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A New Phenoxide Chelated Ir^{III} N-Heterocyclic Carbene Complex and Its Application in Reductive Amination Reactions

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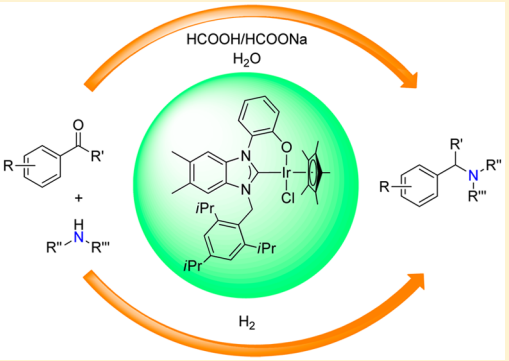
Supporting Information

ABSTRACT: A new phenoxide chelated [Ir(NHC)Cp*Cl] (NHC = N-heterocyclic carbene; Cp* = pentamethylcyclopentadienyl) complex (**3**) has been prepared by reaction of $[IrCp^*Cl_2]_2$ with an in situ prepared NHC−Ag complex in dichloromethane at ambient temperature. The Ir^{III} complex was stable toward air and moisture and was fully characterized by ^1H, ^{13}C NMR, HRMS, and single-crystal X-ray diffraction. The new complex was found to be an active catalyst for transfer hydrogenative reductive amination under aqueous conditions with formate as hydrogen source as well as hydrogenative reductive amination reactions using H_2. Various carbonyl compounds such as aliphatic and aromatic ketones and aldehydes were successfully reacted with amines to give new amines. In comparison with transfer hydrogenative reductive amination, the reductive amination with H_2 is faster and permits higher molar ratios of the substrate to the catalyst (S/C).



INTRODUCTION

Amines are one of the highly valuable compounds in chemical synthesis, widely found in natural products, fine chemicals, pharmaceuticals, and agrochemicals[1] Reductive amination (RA), the coupling of ketones or aldehydes with amines in the presence of a reducing agent, is one of the most powerful methods for one-step synthesis of substituted amines.[2] This method is extremely valuable from a synthetic point of view, since it avoids the isolation of in situ generated imine products, which is not easy due to the limited stability of imines. In most of the RA procedures developed, stoichiometric boron hydride reduction and heterogeneous hydrogenation dominate the scene.[1b,e] However, the use of stoichiometric amounts of boron hydrides generates copious amounts of waste and is associated with other problems such as toxicity issues. One of the most notable drawbacks of heterogeneous catalysts in RA applications is their poor chemoselectivity.[1b] Progress in developing homogeneous catalytic systems, including organometallic hydrogenative[3] and transfer hydrogenative RA protocols,[4] has been made in recent years. *However, there appears to be no catalysts that are highly effective for both hydrogenative and transfer hydrogenative RA reactions.* Such catalysts would be practically advantageous, as a single catalyst could allow one to explore either conditions or a condition that is more desired.

Recently, N-heterocyclic carbenes (NHCs) have emerged as a versatile class of ligands in organometallic chemistry and catalysis. NHCs often form stable complexes with many transition metals irrespective of their oxidation states.[5] Additionally, their tunable character allows for the easy control of the electronic and steric properties at the metal center. In the area of catalysis, NHC-bearing transition metal complexes have found numerous applications. An example is NHC−iridium complexes, which have been successfully employed as catalysts for a number of reactions, such as hydrogenation,[6] transfer hydrogenation (TH),[7] and N-alkylation of amines.[8] However, there are only two studies of RA reactions using NHC−metal complexes. Crabtree and co-workers attempted RA of benzaldehyde with 2-propanol as hydrogen source, using a cationic triazol-5-ylidene complex of iridium(I) as catalyst. A two-step procedure was used. In the first stage, the imine was formed in situ by stirring 1 equiv of aniline with benzaldehyde, and the NHC−Ir(I) catalyst was then added in the second stage to reduce the imine.[9] In a more recent study, a polymer supported NHC−Pd complex was used for hydrogenative RA of different aldehydes and cyclohexanone in aqueous reaction medium at 35 bar of hydrogen pressure.[10]

In this paper, a new phenoxide chelated neutral NHC−Ir(III) complex (**3**) was synthesized and fully characterized. This complex is found to be an active catalyst for RA of various ketones and aldehydes by transfer hydrogenation under aqueous conditions with formate as hydrogen source. Remarkably, the same complex also successfully catalyzes hydrogenative RA of various carbonyl compounds with molecular hydrogen. To the best of our knowledge, this NHC−Ir(III) catalytic system is the first example of a catalyst that is capable of both transfer hydrogenative and hydrogenative RA of various ketones and aldehydes.

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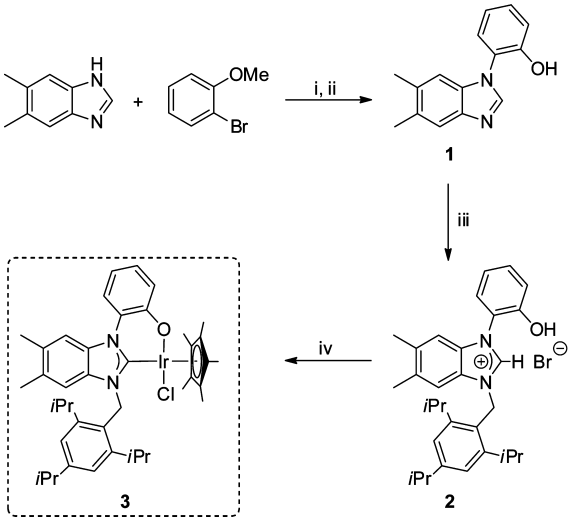
RESULTS AND DISCUSSION

Synthesis and Characterization of the NHC Complex. Scheme 1 outlines the route used for the title complex (**3**). The

Scheme 1. Synthesis of Ligands and Complex (1−3)[a]



[a](i) KOH, Cu_2O, DMSO, 140 °C, 24 h; (ii) HBr (47% aqueous solution), reflux, 48 h then $NaHCO_3$; (iii) 2,4,6-triisopropylbenzyl bromide, MeCN, reflux, 4 h; (iv) Ag_2O, CH_2Cl_2, room temperature, 2 h, then $[IrCp^*Cl_2]_2$, 2 h.

1-(2-hydroxyphenyl)-5,6-dimethylbenzimidazole ligand (**1**) was synthesized via copper catalyzed N-arylation of 5,6-dimethyl-1*H*-benzimidazole with 2-bromoanisole and subsequent demethylation of the corresponding anisole derivative (Scheme 1). The NHC precursor 5,6-dimethylbenzimidazolium salt (**2**) was synthesized by the reaction of **1** with 2,4,6-triisopropylbenzyl bromide in refluxing acetonitrile (Scheme 1). The salt was obtained in 97% yield as a colorless solid. In the ^{1}H NMR spectrum of **2**, the NC*H*N$^+$ proton appears at δ = 8.39 ppm, and this downfield signal indicates the formation of 5,6-dimethylbenzimidazolium salt. The presence of the phenolic OH proton was confirmed by an exchange experiment with D_2O, upon addition of which the signal at δ = 10.08 ppm in the ^{1}H NMR spectrum disappeared.

