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Highly Chemo- and Stereoselective Transfer Semihydrogenation of Alkynes Catalyzed by a Stable, Well-defined Manganese(II) Complex

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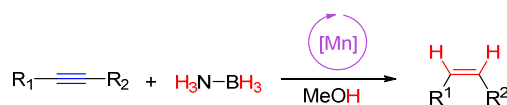
ABSTRACT: Herein we report a manganese catalyzed semihydrogenation of internal alkynes to (*Z*)-alkenes using ammonia borane as a hydrogen donor. The reaction is catalyzed by a pincer complex of the earth abundant manganese(II) salt in the absence of any additives, base or super hydride. The ammonia borane smoothly reduces the manganese pre-catalyst [Mn(II)-PNP][Cl]₂ to the catalytically active species [Mn(I)-PNP]-hydride in the triplet spin state. This manganese hydride is highly stabilized by complexation with the alkyne substrate. Computational DFT analysis studies of the reaction mechanism rationalize the origin of stereoselectivity towards formation of (*Z*)-alkenes.

INTRODUCTION

Stereo-defined alkenes are amongst the most important organic compounds, ubiquitous in chemical, material and pharmaceutical industries.¹ Semihydrogenation of alkynes to alkenes is a very important reaction in organic synthesis.² Until today, triple bond semireduction relies mainly on the use of precious metal catalysis. Among the known heterogeneous catalysts, the palladium based Lindlar catalyst is the most prominent one.³ However, the necessity to use toxic lead salts as additive and the product isomerization under the reaction conditions are the major drawbacks of this method. Besides, various modern heterogeneous catalysts,⁴ homogenous counterparts, such as the Rh-based Wilkinson's and Schrock-Osborn catalyst,⁵ palladium,⁶ ruthenium,⁷ and iridium⁸ catalysts have been intensively investigated for this reaction.

Economic and environmental aspects persuade chemists to replace toxic noble metal catalysts by first row base metal alternatives. In this regard, few homogenous catalytic systems have been reported so far. In 2013, Milstein has reported the use of acridine-based PNP iron catalyst for the (*Z*)-selective semihydrogenation of alkynes followed by rapid isomerization to (*E*)-alkenes under pressurized dihydrogen.⁹ More recently, processes relying on the use of nickel,¹⁰ cobalt¹¹ and copper¹² based catalysts have been disclosed. Nonetheless, these protocols may suffer from the use of high catalyst loading, limited substrate scope, and low levels of chemoselectivity or over-reduction. Despite these advances, new efficient catalytic systems based on earth-abundant metal catalysts would be highly desirable.

During the past months, manganese catalyzed hydrogenation reactions have emerged. However, so far these are limited to the hydrogenation of C=O and C≡N bonds.¹³ To the best of our knowledge, a well-defined manganese complex catalyzing the (transfer) hydrogenation of unsaturated hydrocarbons has never been reported. Therefore, it was not surprising that our initial attempts to employ these complexes in semihydrogenation of alkynes were also unsuccessful.



Scheme 1. Manganese Catalyzed Transfer Semi-Hydrogenation of Alkynes.

The mechanism of the metal hydride catalyzed (*Z*)-selective semireduction of alkynes typically takes place *via* hydrometallation followed by reductive elimination steps, which requires a vacant coordination site on the metal center. However, the recently reported manganese hydrogenation catalysts are hexa-coordinated pincer-Mn(I) complexes. Thus, in order to design a proper catalyst for this transformation, our attention was directed to the use of the five-coordinate manganese(II) dichloride which after activation might be converted to tetra-coordinate manganese(I) hydride. In contrast to the well-established iron(II) and cobalt(II) hydrogenation catalysts, manganese(II) dichloride has been reported to be inactive for the hydrogenation of carbonyl compounds. This might be

attributed to the low stability of the formed Mn(I) hydride in the absence of carbonyl ligands.^{13a,13b}

Ammonia borane (AB) is a low molecular weight (30.87 g mol⁻¹), bench-stable, inexpensive solid bearing both protic N-H and hydric B-H bonds. The good hydrogen capacity (16.9 % wt.) and possibility of recycling its dehydrogenated products has inspired intensive studies towards the use of ammonia borane as H₂ storage molecule. However, reports pertaining to the use of ammonia borane as a chemical reagent and in particular as hydrogen donor are scarce.¹⁴ We report herein the first example of manganese catalyzed transfer hydrogenation of unsaturated carbon-carbon bonds using ammonia borane as an environmentally benign hydrogen donor (Scheme 1).

