ORGANOMETALLICS

pubs.acs.org/Organometallics Article

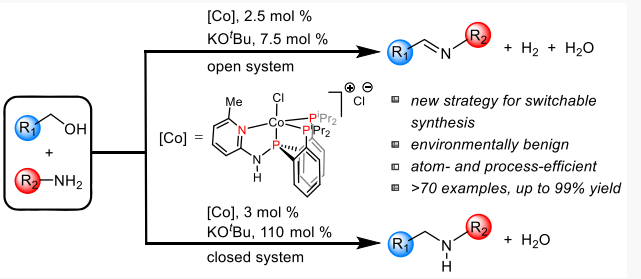
Switchable Imine and Amine Synthesis Catalyzed by a Well-Defined Cobalt Complex

Keshav Paudel,[§] Shi Xu,[§] Oleksandr Hietsoi, Bedraj Pandey, Chuka Onuh, and Keying Ding*

Cite This: https://dx.doi.org/10.1021/acs.organomet.0c00727 Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: Switchable imine and amine synthesis catalyzed by a tripodal ligand-supported well-defined cobalt complex is presented herein. A large variety of primary alcohols and amines were selectively converted to imines or amines in good to excellent yields. It is discovered that the base plays a crucial role on the selectivity. A catalytic amount of base leads to the imine formation, while an excess loading of base results in the amine product. This strategy on product selectivity also strongly depends on the organometallic catalysts in use. We expect that the present study could provide useful insights toward selective organic synthesis and catalyst design.

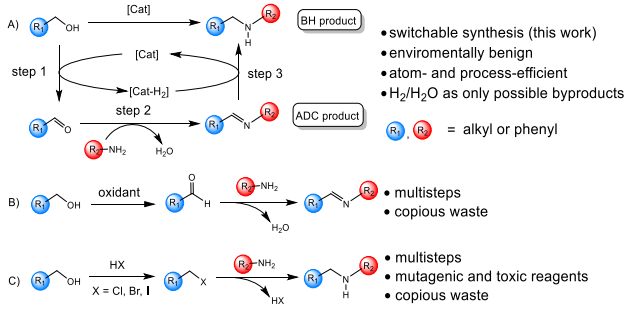


INTRODUCTION

Homogeneous transition-metal-catalyzed carbon−carbon and carbon−heteroatom bond forming reactions are among the pre-eminent organic synthetic methods for high-value products.[1] One such prominent synthetic strategy is acceptorless dehydrogenative coupling (ADC) which has recently attracted enormous interests in academia and fine-chemical industries.[2−5] In a typical ADC pathway, a substrate is first dehydrogenated with the catalyst taking one hydride and one proton (Scheme 1A, steps 1 and 2). The dehydrogenated intermediate is then attacked by a nucleophile, e.g., an amine, leading to an unsaturated product with the loss of a water molecule. In the final step, the hydrogen gas is liberated, regenerating the catalyst. Alternatively, the catalyst bearing a hydride and a proton could reduce the unsaturated product at the final step to afford the saturated product. This is known as the borrowing hydrogen (BH) process (Scheme 1A, steps 1−3).[2−5] Both ADC and BH offer great advantages over conventional methods (Scheme 1B,C): (a) No hydrogen acceptor or oxidant is required. (b) Less waste is generated with water and hydrogen as the only possible byproducts. (c) High atom efficiency can be achieved. (d) Challenging reactants such as normally unreactive alcohols can be used directly. In addition, alcohols are inexpensive, less toxic, readily available, and obtainable from biomass feedstock.[6] In the past decades, precious metal catalysts have been studied intensively for the ADC and BH processes, significantly promoting this field. Due to the increasing economic and environmental concerns, earth-abundant metal catalysts as a desirable alternative to the precious metal catalysts have emerged in a surge of recent discoveries.[7−14]

Imines and amines are important classes of compounds that have ubiquitous applications in pharmaceutical, chemical, and agricultural industries.[15,16] *N*-Alkylation of amines with alcohols catalyzed by earth-abundant metal catalysts to access secondary imines or amines via ADC or BH, respectively, is a promising and environmentally friendly process.[7−14,17−38] However, it remains a great challenge to efficiently tune the selectivity, e.g., imine is normally identified as a major side

Scheme 1. Comparation of the ADC/BH with Conventional Methods for Imine/Amine Synthesis[a]



[a](A) ADC/BH pathways for imine/amine synthesis. (B) Conventional method for imine synthesis. (C) Conventional method for amine synthesis.

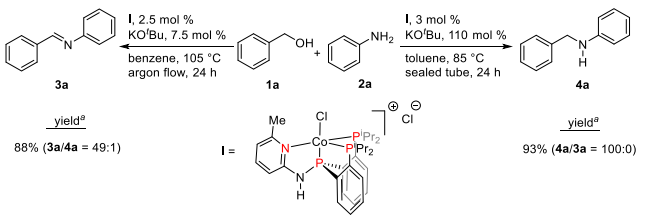
Received: November 15, 2020

product in amine synthesis and *vice versa*. Thus, it is highly desirable to explore the factors that favor either imine or amine product from both practical and mechanistic points of view. Toward this end, new synthetic methods and catalyst design are required. Unfortunately, the current understanding of the selectivity control over imine or amine synthesis via ADC or BH is still limited. In their pioneer work, Hanson, Zhang, and co-workers reported that in a cobalt-catalyzed amine/imine synthesis, the addition of molecular sieves shifts the product from imine to amine.[17,18] However, this method does not seem to be a general one and contradictory results are known, as molecular sieves were also reported to promote imine product instead.[19,20] Furthermore, the heterogeneous nature of molecular sieves exerts challenges to understanding the mechanism. Kirchner and co-workers presented that the choice of the metals leads to different products, in which iron and manganese catalysts afford amine and imine, respectively, in the presence of molecular sieves.[21]

Kempe and co-workers reported an interesting synthetic method wherein the change of base type, i.e., KO^{t}Bu or NaO^{t}Bu, can result in switchable amine/imine synthesis mediated by a manganese catalyst.[22] A large amount of base, i.e., 1.0 and 1.5 equiv with respect to the substrate, is mandatory for amine and imine synthesis, respectively. It is noted that this method is not applicable to the cobalt- and iridium-based analogues. Recently, Srivastava, Srimani, and co-workers reported a similar strategy by changing the type of bases using a manganese catalyst.[38] Harsh reaction conditions, such as 30 mol % base and 140 °C, are required for imine synthesis. Heterogeneous catalysts based on precious metals are also known for selective imine/amine formations.[39,40] Thus, it is highly desirable to develop more general and sustainable strategies to manipulate the ADC or BH process for efficient selectivity control under milder conditions employing base transition metal catalysts.

Recently, we have developed a novel ^{iPr}PPPN^{H}Py^{Me} tetradentate ligand which is designed to offer extraordinary stability to the base transition metal center and may actively participate in catalysis by metal−ligand cooperativity (MLC).[41] Air- and moisture-stable cobalt complex **I** (Scheme 2) has shown great reactivity in dehydrogenation of secondary

Scheme 2. Switchable Synthesis of *N*-Benzylideneaniline and *N*-Benzylaniline Catalyzed by I



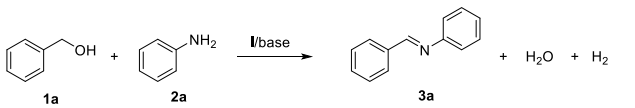
[a]NMR yield, 0.25 mmol scale.

alcohols to ketones,[41] dehydrogenative self-coupling of primary alcohols to esters,[42] and dehydrogenative cross-coupling of primary and secondary alcohols to ketones.[43] Herein, we describe an unprecedented and convenient method using **I** for the highly selective imine/amine synthesis by simply adjusting the base loadings. We expect to provide useful insights that could enable new strategies in selective organic synthesis and catalyst design.