The new neutral phenoxide chelated NHC−Ir complex (**3**) was prepared by transmetalation[11] from the in situ formed NHC−Ag derivative by employing a two-step process (Scheme 1). The NHC−Ag species was not isolated, however. In the second step, addition of $[IrCp^*Cl_2]_2$ to the reaction mixture gave the complex **3** in 93% yield as an air- and moisture-stable yellow solid. Formation of **3** was confirmed by HRMS analysis and NMR spectroscopic analysis, which showed the characteristic Ir−$C_{carbene}$ signal at δ = 174.1 ppm in the ^{13}C NMR spectrum. Meanwhile, the characteristic downfield signal for the NC*H*N$^+$ proton of **2** at δ = 8.39 ppm disappeared in the ^{1}H NMR spectrum. Disappearance of the phenolic OH proton signal at δ = 10.08 ppm in **2** also supports the formation of phenoxide chelated complex **3**. Finally, the structure of complex **3** was determined by single-crystal X-ray diffraction analysis, which confirmed the coordination of NHC and phenoxide group to the iridium center (Figure 1). The average Ir−$C_{carbene}$ (2.003 Å) and Ir−O (2.090 Å) distances are both in the expected range.[8a] It is noted that, while a great number of

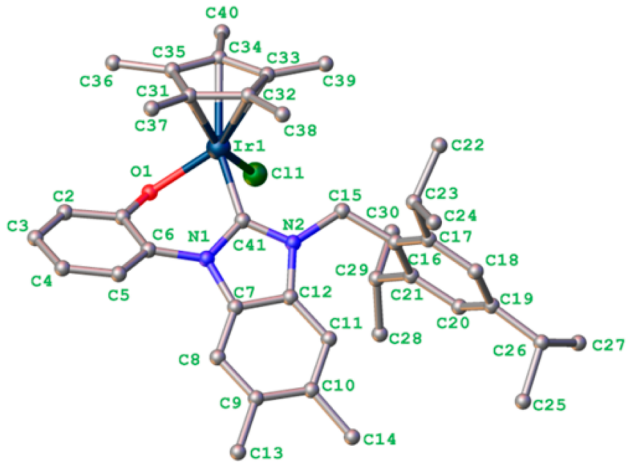


Figure 1. Molecular structure of **3** with hydrogen atoms removed for clarity. The crystal structure includes two symmetry-independent complexes (**3** and **3-A**, only one shown here) in the asymmetric unit with only small differences in bond distances and bond angles. Selected bond lengths [Å] and angles [deg]: **3**: Ir(1)−C(41) 2.003(4), Ir(1)−O(1) 2.092(3), Ir(1)−Cl(1) 2.418(1), C(41)−Ir(1)−O(1) 82.8(2), C(41)−Ir(1)−Cl(1) 88.6(1), O(1)−Ir(1)−Cl(1) 84.2(9). **3-A**: Ir(1A)−C(41A) 2.003(4), Ir(1A)−O(1A) 2.087(3), Ir(1A)−Cl(1A) 2.416(1), C(41A)−Ir(1A)−O(1A) 83.7(1), C(41A)−Ir-(1A)−Cl(1A) 86.1(1), O(1A)−Ir(1A)−Cl(1A) 84.4(9).

chelating−NHC−Ir complexes are known, those featuring a C^O coordination mode are few.[8a,12]

Transfer Hydrogenative RA Reactions in Water. We have recently shown that water is a good solvent for transfer hydrogenative RA with related iridicycle catalysts.[4g] We, therefore, decided to explore whether or not **3** could catalyze aqueous RA, using acetophenone and *p*-anisidine as model substrates and formate as hydrogen source (Figure 2). It is known that both the catalytic activity and the selectivity can be influenced dramatically by the pH of the reaction medium in aqueous RA reactions.[4g] Imine formation from the ketone and amine and the subsequent imine reduction are known to

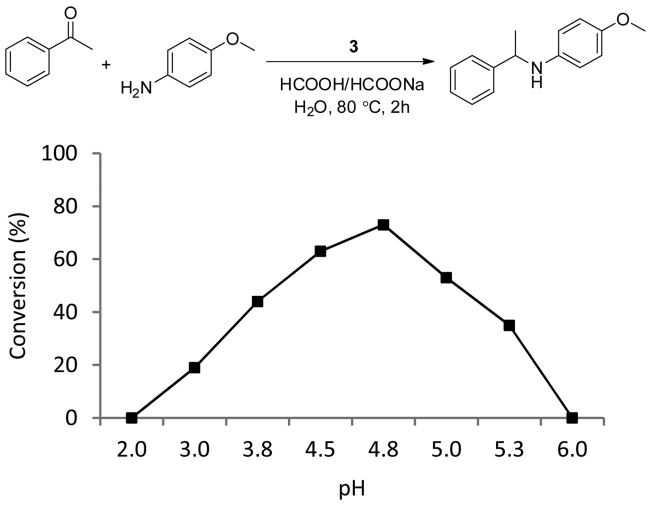


Figure 2. Effect of the pH value on the RA in water. Reaction conditions: acetophenone (0.5 mmol), *p*-anisidine (1.0 mmol), **3** (0.005 mmol, 1 mol %), aqueous HCOOH/HCOONa solution (0.8 mL, 10 mol L^{-1}), 80 °C, 2 h. Conversions were determined by ^{1}H NMR spectroscopy.

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benefit from acidic conditions. With this in mind, we first examined the effect of the solution pH on the model reaction, by using HCOOH and HCOONa to adjust the pH values. The reduction was carried out at 80 °C at a molar ratio of the substrate to the catalyst (S/C) of 100:1 for 2 h. As can be seen in Figure 2, the best catalytic activity was observed at pH 4.8, under which the corresponding amine was obtained in 73% conversion. Pleasingly, in all the pH values examined, the desired amine was observed as the sole product, without any byproduct, e.g., 2-phenylethanol, by reducing acetophenone. This is in contrast to the RA with the iridicycle catalysts, where ketone reduction becomes significant when the solution pH deviates from the optimal value.[4g]

Further studies showed that the reaction temperature is also critical for the completion of the RA reaction with catalyst **3**. The reaction at 80 °C was very fast before reaching approximately 75% conversion. However, it became sluggish thereafter, showing little progress in longer reaction times (e.g., 82% conversion within 24 h). This may result from the decomposition of formic acid at higher reaction temperature, depleting the hydride source. Some related iridium complexes have been shown to be active catalysts for the dehydrogenation of formic acid.[13] Bearing this in mind, we decreased the reaction temperature to 50 °C, and pleasingly, this led to complete conversion of acetophenone to the corresponding amine in 16 h. Percentage conversion was calculated by comparing the methyl proton signals of acetophenone and 4-methoxy-*N*-(1-phenylethyl)aniline in the ^{1}H NMR spectrum of the crude product, and the time-dependent conversions were followed (Figure 3). Under these conditions, the product was

