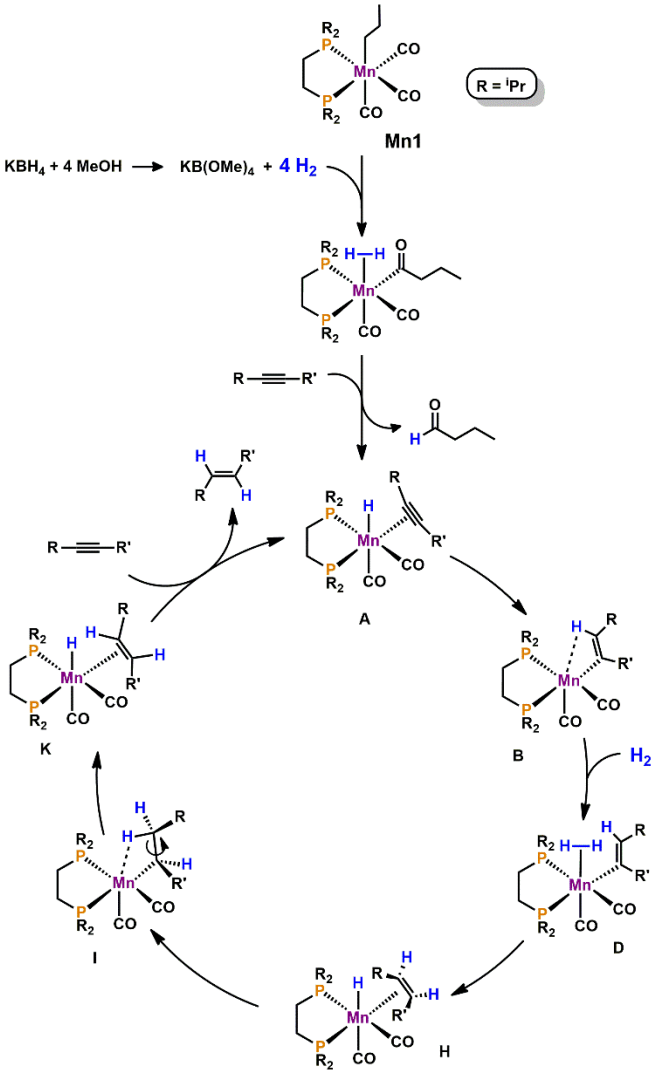


Figure 2. Free Energy Profile Calculated at the PBE0/(SDD,6-31G**) Level for the Semihydrogenation of Phenylacetylene. Free Energies (kcal/mol) are Referred to [Mn(dippe)(CO)$_2$(H)(η^2-PhC≡CPh)] (**A**).

In the next step of the reaction the hydride ligand in **H** migrates to the adjacent olefin C-atom resulting in an alkyl complex stabilized by a C-H agostic interaction in intermediate **I**. This is a facile step with a barrier of 4.6 kcal/mol and a free energy balance of ΔG = -6.1 kcal/mol. In **I**, a switch between the C-H agostic interaction (*Z* to *E* isomerization) yields intermediate **J** ($\Delta G^{\ddagger}$ = 2.9 kcal/mol and ΔG = –0.4 kcal/mol) and finally β-hydrogen elimination to afford the hydride *E*-stilbene intermediate [Mn(dippe)(CO)$_2$(H)(η^2-CH(Ph)=CHPh)] (**K**) with a barrier of 9.2 kcal/mol in an endergonic final step (ΔG = 8.9 kcal/mol).

Closing of the catalytic cycle brings **K** back to **A** with liberation of *E*-stilbene and coordination of a new diphenylacetylene molecule in a favorable process with $\Delta G = -8.2$ kcal/mol.

Scheme 4. Simplified Catalytic Cycle for the *E*-Selective Semihydrogenation of Acetylenes Catalyzed by Mn1.