RESULTS AND DISCUSSION

We started our study with the synthesis of several PNP and NNN manganese pincer complexes (**Mn-1-Mn-4**, Figure 1). These five-coordinated Mn-complexes could be easily prepared by the reaction of the anhydrous manganese dichloride with 1.2 equivalent of the corresponding ligand in THF at room temperature. The synthesis and the characterization of the complexes **Mn-1** and **Mn-2** were recently reported by Beller^{13a} and Kempe,^{13b} respectively. However, these complexes were inactive hydrogenation catalysts. **Mn-3** was prepared from literature report.¹⁵ Furthermore, we have synthesized a new pyridine-based manganese complex **Mn-4** in 80% yield. The crystal structure analysis of **Mn-4** showed that the coordination geometry of the manganese center is distorted square pyramidal (Figure 1).

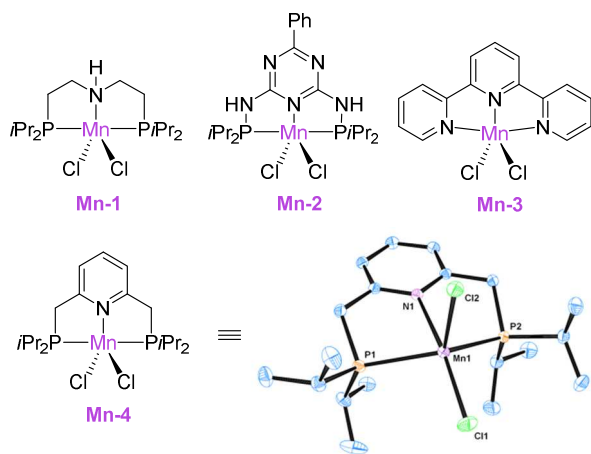


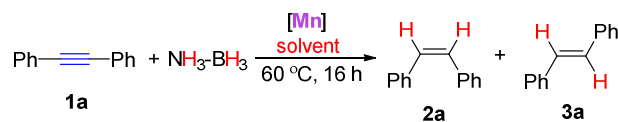
Figure 1. Manganese complexes tested in this study and X-ray crystal structure analysis of **Mn-4** (hydrogen atoms omitted for clarity).

Next, we investigated the catalytic activity of the manganese complexes **Mn-1-Mn-4** in the hydrogenation of diphenylacetylene as a model substrate. Methanol was used as a solvent and ammonia borane as both, the potential catalyst activator and hydrogen donor. The NH-based PNP manganese complex **Mn-1** provided only low conversion (27%) with 84:16 *E/Z* ratio (Table 1, entry 1). Higher

yield (69%) and a slightly higher *Z/E* ratio (88:12) was observed by the application of triazine-based PNP-manganese complex **Mn-2** (Table 1, entry 2). Subsequently, we tested the catalytic performance of the readily available terpyridine-Mn(II) complex **Mn-3**, however, only moderate results were obtained (Table 1, entry 3). To our delight, the newly synthesized pyridyl-based PNP complex **Mn-4** showed full conversion and very good selectivity (97:3, Table 1, entry 4). The use of MnCl₂ as a catalyst afforded low conversion and selectivity (Table 1, entry 5), highlighting the crucial role of the ligand.

Next, different solvents were tested. Replacing MeOH by EtOH resulted in the same conversion but lower *Z/E* ratio (Table 1, entry 6). The promising results in methanol and ethanol have encouraged us to investigate more alcohols such as *i*PrOH and more acidic fluorinated solvents: trifluoroethanol (TFE) and hexafluoroisopropanol (HFIP). However, these alcohols proved to be unsuitable for this reaction (Table 1, entries 7-9). Interestingly, running the reaction in THF or dioxane afforded moderate results (Table 1, entries 10-11). Furthermore, reactions performed in DMF or NMP led to very low conversions, probably due to the strong coordination of these solvents with the catalyst (Table 1, entries 12-13).