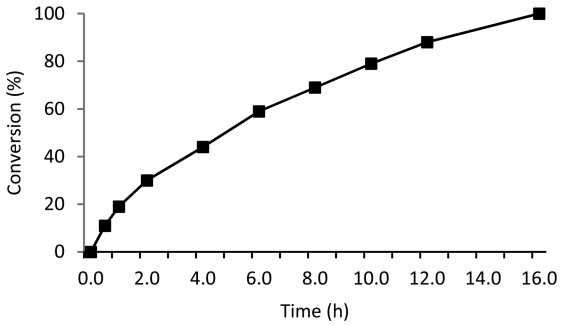

Figure 3. Time course of the RA in water. Reaction conditions: acetophenone (0.5 mmol), *p*-anisidine (1.0 mmol), **3** (0.005 mmol, 1 mol %), aqueous HCOOH/HCOONa solution (0.8 mL, 10 mol L^{-1}), 50 °C. Conversions were determined by ^{1}H NMR spectroscopy.

isolated in 90% yield. Additionally, a control experiment with $[IrCp^*Cl_2]_2$ as catalyst was carried out, and the desired amine obtained only 29% conversion under these conditions in 16 h.

The optimized conditions were applied to various carbonyl compounds and amines (Table 1). Aromatic ketones with electron-withdrawing or electron-donating substituents all reacted with *p*-anisidine, affording good yields (76–90%) in 16 h at 50 °C at an S/C of 100 (Table 1, entries 1–4). Similar activities were observed for the reaction of different aromatic amines with acetophenone (79–83%) (Table 1, entries 5–7). The electronic effects of these substituents on the RA are not obvious for these substrates under the conditions employed.

Reactions of aliphatic ketones with *p*-anisidine were investigated next. These ketones showed higher activity than the aromatic ones. Thus, complete conversions and higher isolated yields (89–92%) were achieved with all the aliphatic ketones examined at a higher S/C of 200 (Table 1, entries 8–11). In addition, the same trend was observed in the reaction of 1-phenylacetone with different aromatic amines, and the corresponding products were isolated with 90–92% yields (Table 1, entries 11–14).

We also explored the RA of aldehydes with amines. As expected, aldehydes were more reactive than aromatic or aliphatic ketones. In the aqueous RA of different aldehydes with *p*-anisidine, full conversions to the desired amines were achieved in 8 h at an S/C of 200. The corresponding amines were isolated in 90–94% yields (Table 1, entries 15–18). However, in comparison with the C^N chelated iridicycle catalysts,[4g,h] the C^O bound NHC **3** is generally less active in the transfer hydrogenative RA.

Hydrogenative RA Reactions. As mentioned, there appears to be no catalyst which can effect both transfer hydrogenative RA and hydrogenative RA reactions. To explore the feasibility of using **3** for hydrogenative RA, the reaction of acetophenone with *p*-anisidine was chosen as a model reaction for hydrogenative RA and examined. As can be seen from Table 2, no reduction was observed in either water or MeOH when using 0.5 mol % **3** at 20 bar of H_2 and 60 °C within 4 h (Table 2, entries 1 and 2). However, with the addition of 10 mol % *p*-toluenesulfonic acid monohydrate (TsOH), a 22% and 73% conversion into the desired amine was observed in water and MeOH, respectively (Table 2, entries 3 and 4). Further studies were then performed in the latter, which revealed that the hydrogenative RA went faster in the presence of both TsOH and 4 Å molecular sieves (MS), affording complete conversion to the desired amine under otherwise the same conditions (Table 2, entry 5). Decreasing the amount of TsOH to 5 mol % afforded a lower conversion (Table 2, entry 6). The addition of the acid and molecular sieves presumably facilitates the formation of the intermediate imine.[3j] Next, we studied the effect of the solvent on the hydrogenative RA and observed that the nature of the solvent affected the conversion of the reaction dramatically. Among the various solvents examined for the reaction, 2,2,2-trifluoroethanol (TFE) and 2-propanol (IPA) showed lower activities compared to MeOH (Table 2, entries 7–13), while others showed no activities at all. A control experiment with $[IrCp^*Cl_2]_2$ as catalyst gave the desired amine in only 17% conversion under the conditions given in Table 2, entry 5.

With the optimized reaction conditions in hand, we then studied the scope of the RA, first using various aromatic ketones and aniline derivatives (Table 3). The results revealed that all the desired products could be afforded in high yields (77–94%) within 4–6 h by using 0.5 mol % of **3** (Table 3, entries 1–7).

Reactions of different aliphatic ketones with *p*-anisidine were then investigated. The hydrogenative RA was completed in 4 h even at a higher S/C of 1000, with the desired amines obtained in good yields (90–93%) (Table 3, entries 8–11). The same trend was observed in the reaction of 1-phenylacetone with different aromatic amines, and the corresponding products were isolated with 91–94% yields (Table 3, entries 11–14). However, secondary amines displayed lover activity, most likely due to their steric hindrance impeding both imine formation and reduction. Thus, a yield of only 25% was obtained for methylphenylamine at an S/C of 200 in 12 h (Table 3, entry 15).

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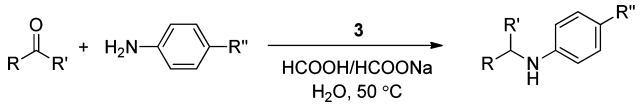
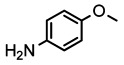
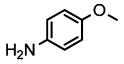
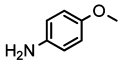
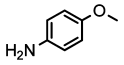
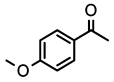
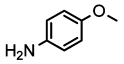
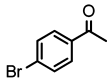
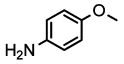
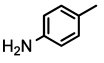
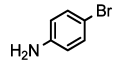
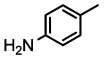
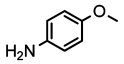
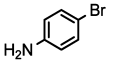
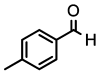
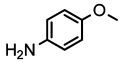
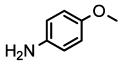
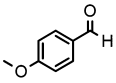
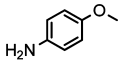
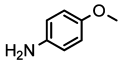
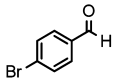
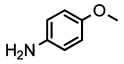
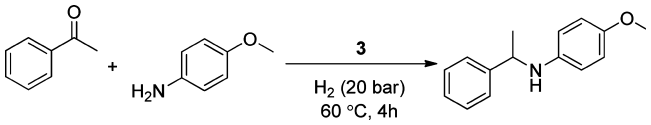
Table 1. Transfer Hydrogenative RA of Ketones and Aldehydes with Different Amines in Water



Entry[a]	Carbonyl	Amine	S/C	Yield [%][b]	Entry[a]	Carbonyl	Amine	S/C	Yield [%][b]
1			100	90	10			200	91
2			100	89	11			200	92
3			100	76	12			200	90
4			100	78	13			200	90
5			100	81	14			200	91
6			100	83	15[c]			200	92
7			100	79	16[c]			200	90
8			200	91	17[c]			200	92
9			200	89	18[c]			200	94

[a]Reaction conditions: ketone or aldehyde (0.5 mmol), amine (1.0 mmol), **3** (0.005 or 0.0025 mmol, 1−0.5 mol %), HCOOH/HCOONa solution (pH 4.8, 0.8 mL), 50 °C, 16 h. [b]Isolated yield. [c]8 h reaction time.