CONCLUSION

In sum, an efficient protocol for the selective semihydrogenation of aryl-aryl, aryl-alkyl and terminal alkynes to afford *E*-alkenes is described. The pre-catalyst is the bench-stable alkyl complex *fac*-Mn(dippe)$(CO)_3(CH_2CH_2CH_3)$ in combination with KBH_4 and MeOH as hydrogen source. The hydrogen gas required for the hydrogenation is formed *in situ* upon alcoholysis of KBH_4. Thus, high pressure equipment is not required. The reaction proceeds at 90°C with catalyst loadings of 0.5 to 2.0 mol% and a reaction time of 20 h. This represents a rare example of a manganese catalyzed hydrogenation of alkynes to give selectively *E*-alkenes. High functional group tolerance including halides, phenols, nitriles, unprotected amines and heterocycles was observed. Even challenging substrates such as alkyl-alkyl alkynes and terminal alkynes allowed high conversions with moderate to good selectivity. The practical applicability of the protocol was demonstrated in the gram-scale synthesis of *E*-stilbene. Mechanistic investigations including DFT calculations and deuterium labelling studies were undertaken to provide a reasonable reaction mechanism showing that initially formed *Z*-isomer undergoes fast isomerization to the afford the thermodynamically more stable *E*-isomer.

SUPPORTING INFORMATION

Synthetic procedures, ^{1}H, $^{13}C\{^{1}H\}$, $^{19}F\{^{1}H\}$, $^{31}P\{H\}$ and ^{11}B NMR spectra of all compounds (PDF)
Cartesian coordinates for DFT-optimized structures (XYZ)

Acknowledgements

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References

(1) (a) Decker, D.; Drexler, H.-J.; Heller, D.; Beweries, T. Homogeneous catalytic transfer semihydrogenation of alkynes - an overview of hydrogen sources, catalysts and reaction mechanisms. *Catal. Sci. Technol.* **2020,** *10*, 6449-6463. (b) Swamy, K. C. K.; Reddy, A. S.; Sandeep, K.; Kalyani, A. Advances in chemoselective and/or stereoselective semihydrogenation of alkynes. *Tetrahedron Lett.* **2018,** *59*, 419-429. (c) Bonrath, W.; Medlock, J. A.; Mueller, M. A., *Catalytic reduction of alkynes and allenes*. In: *Catalytic Reduction in Organic Synthesis 1*, de Vries, J. G., Ed.; Georg Thieme Verlag: **2018**; Vol. 1, pp 195-228. (d) Giacomini, E.; Rupiani, S.; Guidotti, L.; Recanatini, M.; Roberti, M., The Use of Stilbene Scaffold in Medicinal Chemistry and Multi- Target Drug Design. *Curr. Med. Chem.* **2016**, *23*, 2439-2489.

(2) Lopez, N.; Vargas-Fuentes, C. Promoters in the hydrogenation of alkynes in mixtures: insights from density functional theory. *Chem. Commun.* **2012,** *48*, 1379-1391.

(3) Rylander, P. N., *Best Synthetic Methods: Hydrogenation Methods*. Academic Press: Orlando. Florida., **1985**; Chapter 3, pp 53-65.

(4) Lindlar, H.; Dubuis, R., Palladium catalyst for partial reduction of acetylenes. *Org. Synth.* **1966**, *46*, 89-92.

(5) Birch, A. J., Reduction by dissolving metals. I. *J. Chem. Soc.* **1944**, 430-436.

(6) De Thomas, W. R.; Hort, E. V. Catalyst comprising Raney nickel with adsorbed molybdenum compound. US4153578A, **1979**.

(7) Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G., Preparation and properties of tris(triphenylphosphine)halorhodium(I) and some reactions thereof including catalytic homogeneous hydrogenation of olefins and acetylenes and their derivatives. *J. Chem. Soc., A* **1966**, 1711-1732.

