ORGANOMETALLICS

Article

Cite This: *Organometallics* XXXX, XXX, XXX−XXX

pubs.acs.org/Organometallics

A Highly Selective Manganese-Catalyzed Synthesis of Imines under Phosphine-Free Conditions

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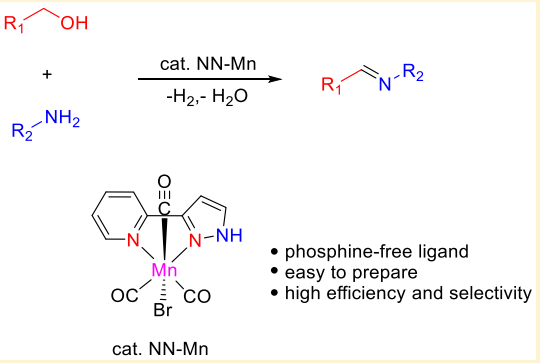
Supporting Information

ABSTRACT: An efficient and highly selective phosphine-free NN-manganese(I) complex catalyst system was developed for the acceptorless dehydrogenative coupling of alcohols with amines to form imines. The coupling reactions underwent at 3 mol % catalyst loading, and a large range of alcohols and amines with diverse functional groups was applied, including challenging diol and diamine. The target imine products were obtained in good to excellent yields. The present work provides an alternative method to construct highly active nonprecious metal complex catalysts based on phosphine-free ligands.



INTRODUCTION

Substituted imines and their derivatives are important building blocks in pharmaceuticals and agricultural chemicals.[1] Moreover, imine-based compounds can act as effective ligands in coordination chemistry to construct versatile transition-metal complex catalysts for catalysis.[2] Typically, imines are synthesized via the reaction of carbonyl compounds, such as aldehydes or ketones, with amines.[3] Significant progress has been made in acceptorless dehydrogenation reactions of alcohols in rencent years. Alcohols can be obtained from lignocellulose, which is a renewable biomass.[4] The catalytic synthesis of imines by acceptorless dehydrogenative coupling (ADC) reactions of alcohols with amines is an attractive green and sustainable route, in which H_2 and H_2O are produced as byproducts. In this direction, pioneering work was reported by Milstein and co-workers[5] in 2010, and they used a PNP-ruthenium pincer complex as the catalyst. Following this report, several catalytic systems for imine synthesis have been developed with precious-metal catalysts.[6] In 2012, Zhang and Hanson introduced the first synthesis of imines catalyzed by the PNP-pincer cobalt complex catalyst **A** (Scheme 1).[7] In 2013, Kumar/Singh et al. employed a Fe-phthalocyanine complex **B** (Scheme 1) as the catalyst to synthesize imines from alcohols and amines.[8] Notably, in 2016 Milstein's group reported the unprecedented dehydrogenative coupling of alcohols and amines catalyzed by pincer-type Mn-PNP complex **C** (Scheme 1).[9] Subsequently, Kirchner and co-workers showed the similar PNP ligand-supported manganese complex **D** (Scheme 1) can also catalyze this reaction.[10] Very recently, Kempe's group reported the base-switchable synthesis of amines or imines from the same alcohol and amine combinations catalyzed by the versatile PNP-type manganese complex **E** (Scheme 1).[11] Despite the significance of such coupling reactions, homogeneous cheap metal complex catalysts mostly contain posphine ligands that are sensitive to air and moisture and difficult to be prepared on a large scale. The development of nonprecious metal complex catalysts possessing phosphine-free ligands is urgent. Intrigued by these studies,[12] we paid much attention to the complexes bearing bidentate phosphine-free ligands. During our investigation of transition-metal complex catalysts, we disclose an efficient and highly selective phosphine-free NN-manganese(I) complex catalyst system, which enables the synthesis of imines from alcohols and amines efficiently and selectively (Scheme 1).

RESULTS AND DISCUSSION

Synthesis and Characterization of Complexes. Initially, we prepared two NN-manganese(I) complexes (**2a**, **2b**) by using ligands **1a**, **1b** with $Mn(CO)_5Br$ in MeOH at room temperature under a nitrogen atmosphere, giving corresponding Mn complexes **2a** and **2b** in 85% and 83% yields,

Received: November 10, 2019

DOI: 10.1021/acs.organomet.9b00769
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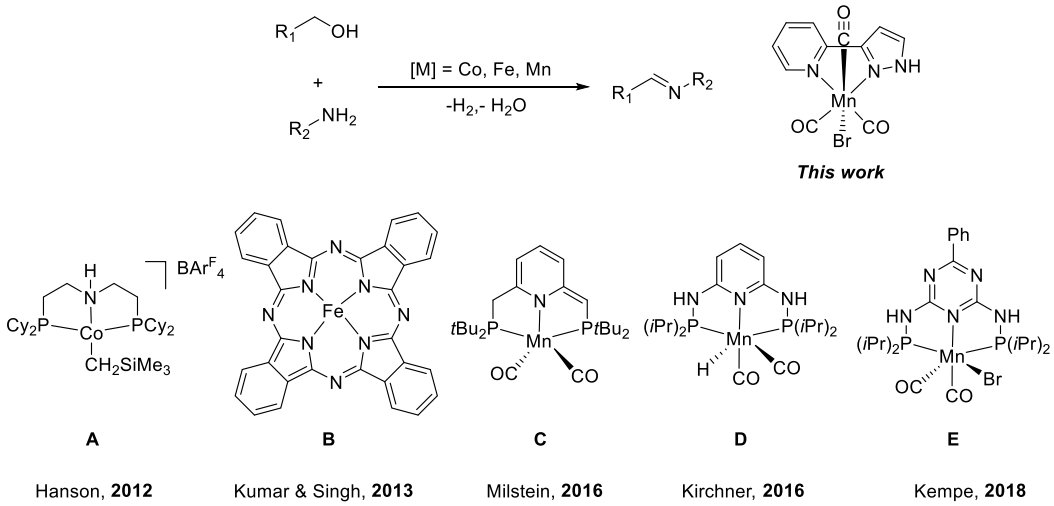
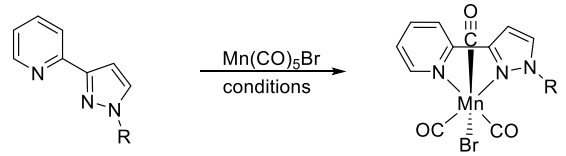
Scheme 1. Synthesis of Imines by Nonprecious Metal Complex Catalysts



respectively (Scheme 2). The NMR analyses of the ligands and their complexes are consistent with the compositions. In the

Scheme 2. Synthesis[a] of Complexes 2a and 2b



1a, R = H
1b, R = Me

2a, 85% (R = H)
2b, 83% (R = Me)

[a]Conditions: **1a** or **1b** (1.0 mmol), $Mn(CO)_5Br$ (1.0 mmol), CH_3OH (25 mL), 0.1 M Pa N_2, 25 °C, 24 h, 85% (**2a**), 83% (**2b**).

^{13}C NMR spectrum, the three coordinating CO groups in complexes appeared at 222.5, 222.1, and 221.6 ppm for **2a** and at 223.3, 223.0, and 220.6 ppm for **2b**. In the infrared spectrum (IR) of complex **2a**, the stretching vibrations of CO ligands gave rise to bands at 1927 and 2036 cm^{-1}. Similarly, carbonyl ligands in complex **2b** were revealed at 1888 and 2013 cm^{-1} in the IR spectral analysis. We attempted to obtain the single crystals of complex **2a** for the X-ray structural analysis, but no success was achieved. To our delight, the molecular structure of methyl-substituted complex **2b** was confirmed by the X-ray single-crystal crystallographic determination (Figure 1, see Supporting Information for details). The structure of complex **2b** exhibits a distorted octahedral geometry, and the central manganese atom of complex **2b** is surrounded by bidentate NN ligand **1b**, three CO groups, and a bromo atom positioning trans to one of the carbonyls (Figure 1). The three coordinating CO ligands are orthogonal to each other and locate in three different chemical environments, in line with the ^{13}C NMR spectrum.