RESULTS AND DISCUSSION

In the ADC/BH route for the imine/amine formation, amine is afforded from the imine hydrogenation step (Scheme 1A, step 3), i.e., the imine-/amine-selectivity-determining step. We initiated our study by probing any strategy that could favor or disfavor this key step. In our previous studies, a base such as KO^{t}Bu is required to activate the cobalt precatalyst.[41−43] Since the base is known to promote transition-metal-catalyzed hydrogenation reactions,[44−46] our initial speculation is that by adjusting the amount of base the amine/imine selectivity might be achieved. Toward this end, we examined our cobalt catalyst in response to the base loadings in transfer hydrogenation of imine. In the model reaction of *N*-benzylideneaniline with benzyl alcohol, an 82% yield of *N*-benzylaniline was obtained using 2.5 mol % **I** and 110 mol % KO^{t}Bu at 85 °C after 24 h. However, when the KO^{t}Bu loading was reduced to a catalytic amount of 7.5 mol %, only 1% of *N*-benzylideneaniline was converted to *N*-benzylaniline. These results suggest a key role of the base: serving as a "switch" for the imine/amine selectivity. Following this hypothesis, we explored the reaction conditions of the alcohol amine coupling reactions for switchable imine/amine synthesis (Tables 1 and

Table 1. Optimization of the Reaction Conditions for Imine Synthesis



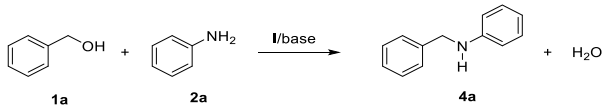
entry[a]	base	base (mol %)	temp (°C)	solvent	yield (%)[b]
1	KO^{t}Bu	0	105	benzene	0
2	KO^{t}Bu	2.5	105	benzene	29
3	KO^{t}Bu	5	105	benzene	74
4	KO^{t}Bu	7.5	105	benzene	88, 0,[c] 79,[d] 74[e]
5	KO^{t}Bu	10	105	benzene	86
6	NaO^{t}Bu	7.5	105	benzene	82
7	KOH	7.5	105	benzene	72
8	$NaHCO_3$	7.5	105	benzene	2
9	K_2CO_3	7.5	105	benzene	4
10	Cs_2CO_3	7.5	105	benzene	9
11	KO^{t}Bu	7.5	105	toluene	72
12	KO^{t}Bu	7.5	105	THF	51
13	KO^{t}Bu	7.5	105	1,4-dioxane	24
14	KO^{t}Bu	7.5	85	benzene	15
15	KO^{t}Bu	7.5	115	benzene	86

[a]Reaction conditions: Benzyl alcohol (0.25 mmol), aniline (0.275 mmol), **I** (2.5 mol %), base, and solvent (1.2 mL) were heated in a 15 mL reaction tube under Ar flow for 24 h. [b]NMR yield using 1,3,5-trimethoxybenzene as internal standard. [c]Without **I**. [d]Isolated yield on 1 mmol scale. [e]Mercury (125 mg) was added to the reaction.

2). Gratifyingly, we found that for efficient imine formation, 2.5 mol % **I** with 7.5 mol % of KO^{t}Bu at 105 °C under argon flow is required. Alternatively, for selective amine generation, 3 mol % **I** with 110 mol % of KO^{t}Bu at 85 °C in a small, closed reaction vessel is needed (Scheme 2). Notably, excellent **3a**/**4a** selectivity was observed and *vice versa*. Both **I** and KO^{t}Bu are crucial for the imine/amine formations. A 1 mmol scale reaction was also performed, leading to very good isolated yields of **3a** and **4a** (79 and 89%, respectively; Scheme 2). H_2

https://dx.doi.org/10.1021/acs.organomet.0c00727
Organometallics XXXX, XXX, XXX−XXX

Table 2. Optimization of the Reaction Conditions for Amine Synthesis



1a 2a 4a

entry[a]	base	base (mol %)	temp (°C)	solvent	yield (%)[b]
1	KO^{t}Bu	0	85	toluene	0
2	KO^{t}Bu	7.5	85	toluene	4
3	KO^{t}Bu	25	85	toluene	47
4	KO^{t}Bu	75	85	toluene	78
5	KO^{t}Bu	110	85	toluene	93, 4,[c] 89,[d] 77[e]
6	KO^{t}Bu	125	85	toluene	93
7	NaO^{t}Bu	110	85	toluene	89
8	KOH	110	85	toluene	78
9	NaOH	110	85	toluene	79
10	K_2CO_3	110	85	toluene	2
11	KO^{t}Bu	110	85	benzene	72
12	KO^{t}Bu	110	85	THF	48
13	KO^{t}Bu	110	85	1,4-dioxane	35
14	KO^{t}Bu	110	65	toluene	22
15	KO^{t}Bu	110	105	toluene	85

[a]Reaction conditions: Benzyl alcohol (0.25 mmol), aniline (0.275 mmol), **I** (3 mol %), base, and solvent (0.75 mL) were heated in a sealed 15 mL reaction tube for 24 h. [b]NMR yield using 1,3,5-trimethoxybenzene as internal standard. [c]Without **I**. [d]Isolated yield on 1 mmol scale. [e]Mercury (125 mg) was added to the reaction.

was confirmed by GC from the gas phase after the imine forming reaction, suggesting an ADC process. Mercury tests indicated homogeneous catalytic processes for both imine and amine formations.

We then examined a comprehensive list of alcohol and amine substrates to explore the scope of this method (Table 3). The presence of electron-donating groups such as −OMe, −Me, −^{i}Pr, and so on attached to the meta or para positions of benzyl alcohol or aniline substrates gave good-to-excellent yields of amine or imine products (Table 3, **3b−3k**; **4b−4k**). The analogous substrates with electron-withdrawing groups like −F and −Cl, also proceeded smoothly to furnish the corresponding products (Table 3, **3l−3q**; **4l−4q**). *ortho*-Substituted substrates also displayed good-to-excellent activity (Table 3, **3r−3s**; **4r−4s**). The substrates bearing naphthalene and pyridine rings were well-tolerated with this method (Table 3, **3t−3w**; **4t−4w**). In addition, amines and imines with alkyl groups could also be accessed. Interestingly, aliphatic amines reacted with both benzyl and alkyl alcohol substrates affording the corresponding imines with excellent yields, but failed for amine formation (Table 3, **3x−3ab**; **4x−4ab**); on the contrary, anilines underwent the catalytic reactions smoothly with alkyl alcohols to give amine products but not for imine generation (Table 3, **3ac−3ai**; **4ac−4ai**). The substrates with nitrile, nitro, and furfuryl groups were not compatible. Also note that our strategy can be employed to selectively synthesize diimine **3aj** or diamine **4aj** from alkylation of 1,3-diaminobenzene (0.275 mmol) with benzyl alcohol (0.5 mmol) in the yields of 83 and 91%, respectively (Scheme 3A).

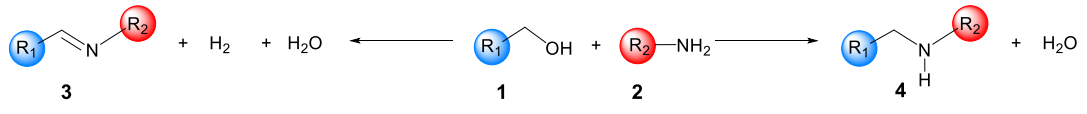
Next, we performed a mechanistic study to understand these reactions. Three derivatives of **I** (**II−IV**, Scheme 3B) were investigated for the amine alcohol coupling reactions. Derivative **II** bearing a dearomatized pyridine arm is synthesized by reacting **I** with 1 equiv of KO^{t}Bu or $KHBEt_3$.[41] **II** shows comparable activity to **I** in both imine and amine formation reactions with 85 and 79% yields, respectively, demonstrating **II** could also be an efficient precatalyst. In order to test if MLC from the N−H linker on the ligand plays a role, [(^{iPr}PPPN^{Me}Py^{Me})]$CoCl_2$ complex **III**[41] with the N−Me linker was employed. An amine yield of 80% was observed which is comparable with **I**, suggesting MLC may not have a crucial effect in amine formation. However, **III** showed dramatically reduced activity toward imine formation leading to only 1% yield. Instead, a large amount of amine (29% yield) and ester (20% yield) side products were generated, indicating poor reactivity and selectivity using **III** as the precatalyst for imine synthesis. To investigate the role of the coordinating pyridine arm, we synthesized **IV** bearing a benzene pendant arm instead. The solid-state structure of **IV** featured a distorted trigonal bipyramidal geometry on the cobalt center (Scheme 3C). As expected, the −NH−Ph arm does not coordinate to the cobalt. The IR spectrum displays a ν(N−H) peak at 3365 cm^{-1}. **IV** showed superior activity toward amine formation with an excellent 93% yield but performed poorly in the imine synthesis without any imine product detected. Interestingly, an amine yield of 75% was observed under the imine forming conditions using **IV**. Taken together, these results indicate the critical roles of both the pyridyl ring and the N−H linker of **I** for the switchable imine/amine synthesis.

