**Bis-NHC–Ag/Pd(OAc)₂ Catalytic System Catalyzed Transfer Hydrogenation Reaction**

Hui-Ju Chen, Chien-Cheng Chiu, Tsui Wang, Dong-Sheng Lee * and Ta-Jung Lu

Department of Chemistry, National Chung Hsing University, Taichung 40227, Taiwan; g106051068@mail.nchu.edu.tw (H.-J.C.); d1020510080@mail.nchu.edu.tw (C.-C.C.); s103051053@mail.nchu.edu.tw (T.W.); tjlu@dragon.nchu.edu.tw (T.-J.L.)

* Correspondence: dslee@mail.nchu.edu.tw; Tel.: +886-4-22862547

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

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$_2$H/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.

| Entry | bis-NHC–Ag/Pd (mol %) | TEAF (equiv) | Solvent | Conv. (%) |
|-------|------------------------|-------------|---------|-----------|
| 1     | 0.5                    | 3.0         | DMF     | 44        |
| 2     | 1.0                    | 5.0         | tBuOH   | 67        |
| 3     | 2.0                    | 7.0         | PhMe    | 42        |
| 4     | 1.0                    | 3.0         | DMF     | 74        |
| 5     | 1.0                    | 4.0         | DMF     | >99       |
| 6     | 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$_2$O 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$_2$O (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$_2$CO$_3$ and K$_3$PO$_4$·H$_2$O 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     | $\text{Z-alkene}$ | $\text{Z-alkane}$ | 98            |
| 2     | $\text{E-alkene}$ | $\text{E-alkane}$ | 99            |
| 3     | $\text{Z-isomerized alkene}$ | $\text{Z-isomerized alkane}$ | 99            |
| 4     | $\text{cis-alkene}$ | $\text{(Z)-alkene}$ | 85            |
| 5     | $\text{trans-alkene}$ | $\text{trans-alkane}$ | 99            |
| 6     | $\text{cis-alkene}$ | $\text{cis-alkane}$ | 99            |
| 7     | $\text{trans-alkene}$ | $\text{trans-alkane}$ | 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-diphenylacetylene 3a as the substrate, the use of a DMF/H$_2$O (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$_2$O (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 alkylnes 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 alkylnes 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.
Entry Substrate Condition 2 Time (h) Conv. (%) 3
1 3a
2 3b
3 3c
4 3d
5 3e
6 3f
7 3g
8 3h

In addition to aryl alkynes, the aliphatic alkynes, 10f and 10g, were also investigated in an aqueous medium.

Table 3. Bis-NHC–Ag/Pd(OAc)2 catalytic system catalyzed transfer hydrogenation.

| Entry | Pd Source | Base | Solvent Ratio (DMF/H2O) | Conv. (%) | Z:E:9a |
|-------|-----------|------|-------------------------|-----------|--------|
| 1     | Pd(OAc)2  | NEt3 | 9/1                     | 100       | 94:6:0 |
| 2     | Pd(OAc)2  | NEt3 | 5/5                     | 100       | 93:7:0 |
| 3     | Pd(OAc)2  | NEt3 | 1/9                     | 82        | 93:7:0 |
| 4     | Pd(OAc)2  | NEt3 | 0/1                     | 32        | 93:7:0 |
| 5     | Pd(OAc)2  | K2CO3| 5/5                     | 24        | 96:4:0 |
| 6     | Pd(OAc)2  | K2PO4·H2O | 5/5 | 36 | 97:3:0 |
| 7     | PdCl2(CH3CN)2 | NEt3 | 5/5                  | 100      | 93:7:0 |
| 8     | PdCl2 | NEt3 | 5/5                     | 89        | 94:6:0 |
| 9     | [PdCl2(C3H7)2] | NEt3 | 5/5                     | 82        | 93:7:0 |

1 Reaction conditions: 3a (1.0 mmol), Pd source (1 mol %), bis-NHC–Ag (0.5 mol %), and HCO2H (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.

| 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     | 3b        | B (9/1)     | 24       | 100 (> 99) 4 | 94:6:0  |
| 3     | 3c        | B (9/1)     | 2        | 100 (97) 5  | 30:70:0 |
| 4     | 3c        | A (5/5)     | 24       | 47          | 100:0:0 |
| 5     | 3d        | 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     | 3e        | 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 HCO2H/TEAF (4 equiv) at 80 °C in DMF/H2O mixed solvent (5 mL) under air atmosphere. 2 Condition A: the reaction was carried out at 80 °C in DMF/H2O (5/5); condition B: the reaction was conducted at 80 °C in DMF/H2O (9/1); condition C: the reaction was carried out at 60 °C in DMF/H2O (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.