(8) (a) Oger, C.; Balas, L.; Durand, T.; Galano, J.-M. Are Alkyne Reductions Chemo-, Regio-, and Stereoselective Enough To Provide Pure (*Z*)-Olefins in Polyfunctionalized Bioactive Molecules? *Chem. Rev.* **2013,** *113*, 1313-1350. (b) 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.

(9) (a) Yadav, S.; Dutta, I.; Saha, S.; Das, S.; Pati, S. K.; Choudhury, J.; Bera, J. K. An Annelated Mesoionic Carbene (MIC) Based Ru(II) Catalyst for Chemo- and Stereoselective Semihydrogenation of Internal and Terminal Alkynes. *Organometallics* **2020,** *39*, 3212-3223. (b) Gong, D.; Hu, B.; Yang, W.; Kong, D.; Xia, H.; Chen, D. A Bidentate Ru(II)-NC Complex as a Catalyst for Semihydrogenation of Alkynes to (E)-Alkenes with Ethanol. *Organometallics* **2020,** *39*, 862-869. (c) Ekebergh, A.; Begon, R.; Kann, N. Ruthenium-Catalyzed E-Selective Alkyne Semihydrogenation with Alcohols as Hydrogen Donors. *J. Org. Chem.* **2020,** *85*, 2966-2975. (d) Yamamoto, K.; Mohara, Y.; Mutoh, Y.; Saito, S. Ruthenium-Catalyzed (Z)-Selective Hydroboration of Terminal Alkynes with Naphthalene-1,8-diaminatoborane. *J. Am. Chem. Soc.* **2019,** *141*, 17042-17047. (e) Neumann, K. T.; Klimczyk, S.; Burhardt, M. N.; Bang-Andersen, B.; Skrydstrup, T.; Lindhardt, A. T. Direct trans-Selective Ruthenium-Catalyzed Reduction of Alkynes in Two-Chamber Reactors and Continuous Flow. *ACS Catal.* **2016,** *6*, 4710-4714. (f) Fetzer, M. N. A.; Tavakoli, G.; Klein, A.; Prechtl, M. H. G. Ruthenium-Catalyzed E-Selective Partial Hydrogenation of Alkynes under Transfer-Hydrogenation Conditions using Paraformaldehyde as Hydrogen Source. *ChemCatChem* **2021,** *13*, 1317-1325.

(10) (a) Jagtap, S. A.; Bhanage, B. M. Ligand Assisted Rhodium Catalyzed Selective Semi-hydrogenation of Alkynes Using Syngas and Molecular Hydrogen. *ChemistrySelect* **2018,** *3*, 713-718. (b) Schrock, R. R.; Osborn, J. A. Catalytic hydrogenation using cationic rhodium complexes. 3. The selective hydrogenation of dienes to monoenes. *J. Am. Chem. Soc.* **1976,** *98*, 4450-4455.

(11) (a) Wang, Y.; Cao, X.; Zhao, L.; Pi, C.; Ji, J.; Cui, X.; Wu, Y. Generalized Chemoselective Transfer Hydrogenation/Hydrodeuteration. *Adv. Synth. Catal.* **2020,** *362*, 4119-4129. (b) Liu, J.; Wei, Z.; Yang, J.; Ge, Y.; Wei, D.; Jackstell, R.; Jiao, H.; Beller, M. Tuning the Selectivity of Palladium Catalysts for Hydroformylation and Semihydrogenation of Alkynes: Experimental and Mechanistic Studies. *ACS Catal.* **2020,** *10*, 12167-12181.

