

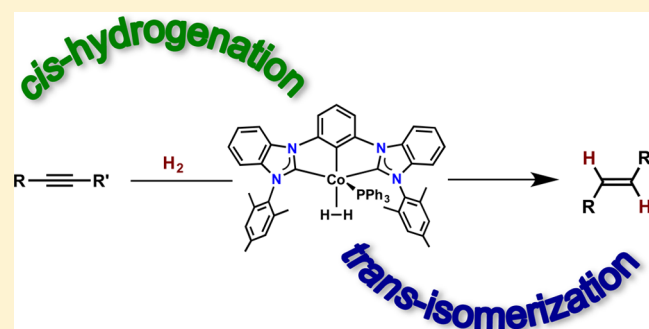
Alkyne Semihydrogenation with a Well-Defined Nonclassical Co–H<sub>2</sub> Catalyst: A H<sub>2</sub> Spin on Isomerization and *E*-Selectivity

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## S Supporting Information

**ABSTRACT:** The reactivity of a Co<sup>I</sup>–H<sub>2</sub> complex was extended toward the semihydrogenation of internal alkynes. Under ambient temperatures and moderate pressures of H<sub>2</sub>, a broad scope of alkynes were semihydrogenated using a Co<sup>I</sup>–N<sub>2</sub> precatalyst, resulting in the formation of *trans*-alkene products. Furthermore, mechanistic studies using <sup>1</sup>H, <sup>2</sup>H, and *para*-hydrogen induced polarization (PHIP) transfer NMR spectroscopy revealed *cis*-hydrogenation of the alkyne occurs first. The Co-mediated alkene isomerization afforded the *E*-selective products from a broad group of alkynes with good yields and *E*/*Z* selectivity.



## INTRODUCTION

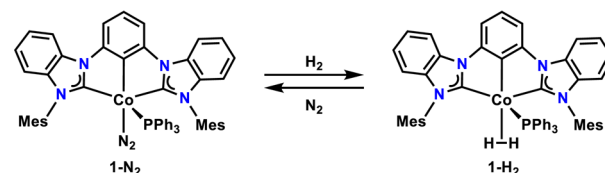
The semihydrogenation of alkynes to alkenes is a noteworthy transformation in the bulk and fine chemical industries.<sup>1</sup> Heterogeneous systems such as Lindlar's catalyst, Pb-poisoned Pd on CaCO<sub>3</sub>,<sup>2</sup> are commonly utilized to accomplish this transformation, yielding the corresponding *Z*-alkene. Homogeneous counterparts such as Wilkinson's catalyst<sup>3</sup> and the widely utilized cationic Schrock–Osborn rhodium system<sup>4,5</sup> are also capable of the semihydrogenation of alkynes to *Z*-alkenes. However, the stereocomplementary formation of *E*-alkenes by means of hydrogenation is much more difficult. This is, in part, due to the nature of H<sub>2</sub> addition, favoring one side of the substrate and thereby adding in a *cis*-manner. Birch-type reductions, which dissolve metals in ammonia, circumvent this challenge by providing good *E*-selectivity; however, the conditions employed for this transformation are incompatible with highly functionalized alkynes. Increased functional group tolerance has been achieved with the use of chromium reagents,<sup>6,7</sup> and more recently, transition-metal systems featuring Ir,<sup>8</sup> Ru,<sup>9</sup> Pd,<sup>10,11</sup> and Co;<sup>12</sup> however, these processes are accompanied by stoichiometric amounts of waste.

Recently, Fürstner<sup>13,14</sup> and Bargon<sup>15</sup> reported *trans*-selective cationic Ru alkyne hydrogenation catalysts, through which direct *trans*-hydrogenation was operative. More commonly, *E*-selectivity is achieved by means of *Z* to *E* isomerization under the catalytic conditions employed. For example, Furukawa and Komatsu<sup>16</sup> have reported a tandem heterogeneous catalytic system consisting of Pd<sub>3</sub>Pb/SiO<sub>2</sub> for alkyne semihydrogenation and RhSb/SiO<sub>2</sub> for *trans*-isomerization yielding *E*-selective products in good yields; however, environmental concerns arise with the use of lead. A heterobimetallic silver–ruthenium system<sup>17</sup> and an iron pincer catalyst<sup>18</sup> have also been reported for the semihydrogenation of alkynes, with the *Z* to *E*

isomerization occurring at elevated temperatures (≥90 °C). The use of atom-economical reagents,<sup>19,20</sup> as well as the reclusion of noble-metal complexes, are important considerations in developing environmentally benign catalytic systems.<sup>21,22</sup>