| Entry | Substrate | Time (h) | 11:12 | GC Yield (%) |
|-------|-----------|----------|-------|--------------|
| 1     | 10a       | 3        | 100:0 | 89           |
| 2     | 10b       | 5        | 0:100 | 34           |
| 3     | 10b       | 0.5      | 100:0 | 92           |
| 4     | 10c       | 3        | 0:100 | 63           |
| 5     | 10c       | 0.5      | 97:3  | 88           |
| 6     | 10c       | 3        | 0:100 | 40           |
| 7     | 10d       | 1        | 100:0 | 83 4         |
| 8     | 10d       | 2        | 0:100 | 80 4         |
| 9     | 10e       | 3        | 100:0 | 72           |
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 13C NMR spectra, found in the Supplementary Materials, were analyzed on a Shimadzu GC-2014 equipped with a capillary flame ionization detector. The synthesis of the bis-NHC–Ag complex was carried out according to our previous report [50].

3.1.1. 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 2 H/TEAF (4 equiv) at 80 °C in DMF/H 2 O (9/1) mixed solvent (5 mL) under air atmosphere. Determined by GC analysis. GC yield is reported and undecane was applied as an internal standard. Isolated yield is reported. The product was 4-ethylaniline. The reaction temperature was 60 °C.

3.1.2. 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 2 H (4 mmol), substrate (1 mmol), and DMF/H 2 O (5 mL). After stirring at 80 °C for 24 h under air, 5 mL of brine were added to the reaction mixture. The aqueous layer was extracted with EtOAc (5 mL × 3). The combined organic phases were obtained with a Finnigan/Thermo Quest MAT 95XL mass spectrometer using either the electron impact (EI) or the electrospray ionization (ESI) method. 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 2 H (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) and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography.

| Entry | Substrate | Time (h) | 11:12 | GC Yield (%) |
|-------|-----------|----------|-------|-------------|
| 10    |           | 2        | 100:0 | 99          |
| 11    |           | 24       | 0:100 | 97          |
| 12    |           | 24       | 100:0 | 78          |
| 13    |           | 24       | 0:100 | 72          |

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

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 2 H (4 mmol), substrate (1 mmol), and DMF/H 2 O (5 mL). After stirring at 80 °C for 24 h under air, 5 mL of brine were added to the reaction mixture. The aqueous layer was extracted with EtOAc (5 mL × 3). The combined organic layers were dried (Na 2 SO 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 N₂

3-Phenylpropanol (2a) (Table 2, entry 1) [63]. ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 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]. ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 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]. ¹H NMR (CDCl₃, 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]. ¹H NMR (CDCl₃, 400 MHz): δ 7.29–7.20 (m, 10H), 6.62 (s, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ 137.2, 130.2, 128.9, 128.2, 127.1.

Aniline (6a) (Table 2, entry 5) [65]. ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 100 MHz): δ 146.3, 129.1, 118.3, 114.9.

(4-(4-Aminophenyl)ethan-1-one (6b) (Table 2, entry 6) [65]. ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 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]. ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 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]. ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 100 MHz): δ 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 ¹H NMR signals at 4.50 ppm (alkyne protons of 3c) and 4.45 ppm (olefin protons of 4c). (Z)-4c: ¹H NMR (CDCl₃, 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 ¹H NMR signals at 6.46 ppm (E-4d) and 5.96 ppm (Z-4d). (Z)-4d: ¹H NMR (CDCl₃, 400 MHz): δ 7.59 (d, J = 7.6 Hz, 2H), 7.40–7.37 (m, 1H), 7.54 (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]. ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 100 MHz): δ 169.1, 137.5, 134.8, 128.9, 128.7, 128.5, 123.8.

Styrene (11a) (Table 5, entry 1) [68]. ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 100 MHz): δ 137.5, 136.8, 128.5, 127.8, 126.2, 113.8.

Ethylbenzene (12a) (Table 5, entry 2) [68]. ¹H NMR (CDCl₃, 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); ¹³C NMR (CDCl₃, 100 MHz): δ 144.2, 128.3, 127.8, 126.5, 28.9, 15.6.