Table 2. Optimization of Conditions for the Hydrogenative RA



entry[a]	solvent	additive	conv. [%][b]
1	H_2O		NR
2	MeOH		NR
3	H_2O	TsOH (10%)	22
4	MeOH	TsOH (10%)	73
5	MeOH	TsOH (10%), 4 Å MS	> 99
6	MeOH	TsOH (5%), 4 Å MS	67
7	TFE	TsOH (10%), 4 Å MS	60
8	IPA	TsOH (10%), 4 Å MS	10
9	PhMe	TsOH (10%), 4 Å MS	NR
10	EtOAc	TsOH (10%), 4 Å MS	NR
11	1,4-Dioxan	TsOH (10%), 4 Å MS	NR
12	MeCN	TsOH (10%), 4 Å MS	NR
13	THF	TsOH (10%), 4 Å MS	NR

[a]Reaction conditions: acetophenone (0.5 mmol), *p*-anisidine (0.75 mmol), **3** (0.0025 mmol, 0.5 mol %), solvent (2 mL), 20 bar of H_2, 60 °C, 4 h. [b]Conversions were determined by ^{1}H NMR spectroscopy.

The RA of aldehydes was also successful. Thus, the reaction of benzaldehyde with *p*-anisidine provided the corresponding secondary amines in good yields (94−96%) at an S/C of 1000 in 4 h (Table 3, entries 16−19). It was observed that *p*-substituted benzaldehydes containing electron-donating or electron-withdrawing groups were all tolerated under the present reaction conditions. Furthermore, we examined the reaction of a secondary amine with benzaldehyde. The corresponding tertiary amine was obtained in 93% yield at an S/C of 1000 within 12 h (Table 3, entry 20).

Comparing the results in Table 1 with those in Table 3 shows that the hydrogenative RA is considerably faster than the transfer hydrogenative RA. Since the hydride complex generated from **3** is coordinatively saturated, the hydride transfer from the hydride to the substrate is likely to proceed via the outer sphere mechanism, i.e., direct hydride addition to a protonated iminium cation without C=N bond coordination to the metal.[2i,14] This mechanism is expected to hold for both modes of RA reactions. The possibility of phenoxide dissociation from the Ir^{III} during the RA appears low. On this ground, the slower RA when using formate as the hydrogen source could stem from a slower step of hydride formation.

CONCLUSIONS

In this report, we have synthesized a new N-heterocyclic carbene ligand containing a phenol moiety that allows, for the first time, the preparation of an Ir^{III}−Cp* complex with a chelating NHC−phenoxide ligand. This complex is found to catalyze successfully both transfer hydrogenative and hydro-

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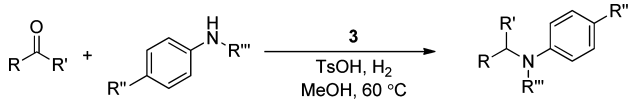
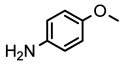
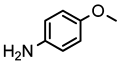
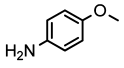
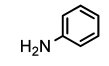
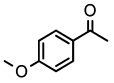
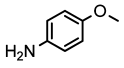
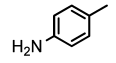
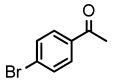
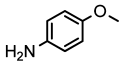
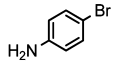
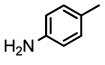
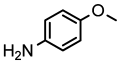
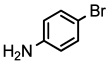
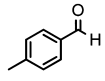
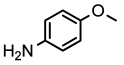
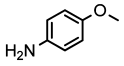
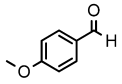
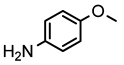
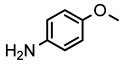
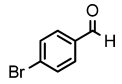
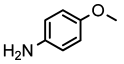
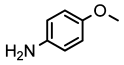
Table 3. Hydrogenative RA of Ketones and Aldehydes with Different Amines



Entry[a]	Ketone	Amine	S/C	Time [h]	Yield [%][b]	Entry[a]	Ketone	Amine	S/C	Time [h]	Yield [%][b]
1			200	4	94	11			1000	4	92
2			200	6	86	12			1000	4	93
3			200	6	77	13			1000	4	91
4			200	6	93	14			1000	4	94
5			200	6	91	15			200	12	25
6			200	6	92	16			1000	4	95
7			200	6	92	17			1000	4	94
8			1000	4	91	18			1000	4	94
9			1000	4	90	19			1000	4	96
10			1000	4	93	20			1000	12	93

[a]Reaction conditions: ketone or aldehyde (0.5 mmol), amine (0.75 mmol), **3** (0.0025 or 0.0005 mmol, 0.5−0.1 mol %), TsOH (10 mol %), 4 Å MS (200 mg), MeOH (2 mL), 20 bar of H_2, 60 °C. [b]Isolated yield.

genative RA of various ketones and aldehydes with aniline derivatives. The reactions proceed with high efficiency to afford the corresponding amines. The hydrogenative RA is faster than the transfer hydrogenative RA and permits higher S/C ratios. This is the first example in which a single catalyst has allowed effectively both transfer hydrogenative and hydrogenative RA of various ketones and aldehydes.