Synthesis of Imines. In an exploration of the optimum conditions, the reaction of phenylmethanol with aniline was studied as a model system for the acceptorless dehydrogenative coupling to form imines (Table 1). The catalytic activities of complex **2a** and **2b** were examined in refluxing toluene of phenylmethanol (0.22 mmol), aniline (0.20 mmol), and *t*BuOK (0.10 mmol) under a nitrogen atmosphere (see Table 1, entries 1 and 2). In the presence of 3 mol % complex

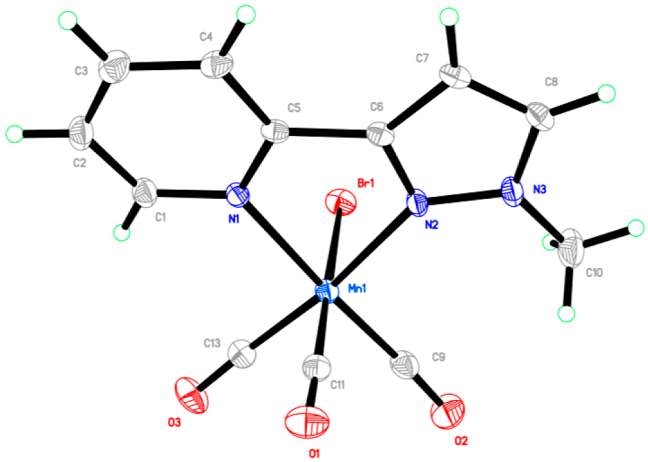


Figure 1. Molecular structure of complex **2b**.

catalyst **2a**, 97% conversion was obtained for **4a** with a higher selectivity (98.1:1.9) for product imine **5a** and product amine **5a′** (see Table 1, entry 1), while complex **2b** yielded 90% conversion for **4a** and 77:23 selectivity for **5a**:**5a′** (see Table 1, entry 2). The high catalytic activity and selectivity of complex **2a** may be derived from the NH functionality.[13] In the same reactions of entry 1, heating the solution in a closed system resulted in only 41% conversion for **4a** (see Table 1, entry 3). Next, the base effect on the reaction was evaluated. Use of *t*BuONa obviously deteriorated the conversion (77%) (see Table 1, entry 4). The case of utilizing KOH under similar conditions gave 93% conversion for **4a** and 29:71 selectivity for **5a**:**5a′** (see Table 1, entry 5), while the reaction proceeded less efficiently with 80% conversion for **4a** employing NaOH as a base (see Table 1, entry 6). When Na_2CO_3 and K_2CO_3 were used as the bases, the conversions for **4a** were dropped from 14% to 3.2% (see Table 1, entries 7 and 8). Different solvents were also screened for the reaction. In refluxing 1,4-dioxane, both the conversion and the selectivity were decreased greatly (see Table1, entry 9). In tetrahydrofuran (thf) or 2-Me-thf, the substrates hardly reacted (see Table 1, entries 10 and 11). Decreasing the catalyst loading to 2 mol % reduced the conversion of **4a** with deteriorated selectivity of **5a**/**5a′** (see Table 1, entry 12). With 4 mol % catalyst loading, there's no evident improvement in conversion of **4a** and selectivity of **5a**/

DOI: 10.1021/acs.organomet.9b00769
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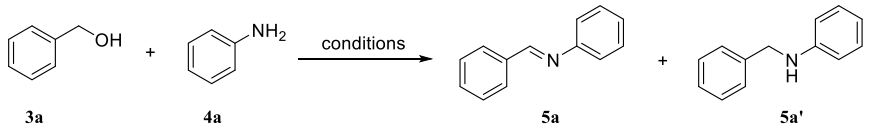
Table 1. Screening of Reaction Conditions[a]

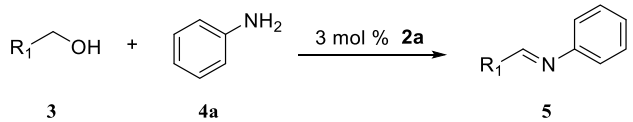


3a 4a 5a 5a'

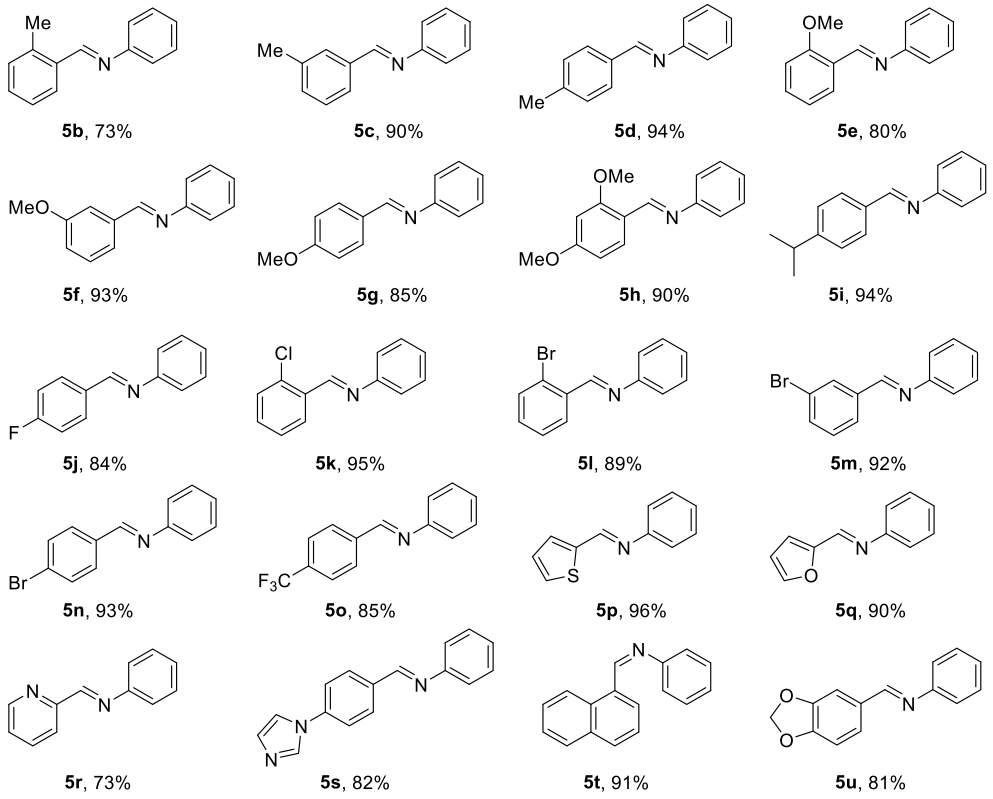
entry	catalyst loading (mol %)	base (0.5 equiv)	solvent (1.5 mL)	conv[b] (%)	5a/5a′ (molar ratio)[b] (%)
1	3	*t*BuOK	toluene	97	98.1:1.9
2[c]	3	*t*BuOK	toluene	90	77:23
3[d]	3	*t*BuOK	toluene	41	99:1
4	3	*t*BuONa	toluene	77	99.5:0.5
5	3	KOH	toluene	93	29:71
6	3	NaOH	toluene	80	99.6:0.4
7	3	Na_2CO_3	toluene	14	81:19
8	3	K_2CO_3	toluene	3.2	100
9	3	*t*BuOK	1,4-dioxane	42	79.4:20.6
10	3	*t*BuOK	thf	0.7	100
11	3	*t*BuOK	2-Me-thf	0.4	100
12	2	*t*BuOK	toluene	85	80:20
13	4	*t*BuOK	toluene	98	98:2
14[e]	**3**	***t*BuOK**	**toluene**	**97**	**99.5:0.5(93)**[f]

[a]Conditions: **3a** (0.22 mmol), **4a** (0.20 mmol), complex catalyst **2a** (0.006 mmol), 110 °C, 0.1 MPa N_2, 24 h. [b]Determined by gas chromatography analysis. [c]Using complex catalyst **2b**. [d]Screening in sealed tube. [e]Adding 5 mg of 4 Å MS. [f]Isolated yield of **5a** given in parentheses.

Table 2. Scope of Primary Alcohols 3[a]



3 4a 5



[a]Conditions: **3** (0.55 mmol), **4a** (0.50 mmol), complex **2a** (0.015 mmol), *t*BuOK (0.25 mmol), 4 Å MS (12.5 mg), toluene (2 mL), 110 °C, 0.1 MPa N_2, 24 h. Yields refer to the isolated products.

