ACS Catalysis

Research Article

pubs.acs.org/acscatalysis

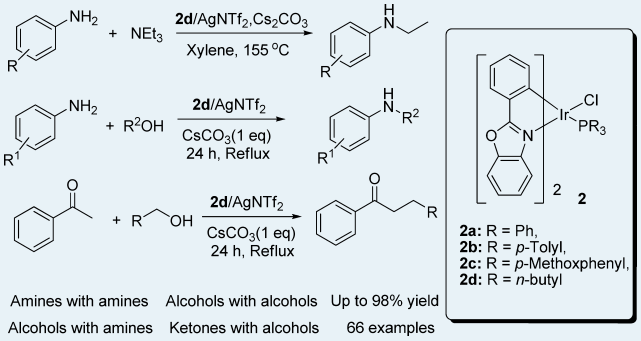
Synthesis, Structures of Benzoxazolyl Iridium(III) Complexes, and Applications on C−C and C−N Bond Formation Reactions under Solvent-Free Conditions: Catalytic Activity Enhanced by Noncoordinating Anion without Silver Effect

Dawei Wang,* Keyan Zhao, Chongying Xu, Hongyan Miao, and Yuqiang Ding*

The Key Laboratory of Food Colloids and Biotechnology, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, Jiangsu Province, China

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 and C−N bond formation reactions from the alkylation of amine with amine, amine with alcohol, ketone with alcohol, and alcohol with alcohol through a borrowing hydrogen reaction. Moreover, these iridium(III) complexes are effective catalysts for the alkylation of amine with alcohol and ketone with alcohol under solvent-free conditions. The catalytic activity of these complexes is greatly enhanced by noncoordinating, while the experiments have excluded the possibility of a "silver effect" (bimetallic catalysis or silver-assisted metal catalysis) from the experiments.



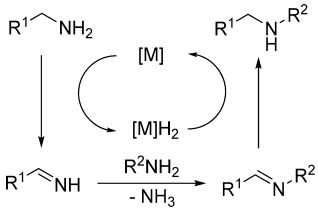
KEYWORDS: *C−C coupling, C−N coupling, solvent-free, iridium complex, noncoordinating anion*

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 the 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 borrow 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, Ru[15] and Ir[16−33] are still shown to be the most effective and promising catalysts for C-alkylation and N-alkylation.

In the related area of iridium-catalyzed N-alkylation and C-alkylation using the borrow hydrogen strategy, several research groups have paid great efforts in this area.[4a,17] Recently, Fujita and co-workers reported the synthesis of indoles and 1,2,3,4-tetrahydroquinolines with the Cp*Ir complex as a catalyst using the borrow hydrogen strategy.[18] Later, they developed multialkylation of aqueous ammonia with alcohols with the water-soluble Cp*Ir−ammine complexes as catalysts. Williams et al. showed amine alkylation using $[Cp^*IrI_2]_2$ 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. Martín-Matute et al. also described several new

Scheme 1. Alkylation of an Amine with Another Amine by Borrowing Hydrogen Reaction



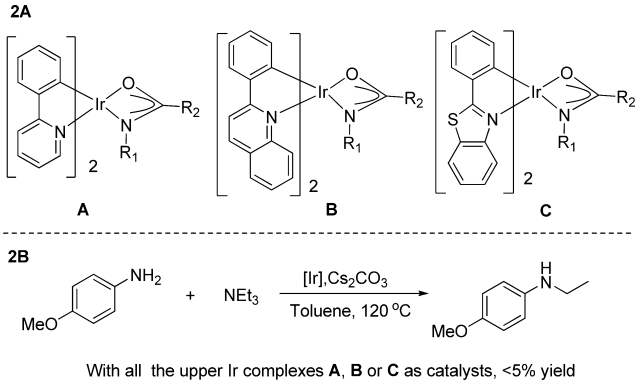
Received: July 11, 2014
Revised: September 18, 2014
Published: September 22, 2014

   dx.doi.org/10.1021/cs5009909 | ACS Catal. 2014, 4, 3910−3918

iridium complexes containing bidentate N-heterocyclic carbenes (NHC), which catalyzed the alkylation of anilines with alcohols.[5k,21] In 2008, Peris et al. reported [$IrCl_2Cp^*$(NHC)] complexes from catalyzed C−N and C−C formation reactions.[22] In 2009, Crabtree et al. 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 et al. investigated $[Cp^*IrCl_2]_2$-catalyzed alkylation of amines with alcohols using a combination of experimental and theoretical methods.[25] In 2014, Li demonstrated that the water-soluble $[Cp^*Ir(6,6'\text{-}(OH)_2bpy)(H_2O)][OTf]_2$ 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, several other groups (Milstein and Gunanathan,[6f] Beller et al.,[5a,f,6b,c] Obora et al.,[28] Huang et al.,[29] Limbach et al.,[30] Sridharan and Bhat,[31] and Ramón et al.[32]) 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