4-Methoxystyrene (11b) (Table 5, entry 3) [69]. ¹H NMR (CDCl₃, 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, 11 Hz, 1H), 5.13 (d, J = 11.2 Hz, 1H), 3.81 (s, 3H); ¹³C NMR (CDCl₃, 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): $\delta$ 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): $\delta$ 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): $\delta$ 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): $\delta$ 137.6, 136.7, 134.8, 129.2, 126.1, 112.7, 21.2.

4-Ethylaniline (12d) (Table 5, entry 8) [70]. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 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): $\delta$ 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); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 155.7, 149.4, 136.9, 136.4, 122.4, 121.1, 118.1.

Dodecene (11g) (Table 5, entry 10) [72]. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 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): $\delta$ 139.7, 114.1, 33.8, 31.9, 29.6, 29.5, 29.2, 29.0, 22.7, 14.1.

Dodecane (12f) (Table 5, entry 11) [73]. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 1.36–1.20 (m, 20H), 0.88 (t, $J = 6.8$ Hz, 6H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 31.9, 29.7, 29.4, 22.7, 14.1.

Undec-10-en-1-ol (12c) (Table 5, entry 12) [74]. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 5.81 (dd, $J = 17.2$, 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): $\delta$ 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): $\delta$ 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): $\delta$ 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-NHC–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)-1H-benzo[d]imidazole in CDCl$_3$, Figure S2: $^{13}$C NMR spectrum of 1-(4-methoxyphenyl)-1H-benzo[d]imidazole in CDCl$_3$, Figure S3: $^1$H NMR spectrum of 5,5′-(pentane-1,5-diyl)bis(1-(4-methoxyphenyl)-1H-benzo[d]imidazol-3-ium) bromide in CD$_2$OD, Figure S4: $^{13}$C NMR spectrum of 5,5′-(pentane-1,5-diyl)bis(1-(4-methoxyphenyl)-1H-benzo[d]imidazol-3-ium) bromide in CD$_2$OD, 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: $^{13}$C 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 CDCl₃, Figure S24: ¹H NMR spectrum of the mixture of (E)-4e and (Z)-4e in CDCl₃, Figure S25: ¹H NMR spectrum of compound (Z)-4f in CDCl₃, Figure S26: ¹³C NMR spectrum of compound (Z)-4f in CDCl₃, Figure S27: ¹H NMR spectrum of compound 11a in CDCl₃, Figure S28: ¹³C NMR spectrum of compound 11a in CDCl₃, Figure S29: ¹H NMR spectrum of compound 12a in CDCl₃, Figure S30: ¹³C NMR spectrum of compound 12a in CDCl₃, Figure S31: ¹H NMR spectrum of compound 11b in CDCl₃, Figure S32: ¹³C NMR spectrum of compound 11b in CDCl₃, Figure S33: ¹H NMR spectrum of compound 12b in CDCl₃, Figure S34: ¹³C NMR spectrum of compound 12b in CDCl₃, Figure S35: ¹H NMR spectrum of compound 11c in CDCl₃, Figure S36: ¹³C NMR spectrum of compound 11c in CDCl₃, Figure S37: ¹H NMR spectrum of compound 12d in CDCl₃, Figure S38: ¹H NMR spectrum of compound 11e in CDCl₃, Figure S39: ¹³C NMR spectrum of compound 11e in CDCl₃, Figure S40: ¹H NMR spectrum of compound 11f in CDCl₃, Figure S41: ¹³C NMR spectrum of compound 11f in CDCl₃, Figure S42: ¹H NMR spectrum of compound 12f in CDCl₃, Figure S43: ¹³C NMR spectrum of compound 12f in CDCl₃, Figure S44: ¹H NMR spectrum of compound 11g in CDCl₃, Figure S45: ¹³C NMR spectrum of compound 11g in CDCl₃, Figure S46: ¹H NMR spectrum of compound 12g in CDCl₃, Figure S47: ¹³C NMR spectrum of compound 12g in CDCl₃.

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.

Funding: This research was funded by the Ministry of Science and Technology of the Republic of China, grant number 107WFA0510613.

Acknowledgments: We thank the National Center for High-performance Computing (NCHC) for providing computational and storage resources.