When the optimized imine reaction was conducted with (benzyl alcohol)-α,α-d_2 and aniline, H/D scrambling was detected with a Ph−CH═N−Ph/Ph−CD═N−Ph ratio of about 1:3 (Scheme 3D), suggesting that the alcohol dehydrogenation step is reversible and involves cobalt hydride species as the intermediate. The amine formation was monitored using a J. Young NMR tube. A triplet of doublets at −15.99 ppm (J = 53.8 Hz (t) and 40.3 Hz (d)) was observed in the ^{1}H NMR spectrum (Scheme 3E). Although **I** is a paramagnetic Co(II) complex, the diamagnetic hydride signal indicates the generation of a Co(I) or Co(III) hydride in the presence of KO^{t}Bu and alcohol/amine substrates, which is analogous to that of other reported Co-based catalytic systems.[47−49] Attempts to isolate the hydride species were unsuccessful. In addition, no product was observed from dehydrogenation of aniline or benzyl amine in the absence of alcohol under the standard conditions, suggesting the amine dehydrogenation pathway could be excluded.

To explore the generality of our method in selective amine/imine synthesis, two representative base transition metal catalysts, **V** and **VI** (Scheme 3B) originally reported for amine synthesis, were examined by our strategy to form imines. Note that both catalytic systems require an excess amount of KO^{t}Bu for amine synthesis.[25,28] **V** and **VI** were prepared according to the published procedures.[50,51] Benzyl alcohol and aniline were chosen as the model substrates. Beller's manganese pincer complex **V** gave a *N*-benzylideneaniline yield of 80% under the analogous imine synthesis conditions with 3.5 mol % **V** and 6 mol % KO^{t}Bu. This demonstrates our strategy is amenable for Beller's catalytic system, although more extensive reaction condition optimization is required to further enhance the productivity. However, Kempe's cobalt pincer complex **VI** with the triazine backbone showed poor activity (3% yield) when subjected to the standard imine synthesis conditions. The stability of the reactive complexes could play a pivotal role, as catalyst degradation was observed during the reaction. Kempe and co-workers proposed a

https://dx.doi.org/10.1021/acs.organomet.0c00727
Organometallics XXXX, XXX, XXX−XXX

Table 3. Switchable Synthesis of Imines 3b−3ai and Amines 4b−4ai from Various Alcohol and Amine Substrates[a,b,c]



Imine	Amine
3b, 89%	4b, 86%
3c, 80%	4c, 80%
3d, 89%	4d, 71%
3e, 85%	4e, 80%
3f, 95%	4f, 97%
3g, 80%	4g, 91%
3h, 89%	4h, 91%
3i, 89%	4i, 92%[d]
3j, 80%	4j, 99%
3k, 89%	4k, 68%
3l, 80%	4l, 77%
3m, 94%	4m, 76%
3n, 62%[e]	4n, 72%
3o, 82%	4o, 84%[e]
3p, 69%	4p, 84%[e]
3q, 89%	4q, trace
3r, 73%	4r, 93%
3s, 77%	4s, 99%[d]
3t, 67%	4t, 90%
3u, 94%	4u, 72%[d]
3v, 76%	4v, 72%
3w, 67%	4w, 78%
3x, 61%[f]	4x, trace
3y, 80%[f]	4y, trace
3z, 85%[f]	4z, trace
3aa, 73%[g]	4aa, trace
3ab, 85%[g]	4ab, trace
3ac, trace	4ac, 99%
3ad-3ai, trace	4ad, n = 20, 90% 4ae, n = 10, 99% 4af, n = 8, 98% 4ag, n = 6, 93% 4ah, n = 4, 99% 4ai, n = 3, 95%

[a]General reaction conditions for imine synthesis: alcohol **1** (0.25 mmol), amine **2** (0.275 mmol), **I** (2.5 mol %), KO^{t}Bu (7.5 mol %), benzene (1.2 mL), Ar flow, 105 °C, 24 h. [b]General reaction conditions for amine synthesis: **1** (0.25 mmol), **2** (0.275 mmol), **I** (3 mol %), KO^{t}Bu (110 mol %), toluene (0.75 mL), 15 mL reaction tube, 85 °C, 24 h. [c]NMR yield using 1,3,5-trimethoxybenzene or nitromethane as internal standard. [d]Alcohol (0.3 mmol) and amine (0.25 mmol) were used. [e]**1** (0.25 mmol) and **2** (0.35 mmol) were used. [f]Reactions were run in a 100 mL pressure vessel for 48 h. [g]Reactions were run in a 100 mL pressure vessel for 24 h.

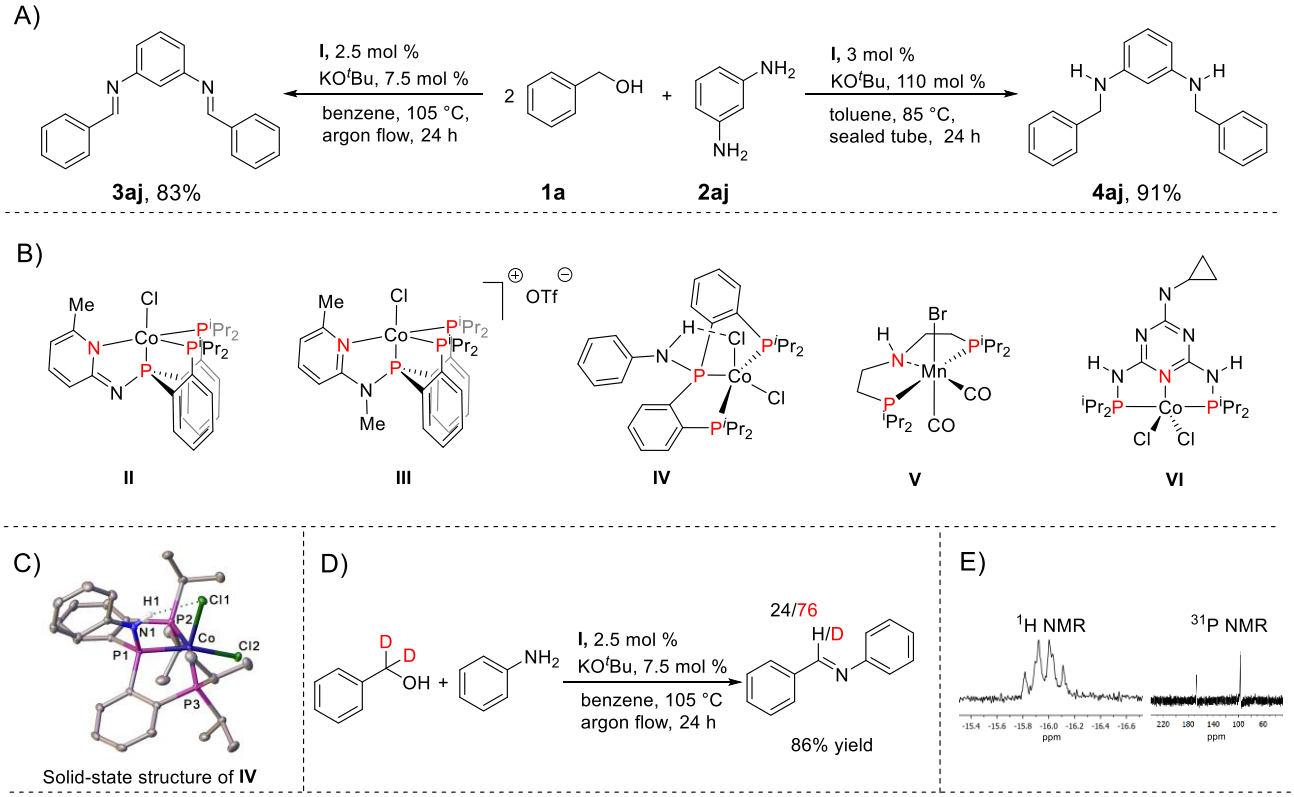
possible stabilization effect from the coordination of the potassium or sodium cation to the nitrogen atoms of the triazine backbone.[22] Under our conditions for imine synthesis, the catalytic amount of KO^{t}Bu may be insufficient to stabilize the catalyst, leading to catalyst degradation. Collectively, considering other known catalytic systems that otherwise require a large amount of base for the imine formation,[22,38] we conclude that our switchable imine/amine synthetic strategy is strongly dependent on the choice of the metal catalysts.