5a′ (see Table 1, entry 13). To our delight, the selectivity for **5a**/**5a′** was further improved if 5 mg of 4 Å MS was added, and product imine **5a** was isolated in 93% yield (see Table 1, entry 14). Different amounts of 4 Å MS, base loading, and the ratio

DOI: 10.1021/acs.organomet.9b00769
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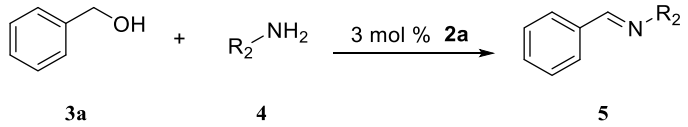
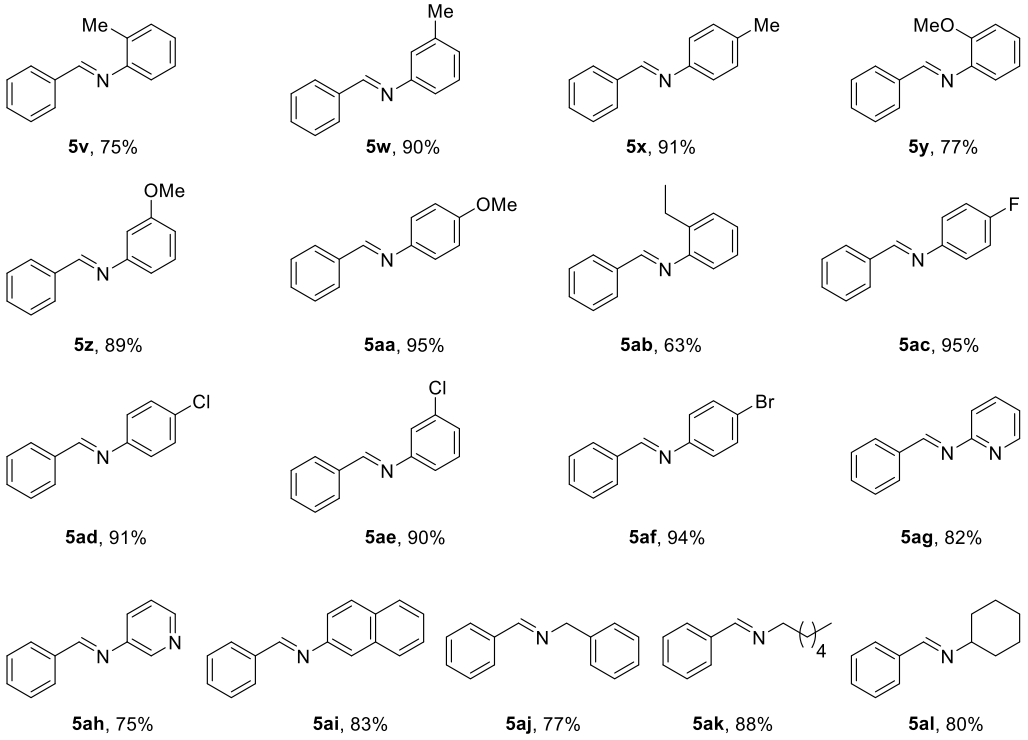
Table 3. Scope of Amines 4[a]



3a **4** **5**



[a]Conditions: **3a** (0.55 mmol), **4** (0.50 mmol), catalyst **2a** (0.015 mmol), *t*BuOK (0.25 mmol), 4 Å MS (12.5 mg), toluene (2 mL), 110 °C, 0.1 MPa N_2, 24 h. Yields refer to the isolated products.

of **3a**/**4a** were also screened for the reaction (see Supporting Information for details).

Under the optimal conditions, the scope of primary alcohols **3** was explored by means of their reactions with aniline (**4a**) (Table 2). Methyl-substituted benzyl alcohol substrates reacted with **4a** to afford the target products **5b**−**5d** in 73%−94% isolated yields and exhibited obvious steric impact on the yields. The reactions of methoxy- and isopropyl-substituted benzyl alcohols with **4a** afforded products **5e**−**5i** in excellent yields (80−94%). It is noted that 2-MeO substituent showed a negative effect on the reaction efficiency. F-, Cl-, and Br- substituents on the aryl group of the benzyl alcohol substrate did not demonstrate distinct electronic effect on the product yields of **5g**−**5l** (84%−95%). *o*-, *m*-, and *p*-Br-substituted benzyl alcohols reacted efficiently with **4a** to give the corresponding products **5l**−**5n**, showing a slight steric effect on the yields (89%−93%). Importantly, the pharmaceutically active trifluoromethyl-substituted benzyl alcohol gave the corresponding product **5o** with excellent isolated yield (85%). Similarly, heteroaromatic substrates, that is, thiophen-2-ylmethanol, and furan-2-ylmethanol, also efficiently underwent the reactions to generate **5p**−**5q** (90%−96%). However, 2-pyridinemethanol reacted with **4a** less efficiently, giving **5r** in 73% yield. Benzyl alcohol-containing imidazol moiety also reacted with **4a** to give **5s** in good yield (82%). 1-Naphthylmethanol efficiently reacted with **4a** to afford **5t** (91%), exhibiting no steric effect. In a similar manner, piperonyl alcohol and **4a** were efficiently converted to **5u** in good isolated yield (81%). We also explored the reactivity of alkyl alcohols, but the substrates were hardly reacted.

Next, the generality of the protocol was investigated by using diverse amines **4** as the coupling partners (Table 3). With methyl substituent anilines as the substrates, their reactions with benzyl alcohol afforded **5v** (75%), **5w** (90%), and **5x** (91%). An evident steric effect was revealed on the reactivity of the *o*-Me-substituted aniline. Similarly, the *o*-, *m*-, and *p*-methoxyls showed an obvious impact on the formation of **5y**−**5aa** (77%−95%) with the order *o*- < *m*- < *p*-methoxyl aniline. The 2-ethyl group diminished the yield of **5ab** (63%). Halogen-substituted anilines also reacted well with **3a** to afford **5ac**−**5af** in 90%−95% yields. Use of pyridin-2-amine as the substrate slightly deteriorated the yield of **5ag** (82%). However, when pyridin-3-amine was used as the substrate, the product yield dropped to 75% for **5ah**. In the case of naphthalen-2-amine, a decent yield was obtained to generate **5ai** (83%). Benzylamine also efficiently reacted with benzyl alcohol **3a**, but its reaction gave the product **5aj** in yield (77%) lower than the corresponding reaction by using aniline **4a** (93%). Alkylamines, such as hexylamine and cyclohexylamine, promoted the reactions to yield the target products **5ak** and **5al** in good yields (80%−88%).

DOI: 10.1021/acs.organomet.9b00769
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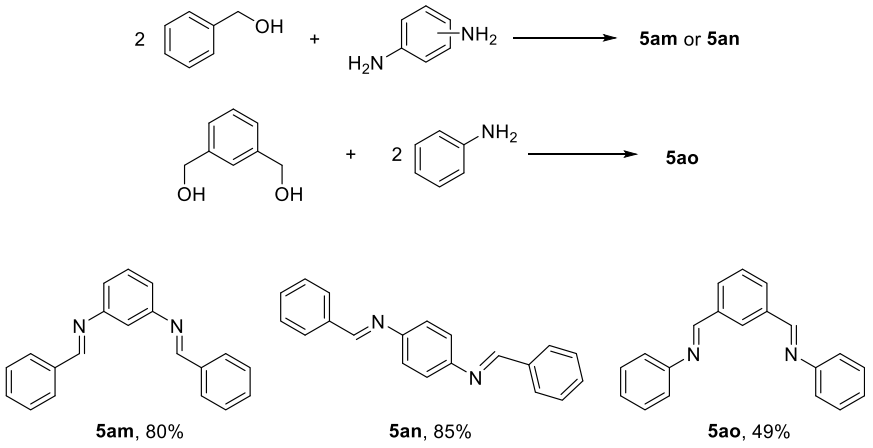
Scheme 3. Synthesis of Diimines