Table 1. Optimization of the Reaction Conditions.^a



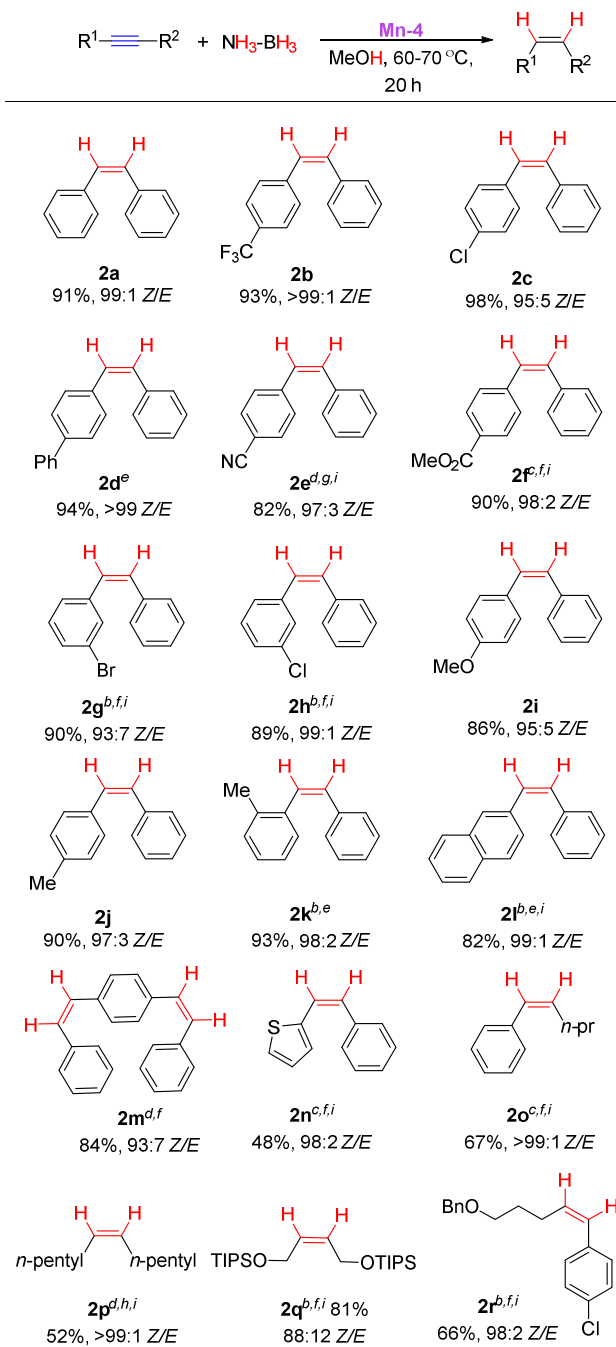
entry	[Mn] (mol %)	solvent	conv.(%)	2a:3a ^c
1	Mn-1 (2)	MeOH	27	84:16
2	Mn-2 (2)	MeOH	69	88:12
3	Mn-3 (2)	MeOH	62	79:21
4	Mn-4 (2)	MeOH	>99	97:03
5	MnCl ₂ (2)	MeOH	29	78:22
6	Mn-4 (2)	EtOH	99	85:15
7	Mn-4 (2)	<i>i</i> PrOH	41	95:05
8	Mn-4 (2)	HFIP	06	ND
9	Mn-4 (2)	TFE	08	ND
10	Mn-4 (2)	THF	87	72:28
11	Mn-4 (2)	Dioxane	63	79:21
12	Mn-4 (2)	DMF	14	80:20
13	Mn-4 (2)	NMP	21	83:17
14	Mn-4 (2)	toluene	14	83:17
15	Mn-4 (2)	hexane	<5	ND
16 ^b	Mn-4 (2)	MeOH	<5	ND
17 ^c	Mn-4 (2)	MeOH	<5	ND
18	Mn-4 (1)	MeOH	>99	99:01
19	Mn-4 (0.5)	MeOH	76	95:05

^aReaction conditions: **1** (0.25 mmol), AB (0.25 mmol), **Mn** catalyst in 1 mL of solvent at 60 °C for 16 h. Conversion was determined by ¹H NMR using mesitylene as the internal standard. *Z/E* ratio was determined by GC analysis. ^bAB (0.025 mmol), HCOOH (0.5 mmol). ^cAB (0.025 mmol), H₂ (10 bar).