CONCLUSIONS

In summary, we reported the couplings of primary alcohols and amines to selectively synthesize imines or amines catalyzed by a well-defined cobalt catalyst. Intriguingly, the product selectivity can be simply controlled by the base loadings and

https://dx.doi.org/10.1021/acs.organomet.0c00727
Organometallics XXXX, XXX, XXX−XXX

Scheme 3. Studies on the Switchable Imine/Amine Formation[a]



[a](A) Switchable synthesis of diimine and diamine using benzyl alcohol and benzenediamine. (B) Base transition metal complexes examined for switchable imine/amine synthesis. (C) Solid-state structure of **IV**. Hydrogen atoms are omitted except the N−H proton. (D) Deuterium labeling experiment of the imine forming reaction using (benzyl alcohol)-α,α-d_2. (E) Cobalt hydride species detected by ^{1}H NMR (left) and ^{31}P NMR (right) from the *in situ* amine forming reaction in a J. Young NMR tube.

strongly depends on the catalysts used. Moreover, the imine forming reaction is environmentally benign with hydrogen and water as the only byproducts. We anticipate that this study could provide insights that lead for more efficient base transition metal catalysts, potentially opening new avenues of research on selective transformations in catalysis.

EXPERIMENTAL SECTION

General Methods. Unless specified, all reactions were performed in an MBraun glovebox under an atmosphere of N_2 or using standard Schlenk techniques with Ar atmosphere. Anhydrous solvents were deoxygenated by sparging with dinitrogen and dried by passing through activated alumina columns of a Pure Solv solvent purification system. $CDCl_3$ was purchased from Cambridge Isotope Lab and dried over molecular sieves (4 Å). (Benzyl alcohol)-α,α-d_2 was purchased from Sigma-Aldrich and used as received. All organic substrates were purchased from Sigma-Aldrich or Fisher Scientific and used as received. KO^{t}Bu (≥98%) was purchased from Sigma-Aldrich and vacuum-sublimed before use. Comparable results were obtained as using KO^{t}Bu (99.99%, Aldrich). All other chemicals were purchased and used as received. NMR spectra were recorded on a JEOL Unity 500 or 300 MHz spectrometer. ^{1}H NMR spectra were referenced to tetramethylsilane (0.00 ppm) using $CDCl_3$ as solvent. ^{13}C NMR were referenced to solvent carbons at 77.0 ppm for $CDCl_3$. ^{31}P NMR spectra were referenced to 85% H_3PO_4 at 0 ppm. Metal complexes (**I**–**III**, **V**, and **VI**) were prepared according to the previously published procedures,[41,50,51] and recrystallized before use. All other reagents were purchased from common suppliers and used without further purification.

Synthesis of the ^{iPr}PPPN^{H}Ph Ligand in IV. In a N_2-filled glovebox, aniline (50 μL, 0.55 mmol) and toluene (4 mL) were loaded into a 100 mL Schlenk flask. NEt_3 (76.2 μL, 0.55 mmol) was dropwise added to the solution over 5 min. The flask was sealed with a rubber septum, taken out of glovebox, and cooled at 0 °C with an ice bath. In the glovebox, bis(2-diisopropylphosphinophenyl)-chlorophosphine (247.5 mg, 0.55 mmol) was measured and dissolved in 3 mL of toluene. The solution was charged into a 5 mL syringe and then dropwise added to the Schlenk flask under Ar flow over 10 min. After the addition was complete, the ice bath was removed, and the mixture was allowed to warm to room temperature. The rubber septum was switched out for a glass stopper, and the reaction mixture was heated to 80 °C for 24 h. After that, the solvent was removed under vacuum, and the Schlenk flask was taken inside the glovebox. Diethyl ether (15 mL) was added into the Schlenk flask to dissolve the powder, and the mixture was filtered through Celite. Colorless crystals were obtained from the solution concentrated at room temperature (229 mg, 82% yield). ^{1}H NMR (500 MHz, 298 K, C_6D_6): δ (ppm) 7.14−7.11 (m, 2H), 7.06−7.04 (m, 2H), 6.84−6.83 (m, 1 H), 6.82 (dd, J = 2.4 and 1.3 Hz, 2H), 6.81−6.80 (m, 1H), 6.77 (t, J = 7.4 Hz, 2H), 6.68−6.65 (m, 2H), 6.44−6.41 (m, 1H), 3.62 (d, $^2J_{HP}$ = 6.1 Hz, N−H, 1H), 1.81−1.73 (m, 2H), 1.65−1.57 (m, 2H), 0.87−0.77 (m, 12H), 0.64−0.56 (m, 12H). ^{31}P {^{1}H} NMR (121 MHz, 298 K, C_6D_6): δ (ppm) 18.59 (dd, J = 164.4 and 156.7 Hz, 1P), −2.23 (d, J = 4.5 Hz, 1P), −3.56 (d, J = 5.2 Hz). ^{13}C{^{1}H} NMR (126 MHz, 298 K, C_6D_6): δ (ppm) 150.6 (dd, J = 11.9, 5.0 Hz), 150.3 (dd, J = 13.9 and 5.2 Hz), 147.3 (d, J = 18.4 Hz), 141.1 (dd, J = 29.6 and 19.2 Hz) 132.2 (s), 131.5 (d, J = 7.6 Hz), 129.0 (s), 128.7 (s), 128.0 (s), 118.6 (s), 115.9 (d, J = 13.1 Hz), 25.4 (d, J = 16.3 Hz), 23.9 (dd, J = 14.6, 5.8 Hz), 20.3 (dd, J = 17.2, 9.8 Hz), 19.9 (d, J = 20.4 Hz), 19.2 (d, J = 8.3 Hz). ESI-HRMS-TOF m/z: [M + H]$^+$ calcd for $C_{30}H_{42}NP_3$, 509.2512. Found, 509.2518.

Synthesis of [(^{iPr}PPPN^{H}Ph)CoCl]Cl Complex (IV). ^{iPr}PPPN^{H}Ph (34 mg, 0.066 mmol) solution in THF was added dropwise to the

https://dx.doi.org/10.1021/acs.organomet.0c00727
Organometallics XXXX, XXX, XXX−XXX

slurry of $CoCl_2$ (8.5 mg, 0.065 mmol) in THF, and the mixture was stirred for overnight at room temperature. The resulted dark-red slurry was filtered via Celite, and the filtrate was dried under vacuum to give a red powder. Red-orange crystals were grown overnight by slow diffusion of ether into the dichloromethane solution of the complex. ^{1}H NMR (500 MHz, 298 K, CD_2Cl_2): δ (ppm) 9.92, 8.61, 7.96, 7.10, 6.24, 4.99, 4.80, 3.19, 1.43, 1.23, 1.12, 0.85, 0.05, −1.08, −2.69, −5.15. μ_{eff} (B.M.): 1.95. UV−vis [CH_2Cl_2; λ, nm (ε, M^{-1} cm^{-1})]: 472 (71.1). Anal. calcd for $C_{30}H_{42}Cl_2CoNP_3$: C, 56.35; H, 6.62; N, 2.19. Found: C, 56.21; H, 6.60; N, 2.18.

Transfer Hydrogenation of Imine. Condition A: Inside a N_2-filled glovebox, an oven-dried 15 mL reaction tube was charged with *N*-benzylideneaniline (45 mg, 0.25 mmol), benzyl alcohol (30 μL, 0.275 mmol), **I** (4.1 mg, 2.5 mol %), KO^{t}Bu (31 mg, 110 mol %), and toluene (0.75 mL). The tube was sealed by a screw cap fitted with a PTFE septa and heated at 85 °C for 24 h. The reaction mixture was filtered through a silica gel plug and analyzed by ^{1}H NMR spectroscopy. *N*-Benzylaniline was observed with 82% yield.