Our interest in hydrogenation began with the discovery of a catalytically active cobalt dihydrogen complex (<sup>Mes</sup>CCC)Co–(H<sub>2</sub>)(PPh<sub>3</sub>), **1-H<sub>2</sub>**, (<sup>Mes</sup>CCC = bis(mesityl-benzimidazol-2-ylidene)phenyl), that was generated from the addition of H<sub>2</sub> to the (<sup>Mes</sup>CCC)Co(N<sub>2</sub>)(PPh<sub>3</sub>) complex, **1-N<sub>2</sub>** (Scheme 1).<sup>23</sup>

Scheme 1. Synthesis of Co–(H<sub>2</sub>), **1-H<sub>2</sub>**, from Co–(N<sub>2</sub>), **1-N<sub>2</sub>**



In our studies, we demonstrated that **1-H<sub>2</sub>** was selective toward the hydrogenation of terminal olefins under ambient conditions, while the hydrogenation of internal olefins proceeded at higher temperatures. With the use of <sup>1</sup>H, <sup>2</sup>H and *para*-hydrogen (*p*-H<sub>2</sub>) induced polarization (PHIP) transfer NMR spectroscopy, we identified catalytically relevant intermediates and established the role of **1-H<sub>2</sub>** in a Co<sup>I</sup>/Co<sup>III</sup> redox process. Interested in further exploring the catalytic reactivity of our complexes using H<sub>2</sub> and informed by the mechanistic insights gleaned from the alkene hydrogenation, we

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Table 1. Control Experiments and Optimization of the Semihydrogenation of Diphenylacetylene

entry	catalyst	mol %	solvent	temp	alkene (conversion) <sup>b</sup>	E/Z
1	1-N <sub>2</sub>	2	THF	30 °C	80% <sup>a</sup>	>99
2	1-N <sub>2</sub>	1	THF	30 °C	82% <sup>a</sup>	>99
3	1-N <sub>2</sub>	1	C <sub>6</sub> H <sub>6</sub>	30 °C	82% <sup>a</sup>	>99
4	1-N <sub>2</sub>	2	THF	40 °C	70% <sup>a</sup>	>99
5	1-N <sub>2</sub>	2	THF	50 °C	60% <sup>a</sup>	>99
6 <sup>c</sup>	1-N <sub>2</sub>	1	THF	30 °C	82% <sup>a</sup>	>99
7	[H <sub>3</sub> ( <sup>Mes</sup> CCC)]Cl <sub>2</sub>	2	THF	30 °C	0%	N/A
8	( <sup>Mes</sup> CCC)CoCl <sub>2</sub> py	2	THF	30 °C	0%	N/A
9	1-N <sub>2</sub> + PPh <sub>3</sub> (1 equiv)	2	THF	30 °C	40%	<1
10	1-N <sub>2</sub> + PPh <sub>3</sub> (10 equiv)	2	THF	30 °C	0%	N/A
11	1-N <sub>2</sub> + Hg	2	THF	30 °C	82% <sup>a</sup>	>99

<sup>a</sup>Remainder was alkane. <sup>b</sup>Measured by GC-MS. <sup>c</sup>1 atm of H<sub>2</sub>.

Table 2. Substrate Scope

<p><b>2a</b> 1 mol % 79% (82%), E:Z &gt; 99</p>	<p><b>2b</b> 2 mol % 90% (96%), E:Z &gt; 99</p>	<p><b>2c</b> 2 mol % 73% (75%), E:Z &gt; 99</p>	<p><b>2d</b> 2 mol % 69% (&gt;99%), E:Z &gt; 81:19</p>	<p><b>2e</b> 3 mol % 86% (89%), E:Z &gt; 99</p>
<p><b>2f</b> 2 mol % 59% (89%), E:Z 99:1</p>	<p><b>2g</b> 2 mol % 86% (97%), E:Z &gt; 99</p>	<p><b>2h</b> 3 mol % 77% (85%), E:Z &gt; 99</p>	<p><b>2i</b> 3 mol % 68% (70%), E:Z &gt; 99</p>	<p><b>2j<sup>a</sup></b> 5 mol % 96% (97%), E:Z 99:1</p>
<p><b>2k</b> 3 mol % 80% (96%), E:Z 90:10</p>	<p><b>2l</b> 2 mol % 68% (78%), E:Z &gt; 99</p>	<p><b>2m</b> 2 mol % 64% (87%), E:Z &gt; 99</p>	<p><b>2n</b> 2 mol % 83% (92%), E:Z &gt; 99</p>	<p><b>2o</b> 2 mol % 66% (95%), E,E:Z,Z &gt; 99</p>