The solvent screening shows that the non-polar solvents; hexane and toluene failed to give the desired product (Table 1, entries 14-15). Moreover, in order to exclude molecular hydrogen as a reactant in described process, the reaction was examined under hydrogen atmosphere (10 bar) in the presence of catalytic amounts of AB. Importantly, only traces of the desired product were detected (Table 1, entry 16). This result suggests that the reaction takes place *via* direct transfer hydrogenation and not *via* AB solvolysis followed by hydrogenation. Also, formic acid has demonstrated to be unsuitable hydrogen donor in this process (Table 1, entry 17).

Following these results, we turned our attention to screening of the reaction conditions with the respect to the catalyst loading (**Mn-4**). Pleasingly, the reaction still proceeded well with a catalyst loading as low as 1 mol % (Table 1, entry 18). Subsequent reduction of the catalyst to 0.5 mol % resulted in lower conversion of 76% after 16 h (Table 1, entry 19).

Table 2. Mn-Catalyzed (Z)-selective Transfer Hydrogenation of Alkynes.^a



^aReaction conditions: **1** (0.5 mmol), AB (0.5 mmol), **Mn-4** (1 mol%) in 2 mL of methanol at 60 °C for 20 h, yields after column chromatography, *E/Z* ratio is determined by GC analysis of the crude reaction mixture; ^b**Mn-4** (2 mol%); ^c**Mn-4** (3 mol%); ^d**Mn-4** (4 mol%); ^eAB (0.75 mmol); ^fAB (1 mmol); ^gAB (1.5 mmol); ^hAB (2 mmol); ⁱ70 °C.

In order to demonstrate the applicability of our manganese catalyst system, we tested the transfer hydrogenation of various internal alkyne substrates bearing different electronic and steric properties (Table 2). Generally, all investigated aromatic substrates with electron-withdrawing groups and electron-donating groups were converted into the corresponding (*Z*)-alkenes with very good yields and excellent (*Z*):(*E*) selectivity **1a-m**. Interestingly, sensitive functional groups such as nitrile, ester and heterocycles were well tolerated under the mild reac-

tion conditions. The semi-transfer hydrogenation could also be applied to the mono- and dialkylacetylene **10** and **1p** after using more catalyst loading and ammonia borane. The protected allyl alcohol **2q** could be obtained in 81% yield and good selectivity. Finally, the pentynol-derived alkyne **1r** could be selectively semihydrogenated in good yield (66%).

Apart from the synthetic value of the conversion of alkynes to alkenes, we decided to investigate the application of the newly developed catalytic system in the purification of alkenes from alkyne impurities, which is a highly important industrial process to valorize the steam cracking bulk feedstocks.⁴⁸ To demonstrate the process feasibility, we hydrogenated diphenylacetylene in the presence of large excess of (*Z*)-stilbene. To our delight, 0.03 mmol of diphenylacetylene could be hydrogenated in the presence 100 equivalent of (*Z*)-stilbene using only 0.0003 mmol of the **Mn-4**. Importantly, (*Z*)-alkenes were obtained with 99% purity with only traces of the isomerized (*E*)-alkene **3a** and no over-hydrogenation product was detected (Scheme 2).

