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Synthesis, Structures of Benzoxazolyl Iridium(III) Complexes and Applications on C-C, C-N Bond Formation Reactions under Solvent-Free Conditions: Catalytic Activity Enhanced by Non-coordinating Anion without Silver Effect

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 Supporting Information

Abstract: Several new bisbenzoxazolyl iridium(III) complexes have been synthesized and characterized through x-ray crystallography. These complexes exhibit excellent catalytic activity in C-C, C-N bond formation reactions from the alkylation of amine with amine, amine with alcohol, ketone with alcohol and alcohol with alcohol through borrowing hydrogen reaction. Moreover, these iridium(III) complexes are effective catalysts for the alkylation of amine with alcohol, ketone with alcohol under solvent-free conditions. The catalytic activity of these complexes is greatly enhanced by non-coordinating, while the experiments have excluded the possibility of "silver effect" (bimetallic catalysis or silver-assisted metal catalysis) from the experiments.

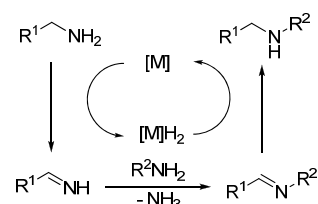
Keywords: C-C coupling, C-N coupling, solvent-free, iridium complex, non-coordinating anion

INTRODUCTION

Transition-metal catalyzed carbon-carbon and carbon-heteroatom bond formation has always been a useful method for the construction of organic molecules.¹ In most cases of cross-coupling reaction, C-X bond activation and breaking are important factors and have therefore guided the mainstream reaction research.^{2,3} Compared to the use of C-X bonds, the use of alcohols or amines as alkylating agents could avoid the use of traditional mutagenic halide reagents, which have received much attraction for their atom-efficient, greener process, which leaves only water or ammonia as a byproduct.⁴ Therefore, the use of alcohols or amines as alternative C-alkylating and N-alkylating agents is necessary and interesting. The borrowing hydrogen methodology involves: 1) oxidation of alcohols or ammonia to the corresponding carbonyl compounds or imines; 2) alkylation of ketones, alcohols or amines to form unsaturated carbonyl compounds or imines; and 3) reduction of the C-C or C-N bonds using the borrowed hydrogen atoms from alcohols or amines (Scheme 1).^{5,6} Generally, among these transformations, the catalyst plays a crucial role in every step. To date, although some metals (Pd,⁷ Au,⁸ Ag,⁹ Cu,¹⁰ Fe,¹¹ Ni,¹² Os,¹³ and Rh,¹⁴) have been studied, Ru¹⁵ and Ir¹⁶⁻³³ are still shown to be

the most effective and promising catalysts for C-alkylation and N-alkylation.

Scheme 1. The alkylation of an amine with another amine by borrowing hydrogen reaction.

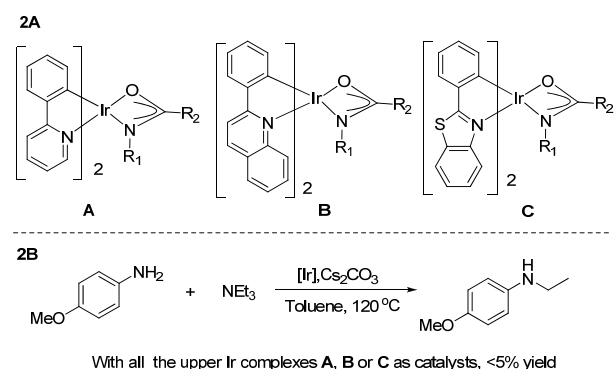


In the related area of iridium-catalyzed N-alkylation and C-alkylation using borrow hydrogen strategy, several research groups have paid great efforts in this area.^{4a,17} Recently, Fujita and Yamaguchi reported the synthesis of indoles and 1,2,3,4-tetrahydroquinolines with Cp*Ir Complex as catalyst using borrow hydrogen strategy.¹⁸ Later they developed multialkylation of aqueous ammonia with alcohols with the water-soluble Cp*Ir-amine complexes as catalysts. Williams showed amine alkylation using [Cp*IrI₂]₂ in water in the absence of any other additives.¹⁹ Kempe *et al* prepared several new iridium complexes containing anionic P,N ligands and their applications in borrow hydrogenation reactions.^{16b,20}