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

References
1. Herrmann, W.A. N-Heterocyclic Carbenes: A New Concept in Organometallic Catalysis. *Angew. Chem. Int. Ed.* 2002, 41, 1290–1309. [CrossRef]
2. Fortman, G.C.; Nolan, S.P. N-Heterocyclic carbene (NHC) ligands and palladium in homogeneous cross-coupling catalysis: A perfect union. *Chem. Soc. Rev.* 2011, 40, 5151–5169. [CrossRef] [PubMed]
3. Hopkinson, M.N.; Richter, C.; Schedler, M.; Glorius, F. An overview of N-heterocyclic carbenes. *Nature* 2014, 510, 485–496. [CrossRef] [PubMed]
4. Froese, R.D.J.; Lombardi, C.; Pompeo, M.; Rucker, R.P.; Organ, M.G. Designing Pd-N-Heterocyclic Carbene Complexes for High Reactivity and Selectivity for Cross-Coupling Applications. *Acc. Chem. Res.* 2017, 50, 2244–2253. [CrossRef] [PubMed]
5. Peris, E. Smart N-Heterocyclic Carbene Ligands in Catalysis. *Chem. Rev.* 2018, 118, 9988–10031. [CrossRef] [PubMed]
6. Marion, N.; Nolan, S.P. Well-Defined N-Heterocyclic Carbenes–Palladium(II) Precatalysts for Cross-Coupling Reactions. *Acc. Chem. Res.* 2008, 41, 1440–1449. [CrossRef] [PubMed]
7. Monot, J.; Brahim, M.M.; Ueng, S.-H.; Robert, C.; Murr, M.D.; Curran, D.P.; Malacria, M.; Fensterbank, L.; Lacôte, E. Suzuki-Miyaura Coupling of NHC-Boranes: A New Addition to the C–C Coupling Toolbox. *Org. Lett.* 2009, 11, 4914–4917. [CrossRef]
8. Kose, O.; Saito, S. Cross-coupling reaction of alcohols for carbon–carbon bond formation using pincer-type NHC/Palladium catalysts. *Org. Biomol. Chem.* 2010, 8, 896–900. [CrossRef]
9. Yong, B.S.; Nolan, S.P. Transition Metal-Carbene Complexes in Homogeneous Catalysis. *Chemtracts: Org. Chem.* 2003, 16, 205–227. [CrossRef]
10. Sprengers, J.W.; Wassenaar, J.; Clement, N.D.; Cavell, K.J.; Elsevier, C.J. Palladium–(N-Heterocyclic Carbene) Hydrogenation Catalysts. *Angew. Chem. Int. Ed.* 2005, 44, 2026–2029. [CrossRef]
11. Liu, L.-J.; Wang, F.; Shi, M. Synthesis of Chiral Bis(N-heterocyclic carbene) Palladium and Rhodium Complexes with 1,1′-Biphenyl Scaffold and Their Application in Asymmetric Catalysis. *Organometallics* 2009, 28, 4416–4420. [CrossRef]
12. Brieger, G.; Nestrick, T.J. Catalytic Transfer Hydrogenation. *Chem. Rev.* 1974, 74, 567–580. [CrossRef]
13. Backvall, J.-E. Transition metal hydrides as active intermediates in hydrogen transfer reactions. *J. Organomet. Chem.* 2002, 652, 105–111. [CrossRef]
14. Gladioli, S.; Alberico, E. Asymmetric transfer hydrogenation: Chiral ligands and applications. *Chem. Soc. Rev.* 2006, 35, 226–236. [CrossRef] [PubMed]
15. Samec, J.S.M.; Backvall, J.-E.; Andersson, P.G.; Brandt, P. Mechanistic aspects of transition metal-catalyzed hydrogen transfer reactions. Chem. Soc. Rev. 2006, 35, 237–248. [CrossRef]

16. Wang, D.; Astruc, D. The Golden Age of Transfer Hydrogenation. Chem. Rev. 2015, 115, 6621–6686. [CrossRef]

17. Lorca, M.; Kuhn, D.; Kuros, M. Selective reduction of aldehydes via BINOL–Zr complex. Tetrahedron Lett. 2001, 42, 6243–6246. [CrossRef]

18. Selvam, P.; Sonavane, S.U.; Mohapatra, S.K.; Jayaram, R.V. Chemoselective Reduction of α,β-Unsaturated Carbonyls over Novel Mesoporous CoNMA Molecular Sieves under Hydrogen Transfer Conditions. Adv. Synth. Catal. 2004, 346, 542–544. [CrossRef]