Scheme 2. Amidate Ancillary Ligand Ir(III) Complexes



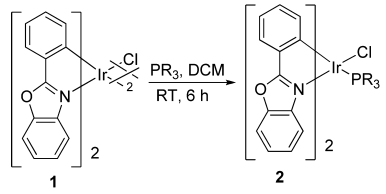
able to bind to the iridium center via the κ2 mode and thereby form a new structure involving a four-member metallocycle.[36] However, when these amide iridium complexes (**1**) were used in the borrowing hydrogen reaction of amines with amines, it was found that they had nearly no catalytic reactivity (Scheme 2B).

Generally, there are two kinds of cyclometalated Ir complexes: neutral and cationic.[37] Neutral complexes (e.g., $Ir(C\wedge N)_3$) 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: $[Ir(C\wedge N)_2L]^+X^-$) are not 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 the synthesis of ionic iridium(III) complexes. We attempted to use the phosphine ligand as an ancillary ligand in order to coordinate with the iridium(III) complex containing 2-benzothiophene (bo). Herein, we report the synthesis and characterizations of benzothienyl iridium(III) complexes with phosphine substituents by X-ray crystallography, and we found that catalytic activity was enhanced by the noncoordinating anion in C−C and C−N formation of alcohols with alcohols and amines with alcohols through the borrowing hydrogen reaction.

RESULTS AND DISCUSSION

Synthesis of Benzoxazolyl Skeleton Phosphine Ligand Ir(III) Complexes 2. The chloro-bridged dimer and phosphine ligand were weighed in an oven-dried Schlenk flask under a nitrogen atmosphere, followed by the addition of dry CH_2Cl_2 as the solvent. The mixture was stirred at room temperature for 6 h producing $[(bo)_2Ir(PR_3)]Cl$ (**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 benzoxazoyl 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 $P\bar{1}$ space group. In the molecular structure of compound **2a**, the Ir(1) atom is coordinated to one tributylphosphine, one chlorine atom, and two benzoxazoyl ligands, and all are in the bidentate-chelating fashion (Figure 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)° and the angle of Cl(1)−Ir(1)−P(1) is 99.60(10)°, while the angle of N(1)−Ir(1)−P(1) is 89.69(4)°. The bond length of Ir(1)−N(1) (2.195(4) Å) is

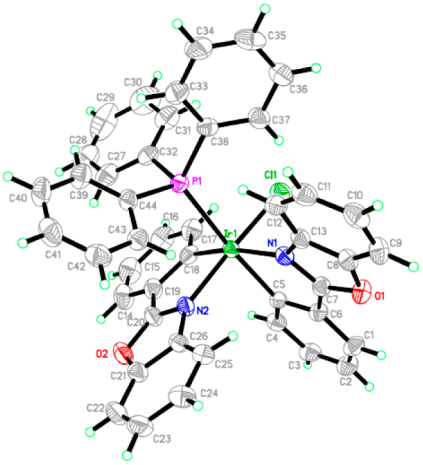


Figure 1. ORTEP diagram of **2a** with thermal ellipsoids shown at the 30% probability level.

dx.doi.org/10.1021/cs5009909 | ACS Catal. 2014, 4, 3910−3918

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 a tri-*n*-butylphosphine ancillary ligand was nearly identical in structure. The single crystal of **2d** (Figure 2) was obtained

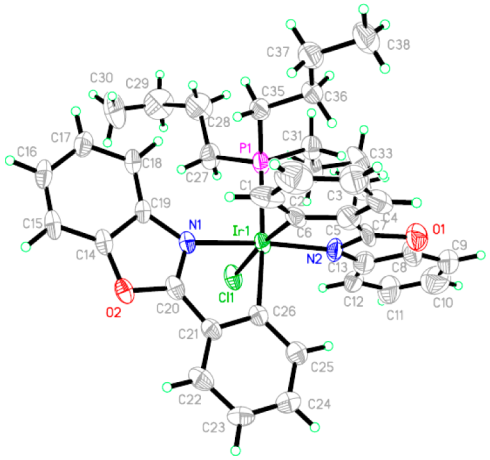


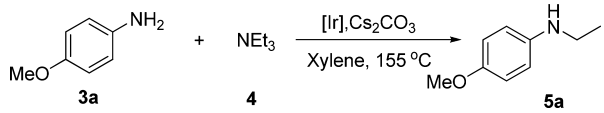
Figure 2. ORTEP diagram of **2d** with thermal ellipsoids shown at the 30% probability level.

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.

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 are shown in Table 1. The chloro-bridged dimer $[\{(bo)_2Ir(\mu\text{-}Cl)\}_2]$ and $[\{(bo)_2Ir(\mu\text{-}Cl)\}_2]$/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).