They also reported iridium-catalyzed C-C bond formation of methyl groups in N-heteroaromatic substrates with simple alcohols. Matute also described several new iridium complexes containing bidentate N-heterocyclic carbenes (NHC), which catalyzed the alkylation of anilines with alcohols.^{5j,21} In 2008, Peris reported [IrCl₂Cp*(NHC)] complexes catalyzed C-N and C-C formation reactions.²² In 2009, Crabtree synthesized the chelating pyrimidine-functionalized N-heterocyclic carbene Ir and Ru complexes, which were also effective for amine alkylation and alkylation of secondary alcohols.²³ In 2010, Ishii reported a method for alkylation of acetates with primary alcohols and diols using an Ir complex.^{16a,24} In 2012, Madsen investigated that [Cp*IrCl₂]₂-catalyzed alkylation of amines with alcohols using a combination of experimental and theoretical methods.²⁵ In 2014, Li demonstrated that the water soluble [Cp*Ir(6,6'-(OH)₂bpy)(H₂O)](OTf)₂ is a general and highly efficient catalyst for the N-alkylation of poor nucleophilic sulfonamides with alcohols as alkylating agents in water.^{16e,26} Very recently, Zhao reported the first chiral N-alkylation using a chiral Ir complex in cooperation with a chiral phosphoric acid through borrowing hydrogen methodology.²⁷ At the same time, many several other groups (Milstein,^{6f} Beller,^{5a,5e,6b,6c} Obora,²⁸ Huang,²⁹ Limbach,³⁰ Sridharan,³¹ Ramón,³² *et al*) have communicated their results in this area.³³ However, with respect to alcohols as alkylating agents, the use of amines as alkylating agents is much more difficult and is less well studied.³⁴

Our research generally focused on cyclometalated iridium complexes, thus leading to the recent discovery of amide cyclometalated Ir(III) complexes (Scheme 2A).³⁵ Amides are able to bind to the iridium center via the κ² mode and thereby form a new structure involving a four-member metallocycle.³⁶ However, when these amide iridium complexes (**1**) were used to borrowing hydrogen reaction of amines with alcohols, it was found that they had nearly no catalytic reactivity (Scheme 2B).

Scheme 2. The amidate ancillary ligand Ir(III) complexes.



Generally, there are two kinds of cyclometalated Ir complexes: neutral and cationic.³⁷ Neutral complexes (e.g., Ir(C[^]N)₃) are of particular interest due to their excellent emission spectra and efficiency.^{38,39} Compared to neutral complexes, although ionic iridium(III) complexes (typical example: [Ir(C[^]N)₂L]⁺X⁻) aren't very suitable for OLED applications due to the difficulty of

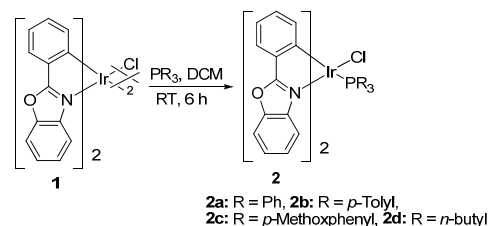
vapor deposition, ionic complexes are easily coordinated with substrates and may provide better catalytic reactivity. Therefore, it was necessary to turn our attention to synthesis of ionic iridium(III) complexes. We attempted phosphine ligand as an ancillary ligand in order to coordinate with iridium(III) complex containing 2-benzothiofene (bo). Herein, we report the synthesis, characterizations of benzothienyl iridium(III) complexes with phosphine substituents by X-ray crystallography, and we found that catalytic activity enhanced by non-coordinating anion in C-C and C-N formation of alcohols with alcohols, amines with alcohols through borrowing hydrogen reaction.

RESULTS AND DISCUSSION

Synthesis of benzoxazolyl skeleton phosphine ligand Ir(III) complexes **2**.

Chloro-bridged dimer and phosphine ligand were weighed into an oven-dried Schlenk flask under a nitrogen atmosphere, followed by dry CH₂Cl₂ as the solvent. The mixture was stirred at room temperature for 6 hours producing [(bo)₂Ir(PR₃)]Cl (**2**) complexes with good yields (Scheme 3).⁴⁰

Scheme 3. Synthesis of benzoxazolyl skeleton phosphine ligand Ir(III) complexes.



Crystal structure of **2a**, and **2d**.

To show the structure of benzoxazolyl skeleton phosphine ancillary ligand Ir(III) complexes **2**, single crystal x-ray diffraction analysis was carried out for complexes **2a** and **2d**. Single-crystal analysis revealed that the compound **2a** belongs to the P-1 space group. In the molecular structure of compound **2a**, the Ir(1) atom is coordinated to one tributylphosphine, one chlorine atom and two benzoxazolyl ligands, and all are in the bidentate-chelating fashion (Fig. 1). The C(5)/N(1) from the benzothiazole is coordinated to Ir(1), forming a nearly planar Ir(1)-C(5)-C(6)-C(7)-N(1) five-member ring, wherein the angle of C(5)-Ir(1)-N(1) is 79.19(16)^o and the angle of Cl(1)-Ir(1)-P(1) is 99.60(10)^o, while the angle of N(1)-Ir(1)-P(1) is 89.69(4)^o. The bond length of Ir(1)-N(1) (2.195(4) Å) is much shorter than that of Ir(1)-P(1) (2.402(12) Å), while the bond length of Ir(1)-Cl(1) (2.370(13) Å) is much longer than that of Ir(1)-C(5) (2.074(4) Å). Another compound with tri-*n*butylphosphine ancillary ligand was nearly identical in structure. The single crystal of **2d** (Fig. 2) was obtained through the slow diffusion of hexane into a dichloromethane solution of the complexes. Overall, there was no large geometric difference among the