Condition B: Inside a N_2-filled glovebox, an oven-dried 15 mL reaction tube was charged with *N*-benzylideneaniline (45 mg, 0.25 mmol), benzyl alcohol (30 μL, 0.275 mmol), **I** (4.1 mg, 2.5 mol %), KO^{t}Bu (2.1 mg, 7.5 mol %), and toluene (0.75 mL). The tube was sealed by a screw cap fitted with a PTFE septa and heated at 85 °C for 24 h. The reaction mixture was filtered through a silica gel plug and analyzed by ^{1}H NMR spectroscopy. Trace amount (<1%) of *N*-benzylaniline was observed.

Synthesis of *N*-Benzylideneaniline 3a. Condition A: Inside a N_2-filled glovebox, an oven-dried 15 mL reaction tube was charged with **I** (4.1 mg, 2.5 mol %), KO^{t}Bu (2.1 mg, 7.5 mol %), benzyl alcohol (0.25 mmol), aniline (0.275 mmol), and benzene (1.2 mL). The tube was then sealed by a screw cap fitted with a PTFE septa and attached to argon flow through a needle. The reaction was carried out at 105 °C for 24 h. 1,3,5-Trimethoxybenzene (8.4 mg, 0.05 mmol) was added to the reaction mixture as internal standard. The mixture was diluted with $CDCl_3$ and filtered through Celite and subjected to NMR analysis. NMR yield: 88%.

Condition B: Inside a N_2-filled glovebox, an oven-dried 100 mL pressure vessel was charged with **I** (4.1 mg, 2.5 mol %), KO^{t}Bu (2.1 mg, 7.5 mol %), benzyl alcohol (0.25 mmol), aniline (0.275 mmol), and benzene (1.2 mL). The vessel was sealed by a PTFE valve and heated to 105 °C for 24 h. 1,3,5-Trimethoxybenzene (8.4 mg, 0.05 mmol) was added to the reaction mixture as internal standard. An aliquot of mixture was filtered through Celite, rinsed with $CDCl_3$, and subjected to NMR analysis. NMR yield: 82%.

Condition C (1 mmol scale): Inside a N_2-filled glovebox, an oven-dried 15 mL reaction tube was charged with **I** (16.4 mg, 2.5 mol %), KO^{t}Bu (8.4 mg, 7.5 mol %), benzyl alcohol (1 mmol), aniline (1.1 mmol), and benzene (3 mL). The tube was then sealed by a screw cap fitted with a PTFE septa and attached to argon flow through a needle. The reaction was carried out at 105 °C for 24 h. At the end of the reaction, the solvent was removed under reduced pressure, and the crude mixture was purified by short-path vacuum distillation. Light yellow powder of **3a** was isolated. Yield: 143 mg (79%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.93−7.91 (m, 2H), 7.51−7.49 (m, 2H), 7.50−7.48 (m, 1H), 7.43−7.39 (m, 2H), 7.27 (m, 1H), 7.25−7.22 (m, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.5, 152.2, 136.3, 131.5, 129.3, 129.0, 128.9, 126.0, 121.0 ppm.

Condition D: Inside a N_2-filled glovebox, an oven-dried 15 mL reaction tube was charged with **II** (3.9 mg, 2.5 mol %), KO^{t}Bu (1.4 mg, 5 mol %), benzyl alcohol (0.25 mmol), aniline (0.275 mmol), and benzene (1.2 mL). The tube was then sealed by a screw cap fitted with a PTFE septa and attached to argon flow through a needle. The reaction was carried out at 105 °C for 24 h. 1,3,5-Trimethoxybenzene (8.4 mg, 0.05 mmol) was added to the reaction mixture as internal standard. The mixture was diluted with $CDCl_3$ and filtered through Celite and subjected to NMR analysis. NMR yield: 85%.

Condition E: Inside a N_2-filled glovebox, an oven-dried 15 mL reaction tube was charged with **III** (4.9 mg, 2.5 mol %), KO^{t}Bu (2.1 mg, 7.5 mol %), benzyl alcohol (0.25 mmol), aniline (0.275 mmol), and benzene (1.2 mL). The tube was then sealed by a screw cap fitted with a PTFE septa and attached to argon flow through a needle. The reaction was carried out at 105 °C for 24 h. 1,3,5-Trimethoxybenzene (8.4 mg, 0.05 mmol) was added to the reaction mixture as internal standard. The mixture was diluted with $CDCl_3$ and filtered through Celite and subjected to NMR analysis. NMR yield: 1%.

Condition E: Inside a N_2-filled glovebox, an oven-dried 15 mL reaction tube was charged with **IV** (3.9 mg, 2.5 mol %), KO^{t}Bu (2.1 mg, 7.5 mol %), benzyl alcohol (0.25 mmol), aniline (0.275 mmol), and benzene (1.2 mL). The tube was then sealed by a screw cap fitted with a PTFE septa and attached to argon flow through a needle. The reaction was carried out at 105 °C for 24 h. 1,3,5-Trimethoxybenzene (8.4 mg, 0.05 mmol) was added to the reaction mixture as internal standard. The mixture was diluted with $CDCl_3$ and filtered through Celite and subjected to NMR analysis. NMR yield: 0%.

Condition G: Inside a N_2-filled glovebox, an oven-dried 15 mL reaction tube was charged with **V** (4.4 mg, 3.5 mol %), KO^{t}Bu (1.7 mg, 6 mol %), benzyl alcohol (0.3 mmol), aniline (0.25 mmol), and benzene (1.2 mL). The tube was then sealed by a screw cap fitted with a PTFE septa and attached to argon flow through a needle. The reaction was carried out at 105 °C for 24 h. 1,3,5-Trimethoxybenzene (8.4 mg, 0.05 mmol) was added to the reaction mixture as internal standard. The mixture was diluted with $CDCl_3$ and filtered through Celite and subjected to NMR analysis. NMR yield: 80%.

Condition H: Inside a N_2-filled glovebox, an oven-dried 15 mL reaction tube was charged with **VI** (3.3 mg, 2.5 mol %), KO^{t}Bu (2.1 mg, 7.5 mol %), benzyl alcohol (0.25 mmol), aniline (0.275 mmol), and benzene (1.2 mL). The tube was then sealed by a screw cap fitted with a PTFE septa and attached to argon flow through a needle. The reaction was carried out at 105 °C for 24 h. 1,3,5-Trimethoxybenzene (8.4 mg, 0.05 mmol) was added to the reaction mixture as internal standard. The mixture was diluted with $CDCl_3$ and filtered through Celite and subjected to NMR analysis. NMR yield: 3%.

Synthesis of *N*-Benzylaniline 4a. Condition A: Inside a N_2-filled glovebox, an oven-dried 15 mL reaction tube was charged with **I** (4.9 mg, 3 mol %), KO^{t}Bu (31 mg, 110 mol %), benzyl alcohol (0.25 mmol), aniline (0.275 mmol), and toluene (0.75 mL). The tube was then sealed by a screw cap fitted with a PTFE septa, taken out of the box, and heated at 85 °C for 24 h. 1,3,5-Trimethoxybenzene (8.4 mg, 0.05 mmol) was added to the reaction mixture as internal standard. An aliquot of mixture was filtered through silica gel and rinsed with diethyl ether (5 mL). The solvent was removed under reduced pressure, and the crude mixture was subjected to NMR analysis to identify the products and determine product yields. NMR yield: 93%.

Condition B (1 mmol scale): Inside a N_2-filled glovebox, an oven-dried 15 mL reaction tube was charged with **I** (19.6 mg, 3 mol %), KO^{t}Bu (124 mg, 110 mol %), benzyl alcohol (1 mmol), aniline (1.1 mmol), and toluene (2 mL). The tube was then sealed by a screw cap fitted with a PTFE septa, taken out of the box, and heated at 85 °C for 24 h. At the end of the reaction, the solvent was removed under reduced pressure, and the crude mixture was passed through a silica gel column using ethyl acetate/hexane (1:10, *v*/*v*) as an eluent. A pale yellow oil of **4a** was isolated. Yield: 163 mg (89%). ^{1}H NMR (500 MHz, CDCl3) δ 7.47−7.52 (m, 4 H), 7.40−7.43 (m, 1 H), 7.31−7.34 (m, 2 H), 6.86−6.89 (m, 1 H), 6.75−6.77 (m, 2 H), 4.43 (s, 2 H), 4.11 (s, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.4, 139.7, 129.5, 128.9, 127.7, 127.4, 117.7, 113.1, 48.5 ppm.