(12) (a) Huang, Z.; Wang, Y.; Leng, X.; Huang, Z. An Amine-Assisted Ionic Monohydride Mechanism Enables Selective Alkyne cis-Semihydrogenation with Ethanol: From Elementary Steps to Catalysis. *J. Am. Chem. Soc.* **2021,** *143*, 4824-4836. (b) Yang, J.; Wang, C.; Sun, Y.; Man, X.; Li, J.; Sun, F. Ligand-controlled iridium-catalyzed semihydrogenation of alkynes with ethanol: highly stereoselective synthesis of *E*- and *Z*-alkenes. *Chem. Commun.* **2019,** *55*, 1903-1906. (c) Wang, C.; Gong, S.; Liang, Z.; Sun, Y.; Cheng, R.; Yang, B.; Liu, Y.; Yang, J.; Sun, F. Ligand-Promoted Iridium-Catalyzed Transfer Hydrogenation of Terminal Alkynes with Ethanol and Its Application. *ACS Omega* **2019,** *4*, 16045-16051. (d) Wang, Y.; Huang, Z.; Leng, X.; Zhu, H.; Liu, G.; Huang, Z. Transfer Hydrogenation of Alkenes Using Ethanol Catalyzed by a NCP Pincer Iridium Complex: Scope and Mechanism. *J. Am. Chem. Soc.* **2018,** *140*, 4417-4429.

(13) (a) Schaub, T. Efficient Industrial Organic Synthesis and the Principles of Green Chemistry. *Chem. Eur. J.* **2021,** *27*, 1865-1869. (b) Ivankovic, A.; Dronjic, A.; Bevanda, A. M.; Talic, S. Review of 12 principles of green chemistry in practice. *Int. J. Sustainable Green Energy* **2017,** *6*, 39-48. (c) Anastas, P.; Eghbali, N. Green Chemistry: Principles and Practice. *Chem. Soc. Rev.* **2010,** *39*, 301-312.

(14) (a) Wen, J.; Wang, F.; Zhang, X. Asymmetric hydrogenation catalyzed by first-row transition metal complexes. *Chem. Soc. Rev.* **2021,** *50*, 3211-3237. (b) Sharma, D. M.; Punji, B. 3d Transition Metal-Catalyzed Hydrogenation of Nitriles and Alkynes. *Chem. Asian J.* **2020,** *15*, 690-708. (c) Teichert, J. F. Homogeneous Hydrogenation with Non-Precious Catalysts. *Wiley-VCH: Weinheim, Germany*, **2020**. (d) Beller, M. Introduction: First Row Metals and Catalysis. *Chem. Rev.* **2019,** *119*, 2089. (e) Gorgas, N.; Kirchner, K. Isoelectronic Manganese and Iron Hydrogenation/Dehydrogenation Catalysts - Similarities and Divergences *Acc. Chem. Res.* **2018**, *51*, 1558-1569. (f) Zell, T.; Langer, R. From Ruthenium to Iron and Manganese-A Mechanistic View on Challenges and Design Principles of Base-Metal Hydrogenation Catalysts. *ChemCatChem* **2018,** *10*, 1930-1940. (g) Filonenko, G. A.; van Putten, R.; Hensen, E. J. M.; Pidko, E. A. Catalytic (De)hydrogenation Promoted by Non-Precious Metals - Co, Fe and Mn: Recent Advances in an Emerging Field. *Chem. Soc. Rev.* **2018**. *47*, 1484-1515. (h) Kallmeier, F.; Kempe, R. Manganese Complexes for (De)Hydrogenation Catalysis: A Comparison to Cobalt and Iron Catalysts. *Angew. Chem., Int. Ed.* **2018**, *57*, 46-60. (i) Chirik, P.; Morris, R. Getting Down to Earth: The Renaissance of Catalysis with Abundant Metals. *Acc. Chem. Res.* **2015,** *48*, 2495. (j) Mukherjee, A.; Milstein, D. Homogeneous Catalysis by Cobalt and Manganese Pincer Complexes *ACS Catal.* **2018**, *8*, 11435−11469.

(15) Gregori, B. J.; Nowakowski, M.; Schoch, A.; Poellath, S.; Zweck, J.; Bauer, M.; Jacobi von Wangelin, A. Stereoselective Chromium-Catalyzed Semi-Hydrogenation of Alkynes. *ChemCatChem* **2020,** *12*, 5359-5363.