complexes. The crystal structures conformed that the synthesized complexes were the designed catalysts.

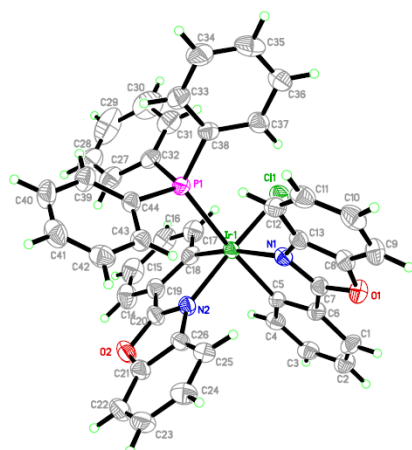


Figure 1. ORTEP diagram of **2a** with thermal ellipsoids shown at the 30% probability level.

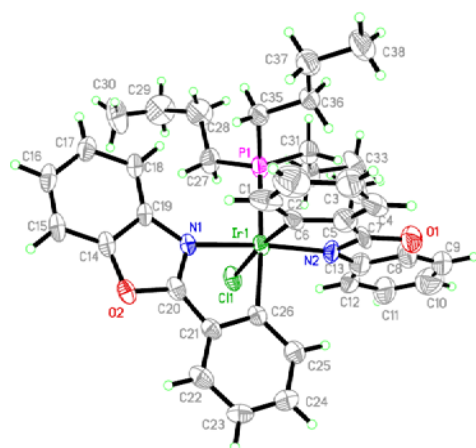
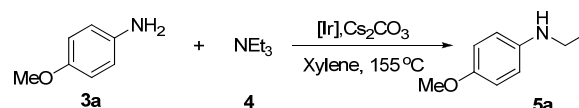


Figure 2. ORTEP diagram of **2d** with thermal ellipsoids shown at the 30% probability level.

Catalytic activity

The N-alkylation of amine with amine was studied after the synthesis of iridium catalysts. In our initial experiments, the classical *p*-anisidine and triethylamine were chosen as the model substrates for reaction examination. First, we checked the effects of catalysts on the reactivity and the results were shown in Table 1. The chloro-bridged dimer $[\{(bo)_2Ir(\mu-Cl)\}_2]$ and $[\{(bo)_2Ir(\mu-Cl)\}_2]/AgOTf$ were added to this reaction (Table 1, entries 2-3), the desired product could not be detected. When iridium complexes with phosphines as ancillary ligands (**2a**, **2b**, **2c** and **2d**) were tested in this reaction, the yields of the product were obtained with approximately 30% yield. It was observed that the catalytic activity of iridium complexes was enhanced by the phosphine ligand (Scheme 2B, and Table 1, entries 4-7).

p-anisidine with NEt_3 .^a



Entry	Catalyst	Yield [%] ^b
1	none	<5
2	$[\{(bo)_2Ir(\mu-Cl)\}_2]$	<5
3	$[\{(bo)_2Ir(\mu-Cl)\}_2]/AgOTf$	<5
4	2a	31
5	2b	33
6	2c	34
7	2d	36
8	2d /AgOTf	69
9	2d /AgBF ₄	61
10	2d /AgSbF ₆	73
11	2d /AgPF ₆	75
12	2d /AgNTf ₂	81
13	2a /AgNTf ₂	77
14	2b /AgNTf ₂	78
15	2c /AgNTf ₂	79
16 ^c	2d /AgNTf ₂	55
17 ^d	2d /AgNTf ₂	81
18 ^e	2d /AgNTf ₂	45
19 ^f	2d /AgNTf ₂	53
20 ^g	2d /AgNTf ₂	67

