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# *Bis*-NHC–Ag/Pd(OAc)$_2$ Catalytic System Catalyzed Transfer Hydrogenation Reaction

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**Abstract:** The *bis*-NHC–Ag/Pd(OAc)$_2$ catalytic system (NHC = *N*-heterocyclic carbene), a combination of *bis*-NHC–Ag complex and Pd(OAc)$_2$, was found to be a smart catalyst in the Pd-catalyzed transfer hydrogenation of various functionalized arenes and internal/terminal alkynes. The catalytic system demonstrated high efficiency for the reduction of a wide range of various functional groups such as carbonyls, alkynes, olefins, and nitro groups in good to excellent yields and high chemoselectivity for the reduction of functional groups. In addition, the protocol was successfully exploited to stereoselectivity for the transformation of alkynes to alkenes in aqueous media under air. This methodology successfully provided an alternative useful protocol for reducing various functional groups and a simple operational protocol for transfer hydrogenation.

**Keywords:** transfer hydrogenation; aqueous; chemoselectivity; bis-NHC–Ag



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## 1. Introduction

Metal-*N*-heterocyclic carbene (NHC) complexes possess a strong metal–carbene bond and these complexes play an important role in organometallic catalysis [1–5]. They have been developed into valuable catalytic systems in various reactions including Pd-catalyzed C–C cross-coupling reactions [6–8], C–N formation [9], hydrogenation [10,11], etc. The transfer hydrogenation reaction in particular has attracted much attention. Transfer hydrogenation [12–16] is one of the useful synthetic methods for various hydrogenated compounds, is inherently safer than direct hydrogenation, and has an easy operational setup. Transfer hydrogenation donors such as 2-propanol [17–21], ethanol [22–24], and formic acid are desirable because of their easy handling. Formic acid in particular has been widely studied as an environmentally friendly transfer hydrogenation agent due to its accessibility and high stability [25–29].

Due to the reductive elimination of the hydrido-palladium complexes of NHC, leading to catalyst deactivation [30–34], Pd–NHC-catalyzed transfer hydrogenation has less successful examples. In 2004, Cavell and co-workers demonstrated the first successful example of a stable tricarbene-Pd-hydrido complex [35], and Pd–NHC-catalyzed transfer hydrogenation has recently attracted much attention. Elsevier et al. and Cazin et al. also illustrated the Pd(NHC)-catalyzed reduction of alkynes employing triethylammonium formate (TEAF) as the hydrogen source. They also proposed a catalytic mechanism to illustrate the formation of *Z*-alkenes in the transfer hydrogenation of alkynes [36–42]. *Bis*-NHC binds to metal to form stable complexes compared to their monodentate NHC complexes. In addition, bis-NHC ligand diversity could be easily accessed by the modification of the linker and the wingtips. In 2013, Elsevier et al. established various *bis*-NHC–Pd complexes and applied them to the semihydrogenation of 1-phenyl-1-propyne [43]. Unfortunately, only 18% conversion was obtained by using formic acid (5.0 eq) as a hydrogen donor at 70 °C in acetonitrile. The authors mentioned that the transfer semihydrogenation gave

a mixture of *Z*-alkene, *E*-alkene, and alkane (over-reduced product) in a 98:2:0 ratio. Although an excellent Z/E ratio was displayed, the challenges are still functional group compatibility, chemoselectivity, stereoselectivity, and the control of over reduction. Therefore, it is desirable to develop an alternative method for efficient transfer hydrogenation. On the other hand, NHC ligands were recently found to play an important role in the synthesis of metallic nanoparticles (MNPs). Pd nanoparticles (Pd NPs) were formed by the decomposition of Pd–NHC bonds in a Pd/NHC catalytic system or by the reduction of the Pd precursor, especially in the presence of aliphatic amines such as triethylamine. The NHC-ligated Pd NPs present an efficient catalytic activity in the catalysis [44–48]. We recently reported an in situ-generated *bis*-NHC/$Pd(OAc)_2$ catalytic system, which was derived from *bis*-benzimidazolium salt and $Pd(OAc)_2$, as a catalyst for the Suzuki–Miyaura reaction, Mizoroki–Heck reaction, and Friedel-Crafts alkylation reaction of indole and nitrostyrene in good to excellent yields (Figure 1a) [49,50]. Motivated by these results we continued our efforts to develop an efficient *bis*-NHC–Ag/$Pd(OAc)_2$ catalytic system to catalyze chemoselective transfer hydrogenation with TEAF as a hydrogen donor (Figure 1b).