EXPERIMENTAL SECTION

Synthesis of 1. To a degassed dimethyl sulfoxide (20 mL) solution of 5,6-dimethyl-1-*H*-benzimidazole (2.19 g, 15.0 mmol) were added 2-bromoanisole (1.87 g, 10.0 mmol), KOH (1.12 g, 20.0 mmol), and Cu_2O (286 mg, 2.0 mmol) under N_2. The resulting mixture was stirred at 140 °C for 24 h under N_2. After cooling to room temperature, the mixture was poured into ethyl acetate (50 mL) and filtered. The filtrate was washed with water (3 × 50 mL) and dried over anhydrous magnesium sulfate. Solvent was evaporated, and to the crude oil was added an aqueous solution of 47% HBr (5.18 g, 30 mmol). The brown solution was allowed to reflux for 48 h under N_2. The solution was then cooled and basified by the addition of anhydrous $NaHCO_3$ until the evolution of CO_2 ceased and a precipitate formed. The precipitate was filtered and washed with water. The resulting crude product was purified via column chromatography on silica gel with ethyl acetate:methanol (9:1) as eluent, affording an off-white powder. Overall yield: 68%, 1.62 g (based on 2-bromoanisole). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.17 (s, 1H; Ar-O*H*, exchanges with D_2O), 8.18 (s, 1H, NC*H*N), 7.51 (s, 1H, Ar-*H*), 7.38 (d, J = 7.6 Hz, 1H, Ar-*H*), 7.34 (t, J = 7.6 Hz, 1H, Ar-*H*), 7.13 (d, J = 7.6 Hz, 1H, Ar-*H*), 7.05 (s, 1H, Ar-*H*), 7.00 (t, J = 7.6 Hz, 1H, Ar-*H*), 2.33 (s, 3H, Ar-C*H*$_3$), 2.29 (s, 3H, Ar-C*H*$_3$); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 152.6 (NCHN), 143.9 (Ar-C), 142.0 (Ar-C), 133.2 (Ar-C), 131.9 (Ar-C), 130.6 (Ar-C), 129.9 (Ar-C), 127.9 (Ar-C), 123.7 (Ar-C), 120.0 (Ar-C), 119.9 (Ar-C), 117.4 (Ar-C), 111.5 (Ar-C), 20.5 (Ar-CH_3), 20.3 (Ar-CH_3); HRMS (CI+): calcd. m/z for $C_{15}H_{15}N_2O$ $[M + H]^+$: 239.1184; found: 239.1189.

Synthesis of 2. To a suspension of **1** (476 mg, 2.0 mmol) in acetonitrile (10 mL) was added 2,4,6-triisopropylbenzyl bromide (653 mg, 2.2 mmol). The resulting mixture was refluxed for 4 h. After cooling to room temperature, the solvent was evaporated. The resulting solid was dissolved in dichloromethane (5 mL), and diethyl ether (20 mL) was added. The colorless solid that separated out was filtered and washed with Et_2O (2 × 20 mL) and dried under reduced pressure. Yield: 97%, 1.04 g. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.08 (s, 1H; Ar-O*H*, exchanges with D_2O), 8.39 (s, 1H, NC*H*N$^+$), 7.82 (d, J = 8.0 Hz, 1H, Ar-*H*), 7.67 (s, 1H, Ar-*H*), 7.34 (s, 1H, Ar-*H*), 7.28 (t, J = 7.6 Hz, 1H, Ar-*H*), 7.26 (d, J = 8.0 Hz, 1H, Ar-*H*), 7.15 (s, 2H, Ar-*H*), 6.96 (t, J = 7.6 Hz, 1H, Ar-*H*), 5.70 (s, 2H, NC*H*$_2$Ar), 3.04 (sep, J

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= 7.2 Hz, 2H, ArC*H*(CH_3)$_2$), 2.94 (sep, *J* = 7.2 Hz, 1H, ArC*H*(CH_3)$_2$), 2.49 (s, 3H, Ar-C*H*$_3$), 2.41 (s, 3H, Ar-C*H*$_3$), 1.28 (d, *J* = 7.2 Hz, 6H, ArCH(CH_3)$_2$), 1.21 (d, *J* = 7.2 Hz, 12H, ArCH(CH_3)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.3 (Ar-*C*), 151.9 (Ar-*C*), 148.9 (NCHN$^+$), 138.8 (Ar-*C*), 138.6 (Ar-*C*), 138.1 (Ar-*C*), 132.1 (Ar-*C*), 131.2 (Ar-*C*), 129.6 (Ar-*C*), 125.6 (Ar-*C*), 122.5 (Ar-*C*), 121.1 (Ar-*C*), 119.8 (Ar-*C*), 119.7 (Ar-*C*), 119.6 (Ar-*C*), 114.1 (Ar-*C*), 113.0 (Ar-*C*), 44.4 (NCH_2Ar), 34.4 (ArC*H*(CH_3)$_2$), 30.1 (ArCH(CH_3)$_2$), 24.4 (ArCH(CH_3)$_2$), 23.9 (ArCH(CH_3)$_2$), 20.8 (Ar-CH_3), 20.7 (Ar-CH_3); HRMS (ES+): calcd. *m*/*z* for $C_{31}H_{39}N_2O$ [*M* − Br]$^+$: 455.3062; found: 455.3059.

Synthesis of 3. Under a nitrogen atmosphere, a mixture of **2** (268 mg, 0.5 mmol) and Ag_2O (463 mg, 2.0 mmol) was suspended in degassed and dry dichloromethane (5 mL) and stirred at ambient temperature for 2 h shielded from light. [IrCp*Cl_2]$_2$ (198 mg, 0.25 mmol) was then added to the suspension, and the reaction mixture was stirred at ambient temperature for an additional 2 h. The resulting suspension was filtered over Celite. The remaining solid was washed with dichloromethane (2 × 5 mL), and the solvent of the filtrate was evaporated. The residue was purified via column chromatography on silica gel with dichloromethane:methanol (9:1) as eluent, affording a yellow powder. Yield: 93%, 380 mg. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.52 (s, 1H, Ar-*H*), 7.18 (s, 1H, Ar-*H*), 7.15 (s, 1H, Ar-*H*), 7.12 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.08 (t, *J* = 8.0 Hz, 1H, Ar-*H*), 6.70 (d, *J* = 14.4 Hz, 1H, NC*H*$_2$Ar), 6.67 (t, *J* = 8.0 Hz, 1H, Ar-*H*), 5.46 (s, 1H, Ar-*H*), 5.30 (d, *J* = 14.4 Hz, 1H, NC*H*$_2$Ar), 3.40 (sep, *J* = 6.8 Hz, 1H, ArC*H*(CH_3)$_2$), 3.25 (sep, *J* = 6.8 Hz, 1H, ArC*H*(CH_3)$_2$), 3.02 (sep, *J* = 6.8 Hz, 1H, ArC*H*(CH_3)$_2$), 2.22 (s, 3H, Ar-C*H*$_3$), 1.92 (s, 3H, Ar-C*H*$_3$), 1.56 (s, 15H, C_5(C*H*$_3$)$_5$), 1.36 (d, *J* = 6.8 Hz, 9H, ArCH(C*H*$_3$)$_2$), 1.25 (d, *J* = 6.8 Hz, 3H, ArCH(C*H*$_3$)$_2$), 1.21 (d, *J* = 6.8 Hz, 3H, ArCH(C*H*$_3$)$_2$), 0.79 (d, *J* = 6.8 Hz, 3H, ArCH(C*H*$_3$)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.1 (Ir-*C*), 163.7 (Ar-*C*), 152.0 (Ar-*C*), 150.7 (Ar-*C*), 148.4 (Ar-*C*), 134.4 (Ar-*C*), 131.4 (Ar-*C*), 131.3 (Ar-*C*), 130.9 (Ar-*C*), 130.5 (Ar-*C*), 126.8 (Ar-*C*), 126.0 (Ar-*C*), 122.2 (Ar-*C*), 121.6 (Ar-*C*), 120.8 (Ar-*C*), 114.8 (Ar-*C*), 113.1 (Ar-*C*), 113.1 (Ar-*C*), 112.5 (Ar-*C*), 88.3 (C_5(CH$_3$)$_5$), 48.3 (NCH_2Ar), 34.7 (ArCH(CH_3)$_2$), 30.4 (ArCH(CH_3)$_2$), 29.2 (ArCH-(CH_3)$_2$), 25.4 (ArCH(CH_3)$_2$), 24.4 (ArCH(CH_3)$_2$), 23.2 (ArCH-(CH_3)$_2$), 23.1 (ArCH(CH_3)$_2$), 20.1 (Ar-CH_3), 20.0 (Ar-CH_3), 8.8 (C_5(CH_3)$_5$); HRMS (ESI+): calcd. *m*/*z* for $C_{41}H_{52}ClIrN_2ONa$ [*M* + Na]$^+$: 839.3284; found: 839.3272.