Condition C: Inside a N_2-filled glovebox, an oven-dried 15 mL reaction tube was charged with **II** (4.6 mg, 3 mol %), KO^{t}Bu (31 mg, 110 mol %), benzyl alcohol (0.25 mmol), aniline (0.275 mmol), and toluene (0.75 mL). The tube was then sealed by a screw cap fitted with a PTFE septa, taken out of the box, and heated at 85 °C for 24 h. 1,3,5-Trimethoxybenzene (8.4 mg, 0.05 mmol) was added to the reaction mixture as internal standard. An aliquot of mixture was filtered through silica gel and rinsed with diethyl ether (5 mL). The solvent was removed under reduced pressure, and the crude mixture was subjected to NMR analysis to identify the products and determine product yields. NMR yield: 79%.

Condition D: Inside a N_2-filled glovebox, an oven-dried 15 mL reaction tube was charged with **III** (5.9 mg, 3 mol %), KO^{t}Bu (31 mg, 110 mol %), benzyl alcohol (0.25 mmol), aniline (0.275 mmol), and

https://dx.doi.org/10.1021/acs.organomet.0c00727
Organometallics XXXX, XXX, XXX−XXX

toluene (0.75 mL). The tube was then sealed by a screw cap fitted with a PTFE septa, taken out of the box, and heated at 85 °C for 24 h. 1,3,5-Trimethoxybenzene (8.4 mg, 0.05 mmol) was added to the reaction mixture as internal standard. An aliquot of mixture was filtered through silica gel and rinsed with diethyl ether (5 mL). The solvent was removed under reduced pressure, and the crude mixture was subjected to NMR analysis to identify the products and determine product yields. NMR yield: 80%.

Condition E: Inside a N_2-filled glovebox, an oven-dried 15 mL reaction tube was charged with **IV** (4.6 mg, 3 mol %), KO^{t}Bu (31 mg, 110 mol %), benzyl alcohol (0.25 mmol), aniline (0.275 mmol), and toluene (0.75 mL). The tube was then sealed by a screw cap fitted with a PTFE septa, taken out of the box, and heated at 85 °C for 24 h. 1,3,5-Trimethoxybenzene (8.4 mg, 0.05 mmol) was added to the reaction mixture as internal standard. An aliquot of mixture was filtered through silica gel and rinsed with diethyl ether (5 mL). The solvent was removed under reduced pressure, and the crude mixture was subjected to NMR analysis to identify the products and determine product yields. NMR yield: 93%.

Condition F: Inside a N_2-filled glovebox, an oven-dried 15 mL reaction tube was charged with **V** (3.7 mg, 3 mol %), KO^{t}Bu (21 mg, 75 mol %), benzyl alcohol (0.25 mmol), aniline (0.275 mmol), and toluene (0.75 mL). The tube was then sealed by a screw cap fitted with a PTFE septa, taken out of the box, and heated at 85 °C for 24 h. 1,3,5-Trimethoxybenzene (8.4 mg, 0.05 mmol) was added to the reaction mixture as internal standard. An aliquot of mixture was filtered through silica gel and rinsed with diethyl ether (5 mL). The solvent was removed under reduced pressure, and the crude mixture was subjected to NMR analysis to identify the products and determine product yields. NMR yield: 74%.

Condition G: Inside a N_2-filled glovebox, an oven-dried 15 mL reaction tube was charged with **VI** (4.0 mg, 3 mol %), KO^{t}Bu (31 mg, 110 mol %), benzyl alcohol (0.25 mmol), aniline (0.275 mmol), and toluene (0.75 mL). The tube was then sealed by a screw cap fitted with a PTFE septa, taken out of the box, and heated at 85 °C for 24 h. 1,3,5-Trimethoxybenzene (8.4 mg, 0.05 mmol) was added to the reaction mixture as internal standard. An aliquot of mixture was filtered through silica gel and rinsed with diethyl ether (5 mL). The solvent was removed under reduced pressure, and the crude mixture was subjected to NMR analysis to identify the products and determine product yields. NMR yield: 86%.

Hydrogen Detection. Inside a N_2-filled glovebox, an oven-dried 100 mL pressure vessel was charged with **I** (16.4 mg, 2.5 mol %), KO^{t}Bu (8.4 mg, 7.5 mol %), benzyl alcohol (1 mmol), aniline (1.1 mmol), and benzene (2 mL). The vessel was sealed by a PTFE valve and heated to 105 °C for 24 h. The headspace gas sample was taken by a needle syringe from the side arm and analyzed via the SRI 8610C Gas Chromatograph with a 5 Å molecular sieves column (Restek CP753415) with N_2 carrier gas.

Homogeneity Test of the Reaction System for Imine Synthesis. Inside a N_2-filled glovebox, an oven-dried 15 mL reaction tube was charged with **I** (4.1 mg, 2.5 mol %), KO^{t}Bu (2.1 mg, 7.5 mol %), benzyl alcohol (0.25 mmol), aniline (0.275 mmol), and benzene (1.2 mL). Mercury (125 mg, 0.625 mmol) was added to the tube which was then sealed by a screw cap fitted with a PTFE septa and attached to argon flow through a needle. The reaction was carried out at 105 °C for 24 h. 1,3,5-Trimethoxybenzene (8.4 mg, 0.05 mmol) was added to the reaction mixture as internal standard. The mixture was diluted with $CDCl_3$, filtered through Celite, and subjected to NMR analysis. NMR yield: 74%.

Homogeneity Test of the Reaction System for Amine Synthesis. Inside a N_2-filled glovebox, an oven-dried 15 mL reaction tube was charged with **I** (4.9 mg, 3 mol %), KO^{t}Bu (31 mg, 110 mol %), benzyl alcohol (0.25 mmol), aniline (0.275 mmol), and toluene (0.75 mL). Mercury (125 mg, 0.625 mmol) was added to the tube which was then sealed by a screw cap fitted with a PTFE septa and heated at 85 °C for 24 h. 1,3,5-Trimethoxybenzene (8.4 mg, 0.05 mmol) was added to the reaction mixture as internal standard. An aliquot of mixture was filtered through silica gel and rinsed with diethyl ether (5 mL). The solvent was removed under reduced pressure, and the crude mixture was subjected to NMR analysis to identify the products and determine product yields. NMR yield: 77%.

Deuterium Labeling Study of Benzyl Alcohol and Aniline Coupling to *N*-Benzylideneaniline. Inside a N_2-filled glovebox, an oven-dried 15 mL reaction tube was charged with (benzyl alcohol)-α,α-d_2 (0.25 mmol), aniline (0.275 mmol), **I** (4.1 mg, 2.5 mol %), KO^{t}Bu (2.1 mg, 7.5 mol %), and benzene (1.2 mL). The tube was sealed by a screw cap fitted with a PTFE septa and attached to argon flow through a needle. The reaction was carried out at 105 °C for 24 h. 1,3,5-Trimethoxybenzene (8.4 mg, 0.05 mmol) was added to the reaction mixture as internal standard. The mixture was diluted with $CDCl_3$, filtered through Celite and subjected to NMR analysis. H/D scrambling was detected with a Ph−CH═N−Ph/Ph−CD═N−Ph ratio of 1:3.

Study of the Cobalt Hydride in the Coupling of Benzyl Alcohol and Aniline to *N*-Benzylaniline. Inside a N_2-filled glovebox, an oven-dried J. Young NMR tube was charged with benzyl alcohol (0.125 mmol), aniline (0.125 mmol), **I** (8.2 mg, 10 mol %), KO^{t}Bu (11.2 mg, 80 mol %), and toluene-d_8 (0.5 mL). The tube was sealed with PTFE cap, and the reaction was monitored by ^{1}H NMR (500 MHz) at 85 °C.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00727.