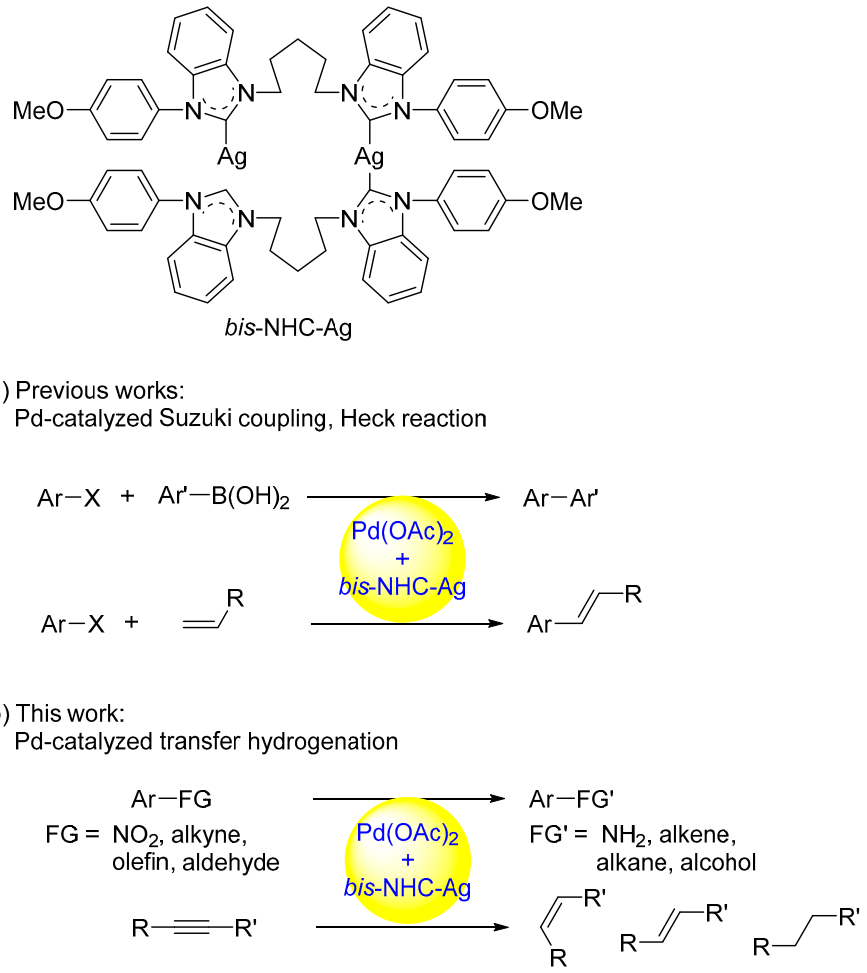



**Figure 1.** Reaction catalyzed by *bis*-NHC–Ag/$Pd(OAc)_2$ catalytic system.

## 2. Results

A testing protocol was examined by using *trans*-cinnamyl alcohol, formic acid, triethylamine, and a *bis*-NHC–Ag/$Pd(OAc)_2$ catalytic system at 80 °C. To screen the optimized reaction conditions fast, various factors such as Pd loading, equivalents of TEAF, and solvents were evaluated (Table 1). Preliminary results illustrated that *N*,*N*-dimethylformamide (DMF) was a suitable solvent for transfer hydrogenation (entry 2 vs. 4). *trans*-cinnamyl

alcohol was hydrogenated completely to 3-phenylpropan-1-ol in the presence of 1.0 mol % catalyst loading and a 4-fold excess of $HCO_2H/NEt_3$ in DMF (entry 5). A dramatic drop in conversion was obtained in the absence of *bis*-NHC–Ag complex (8% conversion, entry 6), which means the *bis*-NHC–Ag/$Pd(OAc)_2$ catalytic system raises the reactivity of the Pd metal center on the catalytic hydrogenation reaction (entry 5 vs. entry 6).

**Table 1.** *Bis*-NHC–Ag/$Pd(OAc)_2$ catalytic system catalyzed transfer hydrogenation reaction of *trans*-cinnamyl alcohol [1].

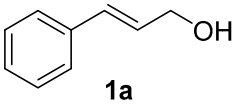
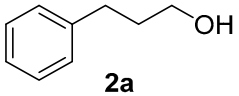
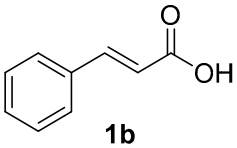
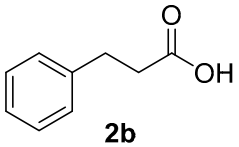
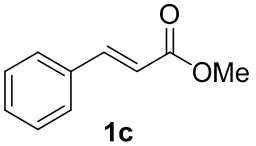
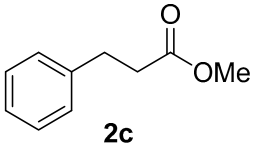
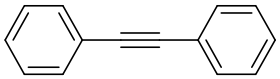
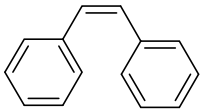
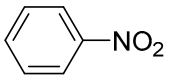
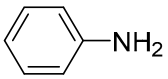
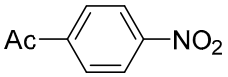
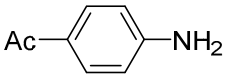
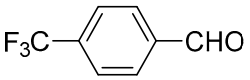
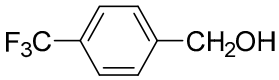
| Entry | *bis*-NHC–Ag/Pd (mol %) | TEAF (equiv) | Solvent | Conv. (%) [2] |
|---|---|---|---|---|
| 1 | 0.5 | 3.0 | DMF | 44 |
| 2 | 1.0 | 5.0 | $^t$BuOH | 67 |
| 3 | 2.0 | 7.0 | PhMe | 42 |
| 4 | 1.0 | 3.0 | DMF | 74 |
| 5 | 1.0 | 4.0 | DMF | >99 |
| 6 [3] | 1.0 | 4.0 | DMF | 8 |

[1] Reaction conditions: *trans*-cinnamyl alcohol (1.0 mmol), $Pd(OAc)_2$ (mol % as indicated), *bis*-NHC–Ag (0.5 equiv to Pd), and TEAF (equiv as indicated) at 80 °C in dry solvent (5 mL) for 24 h under a $N_2$ atmosphere. [2] Determined by 400 MHz $^1$H NMR (in Supplementary Materials). [3] The reaction was carried out in the absence of *bis*-NHC–Ag complex.