Typical Procedure for the Transfer Hydrogenative RA in Water. A reaction tube was charged with a magnetic stir bar, *p*-anisidine (1.0 mmol), and acetophenone (0.5 mmol), followed by catalyst **3** (0.005 or 0.0025 mmol). To the mixture was injected a water solution of HCOOH/HCOONa (0.8 mL, pH 4.8). The resulting mixture was stirred at 50 °C for 8−16 h under N_2. After cooling to room temperature, the solution was adjusted to pH 2−3 with HCl (4 M), stirred for 10 min, and then basified with aqueous NaOH (6 M) to pH 9−10. The resulting solution was extracted with ethyl acetate and dried over anhydrous $MgSO_4$. After evaporating the solvent, the product was purified by flash column chromatography (hexane:ethyl acetate, 20:1−10:1).

Typical Procedure for the Hydrogenative RA. To a glass liner equipped with a stir bar was added 4 Å MS (200 mg), *p*-toluenesulfonic acid (10 mol %), ketone or aldehyde (0.5 mmol), amine (0.75 mmol), catalyst **3** (0.0025 or 0.0005 mmol), and methanol (2 mL). The glass liner was then placed into an autoclave, followed by degassing with H_2 three times. The hydrogenation was carried out at 20 bar H_2 with stirring at 60 °C for 4−12 h. After cooling to room temperature, the hydrogen gas was then carefully released in a fume hood, and the solution was filtered, and concentrated to afford the crude product. The product was purified by flash column chromatography (hexane:ethyl acetate, 20:1−10:1). (***Warning!*** *All the high pressure hydrogenation reactions described here should be carried out with caution due to its potential fire hazards.*)

X-ray Crystallography. Crystallographic data and refinement are provided in Table S1 in the Supporting Information. CCDC 1402303 (**3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00625.

Synthetic procedures, analytical data, NMR spectra, and crystallographic details (PDF)

Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Kobayashi, S.; Ishitani, H. *Chem. Rev.* **1999**, *99*, 1069−1094. (b) Gomez, S.; Peters, J. A.; Maschmeyer, T. *Adv. Synth. Catal.* **2002**, *344*, 1037−1057. (c) Breuer, M.; Ditrich, K.; Habicher, T.; Hauer, B.; Keßeler, M.; Stürmer, R.; Zelinski, T. *Angew. Chem., Int. Ed.* **2004**, *43*, 788−824. (d) Blacker, J.; Martin, J. In *Asymmetric Catalysis on Industrial Scale: Challenges, Approaches and Solutions*; Blaser, H. U., Schmidt, E., Eds.; Wiley-VCH: Weinheim, 2004; pp 201−216. (e) Abdel-Magid, A. F.; Mehrman, S. J. *Org. Process Res. Dev.* **2006**, *10*, 971−1031. (f) Nugent, T. C.; El-Shazly, M. *Adv. Synth. Catal.* **2010**, *352*, 753−819. (g) Guillena, G.; Ramon, D. J.; Yus, M. *Chem. Rev.* **2010**, *110*, 1611−1641.

(2) (a) Tararov, V. I.; Börner, A. *Synlett* **2005**, 203−211. (b) Blaser, H.-U.; Spinder, F. In *Handbook of Homogeneous Hydrogenation*; de Vries, J. G., Elsevier, C. J., Eds.; Wiley-VCH: Weinheim, 2007; pp 1193−1214. (c) You, S. L. *Chem.—Asian J.* **2007**, *2*, 820−827. (d) Tripathi, R. P.; Verma, S. S.; Pandey, J.; Tiwari, V. K. *Curr. Org. Chem.* **2008**, *12*, 1093−1115. (e) Boros, E. E.; Thompson, J. B.; Katamreddy, S. R.; Carpenter, A. J. *J. Org. Chem.* **2009**, *74*, 3587−2590. (f) Sousa, S. C. A.; Fernandes, A. C. *Adv. Synth. Catal.* **2010**, *352*, 2218−2226. (g) Kumar, A.; Sharma, S.; Maurya, R. A. *Adv. Synth. Catal.* **2010**, *352*, 2227−2232. (h) Dangerfield, E. M.; Plunkett, C. H.; Win-Mason, A. L.; Stocker, B. L.; Timmer, M. S. M. *J. Org. Chem.* **2010**, *75*, 5470−5477. (i) Wang, C.; Villa-Marcos, B.; Xiao, J. *Chem. Commun.* **2011**, *47*, 9773−9785. (j) Wei, Y.; Wu, X.; Wang, C.; Xiao, J. *Catal. Today* **2015**, *247*, 104−116.

(3) (a) Blaser, H. U.; Buser, H. P.; Jalett, H. P.; Pugin, B.; Spindler, F. *Synlett* **1999**, 867−868. (b) Gross, T.; Seayad, A. M.; Ahmad, M.; Beller, M. *Org. Lett.* **2002**, *4*, 2055−2058. (c) Chi, Y.; Zhou, Y. G.; Zhang, X. *J. Org. Chem.* **2003**, *68*, 4120−4122. (d) Kadyrov, R.; Riermeier, T. H.; Dingerdissen, U.; Tararov, V.; Börner, A. *J. Org. Chem.* **2003**, *68*, 4067−4070. (e) Bunlaksananusorn, T.; Rampf, F. *Synlett* **2005**, 2682−2684. (f) Imao, D.; Fujihara, S.; Yamamoto, T.; Ohta, T.; Ito, Y. *Tetrahedron* **2005**, *61*, 6988−6992. (g) Robichaud, A.; Ajjou, A. N. *Tetrahedron Lett.* **2006**, *47*, 3633−3636. (h) Bhor, M. D.; Bhanushali, M. J.; Nandurkar, N. S.; Bhanage, B. M. *Tetrahedron Lett.* **2008**, *49*, 965−969. (i) Rubio-Pérez, L.; Pérez-Flores, F. J.; Sharma, P.; Velasco, L.; Cabrera, A. *Org. Lett.* **2009**, *11*, 265−268. (j) Li, C.; Villa-Marcos, B.; Xiao, J. *J. Am. Chem. Soc.* **2009**, *131*, 6967−6969. (k) Villa-