Experimental and crystallographic details, H2 detection by GC chromatography, ^{1}H, ^{31}P, ^{13}C, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra, IR and UV−vis spectra (PDF)

Accession Codes

CCDC 2025592 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

Keying Ding − *Department of Chemistry and Molecular Biosciences Program, Middle Tennessee State University, Murfreesboro, Tennessee 37132, United States;* orcid.org/0000-0002-7367-129X; Email: Keying.Ding@mtsu.edu

Authors

Keshav Paudel − *Department of Chemistry and Molecular Biosciences Program, Middle Tennessee State University, Murfreesboro, Tennessee 37132, United States*

Shi Xu − *Department of Chemistry, Middle Tennessee State University, Murfreesboro, Tennessee 37132, United States*

Oleksandr Hietsoi − *Department of Chemistry, Middle Tennessee State University, Murfreesboro, Tennessee 37132, United States*

Bedraj Pandey − *Department of Chemistry, Middle Tennessee State University, Murfreesboro, Tennessee 37132, United States*

Chuka Onuh − *Department of Chemistry, Middle Tennessee State University, Murfreesboro, Tennessee 37132, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.organomet.0c00727

Author Contributions

[§]K.P. and S.X. contributed equally to this work.

https://dx.doi.org/10.1021/acs.organomet.0c00727
Organometallics XXXX, XXX, XXX−XXX

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge the financial support from National Science Foundation (CHE-1465051 and MRI CHE-1626549). K.D. thanks the Tennessee Board of Regents (TBR-SERS) for partial aid. We also thank FRCAC, URECA, and Clean Energy Fee Funds from Middle Tennessee State University. K.D. thanks Prof. Norma Dunlap for helpful discussions. The following students are acknowledged for their contributions: Latifah Alhthlol, Daniela Taylor, Paeton Poynter, Kerolos Bushra, and David Tyer.

■ REFERENCES

(1) Colacot, T. J. *New Trends in Cross-Coupling: Theory and Applications*; Royal Society of Chemistry: Cambridge, 2014.
(2) Watson, A. J. A.; Williams, J. M. J. The Give and Take of Alcohol Activation. *Science* **2010**, *329*, 635−636.
(3) Dobereiner, G. E.; Crabtree, R. H. Dehydrogenation as a Substrate-Activating Strategy in Homogeneous Transition-Metal Catalysis. *Chem. Rev.* **2010**, *110*, 681−703.
(4) Gunanathan, C.; Milstein, D. Applications of Acceptorless Dehydrogenation and Related Transformations in Chemical Synthesis. *Science* **2013**, *341*, 1229712.
(5) Corma, A.; Navas, J.; Sabater, M. J. Advances in One-Pot Synthesis through Borrowing Hydrogen Catalysis. *Chem. Rev.* **2018**, *118*, 1410−1459.
(6) Barta, K.; Ford, P. C. Catalytic Conversion of Nonfood Woody Biomass Solids to Organic Liquids. *Acc. Chem. Res.* **2014**, *47*, 1503−1512.
(7) Filonenko, G. A.; van Putten, R.; Hensen, E. J. M.; Pidko, E. A. Catalytic (De)Hydrogenation Promoted by Non-precious Metals - Co, Fe and Mn: Recent Advances in an Emerging Field. *Chem. Soc. Rev.* **2018**, *47*, 1459−1483.
(8) Mukherjee, A.; Milstein, D. Homogeneous Catalysis by Cobalt and Manganese Pincer Complexes. *ACS Catal.* **2018**, *8*, 11435−11469.
(9) Kallmeier, F.; Kempe, R. Manganese Complexes for (De)-Hydrogenation Catalysis: A Comparison to Cobalt and Iron Catalysts. *Angew. Chem., Int. Ed.* **2018**, *57*, 46−60.
(10) Gorgas, N.; Kirchner, K. Isoelectronic Manganese and Iron Hydrogenation/Dehydrogenation Catalysts: Similarities and Divergences. *Acc. Chem. Res.* **2018**, *51*, 1558−1569.
(11) Alig, L.; Fritz, M.; Schneider, S. First-Row Transition Metal (De)Hydrogenation Catalysis Based on Functional Pincer Ligands. *Chem. Rev.* **2019**, *119*, 2681−2751.
(12) Irrgang, T.; Kempe, R. 3d-Metal Catalyzed N- and C-Alkylation Reactions via Borrowing Hydrogen or Hydrogen Autotransfer. *Chem. Rev.* **2019**, *119*, 2524−2549.
(13) Ai, W.; Zhong, R.; Liu, X.; Liu, Q. Hydride Transfer Reactions Catalyzed by Cobalt Complexes. *Chem. Rev.* **2019**, *119*, 2876−2953.
(14) Junge, K.; Papa, V.; Beller, M. Cobalt-Pincer Complexes in Catalysis. *Chem. - Eur. J.* **2019**, *25*, 122−143.
(15) Rappoport, Z. J.; Liebman, F. *The Chemistry of Hydroxylamines, Oximes and Hydroxamic Acids*; Wiley, 2009.
(16) Lawrence, S A. *Amine: Synthesis Properties, and Applications*; Cambridge University, 2004.
(17) Zhang, G.; Hanson, S. K. Cobalt-Catalyzed Acceptorless Alcohol Dehydrogenation: Synthesis of Imines from Alcohols and Amines. *Org. Lett.* **2013**, *15*, 650−653.
(18) Zhang, G.; Yin, Z.; Zheng, S. Cobalt-Catalyzed N-Alkylation of Amines with Alcohols. *Org. Lett.* **2016**, *18*, 300−303.
(19) Saha, B.; Wahidur Rahaman, S. M.; Daw, P.; Sengupta, G.; Bera, J. K. Metal-Ligand Cooperation on a Diruthenium Platform: Selective Imine Formation through Acceptorless Dehydrogenative Coupling of Alcohols with Amines. *Chem. - Eur. J.* **2014**, *20*, 6542−6551.
(20) Midya, S. P.; Pitchaimani, J.; Landge, V. G.; Madhu, V.; Balaraman, E. Direct Access to N-alkylated Amines and Imines via Acceptorless Dehydrogenative Coupling Catalyzed by a Cobalt(II)-NNN Pincer Complex. *Catal. Sci. Technol.* **2018**, *8*, 3469−3473.
(21) Mastalir, M.; Glatz, M.; Gorgas, N.; Stöger, B.; Pittenauer, E.; Allmaier, G.; Veiros, L. F.; Kirchner, K. Divergent Coupling of Alcohols and Amines Catalyzed by Isoelectronic Hydride Mn^{I} and Fe^{II} PNP Pincer Complexes. *Chem. - Eur. J.* **2016**, *22*, 12316−12320.
(22) Fertig, R.; Irrgang, T.; Freitag, F.; Zander, J.; Kempe, R. Manganese-Catalyzed and Base-Switchable Synthesis of Amines or Imines via Borrowing Hydrogen or Dehydrogenative Condensation. *ACS Catal.* **2018**, *8*, 8525−8530.
(23) Mukherjee, A.; Nerush, A.; Leitus, G.; Shimon, L. J.; Ben-David, Y.; Espinosa Jalapa, N. A.; Milstein, D. Manganese-Catalyzed Environmentally Benign Dehydrogenative Coupling of Alcohols and Amines to Form Aldimines and H_2: A Catalytic and Mechanistic Study. *J. Am. Chem. Soc.* **2016**, *138*, 4298−4301.
(24) Deibl, N.; Kempe, R. Manganese-Catalyzed Multicomponent Synthesis of Pyrimidines from Alcohols and Amidines. *Angew. Chem., Int. Ed.* **2017**, *56*, 1663−1666.
(25) Elangovan, S.; Neumann, J.; Sortais, J.-P.; Junge, K.; Darcel, C.; Beller, M. Efficient and Selective N-Alkylation of Amines with Alcohols Catalysed by Manganese Pincer Complexes. *Nat. Commun.* **2016**, *7*, 12641.
(26) Neumann, J.; Elangovan, S.; Spannenberg, A.; Junge, K.; Beller, M. Improved and General Manganese-Catalyzed N-Methylation of Aromatic Amines Using Methanol. *Chem. - Eur. J.* **2017**, *23*, 5410−5413.
(27) Bruneau-Voisine, A.; Wang, D.; Dorcet, V.; Roisnel, T.; Darcel, C.; Sortais, J.-B. Mono-N-Methylation of Anilines with Methanol Catalyzed by a Manganese Pincer-Complex. *J. Catal.* **2017**, *347*, 57−62.
(28) Rösler, S.; Ertl, M.; Irrgang, T.; Kempe, R. Cobalt-Catalyzed Alkylation of Aromatic Amines by Alcohols. *Angew. Chem., Int. Ed.* **2015**, *54*, 15046−15050.
(29) Mastalir, M.; Tomsu, G.; Pittenauer, E.; Allmaier, G.; Kirchner, K. Co(II) PCP Pincer Complexes as Catalysts for the Alkylation of Aromatic Amines with Primary Alcohols. *Org. Lett.* **2016**, *18*, 3462−3465.
(30) Midya, S.; Mondal, A.; Begum, A.; Balaraman, E. A Simple Cobalt (II) Chloride Catalyzed N-Alkylation of Amines with Alcohols. *Synthesis* **2017**, *49*, 3957−3961.
(31) Yan, T.; Feringa, B. L.; Barta, K. Iron Catalysed Direct Alkylation of Amines with Alcohols. *Nat. Commun.* **2014**, *5*, 5602.
(32) Yan, T.; Feringa, B. L.; Barta, K. Benzylamines via Iron-Catalyzed Direct Amination of Benzyl Alcohols. *ACS Catal.* **2016**, *6*, 381−388.
(33) Mastalir, M.; Stöger, B.; Pittenauer, E.; Puchberger, M.; Allmaier, G.; Kirchner, K. Air Stable Iron (II) PNP Pincer Complexes as Efficient Catalysts for the Selective Alkylation of Amines with Alcohols. *Adv. Synth. Catal.* **2016**, *358*, 3824−3831.
(34) Brown, T. J.; Cumbes, M.; Diorazio, L. J.; Clarkson, G. J.; Wills, M. Use of (Cyclopentadienone) Iron Tricarbonyl Complexes for C-N Bond Formation Reactions Between Amines and Alcohols. *J. Org. Chem.* **2017**, *82*, 10489−10503.
(35) Bala, M.; Verma, P. K.; Kumar, N.; Sharma, U.; Singh, B. Highly Efficient Iron Phthalocyanine Catalyzed Oxidative Synthesis of Imines from Alcohols and Amines. *Can. J. Chem.* **2013**, *91*, 732−737.
(36) Samuelsen, S.; Santilli, C.; Ahlquist, M. S. G.; Madsen, R. Development and mechanistic investigation of the manganese (III) salen-catalyzed dehydrogenation of alcohols. *Chem. Sci.* **2019**, *10*, 1150−1157.
(37) Liu, Z.; Yang, Z.; Yu, X.; Zhang, H.; Yu, B.; Zhao, Y.; Liu, Z. Efficient Cobalt-Catalyzed Methylation of Amines Using Methanol. *Adv. Synth. Catal.* **2017**, *359*, 4278−4283.
(38) Das, K.; Mondal, A.; Pal, D.; Srivastava, H. K.; Srimani, D. Phosphine-Free Well-Defined Mn(I) Complex-Catalyzed Synthesis of