<sup>a</sup>Heated to 90 °C with 1 atm of H<sub>2</sub>.

turned our attention to the semihydrogenation of alkynes. We hypothesized that the catalytic hydrogenation of internal alkynes using 1-N<sub>2</sub> and H<sub>2</sub> would result in the formation of internal olefins; if this reaction could proceed at low temperatures then further reduction of the olefin by our catalyst would be limited.

Herein we report the catalytic utility of 1-N<sub>2</sub> toward the *E*-selective semihydrogenation of internal alkynes using H<sub>2</sub> under mild conditions. A detailed mechanistic understanding, informed by multinuclear and PHIP transfer NMR studies of

this process, has elucidated that a *cis*-hydrogenation and *trans*-isomerization mechanism is operative.

## RESULTS AND DISCUSSION

**Optimization of Reaction Conditions.** Our initial experiments focused on investigating reaction conditions (catalyst loading, temperature, and solvent), as well as conducting appropriate control experiments, utilizing diphenylacetylene as a model substrate (Table 1). The use of 1-N<sub>2</sub> (2 mol %) in THF at 30 °C and 4 atm of H<sub>2</sub> resulted in 80% conversion to the alkene with a high *E/Z* ratio (Table 1, entry

1). Lowering the catalyst loading to 1% resulted in increased conversion to the alkene (entry 2) and changing the solvent to benzene did not affect the outcome of the reaction (entry 3). Furthermore, increasing the temperature in increments of 10 °C only resulted in higher amounts of the overhydrogenated alkane product, while the *E/Z* ratio of the alkene product remained the same (entries 4 and 5). Lowering the pressure of H<sub>2</sub> to 1 atm did not change the yield of the reaction (entry 6). In addition, the use of the ligand (entry 7) or catalyst precursors (entry 8) resulted in no product formation and only starting material was recovered.

To understand the role of phosphine in the catalytic sequence, the equivalents of PPh<sub>3</sub> were varied (entries 9 and 10). Unsurprisingly, increasing the amounts of PPh<sub>3</sub> did result in lower to no conversion of the alkyne to product likely due to competitive binding of the phosphine and the alkyne to the catalyst. Furthermore, to confirm that this reaction is homogeneous,<sup>24</sup> one drop of mercury was added under catalytic conditions, and no change in product outcome was observed (entry 11).

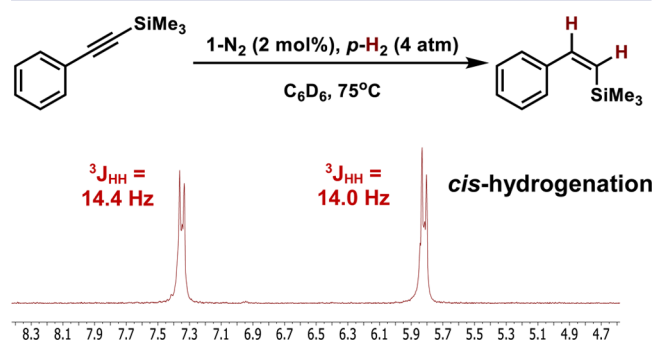
**Substrate Scope.** Encouraged by our preliminary studies and utilizing the optimized reaction conditions (THF as the solvent at 30 °C with 4 atm of H<sub>2</sub>), we sought to investigate the utility of 1-N<sub>2</sub> toward the semihydrogenation of an assortment of substrates bearing a variety of functional groups (Table 2). *Para*-substituted diphenylacetylenes featuring electron-donating and -withdrawing groups (2b and 2c, respectively) proceeded with excellent *E/Z* ratios and good yields. Additionally, an unsymmetric *para*-substituted diphenylacetylene featuring a boronate ester and methoxy group (2e) was tolerated under these conditions, proceeding with good yields and *E/Z* selectivity. Dialkyl-substituted acetylene (2d) resulted in the full conversion to the alkene products with lower selectivity for the *E* isomer; the over-reduced alkane byproducts, however, were not detected by GC-MS.