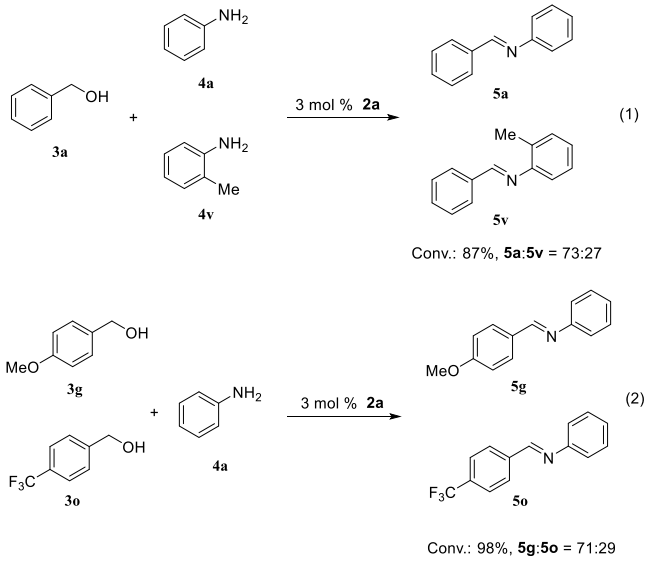


As an important structural unite, diimine compounds play a vital role in constructing ligands in catalytic chemistry and material applications.[14,15] Further, to explore the synthetic potential of the complex catalyst, attempts at synthesis of diimine products were performed (Scheme 3). Benzene-1,3-diamine or benzene-1,4-diamine similarly reacted well with benzyl alcohol to afford diimine products **5am** and **5an** (80% and 85%). For the disubstituted benzyl alcohol 1,3-benzenedimethanol, the product diimine was also acquired in 49% yield.

The control experiments were conducted by reacting **3a** with two different steric effect anilines (aniline **4a**, *o*-toluidine **4v**), and reacting **4a** with two different electronic effect benzyl alcohols ((4-methoxyphenyl)methanol **3g**, (4-(trifluoromethyl)-phenyl)methanol **3o**) under the standard conditions (Scheme 4). With aniline and *o*-methyl substituent aniline as the substrates, their reactions with benzyl alcohol gave 87% conversion and 73:27 selectivity for **5a**/**5v**, and *o*-methyl substituent exhibited a negative steric effect. When **4a** reacted with electron-donating and -withdrawing substituented benzyl alcohols, 98% conversion and 71:29 selectivity for **5g**/**5o** were obtained. The 4-trifluoromethyl substituent demonstrated an obvious negative electronic impact compared to the 4-methoxy group.

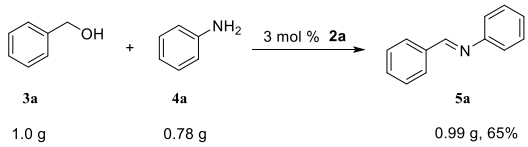
To further probe into the catalyst activity, gram-scale reaction was also performed under the optimized conditions. The target product **5a** was obtained in 65% yield (Scheme 5).

Scheme 4. Control Experiments[a]



[a]Conditions: **3a** (0.55 mmol), **4a** (0.25 mmol), **4v** (0.25 mmol) for eq (1); **3g** (0.275 mmol), **3o** (0.275 mmol), **4a** (0.50 mmol) for eq (2). complex **2a** (0.015 mmol), *t*BuOK (0.25 mmol), 4 Å MS (12.5 mg), toluene (2 mL), 110 °C, 0.1 MPa N_2, 24 h. Determined by gas chromatography analysis.

Scheme 5. Gram-Scale Reaction[a]



[a]Conditions: **3a** (9.25 mmol), **4a** (8.38 mmol), complex **2a** (0.25 mmol), *t*BuOK (4.19 mmol), 4 Å MS (209.5 mg), toluene (30 mL), 110 °C, 0.1 MPa N2, 24 h. Yields refer to the isolated products.

This protocol may offer a potential application for large-scale production. It is noteworthy that the reaction mechanism was explored (Scheme 6) based on those reported work.[9−11,13e,f] Initially, the acceptorless dehydrogenation of a primary alcohol catalyzed by the manganese complex generates the corresponding aldehyde. Considering that the present catalyst is Mn(I), the reaction may involve (1) extrusion of 1 equiv of hydrogen bromide with the base *t*BuOK, forming unsaturated 16-electron mangenese complex, (2) 16-electron mangenese complex interacts with BnOH to form [Mn]-OBn, (3) beta-H elimination of [Mn]-OBn to form [Mn]-H and aldehyde, and (4) the H_2 releases from [Mn]-H and regenerates 16-electron mangenese complex. Subsequent formation of the imine product was achieved by condensation of the in situ generated aldehyde and amine.

CONCLUSIONS

In summmary, we have developed an efficient and highly selective phosphine-free NN-manganese(I) complex catalyst system for the ADC of alcohols with amines to form imines. Functional diimines also can be synthesized by this methodology. The present work provides an alternative method to construct highly active nonprecious metal complex catalysts based on bidentate phosphine-free ligands.

DOI: 10.1021/acs.organomet.9b00769
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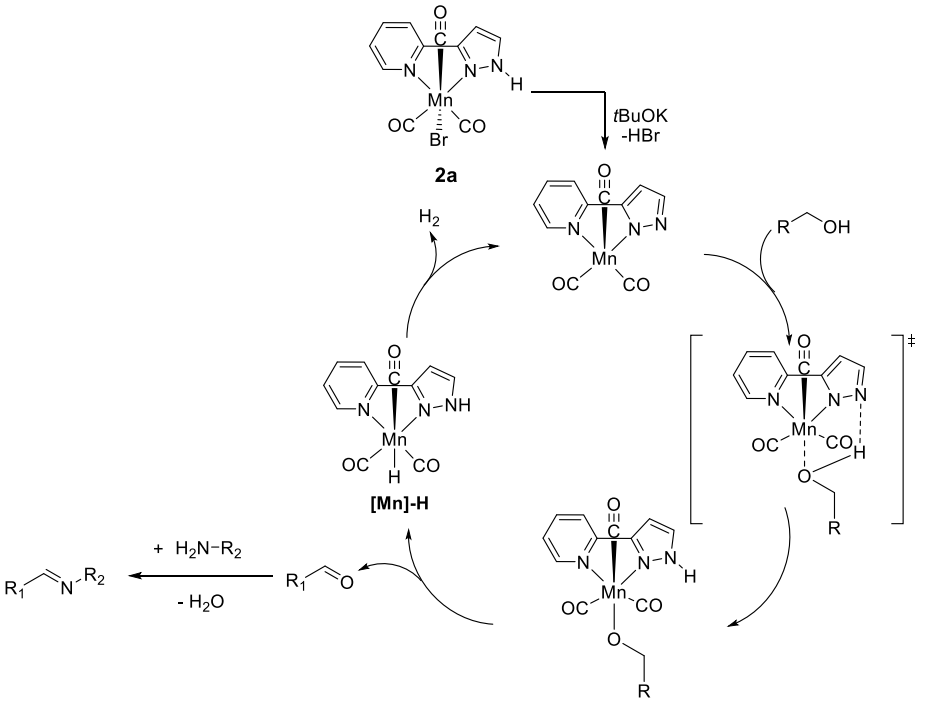
Scheme 6. Proposed Mechanism of the Reaction



EXPERIMENTAL SECTION

General Considerations. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a 600 MHz spectrometer, and all chemical shift values refer to $CDCl_3$ ($\delta(^{1}H)$, 7.26 ppm; $\delta(^{13}C)$, 77.16 ppm), deuterated dimethyl sulfoxide (DMSO-d_6) ($\delta(^{1}H)$, 2.50 ppm; $\delta(^{13}C)$, 39.52 ppm), CD_3COCD_3 ($\delta(^{1}H)$, 2.05 ppm; $\delta(^{13}C)$, 206.26 and 29.84 ppm), and CD_3OD ($\delta(^{1}H)$, 3.31 ppm; $\delta(^{13}C)$, 49.00 ppm). X-ray crystallographic analysis was achieved by Shiyanjia Lab (www.shiyanjia.com). Analytical thin-layer chromatography (TLC) plates were viewed by UV light (254 nm). Column chromatographic purifications were performed on silica gel 160. All the chemical reagents were purchased from commercial sources and used as received unless otherwise indicated.