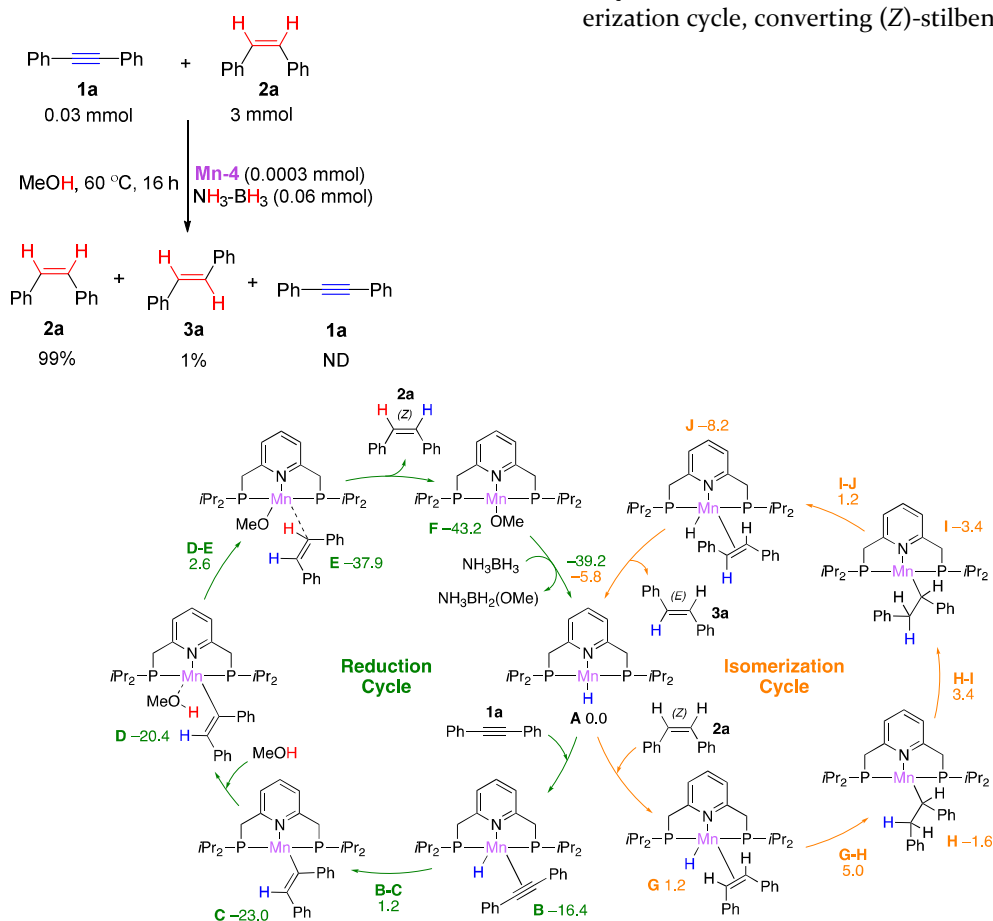


Figure 2. Proposed reaction mechanism for manganese catalyzed semi-transfer hydrogenation of diphenylacetylene (**1a**) into (*Z*)-stilbene (**2a**) (reduction cycle) and internal conversion of (*Z*)-stilbene (**2a**) into (*E*)-stilbene (**3a**), (isomerization cycle). Calculated Gibbs free reaction and activation energies, at 50 °C, are shown in kcal mol⁻¹ at PBE0+D3/TZVP computational level in methanol as solvent.

Calculations indicate that the reaction occurs through a triplet state spin route (Table S1). For example, in the case of the catalytic species **A** the triplet spin state is more

Scheme 2. Showcase of Manganese Catalyzed Purification of *cis*-Alkenes without Isomerization.

With this background knowledge we studied the reaction mechanism for diphenylacetylene reduction into stilbene through DFT modeling (Figure 2).¹⁷ Gibbs free reaction and activation energies were calculated at 50 °C in methanol as a solvent. The pre-catalyst we considered is **Mn-4**, which we suggest can be reduced into the active catalytic [Mn(I)-PNP]-hydride species (**A**, at Figure 2) by NH_3BH_3 . This hypothesis is based on the consideration that thermogravimetric analysis and differential scanning calorimetric studies proved that CoCl_2 to be reduced into cobalt(I) by induction of NH_3BH_3 decomposition. These findings served as the basis for demonstrating the reducing power of NH_3BH_3 towards other compounds such as FeCl_3 and AlCl_3 species.¹⁶ Starting from the proposed active species **A**, two catalytic cycles working simultaneously can be proposed to explain the product distribution. One is the alkyne reduction cycle, converting diphenylacetylene into (*Z*)-stilbene, the second is the alkene isomerization cycle, converting (*Z*)-stilbene into (*E*)-stilbene.

stable than the singlet spin state by 27.5 and 32.4 kcal mol⁻¹ at the PBE/SVP and PBE0+D3(BJ)/TZVP//PVE/SVP levels of theory in methanol. These values are consistent

with the value of 33.5 kcal mol⁻¹ calculated at the OPBE/SVP level in gas phase.¹⁸

The alkyne reduction cycle, converting diphenylacetylene into (*Z*)-stilbene, starts with coordination of diphenylacetylene to the [Mn(I)-PNP]-hydride catalyst **A**, spontaneously forming the stable complex **B**, with a binding Gibbs free energy at 50 °C of -16.4 kcal mol⁻¹ in methanol. The overall structure of **B** (see Figure S2) has a strong metallacycloolefin character, as the C-C-Ph angles are severely bent from 180° in the isolated substrate, to assume an average value of 143°. The C-C bond, 1.34 Å, is close to the value of 1.36 Å as in the isolated (*Z*)-stilbene, compared to 1.23 Å in the isolated diphenylacetylene.