(16) (a) Zubar, V.; Sklyaruk, J.; Brzozowska, A.; Rueping, M. Chemoselective Hydrogenation of Alkynes to (Z)-Alkenes Using an Air-Stable Base Metal Catalyst. *Org. Lett.* **2020,** *22*, 5423-5428. (b) Sklyaruk, J.; Zubar, V.; Borghs, J. C.; Rueping, M. Methanol as the Hydrogen Source in the Selective Transfer Hydrogenation of Alkynes Enabled by a Manganese Pincer Complex. *Org. Lett.* **2020,** *22*, 6067-6071. (c) Garbe, M.; Budweg, S.; Papa, V.; Wei, Z.; Hornke, H.; Bachmann, S.; Scalone, M.; Spannenberg, A.; Jiao, H.; Junge, K.; Beller, M. Chemoselective semihydrogenation of alkynes catalyzed by manganese(I)-PNP pincer complexes. *Catal. Sci. Technol.* **2020,** *10*, 3994-4001. (d) Zhou, Y.-P.; Mo, Z.; Luecke, M.-P.; Driess, M. Stereoselective Transfer Semi-Hydrogenation of Alkynes to *E*-Olefins with N-Heterocyclic Silylene-Manganese Catalysts. *Chem. Eur. J.* **2018,** *24*, 4780-4784. (e) Brzozowska, A.; Azofra, L. M.; Zubar, V.; Atodiresei, I.; Cavallo, L.; Rueping, M.; El-Sepelgy, O. Highly Chemo- and Stereoselective Transfer Semihydrogenation of Alkynes Catalyzed by a Stable, Well-Defined Manganese(II) Complex. *ACS Catal.* **2018,** *8*, 4103-4109.

(17) (a) Gorgas, N.; Bruenig, J.; Stoeger, B.; Vanicek, S.; Tilset, M.; Veiros, L. F.; Kirchner, K. Efficient Z-Selective Semihydrogenation of Internal Alkynes Catalyzed by Cationic Iron(II) Hydride Complexes. *J. Am. Chem. Soc.* **2019,** *141*, 17452-17458. (b) 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. (c) Wienhoefer, G.; Westerhaus, F. A.; Jagadeesh, R. V.; Junge, K.; Junge, H.; Beller, M. Selective iron-catalyzed transfer hydrogenation of terminal alkynes. *Chem. Commun.* **2012,** *48*, 4827-4829. (d) Bianchini, C.; Meli, A.; Peruzzini, M.; Frediani, P.; Bohanna, C.; Esteruelas, M. A.; Oro, L. A. Selective hydrogenation of 1-alkynes to alkenes catalyzed by an iron(II) cis-hydride η^2-dihydrogen complex. A case of intramolecular reaction between η^2-H_2 and σ-vinyl ligands. *Organometallics* **1992,** *11*, 138-145. (e) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Zanobini, F.; Frediani, P. A homogeneous iron(II) system capable of selectivity catalyzing the reduction of terminal alkynes to alkenes and buta-1,3-dienes. *Organometallics* **1989,** *8*, 2080-2082.

(18) (a) Tian, W.-F.; He, Y.-Q.; Song, X.-R.; Ding, H.-X.; Ye, J.; Guo, W.-J.; Xiao, Q. cis-Selective Transfer Semihydrogenation of Alkynes by Merging Visible-Light Catalysis with Cobalt Catalysis. *Adv. Synth. Catal.* **2020,** *362*, 1032-1038. (b) Liu, X.; Liu, B.; Liu, Q. Migratory Hydrogenation of Terminal Alkynes by Base/Cobalt Relay Catalysis. *Angew. Chem., Int. Ed.* **2020,** *59*, 6750-6755. (c) Qi, X.; Liu, X.; Qu, L.-B.; Liu, Q.; Lan, Y. Mechanistic

insight into cobalt-catalyzed stereodivergent semihydrogenation of alkynes: The story of selectivity control. *J. Catal.* **2018,** *362*, 25-34. (d) Fu, S.; Chen, N.-Y.; Liu, X.; Shao, Z.; Luo, S.-P.; 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. (e) Alawisi, H.; Arman, H. D.; Tonzetich, Z. J. Catalytic Hydrogenation of Alkenes and Alkynes by a Cobalt Pincer Complex: Evidence of Roles for Both Co(I) and Co(II). *Organometallics* **2021,** *40*, 1062-1070.