X-ray Crystallographic Studies. The X-ray diffraction studies for complex **2b** were performed on a SMART APEX diffractometer with graphite-monochromated Mo radiation (λ = 0.710 73 Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package. The X-ray crystallographic files, in CIF format, are available from the Cambridge Crystallographic Data Centre on quoting the deposition number CCDC 1920267 for **2b**. Additional crystallographic information is available in the Supporting Information.

General Procedure for the Synthesis of Imines. Under a nitrogen atmosphere a mixture of phenylmethanol (**3a**) (56.9 μL, 0.55 mmol), aniline (**4a**) (45.6 μL, 0.5 mmol), complex **2a** (5.5 mg, 0.015 mmol), 4 Å MS (12.5 mg), and *t*BuOK (28.1 mg, 0.25 mmol) in 2.0 mL of toluene was stirred at 110 °C for 24 h. After it cooled to ambient temperature, the reaction was quenched with 10 mL of water and extracted with ethyl acetate (EtOAc) (3 × 10 mL). The combined organic phase was concentrated under reduced pressure. The resultant residue was subject to purification by column chromatography on silica gel (eluent: *n*-hexane/ethyl ether = 20:1, v/v) to afford **5a** as a white solid (84.3 mg, 93%).

Synthesis of Ligand 1a. Under a nitrogen atmosphere a mixture of (*E*)-3-(dimethylamino)-1-(pyridin-2-yl)prop-2-en-1-one (176.2 mg, 1 mmol) and hydrazine hydrate (1.8 mL) in 5 mL of EtOH was stirred at 80 °C for 2 h. After it cooled to ambient temperature, the reaction was quenched with 20 mL of water and extracted with EtOAc (3 × 15 mL). The combined organic phase was concentrated under reduced pressure. The resultant residue was subject to purification by column chromatography on silica gel (eluent: CH_2Cl_2/CH_3OH = 20:1, v/v) to afford **1a**. 127.7 mg, 88% yield, white solid, ^{1}H NMR ($CDCl_3$, 600 MHz): δ 11.81 (s, 1H), 8.68 (dt, J = 4.9, 1.4 Hz, 1H), 7.76 (d, J = 7.9 Hz, 1H), 7.69 (td, J = 7.6, 1.5 Hz, 1H), 7.65 (d, J = 2.1 Hz, 1H), 7.19 (ddd, J = 7.5, 4.9, 1.2 Hz, 1H), 6.80 (d, J = 2.2 Hz, 1H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz): δ 149.8, 149.4, 145.5, 137.0, 136.6, 122.8, 120.4, 103.6.

Synthesis of Ligand 1b. Under a nitrogen atmosphere a mixture of **1a** (145.2 mg, 1 mmol) and sodium hydride (120 mg, 5 mmol) in 20 mL of THF was stirred at 0 °C for 30 min. And iodomethane (124 μL, 2 mmol) was added to reaction system; after it was stirred for 5 h, the reaction was quenched with 10 mL of methanol and mixed with 20 mL of water, then extracted with EtOAc (3 × 15 mL). The combined organic phase was concentrated under reduced pressure. The resultant residue was subjected to purification by column chromatography on silica gel (eluent: CH_2Cl_2/CH_3OH = 50:1, v/v) to afford **1b**. 143.3 mg, 90% yield, white solid, ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.62 (ddd, J = 4.8, 1.8, 1.0 Hz, 1H), 7.90 (dt, J = 7.8, 1.0 Hz, 1H), 7.70 (td, J = 7.7, 1.8 Hz, 1H), 7.41 (d, J = 2.2 Hz, 1H), 7.18 (ddd, J = 7.4, 4.8, 1.2 Hz, 1H), 6.86 (d, J = 2.3 Hz, 1H), 3.98 (s, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 150 MHz): δ 152.2, 151.7, 149.4, 136.6, 131.6, 122.3, 119.9, 104.4, 39.2.

Synthesis of Complex 2a. Under a nitrogen atmosphere a mixture of **1a** (145.2 mg, 1 mmol) and manganese pentacarbonyl bromide (274.9 mg, 1 mmol) in 30 mL of MeOH was stirred at 25 °C for 24 h. All the volatiles were removed under reduced pressure, and the resultant residue was subject to purification by recrystallization in $CHCl_2/CH_3OH$/*n*-hexane (1/0.1/3, v/v/v) at 25 °C, affording the complex as a yellow solid (309.43 mg, 85%). mp > 320 °C dec. ^{1}H NMR (CD_3SOCD_3, 600 MHz): δ 14.62 (s, 1H), 9.06 (d, J = 5.4 Hz, 1H), 8.22−8.19 (m, 2H), 8.13 (t, J = 7.6 Hz, 1H), 7.56 (t, J = 6.4 Hz, 1H), 7.29 (d, J = 2.4 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (CD_3SOCD_3, 150 MHz): δ 222.5, 222.1, 221.6, 153.9, 151.8, 151.4, 139.7, 135.5, 125.3, 122.3, 104.9. IR (KBr pellets, cm^{-1}): 2036 (ν CO), 1927 (ν CO).

DOI: 10.1021/acs.organomet.9b00769
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Anal. Calcd for $C_{11}H_7BrMnN_3O_3$: C, 36.29; H, 1.94; N, 11.54. Found: C, 36.36; H, 1.98; N, 11.50%.

Synthesis of Complex 2b. Under a nitrogen atmosphere a mixture of **1b** (159.2 mg, 1 mmol) and manganese pentacarbonyl bromide (274.9 mg, 1 mmol) in 30 mL of MeOH was stirred at 25 °C for 24 h. All the volatiles were removed under reduced pressure, and the resultant residue was subject to purification by recrystallization in $CHCl_2/CH_3OH/n$-hexane (1/0.1/3, v/v/v) at 25 °C, affording the complex as a yellow solid (313.8 mg, 83%). mp > 320 °C dec. ^{1}H NMR (CD_3SOCD_3, 600 MHz): δ 9.08 (s, 1H), 8.18 (d, J = 42.8 Hz, 3H), 7.59 (s, 1H), 7.27 (s, 1H), 4.21 (s, 3H). $^{13}C\{^1H\}$ NMR (CD_3SOCD_3, 150 MHz): δ 223.3, 223.0, 220.6, 153.7, 152.0, 151.6, 139.8, 138.4, 125.5, 122.2, 105.0, 40.4. IR (KBr pellets, cm^{-1}): 2013 (ν CO), 1887 (ν CO). Anal. Calcd for $C_{12}H_9BrMnN_3O_3$: C, 38.12; H, 2.40; N, 11.11. Found: C, 38.08; H, 2.37; N, 11.17%.

(E)-N,1-Diphenylmethanimine (5a). 84.3 mg, 93% yield, white solid, ^{1}H NMR (CD_3OD, 600 MHz): δ 8.55 (s, 1H), 7.93−7.92 (m, 2H), 7.53−7.50 (m, 3H), 7.42−7.39 (m, 2H), 7.26−7.24 (m, 3H). $^{13}C\{^1H\}$ NMR (CD_3OD, 150 MHz): δ 162.8, 153.0, 137.4, 132.7, 130.3, 129.9, 129.9, 127.3, 122.0.

(E)-N-Phenyl-1-(o-tolyl)methanimine (5b). 71.3 mg, 73% yield, orange oil, ^{1}H NMR (CD_3COCD_3, 600 MHz): δ 8.84 (s, 1H), 8.10−8.07 (m, 1H), 7.43−7.25 (m, 8H), 2.64 (s, 3H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 150 MHz): δ 159.7, 153.6, 139.7, 135.2, 131.9, 131.8, 130.0, 128.7, 127.0, 126.6, 121.8, 19.5.

(E)-N-Phenyl-1-(m-tolyl)methanimine (5c). 87.9 mg, 90% yield, orange oil, ^{1}H NMR (CD_3COCD_3, 600 MHz): δ 8.54 (s, 1H), 7.79 (s, 1H), 7.75 (d, J = 7.5 Hz, 1H), 7.42−7.38 (m, 3H), 7.35 (d, J = 7.6 Hz, 1H), 7.25−7.22 (m, 3H), 2.41 (s, 3H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 150 MHz): δ 161.2, 153.1, 139.2, 137.5, 132.9, 130.0, 129.9, 129.5, 127.0, 126.6, 121.7, 21.3.