After screening the optimal reaction conditions, the reduction of various functionalized substrates was studied. As illustrated in Table 2, quantitative conversions were observed in the reduction of olefins containing alcohol, acid, and ester functionalities (entries 1–3). Notably, the reduction of 1,2-diphenylacetylene **3a** produced (*Z*)-**4a** as the only product, without the formation of the over-reduced product, 1,2-diphenylethane and (*E*)-**4a** (entry 4, 85%). The reduction of nitrobenzene catalyzed by the *bis*-NHC–Ag/$Pd(OAc)_2$ catalytic system gave aniline **6a** in a 99% isolated yield (entry 5). With a substrate containing two active functional groups, 4-nitroacetophenone **6b**, the catalytic system was found to selectively reduce the nitro group, while no reduction product of the carbonyl group was observed on benzene ring **6b** (entry 6). This demonstrates that the reduction rate of the nitro group is faster than that of ketone. In addition, aldehyde-bearing strong electron-withdrawing group $CF_3$, which could afford the corresponding alcohol **8a** in a 92% yield (entry 7), indicates that our reaction works for both electron-donating and electron-withdrawing substituents.

Recently, numerous studies of Pd-catalyzed transfer hydrogenation using $H_2O$ as the hydrogen agent and the solvent have been reported [51–59]. We turned our attention to the possibility that the transfer hydrogenation of internal/terminal alkynes may also continue in the presence of the *bis*-NHC–Ag/$Pd(OAc)_2$ catalytic system in aqueous media under air. We began to develop a general method for the transfer hydrogenation of internal alkynes by using 1,2-diphenylacetylene **3a** and formic acid (4 equiv) and triethylamine (4 equiv) as the model substrates. As described in Table 3, **3a** was reduced to semihydrogenation product **4a** with a *Z*/*E* ratio of 94/6 in DMF/$H_2O$ (9/1) mixed solvent (entry 1). The over-reduced product **9a** was fully inhibited. When we continued to increase the amount of water, the conversion yields decreased because of the low solubility of **3a**, but (*Z*)-**4a** was still the major product (entries 1–4). Notably, the ratio of (*Z*)-**4a** and (*E*)-**4a** decreased slightly as the amount of water decreased (entries 1–4). *cis*-Stilbene **8a** was afforded as a major product regardless of the proportion of water. This observation is contrary to recent reports, in which *trans*-alkenes were found to be a major product through in situ *Z*→*E* isomerization in the Pd-catalyzed semihydrogenation of internal alkynes in aqueous solution [52,53,56–58]. In addition, $K_2CO_3$ and $K_3PO_4 \cdot H_2O$ were not the best choices as the base, indicating that the basicity of the base might affect the reaction rate (entries 2, 5, and 6) [60]. With Pd(II) sources, **3a** was transformed to olefin efficiently, but $Pd(OAc)_2$ was the best choice (entries 2, 7–9).

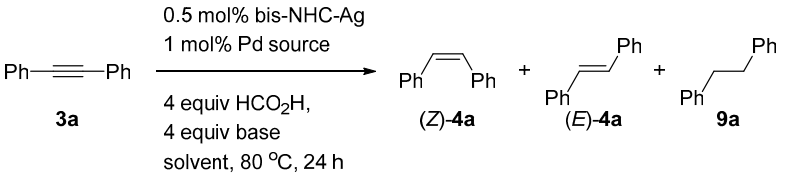
**Table 2.** Transfer hydrogenation catalyzed by *bis*-NHC–Ag/$Pd(OAc)_2$ catalytic system [1].

| Entry | Substrate | Product | Yield (%) [2] |
|---|---|---|---|
| 1 |  **1a** |  **2a** | 98 |
| 2 |  **1b** |  **2b** | 99 |
| 3 |  **1c** |  **2c** | 99 |
| 4 |  **3a** |  (*Z*)-**4a** | 85 |
| 5 |  **5a** |  **6a** | 99 |
| 6 |  **5b** |  **6b** | 99 |
| 7 |  **7a** |  **8a** | 92 |

[1] Reaction conditions: *trans*-cinnamyl alcohol (1.0 mmol), $Pd(OAc)_2$ (1 mol %), *bis*-NHC–Ag (0.5 mol %), and TEAF (4 equiv) at 80 °C in dry DMF (5 mL) for 24 h under a $N_2$ atmosphere. [2] Isolated yield.

Based on this observation, transfer hydrogenation of internal alkynes **3** was subsequently investigated in aqueous media under air. The results summarized in Table 4 showed that various internal alkynes were readily reduced to the corresponding alkenes in moderate to excellent conversion yields. For 1,2-diphenylacetlene **3a** as the substrate, the use of a DMF/$H_2O$ (5/5) solvent system at 80 °C (condition *A*) produced a 100% conversion yield confirmed by GC (Gas Chromatography) with a *Z*/*E* ratio of 93/7 (entry 1). On the other hand, the use of a DMF/$H_2O$ (9/1) solvent system at 80 °C (condition *B*) generated a 100% conversion GC yield and 94/6 *Z*/*E* ratio (entry 2). Surprisingly, the corresponding product **4b** was formed in a 97% isolated yield with a *Z*/*E* ratio of 30/70 under condition B (entry 3) when using heteroaromatic alkynes **3b** as a substrate. That might be the reason why the stereoselectivity of the product is affected by the pyridinyl group, the coordinative moiety [61,62]. It should be mentioned that **3c** was successfully reduced to (*Z*)-**4c** with excellent stereoselectivity under condition B (entry 5). For the semihydrogenation of conjugated alkynes bearing ester **3d**, good performance was demonstrated with a *Z*/*E* ratio of 95/5 under condition B (entry 6). In particular, only (*Z*)-alkenylamide, (*Z*)-**4e**, was prepared in an 83% isolated yield for 1 h at 60 °C (entry 8) and over-reduced amide **9e** was the only product in a quantitative yield for 2 h at 80 °C (entry 7). This illustrated that the excellent chemoselectivity of the reduction of **3e** can be controlled by prolonging the reaction time and conditions.