We next explored the catalytic activity of 1-N<sub>2</sub> toward the reduction of terminal alkynes. The attempted hydrogenation of phenylacetylene resulted in catalyst decomposition, and no hydrogenation of the product was observed. Upon employing a protecting group (trimethylsilyl, TMS), 2f, the reaction proceeded with good *E/Z* selectivity and the silyl group remained intact under these conditions, whereas acidic conditions employed in a Pd-catalyzed alkyne reduction<sup>11</sup> resulted in cleavage of the TMS group. We were able to further extend our system to include methyl, methoxy, and bromo *ortho*-substituted derivatives (2g–2i) of 2f. Interestingly, a derivative featuring an amine group did not proceed well (<1% conversion) under these conditions, likely as a result of binding of the amine to the metal center. A modification of the reaction conditions by increasing the temperature to 90 °C and lowering the H<sub>2</sub> pressure (1 atm) of the reaction successfully obviated this difficulty, resulting in reduction of the substrate, 2j, to the *E* product in high yields. Similarly, a substrate bearing a hydroxyl functionality is tolerated, but proceeded with lower *E/Z* selectivity (2k) under standard reaction conditions. Furthermore, substrates featuring furanyl, thienyl, and imidazolyl groups (2l–2n) exhibited good yields and excellent *E/Z* selectivity under regular reaction conditions. Lastly, we examined the semihydrogenation of a substrate bearing two internal alkynes. Under optimized catalytic conditions, the reduction of 2o resulted in excellent *E/Z* selectivity of both C=C bonds in good yield.

These results clearly show the general applicability of this approach toward the semihydrogenation of a variety of alkynes using H<sub>2</sub> and 1-N<sub>2</sub> under ambient conditions. The retention of excellent *E/Z* selectivity and yield upon a half-gram scale for the semihydrogenation of diphenylacetylene demonstrates the potential of this system in organic synthesis (see SI). However, in some cases less than ideal *E/Z* selectivity and over-reduction of the alkenes were also observed. In an effort to envision the full potential of this system, we sought to elucidate the mechanism of this process in detail, as such studies would promote further progress in limiting over-reduction to alkanes and increasing *E*-selectivity.

**Mechanistic Studies.** Fürstner and co-workers<sup>13</sup> reported a ruthenium system that was competent toward the semihydrogenation of alkynes to *E*-alkenes. A follow-up NMR study employing PHIP transfer, supplemented by computational work<sup>25</sup> and earlier studies of ionic ruthenium platforms by Bargon and co-workers,<sup>15</sup> provided clear evidence of direct *trans*-hydrogenation of alkynes. Accordingly, in an effort to gain insight into the observed semihydrogenation activity of 1-N<sub>2</sub> with H<sub>2</sub>, we turned to multinuclear and PHIP transfer NMR studies. PHIP transfer NMR spectroscopy allows for the possibility of detecting reaction intermediates *in situ* that would otherwise prove elusive with conventional characterization methods.<sup>26–28</sup> This hyperpolarization technique has the possibility of enhancing relevant signals from incoming *p*-H<sub>2</sub> molecules by the inverse order of magnitude over the NMR-governed Boltzmann distribution (10<sup>–5</sup>). However, this effect only occurs if the H atoms of the *p*-H<sub>2</sub> molecule are transferred in a pairwise manner to magnetically distinctive positions on a target compound while remaining magnetically coupled. In the PHIP NMR studies we report, a 45° pulse and a double quantum OPSY (Only Parahydrogen Spectroscopy) filter in the <sup>1</sup>H NMR experiment were employed following introduction of *p*-H<sub>2</sub> at low field (under ALTADENA conditions,<sup>28</sup> see SI).

We first investigated H<sub>2</sub> addition with a set of representative alkynes (2e, 2f, 2h, 2i, and 2l). The addition of *p*-H<sub>2</sub> (4 atm) to a benzene-*d*<sub>6</sub> solution containing 1-N<sub>2</sub> (2 mol %) and 2f (Figures 1 and S10), 2e, 2h, 2i, or 2l (Figures S8–S12) at 30



**Figure 1.** <sup>1</sup>H-OPSY NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz) spectrum of 1-N<sub>2</sub> (2 mol %) and 2f under 4 atm of *p*-H<sub>2</sub> at 75 °C.