(E)-N-Phenyl-1-(p-tolyl)methanimine (5d). 91.8 mg, 94% yield, yellow oil, ^{1}H NMR (CD_3OD, 600 MHz): δ 8.49 (s, 1H), 7.80 (d, J = 8.1 Hz, 2H), 7.40−7.38 (m, 2H), 7.32−7.31 (m, 2H), 7.24−7.21 (m, 3H), 2.41 (s, 3H). $^{13}C\{^1H\}$ NMR (CD_3OD, 150 MHz): δ 162.9, 153.1, 143.6, 134.8, 130.6, 130.3, 130.0, 127.1, 122.0, 21.6.

(E)-1-(2-Methoxyphenyl)-N-phenylmethanimine (5e). 84.5 mg, 80% yield, white solid, ^{1}H NMR (CD_3OD, 600 MHz): δ 8.91 (s, 1H), 8.02 (dd, J = 7.7, 1.8 Hz, 1H), 7.50−7.47 (m, 1H), 7.40−7.37 (m, 2H), 7.24−7.21 (m, 1H), 7.20−7.19 (m, 2H), 7.10−7.08 (m, 1H), 7.05−7.02 (m, 1H), 3.91 (s, 3H). $^{13}C\{^1H\}$ NMR (CD_3OD, 150 MHz): δ 161.2, 158.7, 153.6, 134.4, 130.3, 128.3, 127.1, 125.4, 122.0, 121.8, 112.6, 56.2.

(E)-1-(3-Methoxyphenyl)-N-phenylmethanimine (5f). 98.2 mg, 93% yield, white solid, ^{1}H NMR (CD_3OD, 600 MHz): δ 8.50 (s, 1H), 7.54−7.52 (m, 1H), 7.46−7.43 (m, 1H), 7.41−7.38 (m, 3H), 7.26−7.23 (m, 3H), 7.09−7.07 (m, 1H), 3.86 (s, 3H). $^{13}C\{^1H\}$ NMR (CD_3OD, 150 MHz): δ 162.8, 161.6, 152.9, 138.7, 130.9, 130.3, 127.3, 123.2, 122.0, 119.2, 113.5, 55.8.

(E)-1-(4-Methoxyphenyl)-N-phenylmethanimine (5g). 89.8 mg, 85% yield, white solid, ^{1}H NMR (CD_3OD, 600 MHz): δ 8.45 (s, 1H), 7.86 (d, J = 8.8 Hz, 2H), 7.40−7.37 (m, 2H), 7.23−7.20 (m, 3H), 7.04 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H). $^{13}C\{^1H\}$ NMR (CD_3OD, 150 MHz): δ 164.2, 162.4, 153.2, 131.8, 130.3, 130.1, 126.9, 122.0, 115.3, 56.0.

(E)-1-(2,4-Dimethoxyphenyl)-N-phenylmethanimine (5h). 108.6 mg, 90% yield, white solid, ^{1}H NMR (CD_3COCD_3, 600 MHz): δ 8.79 (s, 1H), 8.06 (d, J = 8.3 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 7.20−7.16 (m, 3H), 6.66−6.64 (m, 2H), 3.94 (s, 3H), 3.89 (s, 3H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 150 MHz): δ 165.0, 162.1, 155.8, 154.2, 129.9, 129.3, 126.0, 121.7, 118.7, 107.1, 98.7, 56.2, 55.9.

(E)-1-(4-Isopropylphenyl)-N-phenylmethanimine (5i). 105.0 mg, 94% yield, yellow liquid, ^{1}H NMR (CD_3COCD_3, 600 MHz): δ 8.54 (s, 1H), 7.89 (d, J = 8.2 Hz, 2H), 7.41−7.39 (m, 4H), 7.24−7.21 (m, 3H), 3.01−2.96 (m, 1H), 1.27 (d, J = 7.0 Hz, 6H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 150 MHz): δ 160.9, 153.4, 153.2, 135.4, 129.9, 129.7, 127.6, 126.5, 121.7, 34.9, 24.1.

(E)-1-(4-Fluorophenyl)-N-phenylmethanimine (5j). 83.7 mg, 84% yield, white solid, ^{1}H NMR (CD_3COCD_3, 600 MHz): δ 8.59 (s, 1H), 8.05−8.03 (m, 2H), 7.42−7.40 (m, 2H), 7.30−7.23 (m, 5H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 150 MHz): δ 166.3, 164.6, 159.7, 152.8, 134.1, 131.8 (d, J_{C-F} = 8.8 Hz), 130.0, 126.8, 121.7, 116.6 (d, J_{C-F} = 22.3 Hz).

(E)-1-(2-Chlorophenyl)-N-phenylmethanimine (5k). 102.5 mg, 95% yield, yellow liquid, ^{1}H NMR (CD_3COCD_3, 600 MHz): δ 8.94 (s, 1H), 8.26−8.24 (m, 1H), 7.55−7.54 (m, 2H), 7.49−7.43 (m, 3H), 7.30−7.27 (m, 3H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 150 MHz): δ 157.0, 152.7, 136.5, 134.1, 133.5, 130.9, 130.1, 129.3, 128.3, 127.3, 121.9.

(E)-1-(2-Bromophenyl)-N-phenylmethanimine (5l). 115.8 mg, 89% yield, white solid, ^{1}H NMR (CD_3COCD_3, 600 MHz): δ 8.87 (s, 1H), 8.23 (dd, J = 7.8, 1.8 Hz, 1H), 7.71 (dd, J = 8.0, 1.0 Hz, 1H), 7.52−7.42 (m, 4H), 7.29−7.28 (m, 3H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 150 MHz): δ 159.3, 152.6, 135.4, 134.1, 133.7, 130.1, 129.7, 128.8, 127.3, 126.4, 121.8.

(E)-1-(3-Bromophenyl)-N-phenylmethanimine (5m). 119.7 mg, 92% yield, white solid, ^{1}H NMR (CD_3COCD_3, 600 MHz): δ 8.58 (s, 1H), 8.16 (t, J = 1.8 Hz, 1H), 7.95−7.93 (m, 1H), 7.70−7.68 (m, 1H), 7.47 (t, J = 7.8 Hz, 1H), 7.43−7.41 (m, 2H), 7.29−7.25 (m, 3H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 150 MHz): δ 159.4, 152.3, 139.7, 134.8, 131.8, 131.6, 130.0, 128.6, 127.1, 123.3, 121.8.

(E)-1-(4-Bromophenyl)-N-phenylmethanimine (5n). 121.0 mg, 93% yield, yellow solid, ^{1}H NMR (CD_3OD, 600 MHz) δ 8.51 (s, 1H), 7.83 (d, J = 8.5 Hz, 2H), 7.66 (d, J = 8.5 Hz, 2H), 7.41−7.38 (m, 2H), 7.25−7.23 (m, 3H). $^{13}C\{^1H\}$ NMR (CD_3OD, 150 MHz): δ 161.2, 152.7, 136.6, 133.1, 131.4, 130.3, 127.5, 126.9, 122.0.

(E)-N-Phenyl-1-(4-(trifluoromethyl)phenyl)methanimine (5o). 105.9 mg, 85% yield, yellow oil, ^{1}H NMR (CD_3COCD_3, 600 MHz): δ 8.72 (s, 1H), 8.19 (d, J = 8.0 Hz, 2H), 7.87−7.86 (m, 2H), 7.45−7.43 (m, 2H), 7.32−7.27 (m, 3H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 150 MHz): δ 159.7, 152.3, 140.9, 132.9 (q, J_{C-F} = 32.2 Hz), 130.1, 130.1, 127.4, 126.5, 126.5, 121.9.

(E)-N-Phenyl-1-(thiophen-2-yl)methanimine (5p). 89.9 mg, 96% yield, yellow oil, ^{1}H NMR (CD_3COCD_3, 600 MHz): δ 8.74 (s, 1H), 7.71 (d, J = 5.0 Hz, 1H), 7.65 (dd, J = 3.6, 1.0 Hz, 1H), 7.41−7.38 (m, 2H), 7.26−7.20 (m, 4H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 150 MHz): δ 154.1, 152.4, 144.1, 133.7, 131.3, 130.0, 128.7, 126.8, 121.8.