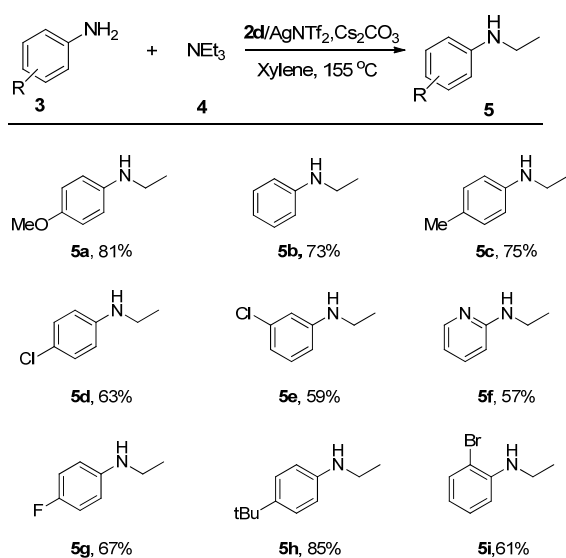
^aReagents and conditions: **3a** (1 mmol), **4** (1 mL), [Ir] loading (2 mol%, 0.02 mmol), AgX loading (2 mol%, 0.02 mmol). CS_2CO_3 (1.1 mmol), xylene (2 mL), 155 °C, 20 h. ^bYields of pure product. ^c[Ir] loading (1 mol%, 0.01 mmol). ^d[Ir] loading (5 mol%, 0.05 mmol). ^eReaction temperature (110 °C). ^fSolvent (1 mL DMF). ^gWithout any base.

The results showed that the yield of the product with **2d** as a catalyst was slightly higher than other phosphine iridium(III) compounds, but the yield was still low (approximately 30%). As we all know, ionic complexes are easily coordinated with substrates and may have better catalytic reactivity. Subsequently, the reaction conditions were further optimized through the variation of a different AgX (Table 1, entries 8-12) in order to produce ionic complexes *in situ*. When these ionic complexes *in situ* formed through the addition of AgX were used to this N-alkylation reaction, the results showed that the yield was significantly increased, while the addition of AgNTf₂ to the reaction was comparatively more effective. Other new Ir(III) complexes such as **2a**, **2b**, **2c** were also found to be effective with AgNTf₂ as the additive under the same condition (Table 1, entries 13-15). Blank inspection showed that the reaction could not occur without iridium catalyst (Table 1, entry 1). By using the other reaction conditions it was found that the decrease in reaction temperature or the change of solvent would lead to decreased product yields (Table 1, entries 18 and 19).

Table 1. Catalysts screening for N-alkylation of *p*-

Decreasing the catalyst loading from 2 mol% to 1 mol% resulted in decreased yield (Table 1, entry 16), while the increase of catalyst loading did not produce an improvement in yield (Table 1, entry 17). Hence, the best reaction conditions are summarized as follows: 2 mol% of **2d**/AgNTf₂ catalyst, 1 equivalent of Cs₂CO₃, xylene as the reaction solvent, and at 155 °C (Table 1, entry 15).

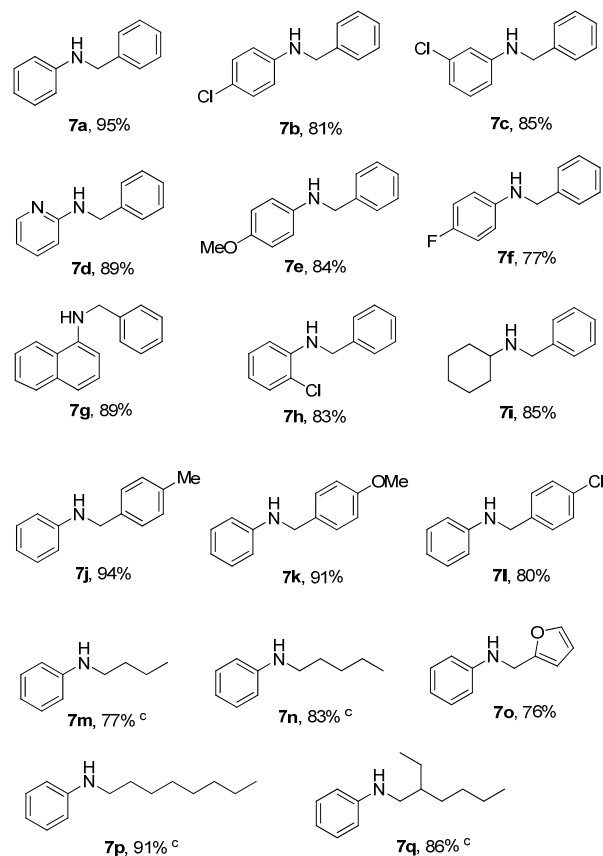
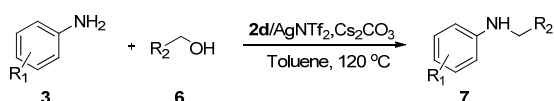
Table 2. Alkylation of amines with amines ^{a, b}



^aReagents and conditions: **3** (1.0 mmol), **4** (1 mL), **2d** (2 mol%, 0.02 mmol), AgNTf₂ (2 mol%, 0.02 mmol), Cs₂CO₃ (1.1 mmol), xylene (2 mL), 155 °C, 20 h. ^bIsolated yield.