This first hydrogenation of the substrate, leading to intermediate **C**, exhibits a Gibbs free activation energy of 17.6 kcal mol⁻¹ via transition state **B-C**. Intermediate **C** presents a *cis* disposition of the Ph substituents on the formed C=C double bond. The overall skeleton of the reacting carbonaceous moiety is perpendicular to the PNP plane, see Figure 3. The formed Mn-C bond is nearly collinear with the Mn-N bond, with a Mn-N-C angle of 161°, and the large distance between Mn and the transferred H atom, 3.17 Å, indicates no agostic interaction.

The next step corresponds to MeOH interaction with the Mn center, leading to intermediate **D**, with a free energy increasing in 2.6 kcal mol⁻¹. The long distance between the Mn and the O atom of MeOH, 3.60 Å, suggests this interaction being dominated by dispersion forces. Indeed, the enthalpy of association (between MeOH and **C** to reach **D**) at the PBE0+D3(BJ)/TZVP//PVE/SVP level amounts to -6.6 kcal mol⁻¹, while at the PBE0+D3/TZVP level, which is after addition of empirical dispersion term, it amounts to -11.1 kcal mol⁻¹. Proton transfer from MeOH to the substrate occurs via transition state **D-E**, indicated to be the rate-limiting step with a relative activation Gibbs free energy of 25.6 kcal mol⁻¹ (energy span from **C** to **D-E**). Once (*Z*)-stilbene is released in a spontaneous process, the formed [Mn]-OMe intermediate **F** reacts with NH₃BH₃ to regenerate the starting [Mn(I)-PNP]-hydride catalytic species **A**.

A key feature of the above reaction pathway is that the initial hydrogen transfer to diphenylacetylene, step **B** to **C**, occurs with formation of a Mn-vinyl bond presenting a *cis* disposition of the Ph substituents. Since no free rotation around the C=C double bond of the substrate is possible, stereoselectivity towards the (*Z*)-alkene is imposed. Our attempts to locate an alternative transition state in which proton transfer from an external MeOH to diphenylacetylene occurs first followed by the hydride transfer from the Mn-H moiety failed.

Furthermore, the potential role of NH₃BH₃ as proton donor instead of MeOH during the **D** to **E** step has been also investigated. The large activation Gibbs free energy of 37.1 kcal mol⁻¹ (relative to **C**) clearly rules out this route in presence of MeOH (Figure S3). Finally, we also analyzed both the reduction and isomerization cycles in THF, where NH₃BH₃ is the sole source of proton (see Figure

S4). Proton transfer from NH₃BH₃ to the substrate via transition state **D'-E'**, with a Gibbs free energy of activation of 35.5 kcal mol⁻¹ is again of high energy, which depresses reactivity. These results are in agreement with experimental solvent screening experiments in Table 1.

The formation of (*E*)-stilbene may also be explained via the alkene isomerization cycle shown in Figure 2. Within this cycle the catalytic species **A** interacts with (*Z*)-stilbene leading to complex **G**. This is a slightly endergonic step, with a binding Gibbs free energy of 1.2 kcal mol⁻¹, which contrasts with the large binding energy of diphenylacetylene to **A** (-16.4 kcal mol⁻¹). Hydride transfer from Mn(I) of **G** to the closest C atom of stilbene leads to intermediate **H**. This hydrogenation transfer exhibits a low relative activation barrier of 5.0 kcal mol⁻¹ and leads to a *sp*³ hybridization of the C atom of stilbene, which indeed allows easy rotation around the C-C bond, step **H** to **I** (the relative rotational activation barrier is calculated to be 5.0 kcal mol⁻¹). β-H transfer to the Mn atom from **I** via transition state **I-J** with Gibbs free energy barrier of 4.6 kcal mol⁻¹ leads to (*E*)-stilbene, intermediate **J**. Finally, dissociation of (*E*)-stilbene from the metal regenerates the catalytic species **A**.