DOI: 10.1021/acs.organomet.5b00625
Organometallics XXXX, XXX, XXX−XXX

Marcos, B.; Li, C.; Mulholland, K. R.; Hogan, P. J.; Xiao, J. *Molecules* **2010**, *15*, 2453−2472. (l) Steinhuebel, D.; Sun, Y.; Matsumura, K.; Sayo, N.; Saito, T. *J. Am. Chem. Soc.* **2009**, *131*, 11316−11317. (m) Pagnoux-Ozherelyeva, A.; Pannetier, N.; Mbaye, M. D.; Gaillard, S.; Renaud, J.-L. *Angew. Chem.* **2012**, *124*, 5060−5064; *Angew. Chem., Int. Ed.* **2012**, *51*, 4976−4980. (n) Chang, M.; Liu, S.; Huang, K.; Zhang, X. *Org. Lett.* **2013**, *15*, 4354−4357. (o) Moulin, S.; Dentel, H.; Pagnoux-Ozherelyeva, A.; Gaillard, S.; Poater, A.; Cavallo, L.; Lohier, J.-F.; Renaud, J.-L. *Chem.—Eur. J.* **2013**, *19*, 17881−17890. (p) Cabrera, A.; Sharma, P.; Pérez-Flores, F. J.; Velasco, L.; Arias, J. L.; Rubio- Pérez, L. *Catal. Sci. Technol.* **2014**, *4*, 2626−2630. (q) Zhou, S.; Fleischer, S.; Jiao, H.; Junge, K.; Beller, M. *Adv. Synth. Catal.* **2014**, *356*, 3451−3455.

(4) (a) Kitamura, M.; Lee, D.; Hayashi, S.; Tanaka, S.; Yoshimura, M. *J. Org. Chem.* **2002**, *67*, 8685−8678. (b) Kadyrov, R.; Riermeier, T. H. *Angew. Chem.* **2003**, *115*, 5630−5632; *Angew. Chem., Int. Ed.* **2003**, *42*, 5472−5474. (c) Williams, G. D.; Pike, R. A.; Wade, C. E.; Wills, M. *Org. Lett.* **2003**, *5*, 4227−4230. (d) Ogo, S.; Uehara, K.; Abura, T.; Fukuzumi, S. *J. Am. Chem. Soc.* **2004**, *126*, 3020−3021. (e) Wang, C.; Pettman, A.; Basca, J.; Xiao, J. *Angew. Chem.* **2010**, *122*, 7710−7714; *Angew. Chem., Int. Ed.* **2010**, *49*, 7548−7552. (f) Zhang, M.; Yang, H.; Zhang, Y.; Zhu, C.; Li, W.; Cheng, Y.; Hu, H. *Chem. Commun.* **2011**, *47*, 6605−6607. (g) Lei, Q.; Wei, Y.; Talwar, D.; Wang, C.; Xue, D.; Xiao, J. *Chem.—Eur. J.* **2013**, *19*, 4021−4029. (h) Talwar, D.; Salguero, N. P.; Robertson, C. M.; Xiao, J. *Chem.—Eur. J.* **2014**, *20*, 245−252. (i) Zhu, M. *Catal. Lett.* **2014**, *144*, 1568−1572.

(5) (a) Crudden, C. M.; Allen, D. P. *Coord. Chem. Rev.* **2004**, *248*, 2247−2273. (b) Normand, A. T.; Cavell, K. J. *Eur. J. Inorg. Chem.* **2008**, *2008*, 2781−2800. (c) Kühl, O. *Funtionalised N-Heterocyclic Carbene Complexes*; Wiley-VCH: Weinheim, 2010. (d) Benhamou, L.; Chardon, E.; Lavigne, G.; Bellemin-Laponnaz, S.; César, V. *Chem. Rev.* **2011**, *111*, 2705−2733. (e) Díez-González, S., Ed. *N-Heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools*; Royal Society of Chemistry: Cambridge, U.K., 2011. (f) Cazin, C. S. J., Ed. *N-Heterocyclic Carbenes in Transition Metal Catalysis and Organocatalysis*; Springer: London, 2011. (g) Nolan, S. P., Ed. *N-Heterocyclic Carbenes: Effective Tools for Organometallic Synthesis*; Wiley-VCH: Weinheim, 2014. (h) Hopkinson, M. N.; Richter, C.; Schedler, M.; Glorius, F. *Nature* **2014**, *510*, 485−496.

(6) (a) Lightfoot, A.; Schnider, P.; Pfaltz, A. *Angew. Chem., Int. Ed.* **1998**, *37*, 2897−2899. (b) Cui, X.; Fan, Y.; Hall, M. B.; Burgess, K. *Chem.—Eur. J.* **2005**, *11*, 6859−6868. (c) Messerle, B. A.; Page, M. J.; Turner, P. *Dalton Trans.* **2006**, 3927−3933. (d) Zhou, J.; Ogle, J. W.; Fan, Y.; Banphavichit(Bee), V.; Zu, Y.; Burgess, K. *Chem.—Eur. J.* **2007**, *13*, 7162−7170. (e) Zhu, Y.; Burgess, K. *Adv. Synth. Catal.* **2008**, *350*, 979−983. (f) Zhao, J.; Burgess, K. *Org. Lett.* **2009**, *11*, 2053−2056. (g) Dobereiner, G. E.; Nova, A.; Schley, N. D.; Hazari, N.; Miller, S. J.; Eisenstein, O.; Crabtree, R. H. *J. Am. Chem. Soc.* **2011**, *133*, 7547−7562. (h) Dunsford, J. J.; Tromp, D. S.; Cavell, K. J.; Elsevier, C. J.; Kariuki, B. M. *Dalton Trans.* **2013**, *42*, 7318−7329. (i) O, W. W. N.; Lough, A. J.; Morris, R. H. *Organometallics* **2013**, *32*, 3808−3818. (j) Kolychev, E. L.; Kronig, S.; Brandhorst, K.; Freytag; Jones, P. G.; Tamm, M. *J. Am. Chem. Soc.* **2013**, *135*, 12448−12459. (k) Schumacher, A.; Bernasconi, M.; Pfaltz, A. *Angew. Chem., Int. Ed.* **2013**, *52*, 7422−7425. (l) Horvath, H.; Katho, A.; Udvardy, A.; Papp, G.; Szikszai, D.; Joo, F. *Organometallics* **2014**, *33*, 6330−6340.