https://dx.doi.org/10.1021/acs.organomet.0c00727
Organometallics XXXX, XXX, XXX−XXX

Amine, Imine, and 2,3-Dihydro-1H-perimidine via Hydrogen Autotransfer or Acceptorless Dehydrogenative Coupling of Amine and Alcohol. *Organometallics* **2019**, *38*, 1815−1825.
(39) Kwon, M. S.; Kim, S.; Park, S.; Bosco, W.; Chidrala, R. K.; Park, J. One-Pot Synthesis of Imines and Secondary Amines by Pd-Catalyzed Coupling of Benzyl Alcohols and Primary Amines. *J. Org. Chem.* **2009**, *74*, 2877−2879.
(40) Cano, R.; Ramón, D. J.; Yus, M. Impregnated Ruthenium on Magnetite as a Recyclable Catalyst for the N-Alkylation of Amines, Sulfonamides, Sulfinamides, and Nitroarenes Using Alcohols as Electrophiles by a Hydrogen Autotransfer Process. *J. Org. Chem.* **2011**, *76*, 5547−5557.
(41) Xu, S.; Alhthlol, L. M.; Paudel, K.; Reinheimer, E.; Tyer, D. L.; Taylor, D. K.; Smith, A. M.; Holzmann, J.; Lozano, E.; Ding, K. Tripodal N, P Mixed-Donor Ligands and Their Cobalt Complexes: Efficient Catalysts for Acceptorless Dehydrogenation of Secondary Alcohols. *Inorg. Chem.* **2018**, *57*, 2394−2397.
(42) Paudel, K.; Pandey, B.; Xu, S.; Taylor, D. K.; Tyer, D. L.; Torres, C. L.; Gallagher, S.; Kong, L.; Ding, K. Cobalt-Catalyzed Acceptorless Dehydrogenative Coupling of Primary Alcohols to Esters. *Org. Lett.* **2018**, *20*, 4478−4481.
(43) Pandey, B.; Xu, S.; Ding, K. Selective Ketone Formations via Cobalt-Catalyzed β-Alkylation of Secondary Alcohols with Primary Alcohols. *Org. Lett.* **2019**, *21*, 7420−7423.
(44) Sandoval, C. A.; Ohkuma, T.; Muñiz, K.; Noyori, R. Mechanism of Asymmetric Hydrogenation of Ketones Catalyzed by BINAP/1,2-Diamine-Ruthenium(II) Complexes. *J. Am. Chem. Soc.* **2003**, *125*, 13490−13503.
(45) Abdur-Rashid, K.; Clapham, S. E.; Hadzovic, A.; Harvey, J. N.; Lough, A. J.; Morris, R. H. Mechanism of the Hydrogenation of Ketones Catalyzed by Trans-Dihydrido(diamine) Ruthenium (II) Complexes. *J. Am. Chem. Soc.* **2002**, *124*, 15104−15118.
(46) Hamilton, R. J.; Bergens, S. H. An Unexpected Possible Role of Base in Asymmetric Catalytic Hydrogenation of Ketones. Synthesis and Characterization of Several Key Catalytic Intermediates. *J. Am. Chem. Soc.* **2006**, *128*, 13700−13701.
(47) Daw, P.; Ben-David, Y.; Milstein, D. Direct Synthesis of Benzimidazoles by Dehydrogenative Coupling of Aromatic Diamines and Alcohols Catalyzed by Cobalt. *ACS Catal.* **2017**, *7*, 7456−7460.
(48) Srimani, D.; Mukherjee, A.; Goldberg, A. F.; Leitus, G.; Diskin Posner, Y.; Shimon, L. J.; Ben-David, Y.; Milstein, D. Cobalt-Catalyzed Hydrogenation of Esters to Alcohols: Unexpected Reactivity Trend Indicates Ester Enolate Intermediacy. *Angew. Chem., Int. Ed.* **2015**, *54*, 12357−12360.
(49) Zhang, G.; Vasudevan, K. V.; Scott, B. L.; Hanson, S. K. Understanding the Mechanisms of Cobalt-Catalyzed Hydrogenation and Dehydrogenation Reactions. *J. Am. Chem. Soc.* **2013**, *135*, 8668−8681.
(50) Elangovan, S.; Topf, C.; Fischer, S.; Jiao, H.; Spannenberg, A.; Baumann, W.; Ludwig, R.; Junge, K.; Beller, M. Selective Catalytic Hydrogenations of Nitriles, Ketones, and Aldehydes by Well-Defined Manganese Pincer Complexes. *J. Am. Chem. Soc.* **2016**, *138*, 8809−8814.
(51) Deibl, N.; Kempe, R. General and Mild Cobalt-Catalyzed C-Alkylation of Unactivated Amides and Esters with Alcohols. *J. Am. Chem. Soc.* **2016**, *138*, 10786−10789.

https://dx.doi.org/10.1021/acs.organomet.0c00727
Organometallics XXXX, XXX, XXX−XXX