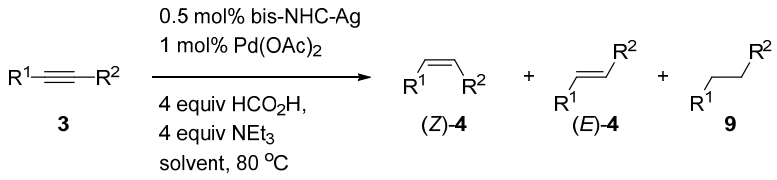
**Table 3.** *Bis*-NHC–Ag/$Pd(OAc)_2$ catalytic system catalyzed transfer hydrogenation [1].

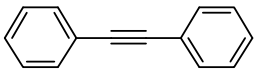
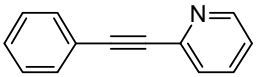
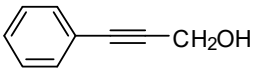
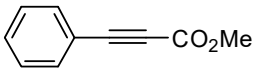
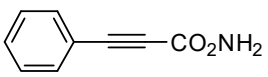



| Entry | Pd Source | Base | Solvent Ratio ($DMF/H_2O$) | Conv. (%)[2] | *Z*:*E*:9a [2] |
|---|---|---|---|---|---|
| 1 | $Pd(OAc)_2$ | $NEt_3$ | 9/1 | 100 | 94:6:0 |
| 2 | $Pd(OAc)_2$ | $NEt_3$ | 5/5 | 100 | 93:7:0 |
| 3 | $Pd(OAc)_2$ | $NEt_3$ | 1/9 | 82 | 93:7:0 |
| 4 | $Pd(OAc)_2$ | $NEt_3$ | 0/1 | 32 | 93:7:0 |
| 5 | $Pd(OAc)_2$ | $K_2CO_3$ | 5/5 | 24 | 96:4:0 |
| 6 | $Pd(OAc)_2$ | $K_3PO_4 \cdot H_2O$ | 5/5 | 36 | 97:3:0 |
| 7 | $PdCl_2(CH_3CN)_2$ | $NEt_3$ | 5/5 | 100 | 93:7:0 |
| 8 | $PdCl_2$ | $NEt_3$ | 5/5 | 89 | 94:6:0 |
| 9 | $[PdCl_2(C_3H_5)_2]$ | $NEt_3$ | 5/5 | 82 | 93:7:0 |

[1] Reaction conditions: **3a** (1.0 mmol), Pd source (1 mol %), *bis*-NHC–Ag (0.5 mol %), and $HCO_2H$ (4 equiv), and base (4 equiv) at 80 °C in solvent (5 mL) for 24 h under air. [2] Determined by GC-FID analysis and undecane was applied as an internal standard.

**Table 4.** Stereoselectivity studies for *bis*-NHC–Ag/$Pd(OAc)_2$ catalytic system catalyzed transfer hydrogenation of internal alkynes in aqueous media [1].·

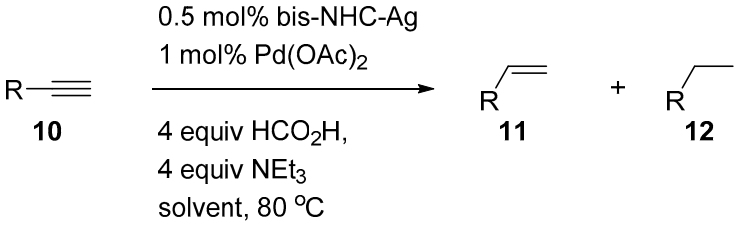



| Entry | Substrate | Condition [2] | Time (h) | Conv. (%) [3] | *Z*:*E*:9 [3] |
|---|---|---|---|---|---|
| 1 |  **3a** | A (5/5) | 24 | 100 (> 99) [4] | 93:7:0 |
| 2 | | B (9/1) | 24 | 100 (> 99) [4] | 94:6:0 |
| 3 |  **3b** | B (9/1) | 2 | 100 (97) [5] | 30:70:0 |
| 4 |  **3c** | A (5/5) | 24 | 47 | 100:0:0 |
| 5 | | B (9/1) | 24 | 100 (80) [5] | 100:0:0 |
| 6 |  **3d** | B (9/1) | 2.5 | 100 (90) [5] | 95:5:0 |
| 7 |  **3e** | B (9/1) | 2 | 100 (> 99) [5] | 0:0:100 |
| 8 | | C (9/1) | 1 | 86 (83) [5] | 100:0:0 |

[1] Reaction conditions: **3** (1.0 mmol), $Pd(OAc)_2$ (1 mol %), *bis*-NHC–Ag (0.5 mol %), and $HCO_2H$/TEAF (4 equiv) at 80 °C in $DMF/H_2O$ mixed solvent (5 mL) under air atmosphere. [2] Condition A: the reaction was carried out at 80 °C in $DMF/H_2O$ (5/5); condition B: the reaction was conducted at 80 °C in $DMF/H_2O$ (9/1); condition C: the reaction was carried out at 60 °C in $DMF/H_2O$ (9/1). [3] Determined by GC or 400 MHz NMR analysis (in Supplementary Materials). [4] GC yield is reported in parentheses and undecane was applied as an internal standard. [5] Isolated yield is reported in parentheses.