19. Miecznikowski, J.R.; Crabtree, R.H. Hydrogen Transfer Reduction of Aldehydes with Alkali-Metal Carbonates and Iridium NHC Complexes. Organometallics 2004, 23, 629–631. [CrossRef]

20. Naskar, S.; Bhattacharjee, M. Ruthenium cationic properties of transfer hydrogenation of aldehydes: Synthesis and catalytic properties of [(PPPh2)2Ru(CH2CN)3Cl]*[A*] (A* = BPh4 or ClO4) and structure of [(PPPh2)2Ru(CH2CN)3Cl]*[BPh4]. J. Organomet. Chem. 2005, 690, 5006–5010. [CrossRef]

21. Baratta, W.; Siega, K.; Rigo, P. Fast and Chemoselective Transfer Hydrogenation of Aldehydes Catalyzed by a Terdentate CNN Complex [RuCl(CN)2(dpbb)]. Adv. Synth. Catal. 2007, 349, 1633–1636. [CrossRef]

22. Zweifel, T.; Naubron, J.V.; Büttner, T.; Ott, T.; Grützmacher, H. Ethanol as Hydrogen Donor: Highly Efficient Transfer Hydrogenations with Rhodium(I) Amides. Angew. Chem. Int. Ed. 2008, 47, 3245–3249. [CrossRef] [PubMed]

23. Wang, D.; Deraedt, C.; Ruiz, J.; Astruc, D. Sodium hydroxide-catalyzed transfer hydrogenation of carbonyl compounds and nitroarenes using ethanol or isopropanol as both solvent and hydrogen donor. J. Mol. Catal. A. Chem. 2015, 400, 14–21. [CrossRef]

24. Castellanos-Blanco, N.; Arévalo, A.; Garcia, J.J. Nickel-Catalyzed Transfer Hydrogenation of Ketones Using Ethanol as Solvent and Hydrogen Donor. Dalton Trans. 2016, 45, 13604–13614. [CrossRef] [PubMed]

25. Enthaler, S. Carbon Dioxide-The Hydrogen-Storage Material of the Future? ChemSusChem 2008, 1, 801–804. [CrossRef] [PubMed]

26. Jou, F. Breakthroughs in hydrogen storage-Formic Acid as a Sustainable Storage Material for Hydrogen. ChemSusChem 2008, 1, 805–808. [CrossRef] [PubMed]

27. Johnson, T.C.; Morris, D.J.; Wills, M. Hydrogen generation from formic acid and alcohols using homogeneous catalysts. Chem. Soc. Rev. 2010, 39, 81–88. [CrossRef]

28. Bodden, A.; Gartner, F.; Federsel, C.; Sponholz, P.; Mellmann, D.; Jackstell, R.; Junge, H.; Beller, M. CO2= “Neutral” Hydrogen Storage Based on Bicarbonates and Formates. Angew. Chem. Int. Ed. 2011, 50, 6411–6414. [CrossRef]

29. Bi, Q.-Y.; Lin, J.-D.; Liu, Y.-M.; He, H.-Y.; Huang, F.-Q.; Cao, Y. Dehydrogenation of Formic Acid at Room Temperature: Boosting Palladium Nanoparticle Efficiency by Coupling with Pyridinic Nitrogen-Doped Carbon. Angew. Chem. Int. Ed. 2016, 55, 11849–11853. [CrossRef]

30. Cavell, K.J.; McGuinness, D.S. Redox processes involving hydrocarbylmetal (N-heterocyclic carbene) complexes and associated imidazolium salts: Ramifications for catalysis. Coord. Chem. Rev. 2004, 248, 671–681. [CrossRef]

31. McGuinness, D.S.; Green, M.J.; Cavell, K.J.; Skelton, B.W.; White, A.H. Synthesis and reaction chemistry of mixed ligand methylpalladium–carbene complexes. J. Organomet. Chem. 1998, 565, 165–178. [CrossRef]

32. McGuinness, D.S.; Cavell, K.J.; Skelton, B.W.; White, A.H. Zerovalent Palladium and Nickel Complexes of Heterocyclic Carbeneres: Oxidative Addition of Organic Halides, Carbon–Carbon Coupling Processes, and the Heck Reaction. Organometallics 1999, 18, 1596–1605. [CrossRef]