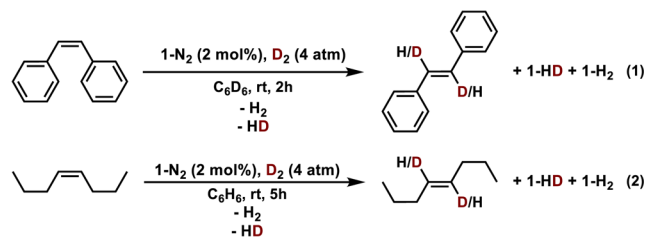
and 75 °C<sup>30</sup> each resulted in the enhancement of the resulting alkene product resonances. Based on the coupling constant of the resulting hyperpolarized alkene product of 2f (<sup>3</sup>J<sub>HH</sub> = 14.4 and 14.0 Hz), it was determined that *cis*-addition occurs under catalytic conditions. Furthermore, 2e, 2h, 2i, and 2l all displayed alkene coupling constants consistent with *cis*-addition and no signals corresponding to the *trans*-alkene products were

observed by the PHIP transfer NMR experiments in this set of alkynes. In addition, these data also demonstrate that both H atoms of  $p$ -H<sub>2</sub> add to the alkyne in a concerted fashion, similar to our previously reported olefin hydrogenation with **1-N<sub>2</sub>**.<sup>23</sup> Since *trans*-hydrogenation is not operative in the catalytic process and the more thermodynamically stable *E*-alkene products are formed throughout, we hypothesized that the generated *cis*-alkenes are converted to *trans*-alkenes via a cobalt-mediated isomerization process. Even though the *Z* to *E* isomerization is thermodynamically favorable, examples of cobalt-mediated systems capable of such processes are rare.<sup>12,31</sup>

To test our hypothesis, a solution consisting of *cis*-stilbene and **1-N<sub>2</sub>** (2 mol %) was stirred at room temperature under 4 atm of H<sub>2</sub> for 2 h. The formation of *trans*-stilbene (78%) from *cis*-stilbene (22%) was detected by GC-MS. When H<sub>2</sub> gas was omitted, no isomerization occurred at 30 °C, but 30% isomerization to *trans*-stilbene was observed after heating the reaction to 80 °C for 18 h. Nevertheless, under catalytic conditions, the involvement of **1-H<sub>2</sub>** is clearly evident (*vide infra*) in the formation of *trans*-alkenes.

To understand if  $\beta$ -hydride elimination of a Co<sup>III</sup>-alkyl intermediate may be involved in the isomerization process, isotopic labeling experiments were performed. A solution of **1-N<sub>2</sub>** (2 mol %) and *cis*-stilbene under 4 atm of D<sub>2</sub> at room temperature was monitored by <sup>1</sup>H and <sup>2</sup>H NMR spectroscopy (Scheme 2, eq 1). From the <sup>2</sup>H NMR spectrum, the

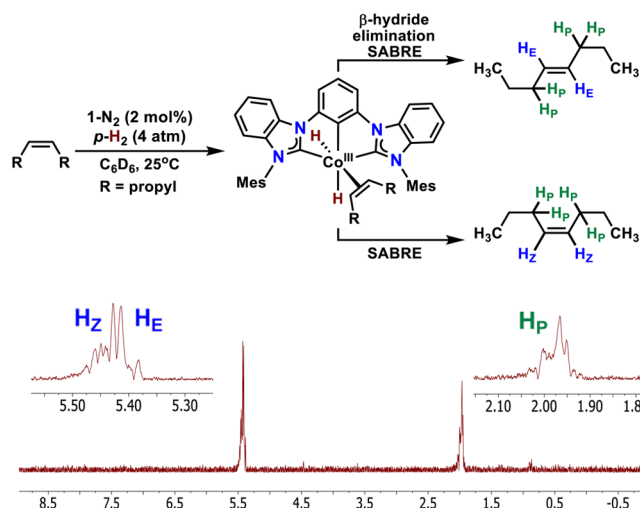
#### Scheme 2. Deuterium Incorporation and Scrambling