Similarly, the catalytic system was efficiently used to employ in the reduction of various terminal alkynes **10** (Table 5). The catalytic system was effective in the hydrogenation of phenylacetylene under condition B and styrene was observed with an 89% GC yield (entry 1). On the contrary, ethylbenzene **12a** was obtained when the reaction time was spread to 5 h (entry 2). It was also noted that the terminal-alkyne-bearing electron-donating group on the benzene ring, i.e., **10b**, **10c**, and **10d**, was easily reduced to the corresponding olefins within 30 min with conversion yields of 82–92% (entries 3 and 5). Completely reduced products, saturated alkanes **12**, were achieved by extending reaction time to 3 h and moderate GC yields in the range 40–68% were obtained (entries 4 and 6). Notably, 4-nitrophenylacetylene, **10d**, shows that the catalytic system displays excellent chemoselectivity between the alkyne and nitro groups (entry 7). Interestingly, the complete reduction product, 4-ethylaniline **12d**, was generated in an 80% isolated yield when increasing reaction time to 2 h (entry 8). In addition, the catalytic system also tolerates well functionalities such as alcohol, methoxy, and nitro groups. Heteroaryl alkyne, **10e**, was reduced to the corresponding olefin in a 72% GC yield (entry 9). In addition to aryl alkynes, the aliphatic alkynes, **10f** and **10g**, were also investigated in an aqueous medium under air. The semi-reduction products, **11f** and **11g**, were obtained in 99% and 78% isolated yields (entries 10 and 12), while the over-reduction products, **12f** and **12g**, were given in 97% and 72% isolated yields, respectively (entries 11 and 13).

**Table 5.** Chemoselectivity studies for *bis*-NHC–Ag/$Pd(OAc)_2$ catalytic system catalyzed transfer hydrogenation of terminal alkynes in aqueous media [1].



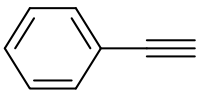
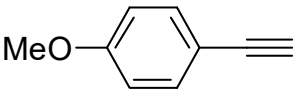
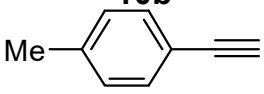
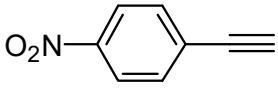
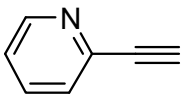
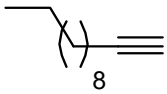
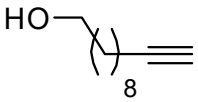

| Entry | Substrate | Time (h) | 11:12 [2] | GC Yield (%) [3] |
|---|---|---|---|---|
| 1 |  **10a** | 3 | 100:0 | 89 |
| 2 | | 5 | 0:100 | 34 |
| 3 |  **10b** | 0.5 | 100:0 | 92 |
| 4 | | 3 | 0:100 | 63 |
| 5 |  **10c** | 0.5 | 97:3 | 88 |
| 6 | | 3 | 0:100 | 40 |
| 7 |  **10d** | 1 | 100:0 | 83 [4] |
| 8 | | 2 | 0:100 [5] | 80 [4] |
| 9 |  **10e** | 3 | 100:0 | 72 |

**Table 5.** *Cont.*

| Entry | Substrate | Time (h) | 11:12 [2] | GC Yield (%) [3] |
|---|---|---|---|---|
| 10 |  **10f** | 2 | 100:0 | 99 [4] |
| 11 | | 24 | 0:100 | 97 [4] |
| 12 [6] |  **10g** | 24 | 100:0 | 78 [4] |
| 13 | | 24 | 0:100 | 72 [4] |

[1] Reaction conditions: **10** (1.0 mmol), $Pd(OAc)_2$ (1 mol %), *bis*-NHC–Ag (0.5 mol %), and $HCO_2H$/TEAF (4 equiv) at 80 °C in DMF/$H_2O$ (9/1) mixed solvent (5 mL) under air atmosphere. [2] Determined by GC analysis. [3] GC yield is reported and undecane was applied as an internal standard. [4] Isolated yield is reported. [5] The product was 4-ethylaniline. [6] The reaction temperature was 60 °C.

## 3. Materials and Methods

### *3.1. General Methods*

Unless otherwise noted, commercially available materials, which were received from Aldrich and Acros, were used without further purification. Anhydrous solvent, DMF, was received from Aldrich. Acetonitrile was obtained by distillation over calcium hydride. Toluene and *t*-BuOH were distilled and used after treatment with sodium. Reactions were monitored with pre-coated silica gel 60 (F-254) plates. The purification of products was performed by column chromatography (silica gel, 0.040–0.063 μm) eluting with *n*-hexane/ethyl acetate. $^1H$ and $^{13}C$ NMR spectra, found in the Supplementary Materials, were analyzed with an Agilent Mercury 400 spectrometer. *J*-values are given in Hz. Chemical shifts (δ) were recorded from $CDCl_3$ (δ = 7.26 ppm) in the $^1H$ NMR spectra and the central peak of $CDCl_3$ (δ = 77.0 ppm) in the $^{13}C$ NMR spectra. GC-FID (Gas Chromatography-flame ionization detector) was analyzed on a Shimadzu GC-2014 equipped with a capillary column (SPB®-5, 60 m × 0.25 mm × 0.25 μm). The conversion yields, GC-yield, and ratios were determined by using undecane as an internal standard. High-resolution mass spectra were obtained with a Finnigan/Thermo Quest MAT 95XL mass spectrometer using either the electron impact (EI) or the electrospray ionization (ESI) method. The synthesis of the *bis*-NHC–Ag complex was carried out according to our previous report [50].