With the optimized reaction conditions in hand, we further employed the above methods to aromatic amines and triethylamine. The results were summarized in Table 2. The experiments showed that different N-alkylated anilines were obtained with moderate to good yields through the use of the catalyst **2d**/AgNTf₂. Generally, the reaction had good substituent tolerance. The substituents with different electronic properties on the aryl ring of aromatic amines significantly affected the reaction yields. Most often, the aromatic amines possessing electron-donating groups gave the corresponding products in higher yields as compared to the electron-poor ones.

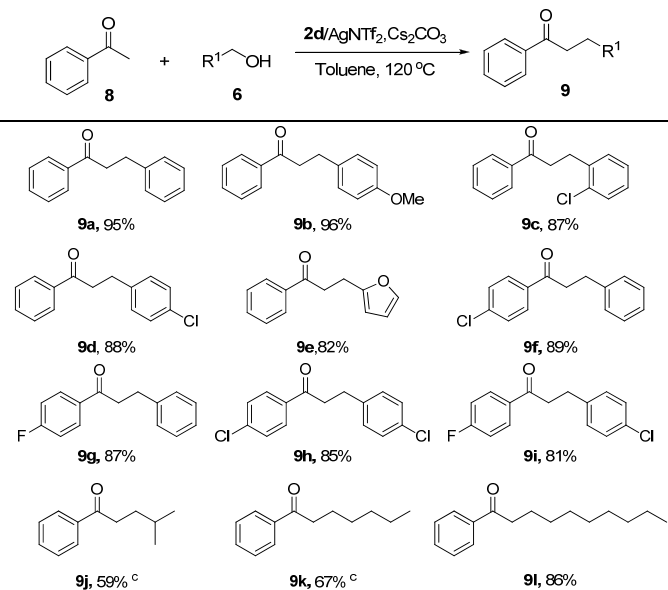
Table 3. Alkylation of amines with alcohols ^{a, b}



^aReagents and conditions: **3** (1.0 mmol), **6** (1.1 mmol), **2d** (2 mol%, 0.02 mmol), AgNTf₂ (2 mol%, 0.02 mmol), Cs₂CO₃ (1.1 mmol), toluene (2 mL), 120 °C, 16 h. ^bIsolated yield. ^c**6** (3 mmol).

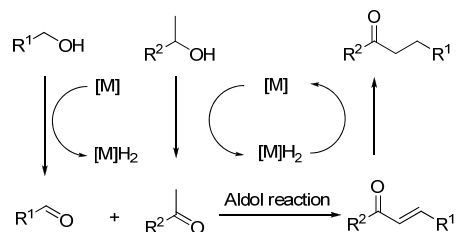
Encouraged by such promising results, we further employed the above methods to other phenyl amines and various alcohols. The results were summarized in Table 3. The results showed different N-alkylated anilines were obtained with good to excellent yields through the use of the catalyst **2d**. Additionally, the effect of substituents on the aromatic ring of amine was explored. It was observed that anilines with electron-donating or electron-withdrawing substituents could react under the optimal reaction conditions with overall yields ranging from 77% to 95%. Subsequently, the amination reactions of different alcohols were explored. Clearly, aromatic alcohols—including *p*-methylbenzyl alcohol, *p*-methoxybenzyl alcohol, *p*-chlorobenzyl alcohol and furyl alcohol—could react smoothly and give yields ranging from 76% to 94%.

We were pleased to find that aliphatic alcohols were effective with this methodology (Table 3). The experiments showed that the N-alkylated products were also achieved with good to excellent yields. The substituent group of aliphatic alcohols had a minimal influence on the reaction. The yields of the corresponding N-alkyl amines were separated with 76% to 91%.