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's (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 $AgNTf_2$ to the reaction was comparatively more effective. Other new Ir(III) complexes such as **2a**, **2b**, and **2c** were also found to be effective with $AgNTf_2$ as the additive under the same conditions (Table 1, entries 13−15). Blank inspection showed that the reaction could not occur without an iridium catalyst (Table 1, entry 1). By using the other reaction conditions, it was found that a decrease in reaction temperature or a change of solvent would lead to decreased product yields

Table 1. Catalysts Screening for N-Alkylation of *p*-Anisidine with NEt_3[a]



entry	catalyst	yield [%][b]
1	none	<5
2	$[\{(bo)_2Ir(\mu\text{-}Cl)\}_2]$	<5
3	$[\{(bo)_2Ir(\mu\text{-}Cl)\}_2]$/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

[a]Reagents 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. [b]Yields of pure product. [c][Ir] loading (1 mol %, 0.01 mmol). [d][Ir] loading (5 mol %, 0.05 mmol). [e]Reaction temperature (110 °C). [f]Solvent (1 mL DMF). [g]Without any base.

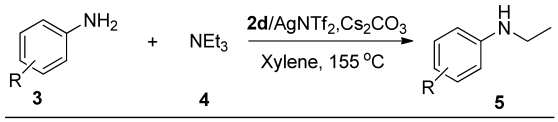
(Table 1, entries 18 and 19). Decreasing the catalyst loading from 2 mol % to 1 mol % resulted in decreased yield (Table 1, entry 16), while the increase of catalyst loading did not produce an improvement in yield (Table 1, entry 17). Hence, the best reaction conditions are summarized as follows: 2 mol % of **2d**/$AgNTf_2$ catalyst, 1 equiv of Cs_2CO_3, xylene as the reaction solvent, and a temperature of 155 °C (Table 1, entry 15).

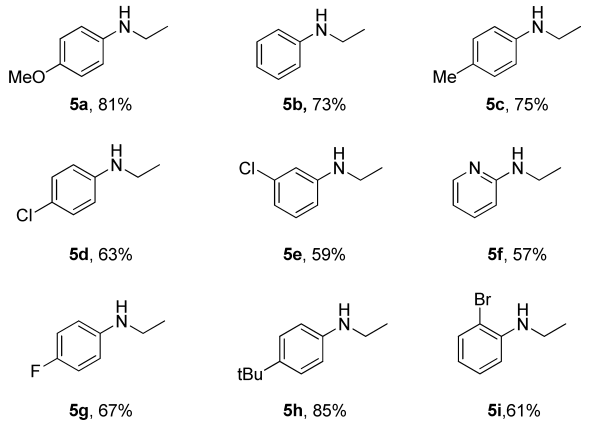
With the optimized reaction conditions in hand, we further employed the above methods to aromatic amines and triethylamine. The results were summarized in Table 2. The experiments showed that different *N*-alkylated anilines were obtained with moderate to good yields through the use of the catalyst **2d**/$AgNTf_2$. 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.

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

dx.doi.org/10.1021/cs5009909 | *ACS Catal.* 2014, 4, 3910−3918

Table 2. Alkylation of Amines with Amines[a,b]





[a]Reagents and conditions: **3** (1.0 mmol), **4** (1 mL), **2d** (2 mol %, 0.02 mmol), $AgNTf_2$ (2 mol %, 0.02 mmol), Cs_2CO_3 (1.1 mmol), xylene (2 mL), 155 °C, 20 h. [b]Isolated yield.

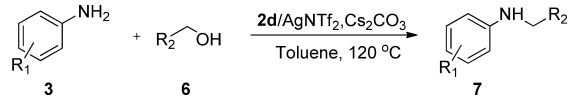
ranging from 77% to 95%. Subsequently, the amination reactions of different alcohols were explored. Clearly, aromatic alcohols—including *p*-methylbenzyl alcohol, *p*-methoxylbenzyl alcohol, *p*-chlorobenzyl alcohol, and furyl alcohol—could react smoothly and give yields ranging from 76% to 94%.