### *3.2. Description of the Screening Experiments*

#### 3.2.1. General Procedures for Transfer Hydrogenation Reactions in Organic Solvent under $N_2$

A Schlenk tube was charged with *bis*-NHC–Ag complex (0.5 mol %), $Pd(OAc)_2$ (1 mol %), $NEt_3$ (4 mmol), $HCO_2H$ (4 mmol), substrate (1 mmol), and DMF (5 mL). After stirring at 80 °C for 24 h under $N_2$, 5 mL of brine were added to the reaction mixture. The aqueous phase was extracted with EtOAc (5 mL × 3). The combined organic phases were dried ($Na_2SO_4$) and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography.

#### 3.2.2. General Procedures for Transfer Hydrogenation Reactions in Aqueous Media under Air

A Schlenk tube was charged with *bis*-NHC–Ag complex (0.5 mol %), $Pd(OAc)_2$ (1 mol %), $NEt_3$ (4 mmol), $HCO_2H$ (4 mmol), substrate **3** (1 mmol), and DMF/$H_2O$ (5 mL). After stirring at 80 °C for 24 h under air, 5 mL of brine were added to the resulting solution. After extracting the aqueous layer with EtOAc (5 mL × 3), the combined organic layers were dried ($Na_2SO_4$) and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography.

### *3.3. Analytical Data of the Reduction Products*

#### 3.3.1. Transfer Hydrogenation Reactions in Organic Solvent under $N_2$

3-Phenylpropanol (**2a**) (Table 2, entry 1) [63]. $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.31−7.18 (m, 5H), 3.68 (t, *J* = 7.6 Hz, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 1.92 (quintet, *J* = 7.6 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 141.7, 128.3, 128.2, 125.7, 61.8, 34.0, 31.9.

3-Phenylpropanoic acid (**2b**) (Table 2, entry 2) [64]. $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.32−7.21 (m, 5H), 2.97 (t, *J* = 7.6 Hz, 2H), 2.69 (t, *J* = 7.6 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 179.5, 140.1, 128.5, 128.2, 126.3, 35.6, 30.5.

Methyl 3-phenylpropanate (**2c**) (Table 2, entry 3) [64]. $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.31−7.27 (m, 2H), 7.33−7.19 (m, 3H), 3.67 (s, 3H), 2.95 (t, *J* = 8.0 Hz, 2H), 2.64 (t, *J* = 8.0 Hz, 2H).

*cis*-Stilbene (**4a**) (Table 2, entry 4) [36]. $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.29–7.20 (m, 10H), 6.62 (s, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 137.2, 130.2, 128.9, 128.2, 127.1.

Aniline (**6a**) (Table 2, entry 5) [65]. $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.17 (t, *J* = 7.6 Hz, 2H), 6.77 (t, *J* = 7.6 Hz, 1H), 6.70 (d, *J* = 7.6 Hz, 2H), 3.65 (br, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 146.3, 129.1, 118.3, 114.9.

1-(4-Aminophenyl)ethan-1one (**6b**) (Table 2, entry 6) [65]. $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.81 (d, *J* = 8.4 Hz, 2H), 6.65 (d, *J* = 8.4 Hz, 2H), 4.11 (br, 2H), 2.51 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 186.5, 151.1, 130.8, 127.7, 113.6, 26.1.

(4-(Trifluoromethyl)phenyl)methanol (**8a**) (Table 2, entry 7) [63]. $^1$H NMR ($CDCl_3$, 400 MHz): δ $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.51 (d, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 7.6 Hz, 2H), 4.58 (s, 2H), 3.99 (bs, 1H, OH); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 144.6, 129.4 (q, $J_{C-F}$ = 32.1 Hz), 126.7, 125.2, 124.1 (q, $J_{C-F}$ = 270.5 Hz), 63.8.

#### 3.3.2. Transfer Hydrogenation Reactions in Aqueous Media under Air

(*E*)-2-Styrylpyridine (**4b**) (Table 4, entry 3) [62]. $^1$H NMR ($CDCl_3$, 400 MHz): δ 8.61 (d, *J* = 4.8 Hz, 1H), 7.69−7.64 (m, 2H), 7.64 (d, *J* = 16.0 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.43−7.36 (m, 3H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 16.0 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz): 145.7, 128.4, 127.4, 125.3, 70.3, 25.1.

The mixture of 3-phenyl-2-propyn-1-ol (**3c**) and (*Z*)-cinnamyl alcohol (**4c**) (Table 4, entry 4) [66]. The ratio (**3c**/**4c** = 84/16) was determined by $^1$H NMR signals at 4.50 ppm (alkyne protons of **3c**) and 4.45 ppm (olefin protons of **4c**). (*Z*)-**4c**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.37−7.20 (m, 5H), 6.58 (d, *J* = 11.6 Hz, 1H), 5.88 (dt, *J* = 11.6, 6.0 Hz, 1H), 4.45 (d, *J* = 6.0 Hz, 2H), 1.50 (br, 1H).

The mixture of (Z/E)-Methyl cinnamate (*Z*-**4d** and *E*-**4d**) (Table 4, entry 6) [67]. The ratio (**Z-4d**/**E-4d** = 95/5) was determined by $^1$H NMR signals at 6.46 ppm (**E-4d**) and 5.96 ppm (**Z-4d**). (*Z*)-**4d**: $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.59 (d, *J* = 7.6 Hz, 2H), 7.40−7.37 (m, 1H), 7.34 (t, *J* = 7.6 Hz, 2H), 6.96 (d, *J* = 12.4 Hz, 1H), 5.96 (d, *J* = 12.4 Hz, 1H), 3.71 (s, 3H).