33. Arnold, P.L.; Cloke, G.N.; Geldbach, T.; Hitchcock, P.B. Metal Vapor Synthesis as a Straightforward Rout to Group 10 Homoleptic Carbene Complexes. Organometallics 1999, 18, 3228–3233. [CrossRef]

34. Cavell, K.J. N-Heterocyclic carbenes/imidazolium salts as substrates in catalysis: The catalytic 2-substitution and annulation of heterocyclic compounds. Dalton Trans. 2008, 6676–6685. [CrossRef]

35. Clement, N.D.; Cavell, K.J.; Jones, C.; Elsevier, C.J. Oxidative Addition of Imidazolium Salts to Ni0 and Pd0: Synthesis and Structural Characterization of Unusually Stable Metal-Hydride Complexes. Angew. Chem. Int. Ed. 2004, 43, 1277–1279.

36. Hauwert, P.; Maestri, G.; Sprengers, J.W.; Catellani, M.; Elsevier, C.J. Transfer Semihydrogenation of Alkynes Catalyzed by a Zero-Valent Palladium N-Heterocyclic Carbene Complex. Angew. Chem. Int. Ed. 2008, 47, 3223–3226. [CrossRef]

37. Hauwert, P.; Boeierlei, R.; Warsink, S.; Weigand, J.J.; Elsevier, C.J. Mechanism of Pd(NHC)-Catalyzed Transfer Hydrogenation of Alkenes. J. Am. Chem. Soc. 2010, 132, 16900–16910. [CrossRef]

38. Warsink, S.; Bosman, S.; Weigand, J.J.; Elsevier, C.J. Rigid pyriyl substituted NH2 ligands, their Pd(0) complexes and their application in selective transfer semihydrogenation of alkenes. Appl. Organomet. Chem. 2011, 25, 276–282. [CrossRef]

39. Tromp, D.S.; Hauwert, P.; Elsevier, C.J. Synthesis of bis-N-alkyl imidazolium salts and their palladium(0)(NHC)(η2-MA)2 complexes. Appl. Organometallic Chem. 2012, 26, 335–341. [CrossRef]

40. Hauwert, P.; Dunsford, J.J.; Tromp, D.S.; Weigand, J.J.; Lutz, M.; Cavell, K.J.; Elsevier, C.J. Zerovalent [Pd(NHC)(alkene)]2 Complexes Bearing Expanded-Ring N-Heterocyclic Carbene Ligands in Transfer Hydrogenation of Alkenes. Organometallics 2013, 32, 131–140. [CrossRef]

41. Drost, R.M.; Bouwens, T.; van Leeuwen, N.P.; de Bruin, B.; Elsevier, C.J. Convenient Transfer Semihydrogenation Methodology for Alkenes using a Pd0-NHC Precatalyst. ACS Catal. 2014, 4, 1349–1357. [CrossRef]

42. Broggi, J.; Jurčík, V.; Songis, O.; Poater, A.; Cavallo, L.; Slawin, A.M.Z.; Cazin, C.S.J. The Isolation of [Pd(OC(O)H)(H)(NHC)(PR3)] (NHC = N-Heterocyclic Carbene) and Its Role in Alene and Alynes Reductions Using Formic Acid. J. Am. Chem. Soc. 2013, 135, 4588–4591. [CrossRef] [PubMed]
43. Sluijter, S.N.; Warsink, S.; Lutz, M.; Elsevier, C.J. Synthesis of palladium(0) and -(II) complexes with chelating bis(N-heterocyclic carbene) ligands and their application in semihydrogenation. *Dalton Trans.* 2013, 42, 7365–7372. [CrossRef] [PubMed]

44. Ranganath, K.V.S.; Kloesges, J.; Schafer, A.H.; Clorius, F. Asymmetric Nanocatalysis: N-Heterocyclic Carbenes as Chiral Modifiers of FeO$_3$/Pd nanoparticles. *Angew. Chem. Int. Ed.* 2010, 49, 7786–7789. [CrossRef] [PubMed]

45. Planellas, M.; Pleixats, R.; Shafir, A. Palladium Nanoparticles in Suzuki Cross-Couplings: Tapping into the Potential of Tris-Imidazolium Salts for Nanoparticle Stabilization. *Adv. Synth. Catal.* 2012, 354, 651–662. [CrossRef]