Table 4. Alkylation of ketone with alcohols. ^{a, b}

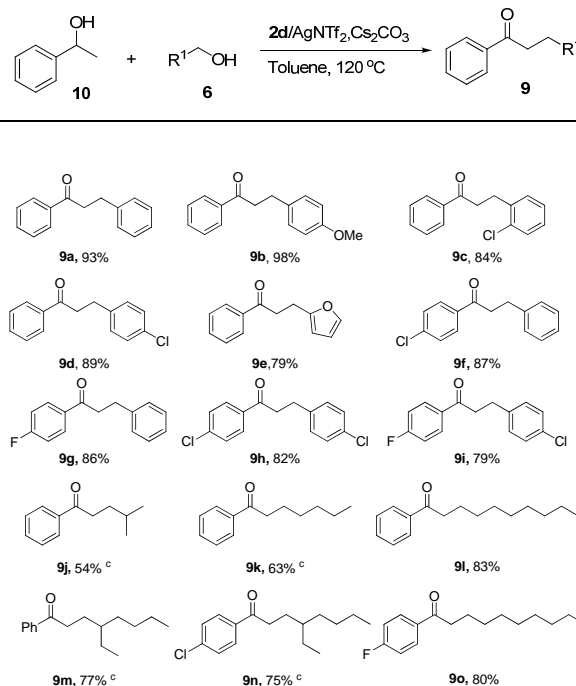
^a Reagents and conditions: **8** (1.0 mmol), **6** (1.1 mmol), **2d** (2 mol%, 0.02 mmol), AgNTf₂ (2 mol%, 0.02 mmol), Cs₂CO₃ (1.1 mmol), toluene (2 mL), 120 °C, 16 h. ^b Isolated yield. ^c **6** (2 mmol).

Next, we challenged the alkylation of ketone with alcohols, proceeding via dehydrogenation reactions and aldol condensation. The results were summarized in Table 4. Generally, all the substrates were converted completely to produce the corresponding ketones. High yields were obtained regardless of the electronic properties and steric hindrance of substituent groups. The substitution patterns of pyridyl, furyl and thienyl-heterocyclic alcohols had little influence on the formation of desired products under the optimal reaction conditions with moderate to good yields.

Scheme 4. C-C formation of primary and secondary alcohols.

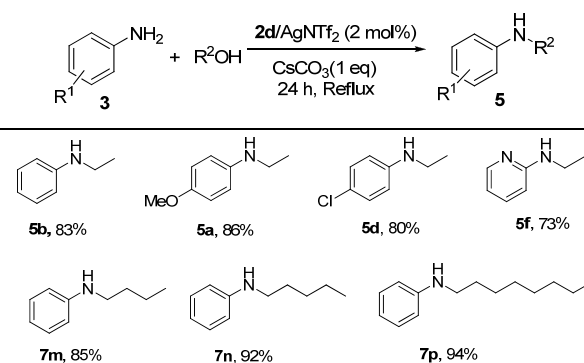
Previously, the development of borrowing hydrogen reactions with respect to alcohols with alcohols was a more difficult and promising area,^{5,6} as alcohols were the very common materials and only water was produced as a byproduct. This transformation has one key step--the successive dehydrogenation of alcohols to carbonyl compounds--and the reaction process was as shown in Scheme 4. Here, we also attempted the reaction under optimized reaction conditions. So, the reaction of a series of secondary and primary alcohols was set up and investigated (Table 5). The reactions of phenylethanol with different types of aromatic alcohols occurred well, providing moderate to excellent yields. Chlorinated aromatic alcohol and electron-donating substituents were well tolerated in the reactions, while furyl-, thienyl-,

pyridyl-heterocyclic alcohols could react well under the optimal reaction conditions with the overall yield ranging from 78% to 87%. Additionally, we also tried to the borrowing hydrogen reaction of phenylethanol with aliphatic alcohols. We chose *iso*-octyl alcohol, *1*-pentanol, *n*-propanol and *isobutanol* as being representative. The corresponding target products were all separated smoothly, while the yields were significantly lower than those of aromatic alcohols.

Table 5. The alkylation of two alcohols. ^{a, b}

^a Reagents and conditions: **8** (1.0 mmol), **6** (1.1 mmol), **2d** (2 mol%, 0.02 mmol), AgNTf₂ (2 mol%, 0.02 mmol), Cs₂CO₃ (1.1 mmol), toluene (2 mL), 120 °C, 16 h. ^b Isolated yield. ^c **6** (3 mmol).

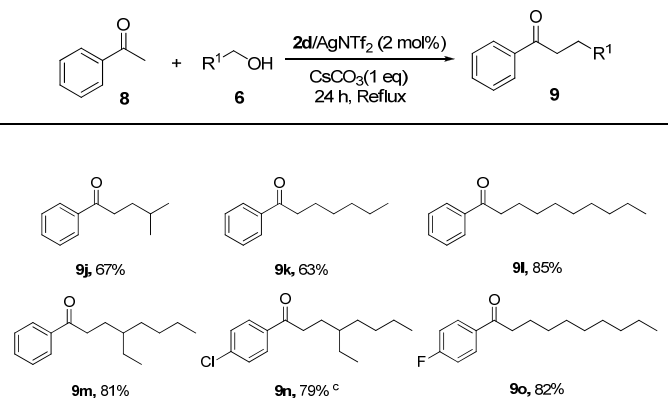
Moreover, we also explored the borrowing hydrogen reaction of an amine under solvent-free conditions. To our surprised, the desired products were separated with good to excellent yields (Table 6).