incorporation of deuterium into *trans*-stilbene and 1,2-diphenylethane was observed, in addition to the formation of HD gas (Figure S4). The <sup>1</sup>H NMR spectrum also revealed the formation of H<sub>2</sub> and HD, as well as **1-HD** and **1-H<sub>2</sub>** (Figure S3). Furthermore, similar results were observed when using *cis*-4-octene (Scheme 2, eq 2 and Figures S5 and S6) and 55% deuterium incorporation only into the olefinic region of *trans*-4-octene was observed after 5 h. These results support  $\beta$ -hydride elimination from a Co<sup>III</sup>-alkyl intermediate and is the basis for the observed *E*-selectivity in the semihydrogenation of alkynes.

In an effort to gain further insight into the catalytic reaction, a solution consisting of **1-N<sub>2</sub>** (2 mol %) and *cis*-4-octene under 4 atm of  $p$ -H<sub>2</sub> in benzene-*d*<sub>6</sub> was monitored by <sup>1</sup>H-OPSY NMR spectroscopy (Figures 2 and S13–S15). Polarization of the olefinic and the  $\alpha$ -carbon protons of *cis*-4-octene, as well as the isomerized *trans*-4-octene, were observed. Akin to the deuterium studies, reduction of the substrate did not occur. This polarization is due to a SABRE (Signal Amplification By Reversible Exchange) effect.<sup>32,33</sup> This effect polarizes the substrate using  $p$ -H<sub>2</sub> without a chemical modification to the substrate. Duckett and co-workers<sup>32,33</sup> cited the importance of reversible binding of a substrate for this effect and provided a theoretical rationale for this process.<sup>34</sup>

On account of the <sup>1</sup>H, <sup>2</sup>H, and PHIP transfer NMR studies, a comprehensive mechanistic pathway for the catalytic semi-



**Figure 2.** <sup>1</sup>H-OPSY NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz) spectrum of **1-N<sub>2</sub>** (2 mol %) and *cis*-4-octene under 4 atm of  $p$ -H<sub>2</sub> at 25 °C.

hydrogenation of alkynes with **1-N<sub>2</sub>** is presented in Figure 3 (*cis*-hydrogenation). We have previously reported the formation of **1-H<sub>2</sub>** from **1-N<sub>2</sub>** under a H<sub>2</sub> atmosphere, as well as the reverse under a N<sub>2</sub> atmosphere.<sup>23</sup> Inhibition of hydrogenation by the addition of excess PPh<sub>3</sub> (*vide supra*) supports ligand-substrate exchange between **1-H<sub>2</sub>** and **1-I**. The alkyne dihydrogen complex, **I-1**, is generated in the presence of alkyne and, upon oxidative addition of H<sub>2</sub> onto the metal center, intermediate **I-2** results. The observation of the PHIP enhanced *cis*-alkene product requires the formation of intermediate **I-2**.

Next, migratory insertion of the alkyne forms a Co<sup>III</sup>-( $\eta^1$ -vinyl) hydride/dihydrogen species, **I-3**. Finally, reductive elimination of the *cis*-alkene and coordination of PPh<sub>3</sub> regenerates the active species, **1-H<sub>2</sub>**. Isomerization to the *trans*-alkene products (Figure 3) commences with the coordination of the *cis*-olefin to **1-H<sub>2</sub>** by phosphine displacement, resulting in **I-4**. The polarization of 4-octene through the SABRE effect indicates **I-4** and **I-5** are reversible. Following oxidative addition of H<sub>2</sub> onto the cobalt center, migratory insertion results in the Co<sup>III</sup>-alkyl dihydrogen/hydride species (**I-6** and **I-7**). The formation of HD and H<sub>2</sub> established from deuterium studies is a result of the exchange between **I-6** and **I-7** and confirms that  $\beta$ -hydride elimination is operative in the isomerization of *cis*-alkene to *trans*-alkene (Figure 3, pathway a). This is further supported by deuterium incorporation into the *trans*-olefin exclusively upon *cis*-olefin isomerization using D<sub>2</sub>. Therefore, formation of **I-5** from **I-6** or **I-7** does not occur. In competition with  $\beta$ -hydride elimination, reductive elimination of the alkane product (Figure 3, pathway b), albeit kinetically slower, is also operative.