46. Khazipov, O.V.; Chevchenko, M.A.; Chemenko, A.Y.; Astakhov, A.V.; Pasyukov, D.V.; Eremin, D.B.; Zubavivhus, Y.V.; Khrustalev, V.N.; Chemyshev, V.M.; Ananikov, V.P. Fast and Slow Release of Catalytically Active Species in Metal/NHC Systems Induced by Aliphatic Amines. *Organometallics* 2018, 37, 1483–1492. [CrossRef]

47. Chemyshev, V.M.; Denisova, E.A.; Eremin, D.B.; Ananikov, V.P. The key role of R-NHC couplings (R = C, H, heteroatom) and M–NHC bond cleavage in the evolution of M/NHC complexes and formation of catalytically active species. *Chem. Sci.* 2020, 11, 6957–6977. [CrossRef]

48. Cerezo-Navarrete, C.; Lara, P.; Martinez-Prieto, L.M. Organometallic Nanoparticles Ligated by NHCs: Synthesis, Surface Chemistry and Ligand Effects. *Catalysts* 2020, 10, 1144. [CrossRef]

49. Lin, Y.-R.; Chiu, C.-C.; Chiu, H.-T.; Lee, D.-S.; Lu, T.-J. Bis-benzimidazolium-palladium system catalyzed Suzuki-Miyaura coupling reaction of aryl bromides under mild conditions. *Appl. Organometal. Chem.* 2018, 32, e3896. [CrossRef]

50. Chiu, C.-C.; Chiu, H.-T.; Lee, D.-S.; Lu, T.-J. An efficient class of bis-NHC salts: Applications in Pd-catalyzed reactions under mild reaction conditions. *RSC Adv.* 2018, 8, 26407–26415. [CrossRef]

51. Arterburn, J.B.; Pannala, M.; Gonzalez, A.M.; Chamberlin, R.M. Palladium-catalyzed transfer hydrogenation in alkaline aqueous medium. *Tetrahedron Lett.* 2000, 41, 7847–7849. [CrossRef]

52. Shirakawa, E.; Otuska, H.; Hayashi, T. Reduction of alkynes into 1,2-dideuterioalkenes with hexamethyldisilane and deuterium oxide in the presence of a palladium catalyst. *Chem. Commun.* 2005, 2005, 5885–5886. [CrossRef]

53. Luo, F.; Pan, C.; Wang, W.; Ye, Z.; Cheng, J. Palladium-catalyzed reduction of alkynes employing HSiEt$_3$: Stereoselective synthesis of trans- and cis-alkenes. *Tetrahedron* 2010, 66, 1399–1403. [CrossRef]

54. Xuan, Q.; Song, Q. Diboron-Assisted Palladium-Catalyzed Hydrogenation of N-Heteroaromatics with Water as Hydrogen Donor and Solvent. *Org. Lett.* 2016, 18, 4250–4253. [CrossRef] [PubMed]

55. Liu, T.; Zeng, Y.; Zhang, H.; Wei, T.; Wu, X.; Li, N. Facile Pd-catalyzed chemoselective transfer hydrogenation of olefins using formic acid in water. *Tetrahedron Lett.* 2016, 57, 4845–4849. [CrossRef]

56. Rao, S.; Prabhu, K.R. Stereodivergent Alkyne Reduction by using Water as the Hydrogen Source. *Chem. Eur. J.* 2018, 24, 13954–13962. [CrossRef]

57. Zhao, C.-Q.; Chen, T.-G.; Giu, H.; Wei, L.; Fang, P.; Mei, T.-S. Water as a hydrogenating agent: Stereodivergent Pd-catalyzed semihydrogenation of alkynes. *Org. Lett.* 2019, 21, 1412–1416. [CrossRef]

58. Wang, W.; Gao, L.; Wei, H.; Qi, Z.-H.; Zeng, G.; Cheng, X.; Wang, G.; Ma, J. Selectivity control of Pd-(PMe$_3$)$_2$-catalyzed hydrogenation of internal alkynes to E-alkenies by reaction time and water content in formic acid. *Dalton Trans.* 2019, 48, 10033–10042. [CrossRef]

59. De, S.; Udvardy, A.; Czégregé, C.E.; Joó, F. Poly-N-heterocyclic carbene complexes with applications in aqueous media. *Coord. Chem. Rev.* 2019, 400, 213038. [CrossRef]