Table 6. The alkylation of amine with alcohol under solvent-free conditions. ^{a, b}

^a Reagents and conditions: **3** (1.0 mmol), R^2-OH (1 mL), **2d** (2 mol%, 0.02 mmol), AgNTf₂ (2 mol%, 0.02 mmol), Cs₂CO₃ (1 mmol), Reflux, 24 h. ^b Isolated yield.

Furthermore, the borrowing hydrogen reaction of acetophenone was examined under solvent-free conditions. Generally, all the acetophenones were converted to the corresponding ketones with moderate to good yields (Table 7). This reaction under solvent-free conditions provides an effective, green method for the alkylation of amines and ketones with alcohols.

Table 7. The alkylation of acetophenone with alcohol under solvent-free conditions. ^{a, b}



^a Reagents and conditions: **8** (1.0 mmol), R²OH (1 mL), **2d** (2 mol%, 0.02 mmol), AgNTf₂ (2 mol%, 0.02 mmol), Cs₂CO₃ (1 mmol), Reflux, 24 h. ^b Isolated yield.

Compared to the reported methods, the catalyst loading is still around 1-2 mol%, a very common catalyst loading in iridium-catalyzed borrow hydrogen reactions. After all, several new catalysts were synthesized and an alternative method to alkylation reactions was provided. Importantly, these complexes were systematically studied and proved to be effective for almost all the kinds of the alkylation reactions, such as: amine with amine, amine with alcohol, ketone with alcohol, alcohol with alcohol, even under solvent-free conditions.

In 2012, Shi and co-workers revealed a long-overlooked "silver effect" in gold catalysis, which led to the revision of silver-involved reactions.⁴¹ They found that many reactions involving silver (AgCl or silver nanoparticle, in most cases) actually comprised bimetallic catalysis or silver-assisted metal catalysis. Here, we have a concern about the "silver effect" for this transformation, i.e., the question of whether this phenomenon exists in the iridium catalyzed reaction. Therefore, the "silver effect" test must be applied in this reaction.

Table 8. Verification test of silver effect. ^{a, b}

Entry	Catalyst	Conditions	Yield [%] ^b
1	[(bo) ₂ Ir(PBu ₃) ₂]Cl (2d)	-	43
2	2d /AgNTf ₂	No filtration	95
3	2d /AgNTf ₂	After filtration	92

4	2d /AgOTf	No filtration	83
5	2d /AgOTf	After filtration	79
6	2d /AgSbF ₆	No filtration	88
7	2d /AgSbF ₆	After filtration	83

^a Reagents and conditions: **3a** (1.0 mmol), **6a** (1.1 mmol), **2d** (2 mol%, 0.02 mmol), AgX (2 mol%, 0.02 mmol), Cs₂CO₃ (1.1 mmol), toluene (2 mL), 120 °C, 16 h. The filtration was conducted to remove AgCl through celite. ^b Isolated yield.

As indicated in Table 8, the test of silver salts was conducted. The complex [(bo)₂Ir(PBu₃)₂]NTf₂, which was performed in order to remove AgCl through celite could also catalyze the reaction smoothly and give nearly the same result (Table 8). Similar results were also observed with AgOTf and AgSbF₆ as additives. So, silver does not play a role in this reaction, and the effective catalyst is iridium.

CONCLUSION

In conclusion, several new types of bisbenzoxazolyli iridium(III) complexes have been synthesized and characterized through x-ray crystallography. The experiments showed that these complexes exhibit good catalytic activity in borrowing hydrogen for C-C or C-N bond formation under mild conditions. Moreover, these iridium(III) complexes are effective catalysts for the alkylation of amine with alcohol, ketone with alcohol under solvent-free conditions. The catalytic activity of these complexes is greatly enhanced by non-coordinating anion, while the experiments have excluded the possibility of "silver effect" (bimetallic catalysis or silver-assisted metal catalysis) from the experiments.

EXPERIMENTAL DETAILS

Materials. IrCl₃·3H₂O and other chemicals were obtained from commercial resource and used without further purification. Chloro-bridged dimer (bo)₂Ir(μ-Cl)₂Ir(bo)₂ was prepared according to the reported literatures. All solvents were dried by standard methods.