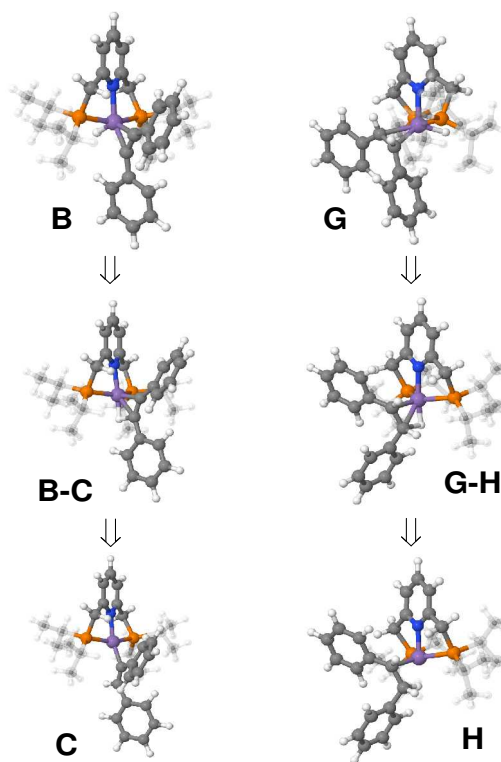


Figure 3. Minima and transition states for the hydride transfer steps in the reduction (**B** to **C**) and isomerization (**G** to **H**) cycles. (For clarity, *i*Pr₂ groups are in soft color).

Comparison between the reduction and the isomerization cycles shows that coordination of diphenylacetylene to the catalytic species **A** is favored by 17.6 kcal mol⁻¹ over (*Z*)-stilbene coordination (-16.4 vs. 1.2 kcal mol⁻¹). Steric

effects play a minor role in determining this large difference in the binding energies, as a similarly large difference, 14.0 kcal mol⁻¹, is calculated for coordination of diphenylacetylene and (*Z*)-stilbene to a model system where the *i*Pr substituents on the P atoms of PNP ligands are replaced by smaller methyl groups, -17.3 and -3.3 kcal mol⁻¹, respectively. Further, coordination of the simplest alkyne (acetylene) and alkene (ethylene) to this model system with methyl substituents on the P atoms, displays again a large difference in the binding Gibbs free energies, -18.3 and -7.8 kcal mol⁻¹, confirming that preferential alkyne coordination over alkene coordination is dominated by electronic effects.

Considering that the substrate coordinated intermediates **B** and **G** are connected by intermediate **A**, the Curtin-Hammett principle can be used to relate the faster kinetics of the alkyne reduction cycle to the energy difference between the highest lying transition states along the two cycles, which is transition states **D-E** and **G-H**. Consistently with the experimental evidence, the former, along the alkyne reduction cycle, is favored by 2.4 kcal mol⁻¹ over the latter, taking place along the alkene isomerization cycle.

Conclusions

A new manganese catalyzed hydrogenation of unsaturated hydrocarbons is reported herein.¹⁹ Notably, the newly developed catalytic system is based on an earth-abundant metal which is shown to be highly active for semi transfer hydrogenation of internal alkynes under base and super hydride free conditions. Ammonia borane was used as both, potential hydrogen donor and catalyst activator. Under mild conditions a broad scope of internal alkynes bearing different functional groups are converted to (*Z*)-alkenes in up to 98% yield and >99:1 (*Z*):(*E*) selectivity. Importantly, this base-metal catalyst allows for the purification of alkenes from alkyne impurities without alkene isomerization. The ammonia borane smoothly reduces the manganese pre-catalyst [Mn(II)-PNP][Cl]₂ to the active catalytic species [Mn(I)-PNP]-hydride in the triplet spin state which is highly stabilized by the complexation with the alkyne substrate. DFT calculations indicate that two catalytic cycles, one for hydrogenation of diphenylacetylene to (*Z*)-stilbene (the reduction cycle), the other for isomerization of (*Z*) to (*E*)-stilbene (the isomerization cycle), are in competition. The strong thermodynamics control imposed during the early catalyst-substrate coordination steps explains the selectivity showed by the [Mn(I)-PNP]-hydride species for the preferred reduction of diphenylacetylene into (*Z*)-stilbene over the (*E*) isomer.

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Notes

The authors declare no competing financial interest

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.XXXXXXX.

Experimental and DFT details (PDF)
 Crystallographic data (CIF)
 Optimized geometries (XYZ)

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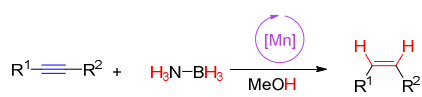
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- A new base metal catalyst
- (Z)-selectivity up to >99:1
- very high functional group tolerance
- Base and super hydride free reaction