(Z)-3-Phenylacrylamide (**4e**) (Table 4, entry 8) [57]. $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.48 (d, *J* = 6.8 Hz, 2H), 7.38−7.32 (m, 3H), 6.86 (d, *J* = 12.4 Hz, 1H), 5.99 (d, *J* = 12.4 Hz, 1H), 5.47 (br, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 169.1, 137.5, 134.8, 128.9, 128.7, 128.5, 123.8.

Styrene (**11a**) (Table 5, entry 1) [68]. $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.41 (d, *J* = 6.8 Hz, 2H), 7.32 (t, *J* = 6.8 Hz, 2H), 7.25 (t, *J* = 6.8 Hz, 1H), 6.72 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.75 (d, *J* = 17.6 Hz, 1H), 5.24 (d, *J* = 10.8 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 137.5, 136.8, 128.5, 127.8, 126.2, 113.8.

Ethylbenzene (**12a**) (Table 5, entry 2) [68]. $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.29 (t, *J* = 7.2 Hz, 2H), 7.21 (d, *J* = 7.2 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 2.66 (q, *J* = 7.6 Hz, 2H), 1.25 (t, *J* = 7.6 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 144.2, 128.3, 127.8, 125.6, 28.9, 15.6.

4-Methoxystyrene (**11b**) (Table 5, entry 3) [69]. $^1$H NMR ($CDCl_3$, 400 MHz): δ 7.35 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 6.67 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.61 (d, *J* = 17.6, Hz, 1H), 5.13 (d, *J* = 11.2 Hz, 1H), 3.81 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 159.3, 136.2, 130.4, 127.4, 113.9, 111.6, 53.3.

4-Ethylanisole (**12b**) (Table 5, entry 4) [68]. $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 7.12 (d, *J* = 7.6 Hz, 2H), 6.84 (d, *J* = 7.6 Hz, 2H), 3.80 (s, 3H), 2.60 (q, *J* = 7.6 Hz, 2H), 1.22 (t, *J* = 7.6 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 157.6, 136.4, 128.7, 113.7, 55.3, 27.9, 15.9.

4-Methylstyrene (**11c**) (Table 5, entry 5) [69]. $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 7.32 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.70 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.76 (d, *J* = 17.6 Hz, 1H), 5.19 (d, *J* = 10.8 Hz, 1H), 2.35 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 137.6, 136.7, 134.8, 129.2, 126.1, 112.7, 21.2.

4-Ethylaniline (**12**d) (Table 5, entry 8) [70]. $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 6.99 (d, *J* = 8.4 Hz, 2H), 6.63 (d, *J* = 8.4 Hz, 2H), 3.55 (br, 2H), 2.54 (q, *J* = 7.6 Hz, 2H), 1.19 (t, *J* = 7.6 Hz, 3H).

2-Vinylpyridine (**11e**) (Table 5, entry 9) [71]. $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 8.57 (d, *J* = 4.0 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.82 (dd, *J* = 17.2, 10.8 Hz, 1H), 6.20 (d, *J* = 17.2 Hz, 1H) 5.48 (d, *J* = 10.8 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 155.7, 149.4, 136.9, 136.4, 122.4, 121.1, 118.1.

Dodec-1-ene (**11f**) (Table 5, entry 10) [72]. $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 5.82 (m, 1H), 4.99 (d, *J* = 17.2 Hz, 1H), 4.93 (d, *J* = 9.6 Hz, 1H), 2.05−2.01 (m, 2H), 1.39−1.26 (m, 16H), 0.88 (s, *J* = 6.8 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 139.7, 114.1, 33.8, 31.9, 29.6, 29.5, 29.5, 29.2, 29.0, 22.7, 14.1.

Dodecane (**12f**) (Table 5, entry 11) [73]. $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 1.36–1.20 (m, 20H), 0.88 (t, *J* = 6.8 Hz, 6H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 31.9, 29.7, 29.4, 22.7, 14.1.

Undec-10-en-1-ol (**11g**) (Table 5, entry 12) [74]. $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 5.81 (ddd, *J* = 17.2, 10.4, 6.8 Hz, 1H), 4.99 (dd, *J* = 17.2, 0.8 Hz, 1H), 4.93 (dd, *J* = 10.4, 0.8 Hz, 1H), 3.64 (t, *J* = 6.8 Hz, 2H), 2.04 (dd, *J* = 13.6, 6.8 Hz, 2H), 1.69−1.51 (m, 2H), 1.50−1.18 (m, 13H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 139.2, 114.1, 63.1, 33.8, 32.8, 29.5, 29.4, 29.1, 28.9, 25.7.

Undecan-1-ol (**12g**) (Table 5, entry 13) [72]. $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 3.64 (t, *J* = 6.8 Hz, 2H), 1.51–1.62 (m, 2H), 1.40–1.19 (m, 16H), 0.88 (t, *J* = 6.8 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 63.0, 32.7, 31.9, 29.6, 29.4, 29.3, 25.7, 22.6, 14.1.