60. Liu, J.-Q.; Gou, X.-X.; Han, Y.-F. Chelating Bis(N-Heterocyclic Carbene) Palladium-Catalyzed Reactions. *Chem. Asian J.* 2018, 13, 2257–2276. [CrossRef]

61. Enthaler, S.; Haberberger, M.; Irran, E. Highly Selective Iron-Catalyzed Synthesis of Alkenes by the Reduction of Alkynes. *Chem. Asian J.* 2011, 6, 1613–1623. [CrossRef] [PubMed]

62. Iwasaki, R.; Tanaka, E.; Ichihashi, T.; Idenoto, Y.; Endo, K. Semireduction of Alkynes Using Formic Acid with Reusable Pd-Catalysts. *J. Org. Chem.* 2018, 83, 13574–13579. [CrossRef] [PubMed]

63. Jia, Z.; Zhou, F.; Liu, M.; Li, X.; Chan, A.S.C.; Li, C.J. Silver-Catalyzed Hydrogenation of Aldehydes in Water. *Angew. Chem. Int. Ed.* 2013, 52, 11871–11874. [CrossRef]

64. Jurčík, V.; Nolan, S.P.; Cazin, C.S.J. Hydrogenation of C=C Multiple Bonds Mediated by [Pd(NHC)(PCy$_3$)$_2$] (NHC = N-Heterocyclic Carbene) under Mild Reaction Conditions. *Chem. Eur. J.* 2009, 15, 2509–2511. [CrossRef] [PubMed]

65. Zhou, Y.; Zhou, H.; Liu, S.; Pi, D.; Shen, G. Water as a hydrogen source in palladium-catalyzed reduction and reductive amination of nitroarenes mediated by diboronic acid. *Tetrahedron* 2017, 73, 3898–3904. [CrossRef]

66. Zhao, Y.; Liu, Q.; Li, J.; Liu, Z.; Zhou, B. Highly Selective Semihydrogenation of Phentalkynes to (Z)-Styrenes Using Hantzsch Ester 1,4-Dihydropyridine Catalyzed by Pd/C. *Synlett* 2010, 2010, 1870–1872. [CrossRef]

67. Byrne, P.A.; Gilheaney, D.G. Unequivocal experimental evidence for a unified Li salt-free Wittig reaction mechanism for all phosphonium ylide types: Reactions with b-heteroatom substituted aldehydes are consistently selective for cis-oxaphosphetane derived products. *J. Am. Chem. Soc.* 2012, 134, 9225–9239. [CrossRef]

68. Espinal-Viguri, M.; Neale, S.E.; Coles, N.T.; Macgregor, S.A.; Webster, R.L. Room Temperature Iron-Catalyzed Transfer Hydrogenation and Regioselective Deuteration of Carbon-Carbon Double Bonds. *J. Am. Chem. Soc.* 2019, 141, 572–582. [CrossRef]

69. Chen, W.; Tao, H.; Huang, W.; Wang, G.; Li, S.; Cheng, X.; Li, G. Hantzsch Ester as a Photosensitizer for the Visible-Light-Induced Degradation of Vicinal Dibromo Compounds. *Chem. Eur. J.* 2016, 22, 9546–9550. [CrossRef]
70. Zhou, M.; Li, T.; Xu, B. Easy-handling and Low-leaching Heterogeneous Palladium and Platinum Catalysis via Coating with a Silicone Elastomer. *Tetrahedron Lett.*, **2019**, *60*, 948–952. [CrossRef]

71. Buxaderas, E.; Volpe, M.A.; Radivoy, G. Selective Semi-hydrogenation of Terminal Alkynes Promoted by Bimetallic Cu-Pd Nanoparticles. *Synthesis* **2018**, *51*, 1466–1472.

72. Bao, H.; Zhou, B.; Jin, H.; Liu, Y. Diboron-Assisted Copper-Catalyzed Z-Selective Semihydrogenation of Alkynes Using Ethanol as a Hydrogen Donor. *J. Org. Chem.* **2019**, *84*, 3579–3589. [CrossRef]

73. 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. [CrossRef]

74. Zhao, S.; Mankad, N.P. Cu-Catalyzed Hydroxymethylation of Unactivated Alkyl Iodides with CO to Provide One-Carbon-Extended Alcohols. *Angew. Chem. Int. Ed.* **2018**, *57*, 5867–5870. [CrossRef] [PubMed]