(19) (a) Li, K.; Yang, C.; Chen, J.; Pan, C.; Fan, R.; Zhou, Y.; Luo, Y.; Yang, D.; Fan, B. Anion Controlled Stereodivergent Semi-Hydrogenation of Alkynes using Water as Hydrogen Source. *Asian J. Org. Chem.* **2021,** *10*, 2143-2146. (b) Thiel, N. O.; Kaewmee, B.; Tran Ngoc, T.; Teichert, J. F. A Simple Nickel Catalyst Enabling an E-Selective Alkyne Semihydrogenation. *Chem. Eur. J.* **2020,** *26*, 1597-1603. (c) Murugesan, K.; Bheeter, C. B.; Linnebank, P. R.; Spannenberg, A.; Reek, J. N. H.; Jagadeesh, R. V.; Beller, M. Nickel-catalyzed stereodivergent synthesis of E- and Z-alkenes by hydrogenation of alkynes. *ChemSusChem* **2019,** *12*, 3363-3369. (d) Wen, X.; Shi, X.; Qiao, X.; Wu, Z.; Bai, G. Ligand-free nickel-catalyzed semihydrogenation of alkynes with sodium borohydride: a highly efficient and selective process for cis-alkenes under ambient conditions. *Chem. Commun.* **2017,** *53*, 5372-5375. (e) Reyes-Sanchez, A.; Canavera-Buelvas, F.; Barrios-Francisco, R.; Cifuentes-Vaca, O. L.; Flores-Alamo, M.; Garcia, J. J. Nickel-Catalyzed Transfer Semihydrogenation and Hydroamination of Aromatic Alkynes Using Amines As Hydrogen Donors. *Organometallics* **2011,** *30*, 3340-3345.

(20) (a) Kaicharla, T.; Zimmermann, B. M.; Oestreich, M.; Teichert, J. F. Using alcohols as simple H_2-equivalents for copper-catalysed transfer semihydrogenations of alkynes. *Chem. Commun.* **2019,** *55*, 13410-13413. (b) Cao, H.; Chen, T.; Zhou, Y.; Han, D.; Yin, S.-F.; Han, L.-B. Copper-Catalyzed Selective Semihydrogenation of Terminal Alkynes with Hypophosphorous Acid. *Adv. Synth. Catal.* **2014,** *356*, 765-769.

(21) Alig, L.; Fritz, M.; Schneider, S. First-Row Transition Metal (De)Hydrogenation Catalysis Based On Functional Pincer Ligands. *Chem. Rev.* **2019,** *119*, 2681-2751.

(22) (a) Weber, S.; Bruenig, J.; Veiros, L. F.; Kirchner, K. Manganese-Catalyzed Hydrogenation of Ketones under Mild and Base-free Conditions. *Organometallics* **2021,** *40*, 1388-1394. (b) Weber, S.; Stoeger, B.; Kirchner, K. Hydrogenation of Nitriles and Ketones Catalyzed by an Air-Stable Bisphosphine Mn(I) Complex. *Org. Lett.* **2018,** *20*, 7212-7215.

(23) Weber, S.; Veiros, L. F.; Kirchner, K. Old Concepts, New Application - Additive-Free Hydrogenation of Nitriles Catalyzed by an Air Stable Alkyl Mn(I) Complex. *Adv. Synth. Catal.* **2019,** *361*, 5412-5420.