Preparation of complex 2a. A solution of [(bo)₂Ir(μ-Cl)₂] (0.1 mmol) and tributylphosphine (0.22 mmol) in CH₂Cl₂ (10 mL) was stirred at temperature overnight under a nitrogen atmosphere. The mixture was filtered off and the solvent removed under vacuum. The crude product was further recrystallized in CH₂Cl₂ / hexane and a desired product **2a** was obtained (yield: 84%). ¹H NMR (400 MHz, CDCl₃) δ 8.51 (d, *J* = 8.1 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.29-7.16 (m, 9H), 7.03 (dd, *J* = 14.7, 7.4 Hz, 4H), 6.96-6.84 (m, 9H), 6.82-6.73 (m, 2H), 6.68-6.61 (m, 1H), 6.32 (d, *J* = 7.8 Hz, 1H), 6.14 (dd, *J* = 7.5, 4.6 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 178.72 (d, *J* = 9.1 Hz), 175.87, 160.40, 159.37, 150.16, 149.85, 146.68 (d, *J* = 4.8 Hz), 139.13, 138.53, 134.87 (d, *J* = 9.7 Hz), 134.30-133.85 (m), 132.71 (d, *J* = 6.0 Hz), 132.30, 132.16, 131.91, 131.15, 129.44, 129.23, 128.86, 128.58, 127.40 (d, *J* = 9.1 Hz), 125.99 (d, *J* = 4.0 Hz), 125.75, 125.14 (d, *J* = 5.6 Hz), 124.68, 124.29, 122.87, 121.46, 120.30, 118.65, 111.50, 110.42; ³¹P NMR (162 MHz,

CDCl₃) δ -9.24; Anal. Calcd for C₄₄H₃₁ClIrN₂O₂P: C, 60.16, H, 3.56, N, 3.19; Found: C, 59.93, H, 3.75, N, 3.06; CCDC number: 1009985.

General procedure for N-alkylation of aromatic amines with aliphatic amines.

A solution of **2d** (2 mol%, 0.02 mmol), AgNTf₂ (2 mol%, 0.02 mmol) and xylene (1 mL) were stirred in a Schlenk tube under N₂ at room temperature for a moment. Subsequently, aromatic amine (1.0 mmol), aliphatic amine (1.0 mL), and caesium carbonate (1.0 mmol) were added. The mixture was heated under 155 °C for 20 h and then cooled to room temperature. The resulting solution was directly purified by column chromatography with petroleum ether/ethyl acetate (10:1) as eluent to give the desired product **5**.

General procedure for N-alkylation of aromatic amines with primary alcohols.

A solution of **2d** (2 mol%, 0.02 mmol), AgNTf₂ (2 mol%, 0.02 mmol) and toluene (1 mL) were stirred in a Schlenk tube under N₂ at room temperature for a moment. Subsequently, aromatic amine (1.1 mmol), primary alcohol (1.0 mmol), and caesium carbonate (1.0 mmol) were added. The mixture was heated under 120 °C for 24 h and then cooled to room temperature. The resulting solution was directly purified by column chromatography with petroleum ether/ethyl acetate (20:1) as eluent to give the desired product **7**.

General procedure for C-alkylation of secondary alcohols with primary alcohols.

A solution of **2d** (2 mol%, 0.02 mmol), AgNTf₂ (2 mol%, 0.02 mmol) and toluene (1 mL) were stirred in a Schlenk tube under N₂ at room temperature for a moment. Subsequently, secondary alcohol (1.1 mmol), primary alcohol (1.0 mmol), and caesium carbonate (1.0 mmol) were added. The mixture was heated under 120 °C for 16 h and then cooled to room temperature. The resulting solution was directly purified by column chromatography with petroleum ether/ethyl acetate (10:1) as eluent to give the desired product **9**.

General procedure for the alkylation of amine with alcohol under solvent-free conditions.

A solution of **2d** (2 mol%, 0.02 mmol), AgNTf₂ (2 mol%, 0.02 mmol) and alcohol (1 mL) were stirred in a Schlenk tube under N₂ at room temperature for a moment. Subsequently, aromatic amine (1 mmol), and caesium carbonate (1 mmol), was added. The mixture was heated under reflux for 24 h and then cooled to room temperature. The resulting solution was directly purified by column chromatography with petroleum ether/ethyl acetate (20:1) as eluent to give the desired product.

General procedure for the alkylation of acetophenone with alcohol under solvent-free conditions.

A solution of **2d** (2 mol%, 0.02 mmol), AgNTf₂ (2 mol%, 0.02 mmol) and alcohol (1 mL) were stirred in a Schlenk tube under N₂ at room temperature for a moment. Subsequently, acetophenone (1 mmol), and caesium carbonate (1 mmol), was added. The mixture was heated

under reflux for 24 h and then cooled to room temperature. The resulting solution was directly purified by column chromatography with petroleum ether/ethyl acetate (10:1) as eluent to give the desired product.

ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures, ¹H NMR, ¹³C NMR, ³¹P NMR spectra and CIF files giving crystallographic data for **2a-2d** and ¹H NMR, ¹³C NMR spectra for **5**, **7**, and **9**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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