## CONCLUSION

In conclusion, we have extended the catalytic utility of **1-N<sub>2</sub>** toward the semihydrogenation of a broad scope of internal alkynes with excellent selectivity toward *E*-alkenes. The use of <sup>1</sup>H, <sup>2</sup>H, and PHIP transfer NMR spectroscopic studies has enabled the identification of key reaction intermediates in this process, establishing that *cis*-hydrogenation occurs first and is then followed by *trans*-isomerization under a H<sub>2</sub> atmosphere to yield the corresponding *E*-alkenes. Finally, this system signifies an atom-economical route toward the formation of *E*-alkenes



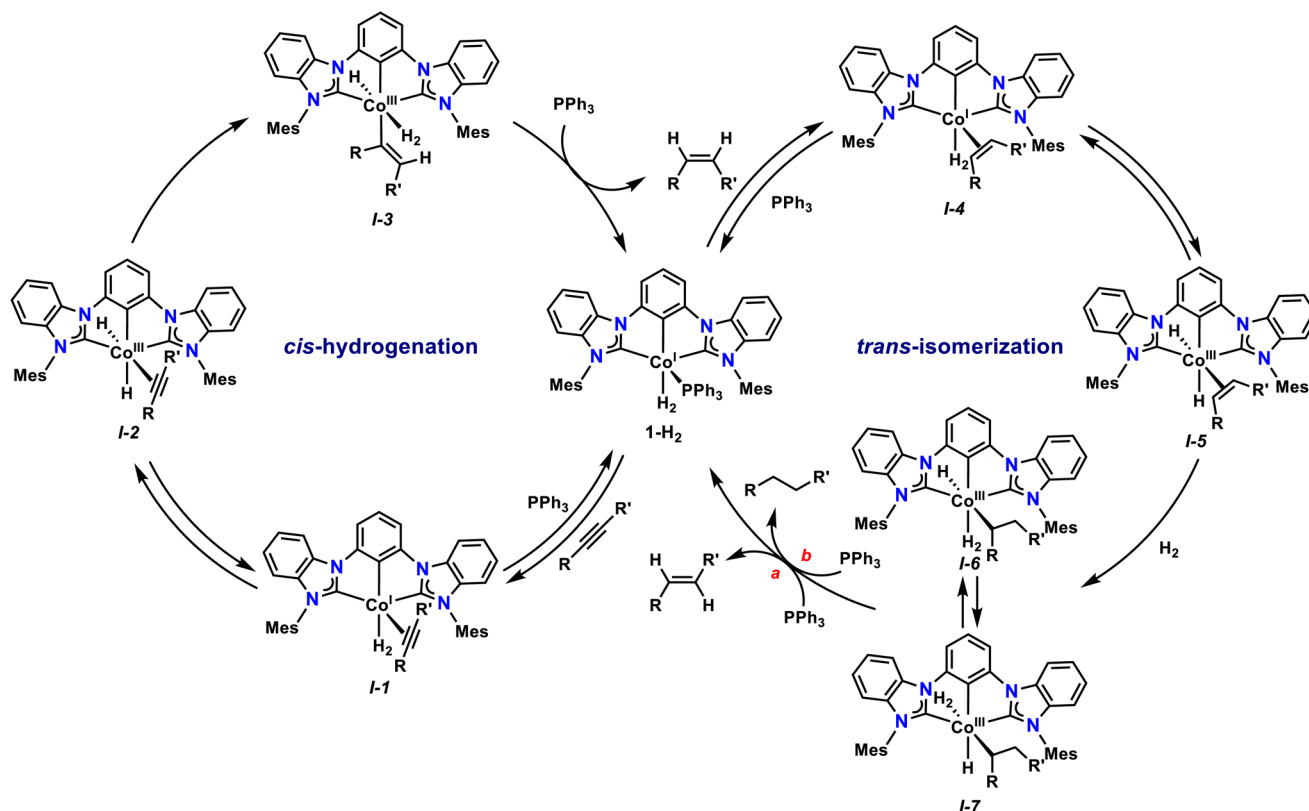


Figure 3. Proposed catalytic cycle for the *cis*-hydrogenation of internal alkynes, followed by *trans*-isomerization using **1-H<sub>2</sub>**.

under mild conditions and mechanistic insights into this process can guide further development in this area.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b08128.

Experimental data (PDF)

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### Notes

The authors declare no competing financial interest.

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