(24) Weber, S.; Stoeger, B.; Veiros, L. F.; Kirchner, K. Rethinking Basic Concepts-Hydrogenation of Alkenes Catalyzed by Bench-Stable Alkyl Mn(I) Complexes. *ACS Catal.* **2019,** *9*, 9715-9720.

(25) Kostera, S.; Weber, S.; Peruzzini, M.; Veiros, L. F.; Kirchner, K.; Gonsalvi, L. Carbon Dioxide Hydrogenation to Formate Catalyzed by a Bench-Stable, Non-Pincer-Type Mn(I) Alkylcarbonyl Complex. *Organometallics* **2021,** *40*, 1213-1220.

(26) Weber, S.; Stoger, B.; Zobernig, D.; Veiros, L. F.; Kirchner, K. Hydroboration of Terminal Alkenes and trans-1,2-Diboration of Terminal Alkynes Catalyzed by a Mn(I) Alkyl Complex. *Angew. Chem., Int. Ed.* **2021**, in press (DOI: 10.1002/anie.202110736).

(27) Weber, S.; Glavic, M.; Stöger, B.; Pittenauer, E.; Veiros, L. F.; Kirchner, K. Manganese-Catalyzed Dehydrogenative Silylation of Alkenes Following Two Parallel Pathways. *J. Am. Chem. Soc.* **2021**, in press (DOI: 10.1021/jacs.1c09175).

(28) Weber, S.; Veiros, L. F.; Kirchner, K. Selective Manganese-Catalyzed Dimerization and Cross-Coupling of Terminal Alkynes. *ACS Catal.* **2021,** *11*, 6474-6483.

(29) (a) Abdelhamid, H. N., A review on hydrogen generation from the hydrolysis of sodium borohydride. *Int. J. Hydrogen Energy* **2021**, *46*, 726-765. (b) Ramya, K.; Dhathathreyan, K. S.; Sreenivas, J.; Kumar, S.; Narasimhan, S., Hydrogen production by alcoholysis of sodium borohydride. *Int. J. Energy Res.* **2013**, *37*, 1889-1895. (c) Hannauer, J.; Demirci, U. B.; Pastor, G.; Geantet, C.; Herrmann, J. M.; Miele, P. Hydrogen release through catalyzed methanolysis of solid sodium borohydride *Energy Environ. Sci.* **2010**, *3*, 1796-1803. (d) Lo, C.-T. F.; Karan, K.; Davis, B. R. Kinetic Studies of Reaction between Sodium Borohydride and Methanol, Water, and Their Mixtures *Ind. Eng. Chem. Res.* **2007,** *46,* 5478-5484. (e) Davis, R. E.; Gottbrath, J. A. Boron Hydrides. V. Methanolysis of Sodium Borohydride *J. Am. Chem. Soc.* **1962**, *84*, 895-898.

(30) Jin, L.; Liang, X.; Wang, J.; Zhan, Z.; Guan, L.; Li, X.; Chen, Y.; Luo, J.; Wang, X.; Wang, Z. Insecticidal composition containing insect pheromone, thiacloprid and novaluron, and application thereof. CN107668061A, **2018**.

(31) (a) Clapham, S. E.; Hadzovic, A.; Morris, R. H., Mechanisms of the H_2-hydrogenation and transfer hydrogenation of polar bonds catalyzed by ruthenium hydride complexes. *Coord. Chem. Rev.* **2004**, *248*, 2201-

2237. (b) Smith, N. E.; Bernskoetter, W. H.; Hazari, N., The Role of Proton Shuttles in the Reversible Activation of Hydrogen via Metal-Ligand Cooperation. *J. Am. Chem. Soc.* **2019**, *141*, 17350-17360.

(32) (a) Parr, R. G.;Yang, W. Density Functional Theory of Atoms and Molecules; Oxford University Press: New York, **1989**. (b) Calculations performed at the PBE0/(SDD,6-31G**) level using the GAUSSIAN 09 package. Solvent effects (MeOH) were considered using the PCM/SMD model. A full account of the computational details and a complete list of references are provided as SI.