(7) (a) Albrecht, M.; Miecznikowski, J. R.; Samuel, A.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2002**, *21*, 3596−3604. (b) Corberán, R.; Sanaú, M.; Peris, E. *Organometallics* **2007**, *26*, 3492−3498. (c) Pontes da Costa, A.; Viciano, M.; Sanau, M.; Merino, S.; Tejeda, J.; Peris, E.; Royo, B. *Organometallics* **2008**, *27*, 1305−1309. (d) Türkmen, H.; Pape, T.; Hahn, F. E.; Çetinkaya, B. *Eur. J. Inorg. Chem.* **2008**, *2008*, 5418−5423. (e) Türkmen, H.; Pape, T.; Hahn, F. E.; Çetinkaya, B. *Organometallics* **2008**, *27*, 571−575. (f) Corberán, R.; Peris, E. *Organometallics* **2008**, *27*, 1954−1958. (g) Zinner, S. C.; Rentzsch, C. F.; Herdtweck, E.; Herrmann, W. A.; Kühn, F. E. *Dalton Trans.* **2009**, 7055−7062. (h) Gnanamgari, D.; Sauer, E. L. O.; Schley, N. D.; Butler, C.; Incarvito, C. D.; Crabtree, R. H. *Organometallics* **2009**, *28*, 321−325. (i) Binobaid, A.; Iglesias, M.; Beetstra, D.; Dervisi, A.; Fallis, I.; Cavell, K. J. *Eur. J. Inorg. Chem.* **2010**, *2010*, 5426−5431. (j) Jimènez, M. V.; Fernàndez-Tornos, J.; Perèz-Torrente, J. J.; Modrego, F. J.; Winterle, S.; Cunchillos, C.; Lahoz, F. J.; Oro, L. A. *Organometallics* **2011**, *30*, 5493−5508. (k) Gong, X.; Zhang, H.; Li, X. *Tetrahedron Lett.* **2011**, *52*, 5596−5600. (l) Azua, A.; Mata, J. A.; Peris, E. *Organometallics* **2011**, *30*, 5532−5536. (m) Chiyojima, H.; Sakaguchi, S. *Tetrahedron Lett.* **2011**, *52*, 6788−6791. (n) Azua, A.; Sanz, S.; Peris, E. *Chem.—Eur. J.* **2011**, *17*, 3963−3967. (o) Azua, A.; Mata, J. A.; Peris, E.; Lamaty, F.; Martinez, J.; Colacino, E. *Organometallics* **2012**, *31*, 3911−3919. (p) Gonell, S.; Poyatos, M.; Mata, J. A.; Peris, E. *Organometallics* **2012**, *31*, 5606−5614. (q) Ashley, J. M.; Farnaby, J. H.; Hazari, N.; Kim, K. E.; Luzik, E. D., Jr; Meehan, R. E.; Meyer, E.; Schley, N. D.; Schmeier, T. J.; Tailor, A. N. *Inorg. Chim. Acta* **2012**, *380*, 399−410. (r) Gülcemal, S.; Gökçe, A. G.; Çetinkaya, B. *Inorg. Chem.* **2013**, *52*, 10601−10609. (s) Gülcemal, S.; Gökçe, A. G.; Çetinkaya, B. *Dalton Trans.* **2013**, *42*, 7305−7311. (t) Blanco, M.; Alvarez, P.; Blanco, C.; Jimenez, M. V.; Fernandez-Tornos, J.; Perez-Torrente, J. J.; Oro, L. A.; Menendez, R. *ACS Catal.* **2013**, *3*, 1307−1317. (u) O, W. W. N.; Lough, A. J.; Morris, R. H. *Organometallics* **2013**, *32*, 3808−3818. (v) Riener, K.; Bitzer, M. J.; Pöthig, A.; Raba, A.; Cokoja, M.; Herrmann, W. A.; Kühn, F. E. *Inorg. Chem.* **2014**, *53*, 12767−12777. (w) Modugno, G.; Monney, A.; Bonchio, M.; Albrecht, M.; Carraro, M. *Eur. J. Inorg. Chem.* **2014**, *2014*, 2356−2360. (x) Sabater, S.; Baya, M.; Mata, J. A. *Organometallics* **2014**, *33*, 6830−6839. (y) Hintermair, U.; Campos, J.; Brewster, T. P.; Pratt, L. M.; Schley, N. D.; Crabtree, R. H. *ACS Catal.* **2014**, *4*, 99−108. (z) Gülcemal, D.; Gökçe, A. G.; Gülcemal, S.; Çetinkaya, B. *RSC Adv.* **2014**, *4*, 26222−26230.

(8) (a) Bartoszewicz, A.; Marcos, R.; Sahoo, S.; Inge, A. K.; Zou, X.; Martin-Matute, B. *Chem.—Eur. J.* **2012**, *18*, 14510−14519. (b) Li, J.-Q.; Andersson, P. G. *Chem. Commun.* **2013**, *49*, 6131−6133. (c) Wang, D.; Guo, X.-Q.; Wang, C.-X.; Wang, Y.-N.; Zhong, R.; Zhu, X.-H.; Cai, L.-H.; Gao, Z.-W.; Hou, X.-F. *Adv. Synth. Catal.* **2013**, *355*, 1117−1125.

(9) Gnanamgari, D.; Moores, A.; Rajaseelan, E.; Crabtree, R. H. *Organometallics* **2007**, *26*, 1226−1230.

(10) Bagal, D. B.; Watile, R. A.; Khedkar, M. V.; Dhake, K. P.; Bhanage, B. M. *Catal. Sci. Technol.* **2012**, *2*, 354−358.

(11) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972−975.

(12) (a) Chianese, A. R.; Crabtree, R. H. *Organometallics* **2005**, *24*, 4432−4436. (b) Weinberg, D. R.; Hazari, N.; Labinger, J. A.; Bercaw, J. E. *Organometallics* **2010**, *29*, 89−100. (c) Iglesias, M.; Perez-Nicolas, M.; Miguel, P. J. S.; Polo, V.; Fernandez-Alvarez, F. J.; Perez-Torrente, J. J.; Oro, L. A. *Chem. Commun.* **2012**, *48*, 9480−9482. (d) Iglesias, M.; Miguel, P. J. S.; Polo, V.; Fernandez-Alvarez, F. J.; Perez-Torrentea, J. J.; Oro, L. A. *Chem.—Eur. J.* **2013**, *19*, 17559−17566.

(13) Barnard, J. H.; Wang, C.; Berry, N. G.; Xiao, J. *Chem. Sci.* **2013**, *4*, 1234−1244.

(14) (a) Clapham, S. E.; Hadzovic, A.; Morris, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2201−2237. (b) Magee, M. P.; Norton, J. R. *J. Am. Chem. Soc.* **2001**, *123*, 1778−1779. (c) Guan, H. R.; Iimura, M.; Magee, M. P.; Norton, J. R.; Zhu, G. *J. Am. Chem. Soc.* **2005**, *127*, 7805−7814. (d) Zhou, H. F.; Li, Z. W.; Wang, Z. J.; Wang, T. L.; Xu, L. J.; He, Y.; Fan, Q. H.; Pan, J.; Gu, L. Q.; Chan, A. S. C. *Angew. Chem.* **2008**, *120*, 8592−8595; *Angew. Chem., Int. Ed.* **2008**, *47*, 8464−8467.

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Organometallics XXXX, XXX, XXX−XXX