(E)-1-(Furan-2-yl)-N-phenylmethanimine (5q). 77.0 mg, 90% yield, white solid, ^{1}H NMR (CD_3COCD_3, 600 MHz): δ 8.41 (s, 1H), 7.80 (s, 1H), 7.41−7.38 (m, 2H), 7.25−7.23 (m, 3H), 7.10 (d, J = 2.7 Hz, 1H), 6.66 (dd, J = 3.4, 1.8 Hz, 1H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 150 MHz): δ 153.7, 152.7, 148.9, 146.7, 130.0, 126.8, 121.7, 116.5, 113.1.

(E)-N-Phenyl-1-(pyridin-2-yl)methanimine (5r). 66.5 mg, 73% yield, white liquid, ^{1}H NMR (CD_3COCD_3, 600 MHz): δ 8.71 (m, 1H), 8.59 (s, 1H), 8.23−8.22 (m, 1H), 7.94 (td, J = 7.7, 1.7 Hz, 1H), 7.51−7.44 (m, 3H), 7.34−7.28 (m, 3H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 150 MHz): δ 161.7, 155.7, 152.1, 150.6, 137.6, 130.1, 127.5, 126.2, 121.9, 121.8.

(E)-1-(4-(1H-Imidazol-1-yl)phenyl)-N-phenylmethanimine (5s). 101.4 mg, 82% yield, white solid, ^{1}H NMR (CD_3COCD_3, 600 MHz): δ 8.65 (s, 1H), 8.21 (s, 1H), 8.13−8.11 (m, 2H), 7.79 (d, J = 8.6 Hz, 2H), 7.70 (t, J = 1.5 Hz, 1H), 7.44−7.41 (m, 2H), 7.29−7.24 (m, 3H), 7.16 (s, 1H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 150 MHz): δ 159.8, 152.7, 140.4, 136.3, 136.0, 131.4, 131.2, 130.0, 126.9, 121.8, 121.5, 118.5.

(E)-1-(Naphthalen-1-yl)-N-phenylmethanimine (5t). 105.2 mg, 91% yield, yellow solid, ^{1}H NMR (CD_3OD, 600 MHz): δ 9.16 (s, 1H), 9.00 (d, J = 8.5 Hz, 1H), 8.08−8.07 (dd, J = 7.2, 1.2 Hz, 1H), 8.01−7.93 (m, 2H), 7.62−7.53 (m, 3H), 7.44−7.41 (m, 2H), 7.31−7.25 (m, 3H). $^{13}C\{^1H\}$ NMR (CD_3OD, 150 MHz): δ 161.9, 153.6, 135.4, 133.1, 132.8, 132.7, 130.6, 130.3, 129.8, 128.5, 127.3, 127.2, 126.3, 125.2, 122.0.

(E)-1-(Benzo[d][1,3]dioxol-5-yl)-N-phenylmethanimine (5u). 91.2 mg, 81% yield, white solid, ^{1}H NMR (CD_3OD, 600 MHz): δ 8.40 (s, 1H), 7.48 (s, 1H), 7.39−7.34 (m, 3H), 7.23−7.19 (m, 3H), 6.92 (d, J = 8.0 Hz, 1H), 6.04 (s, 2H). $^{13}C\{^1H\}$ NMR (CD_3OD, 150 MHz): δ 162.1, 153.0, 152.3, 150.0, 132.2, 130.3, 127.4, 127.0, 122.0, 109.2, 107.4, 103.2.

DOI: 10.1021/acs.organomet.9b00769
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(E)-1-Phenyl-N-(o-tolyl)methanimine (5v). 73.2 mg, 75% yield, orange oil, ^{1}H NMR (CD_3COCD_3, 600 MHz): δ 8.48 (s, 1H), 8.00−7.98 (m, 2H), 7.53−7.52 (m, 3H), 7.24−7.21 (m, 2H), 7.12 (t, J = 7.4 Hz, 1H), 7.02−7.01 (m, 1H), 2.34 (s, 3H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 150 MHz): δ 160.2, 151.9, 137.7, 132.6, 132.1, 131.0, 129.6, 129.5, 127.6, 126.5, 118.4, 17.9.

(E)-1-Phenyl-N-(m-tolyl)methanimine (5w). 87.9 mg, 90% yield, yellow liquid, ^{1}H NMR (CD_3COCD_3, 600 MHz): δ 8.57 (s, 1H), 7.97−7.96 (m, 2H), 7.52−7.51 (m, 3H), 7.28 (t, J = 7.7 Hz, 1H), 7.08−7.04 (m, 3H), 2.36 (s, 3H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 150 MHz): δ 160.7, 153.0, 139.6, 137.6, 132.1, 129.8, 129.6, 129.5, 127.4, 122.4, 118.8, 21.4.

(E)-1-Phenyl-N-(p-tolyl)methanimine (5x). 88.8 mg, 91% yield, yellow liquid, ^{1}H NMR (CD_3COCD_3, 600 MHz): δ 8.59 (s, 1H), 7.96−7.94 (m, 2H), 7.51−7.50 (m, 3H), 7.22−7.17 (m, 4H), 2.34 (s, 3H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 150 MHz): δ 160.1, 150.4, 137.7, 136.4, 132.0, 130.5, 129.6, 129.5, 121.7, 21.0.

(E)-N-(2-Methoxyphenyl)-1-phenylmethanimine (5y). 81.3 mg, 77% yield, yellow oil, ^{1}H NMR (CD_3COCD_3, 600 MHz): δ 8.53 (s, 1H), 7.96−7.95 (m, 2H), 7.52−7.50 (m, 3H), 7.19−7.16 (m, 1H), 7.06−7.02 (m, 2H), 6.96 (td, J = 7.5, 1.2 Hz, 1H), 3.83 (s, 3H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 150 MHz): δ 161.8, 153.1, 142.9, 137.8, 132.0, 129.5, 129.5, 127.2, 121.8, 121.5, 113.0, 56.1.

(E)-N-Benzylidine-3-methoxyaniline (5z). 94.0 mg, 89% yield, yellow liquid, ^{1}H NMR (CD_3COCD_3, 600 MHz): δ 8.58 (s, 1H), 7.97−7.96 (m, 2H), 7.52−7.49 (m, 3H), 7.32−7.29 (m, 1H), 6.85−6.81 (m, 3H), 3.83 (s, 3H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 150 MHz): δ 161.4, 161.1, 154.4, 137.4, 132.1, 130.7, 129.6, 129.5, 113.9, 112.4, 107.2, 55.6.

(E)-N-(4-Methoxyphenyl)-1-phenylmethanimine (5aa). 100.4 mg, 95% yield, white solid, ^{1}H NMR (CD_3OD, 600 MHz): δ 8.53 (s, 1H), 7.89−7.87 (m, 2H), 7.48−7.46 (m, 3H), 7.26−7.24 (m, 2H), 6.95−6.94 (m, 2H), 3.79 (s, 3H). $^{13}C\{^1H\}$ NMR (CD_3OD, 150 MHz): δ 160.7, 160.1, 145.6, 137.6, 132.3, 129.8, 129.7, 123.3, 115.5, 55.9.

(E)-N-(2-Ethylphenyl)-1-phenylmethanimine (5ab). 65.9 mg, 63% yield, yellow oil, ^{1}H NMR (CD_3COCD_3, 600 MHz): δ 8.51 (s, 1H), 8.00−7.98 (m, 2H), 7.53−7.52 (m, 3H), 7.26−7.15 (m, 3H), 7.03 (dd, J = 7.7, 1.3 Hz, 1H), 2.79 (q, J = 7.5 Hz, 2H), 1.17 (t, J = 7.6 Hz, 3H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 150 MHz): δ 160.3, 151.3, 138.8, 137.7, 132.1, 129.6, 129.5, 129.5, 127.7, 126.8, 118.5, 25.5, 15.5.