## 4. Conclusions

In summary, we have developed a practical and efficient in-situ-generated *bis*-*N*HC–Pd catalytic system which was applied in the transfer hydrogenation of various functionalized arenes in good to high yields with excellent chemoselectivity. The catalytic system was also applied in the semihydrogenation of internal alkynes to provide outstanding stereoselectivity. The chemoselectivity was shown in the reduction of terminal alkynes by controlling the reaction time and conditions. The simplicity of the procedure is outlined by the application of the commercially available triethylammonium formate as a hydrogen source under mild and non-inert conditions.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/2073-4344/11/1/8/s1, Figure S1: $^{1}$H NMR spectrum of 1-(4-methoxyphenyl)-1*H*-benzo[d]imidazole in $CDCl_3$, Figure S2: $^{13}$C NMR spectrum of 1-(4-methoxyphenyl)-1*H*-benzo[d]imidazole in $CDCl_3$, Figure S3: $^{1}$H NMR spectrum of 5,5′-(pentane-1,5-diyl)bis(1-(4-methoxyphenyl)-1*H*-benzo[d]imidazol-3-ium) bromide in $CD_3OD$, Figure S4: $^{13}$C NMR spectrum of 5,5′-(pentane-1,5-diyl)bis(1-(4-methoxyphenyl)-1*H*-benzo[d]imidazol-3-ium) bromide in $CD_3OD$, Figure S5: $^{1}$H NMR spectrum of bis-NHC–Ag complex in DMSO-$d_6$, Figure S6: $^{13}$C NMR spectrum of bis-NHC–Ag complex in DMSO-$d_6$, Figure S7: $^{1}$H NMR spectrum of compound **2a** in $CDCl_3$, Figure S8: $^{13}$C NMR spectrum of compound **2a** in $CDCl_3$, Figure S9: $^{1}$H NMR spectrum of compound **2b** in $CDCl_3$, Figure S10: $^{13}$C NMR spectrum of compound **2b** in $CDCl_3$, Figure S11: $^{1}$H NMR spectrum of compound **2c** in $CDCl_3$, Figure S12: $^{1}$H NMR spectrum of compound **(*Z*)-4a** in $CDCl_3$, Figure S13: $^{13}$C NMR spectrum of compound **(*Z*)-4a** in $CDCl_3$, Figure S14: $^{1}$H NMR spectrum of compound **6a** in $CDCl_3$, Figure S15: $^{13}$C NMR spectrum of compound **6a** in $CDCl_3$, Figure S16: $^{1}$H NMR spectrum of compound **6b** in $CDCl_3$, Figure S17: $^{13}$C NMR spectrum of compound **6b** in $CDCl_3$, Figure S18: $^{1}$H NMR spectrum of compound **8a** in $CDCl_3$, Figure S19: $^{13}$C NMR spectrum of compound **8a** in $CDCl_3$, Figure S20: $^{1}$H NMR spectrum of compound **(*E*)-4b** in $CDCl_3$, Figure S21: $^{13}$C NMR spectrum of compound **(*E*)-4b** in $CDCl_3$, Figure S22: $^{1}$H NMR spectrum of the mixture of **(*Z*)-4c and 3c** in $CDCl_3$, Figure S23: $^{1}$H

NMR spectrum of the mixture of **(*Z*)-4d, (*E*)-4d, and 9d** in $CDCl_3$, Figure S24: $^1H$ NMR spectrum of the mixture of **(*E*)-4e** and **(*Z*)-4e** in $CDCl_3$, Figure S25: $^1H$ NMR spectrum of compound **(*Z*)-4f** in $CDCl_3$, Figure S26: $^{13}C$ NMR spectrum of compound **(*Z*)-4f** in $CDCl_3$, Figure S27: $^1H$ NMR spectrum of compound **11a** in $CDCl_3$, Figure S28: $^{13}C$ NMR spectrum of compound **11a** in $CDCl_3$, Figure S29: $^1H$ NMR spectrum of compound **12a** in $CDCl_3$, Figure S30: $^{13}C$ NMR spectrum of compound **12a** in $CDCl_3$, Figure S31: $^1H$ NMR spectrum of compound **11b** in $CDCl_3$, Figure S32: $^{13}C$ NMR spectrum of compound **11b** in $CDCl_3$, Figure S33: $^1H$ NMR spectrum of compound **12b** in $CDCl_3$, Figure S34: $^{13}C$ NMR spectrum of compound **12b** in $CDCl_3$, Figure S35: $^1H$ NMR spectrum of compound **11c** in $CDCl_3$, Figure S36: $^{13}C$ NMR spectrum of compound **11c** in $CDCl_3$, Figure S37: $^1H$ NMR spectrum of compound **12d** in $CDCl_3$, Figure S38: $^1H$ NMR spectrum of compound **11e** in $CDCl_3$, Figure S39: $^{13}C$ NMR spectrum of compound **11e** in $CDCl_3$, Figure S40: $^1H$ NMR spectrum of compound **11f** in $CDCl_3$, Figure S41: $^{13}C$ NMR spectrum of compound **11f** in $CDCl_3$, Figure S42: $^1H$ NMR spectrum of compound **12f** in $CDCl_3$, Figure S43: $^{13}C$ NMR spectrum of compound **12f** in $CDCl_3$, Figure S44: $^1H$ NMR spectrum of compound **11g** in $CDCl_3$, Figure S45: $^{13}C$ NMR spectrum of compound **11g** in $CDCl_3$, Figure S46: $^1H$ NMR spectrum of compound **12g** in $CDCl_3$, Figure S47: $^{13}C$ NMR spectrum of compound **12g** in $CDCl_3$.

**Author Contributions:** Conceptualization, C.-C.C. and D.-S.L.; methodology, H.-J.C. and C.-C.C.; validation, H.-J.C., C.-C.C., and T.W.; formal analysis, H.-J.C., C.-C.C., and T.W.; investigation, H.-J.C. and C.-C.C.; resources, C.-C.C. and D.-S.L.; data curation, H.-J.C., C.-C.C., and T.W.; writing—original draft preparation, D.-S.L.; writing—review and editing, T.-J.L.; supervision, D.-S.L.; project administration, D.-S.L.; funding acquisition, D.-S.L. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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