(E)-N-(4-Fluorophenyl)-1-phenylmethanimine (5ac). 94.6 mg, 95% yield, white solid, ^{1}H NMR (CD_3COCD_3, 600 MHz): δ 8.60 (s, 1H), 7.97−7.96 (m, 2H), 7.53−7.50 (m, 3H), 7.33−7.31 (m, 2H), 7.19−7.16 (m, 2H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 150 MHz): δ 162.8, 161.1 (d, J_{C-F} = 1.8 Hz), 149.2, 137.4, 132.2, 129.6 (d, J_{C-F} = 3.3 Hz), 123.5 (d, J_{C-F} = 8.3 Hz), 116.6, 116.5.

(E)-N-(4-Chlorophenyl)-1-phenylmethanimine (5ad). 98.1 mg, 91% yield, white solid, ^{1}H NMR (CD_3COCD_3, 600 MHz): δ 8.60 (s, 1H), 7.97 (d, J = 6.2 Hz, 2H), 7.54−7.50 (m, 3H), 7.43 (d, J = 8.7 Hz, 2H), 7.28 (d, J = 8.7 Hz, 2H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 150 MHz): δ 161.8, 151.7, 137.2, 132.4, 131.7, 130.0, 129.7, 129.6, 123.4.

N-(3-Chlorophenyl)-1-phenylmethanimine (5ae). 97.1 mg, 90% yield, yellow oil, ^{1}H NMR (CD_3COCD_3, 600 MHz): δ 8.60 (s, 1H), 7.99−7.97 (m, 2H), 7.55−7.51 (m, 3H), 7.42 (t, J = 7.9 Hz, 1H), 7.29−7.26 (m, 2H), 7.22−7.20 (m, 1H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 150 MHz): δ 162.6, 154.5, 137.1, 135.1, 132.5, 131.4, 129.8, 129.6, 126.4, 121.6, 120.6.

(E)-N-(4-Bromophenyl)-1-phenylmethanimine (5af). 122.3 mg, 94% yield, white solid, ^{1}H NMR (CD_3COCD_3, 600 MHz): δ 8.60 (s, 1H), 7.97 (d, J = 6.6 Hz, 2H), 7.58−7.51 (m, 5H), 7.22 (d, J = 8.5 Hz, 2H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 150 MHz): δ 161.4, 151.7, 136.8, 132.5, 132.0, 129.3, 129.2, 123.4, 119.1.

(E)-1-Phenyl-N-(pyridin-2-yl)methanimine (5ag). 74.7 mg, 82% yield, white solid, ^{1}H NMR (CD_3COCD_3, 600 MHz): δ 9.23 (s, 1H), 8.50−8.49 (m, 1H), 8.06−8.05 (m, 2H), 7.86 (td, J = 7.6, 1.9 Hz, 1H), 7.57−7.53 (m, 3H), 7.34 (dt, J = 7.9, 1.0 Hz, 1H), 7.27 (ddd, J = 7.4, 4.8, 1.1 Hz, 1H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 150 MHz): δ 163.2, 161.8, 149.8, 139.1, 137.1, 132.8, 130.2, 129.7, 122.9, 120.9.

(E)-1-Phenyl-N-(pyridin-3-yl)methanimine (5ah). 68.3 mg, 75% yield, white liquid, ^{1}H NMR (CD_3COCD_3, 600 MHz): δ 8.66 (s, 1H), 8.50 (d, J = 2.6 Hz, 1H), 8.46 (dd, J = 4.7, 1.5 Hz, 1H), 8.01−7.99 (m, 2H), 7.66−7.64 (m, 1H), 7.57−7.53 (m, 3H), 7.42−7.40 (m, 1H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 150 MHz): δ 163.2, 148.6, 148.0, 143.8, 137.1, 132.6, 129.8, 129.7, 128.1, 124.6.

(E)-N-(Naphthalen-2-yl)-1-phenylmethanimine (5ai). 96.0 mg, 83% yield, white solid, ^{1}H NMR (CD_3COCD_3, 600 MHz): δ 8.75 (s, 1H), 8.04−8.02 (m, 2H), 7.96−7.91 (m, 3H), 7.71 (d, J = 1.8 Hz, 1H), 7.56−7.46 (m, 6H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 150 MHz): δ 161.4, 150.6, 137.6, 135.2, 133.0, 132.2, 129.8, 129.7, 129.7, 128.7, 128.6, 127.3, 126.2, 122.0, 118.6.

(E)-N-Benzyl-1-phenylmethanimine (5aj). 75.2 mg, 77% yield, orange oil, ^{1}H NMR (CD_3COCD_3, 600 MHz): δ 8.50 (s, 1H), 7.84−7.82 (m, 2H), 7.46−7.44 (m, 3H), 7.37−7.33 (m, 4H), 7.26−7.23 (m, 1H), 4.80 (s, 2H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 150 MHz): δ 162.4, 140.9, 137.6, 131.4, 129.4, 129.2, 129.0, 128.8, 127.6, 65.4.

(E)-N-Hexyl-1-phenylmethanimine (5ak). 83.3 mg, 88% yield, white oil, ^{1}H NMR (CD_3COCD_3, 600 MHz): δ 8.33 (s, 1H), 7.78−7.76 (m, 2H), 7.43−7.42 (m, 3H), 3.58 (td, J = 6.9, 1.5 Hz, 2H), 1.68−1.63 (m, 2H), 1.39−1.29 (m, 6H), 0.90−0.87 (m, 3H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 150 MHz): δ 161.0, 137.8, 131.2, 129.4, 128.7, 62.0, 32.4, 31.7, 27.8, 23.3, 14.3.

(E)-N-Cyclohexyl-1-phenylmethanimine (5al). 74.9 mg, 80% yield, yellow liquid, ^{1}H NMR (CD_3OD, 600 MHz): δ 8.38 (s, 1H), 7.74−7.73 (m, 2H), 7.44−7.43 (m, 3H), 3.28−3.23 (m, 1H), 1.87−1.84 (m, 2H), 1.77−1.70 (m, 3H), 1.62−1.55 (m, 2H), 1.46−1.38 (m, 3H). $^{13}C\{^1H\}$ NMR (CD_3OD, 150 MHz): δ 162.3, 137.3, 132.0, 129.7, 129.3, 71.3, 35.3, 26.7, 25.9.

(1E,1′E)-N,N′-(1,3-Phenylene)bis(1-phenylmethanimine) (5am). 113.7 mg, 80% yield, yellow solid, ^{1}H NMR (CD_3COCD_3, 600 MHz): δ 8.67 (s, 2H), 8.01−7.99 (m, 4H), 7.54−7.53 (m, 6H), 7.46−7.43 (m, 1H), 7.16−7.15 (m, 3H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 150 MHz): δ 161.5, 154.0, 137.5, 132.2, 130.6, 129.6, 129.6, 119.5, 113.9.

(1E,1′E)-N,N′-(1,4-Phenylene)bis(1-phenylmethanimine) (5an). 120.9 mg, 85% yield, pale yellow solid, ^{1}H NMR (CD_3COCD_3, 600 MHz): 8.67 (s, 2H), 8.00−7.98 (m, 4H), 7.54−7.52 (m, 6H), 7.36 (s, 4H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 150 MHz): δ 160.4, 150.9, 137.6, 132.1, 129.6, 129.6, 122.8.

(1E,1′E)-1,1′-(1,3-Phenylene)bis(N-phenylmethanimine) (5ao). 69.7 mg, 49% yield, yellow solid, ^{1}H NMR (CD_3COCD_3, 600 MHz): δ 8.71 (s, 2H), 8.57 (s, 1H), 8.13 (dd, J = 7.6, 1.4 Hz, 2H), 7.68 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 7.8 Hz, 4H), 7.33−7.31 (m, 4H), 7.28−7.25 (m, 2H). $^{13}C\{^1H\}$ NMR (CD_3COCD_3, 150 MHz): δ 160.5, 152.8, 138.1, 132.2, 130.1, 130.0, 129.5, 127.0, 121.8.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.9b00769.

NMR spectra of the new compounds and the X-ray crystallographic data for **2b** (PDF)

Crystallographic X-ray data for **2b** (XYZ)

Accession Codes

CCDC 1920267 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.

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DOI: 10.1021/acs.organomet.9b00769
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Notes

The authors declare the following competing financial interest(s): The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to the National Natural Science Foundation of China (21801158) and the Open Project Fund of Qingdao University of Technology (QUTSEME201934) for support of this research. We thank Prof. Z.-K. Yu (DICP) for helpful discussion.

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