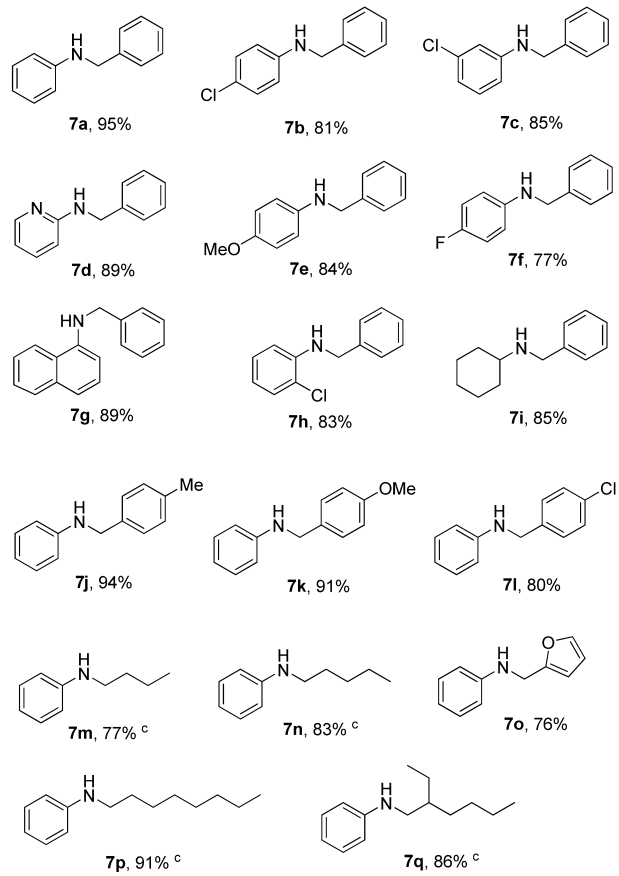
We were pleased to find that aliphatic alcohols were effective with this methodology (Table 3). The experiments showed that the *N*-alkylated products were also achieved with good to excellent yields. The substituent group of aliphatic alcohols had a minimal influence on the reaction. The yields of the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

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 furyl-heterocyclic alcohols had little influence on the formation of desired products under the optimal reaction conditions with moderate to good yields.

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 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 performed well, providing moderate to excellent yields. Chlorinated aromatic alcohol and electron-donating substituents were well tolerated in the reactions, while furyl-heterocyclic alcohol could react well under the optimal reaction conditions with the overall yield (79%). Additionally, we also tried the borrowing hydrogen reaction of phenylethanol with aliphatic alcohols. We chose *iso*-

Table 3. Alkylation of Amines with Alcohols[a,b]





[a]Reagents and conditions: **3** (1.0 mmol), **6** (1.1 mmol), **2d** (2 mol %, 0.02 mmol), $AgNTf_2$ (2 mol %, 0.02 mmol), Cs_2CO_3 (1.1 mmol), toluene (2 mL), 120 °C, 16 h. [b]Isolated yield. [c]**6** (3 mmol).

octyl alcohol, 1-pentanol, *n*-propanol, and *iso*-butanol as being representative. The corresponding target products were all separated smoothly, while the yields were significantly lower than those of aromatic alcohols.

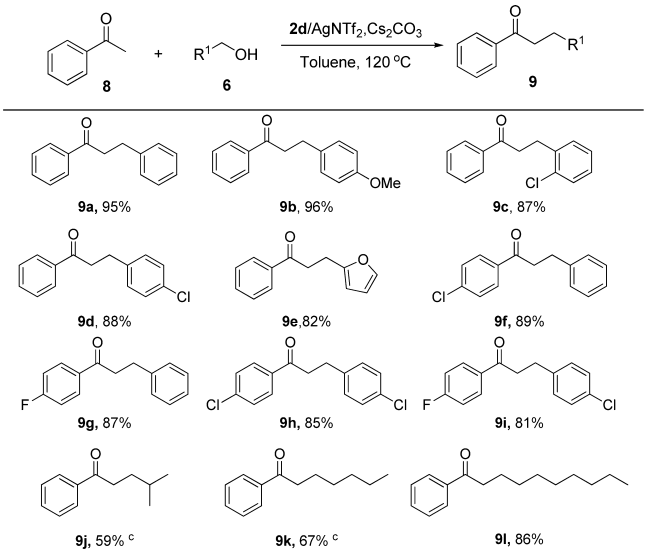
Moreover, we also explored the borrowing hydrogen reaction of an amine under solvent-free conditions. To our surprise, the desired products were separated with good to excellent yields (Table 6).

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.

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

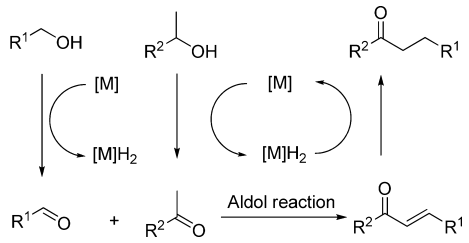
dx.doi.org/10.1021/cs5009909 | ACS Catal. 2014, 4, 3910−3918

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), $AgNTf_2$ (2 mol %, 0.02 mmol), Cs_2CO_3 (1.1 mmol), toluene (2 mL), 120 °C, 16 h. [b]Isolated yield. [c]**6** (2 mmol).

Scheme 4. C−C Formation of Primary and Secondary Alcohols



with amine, amine with alcohol, ketone with alcohol, and alcohol with alcohol, even under solvent-free conditions.

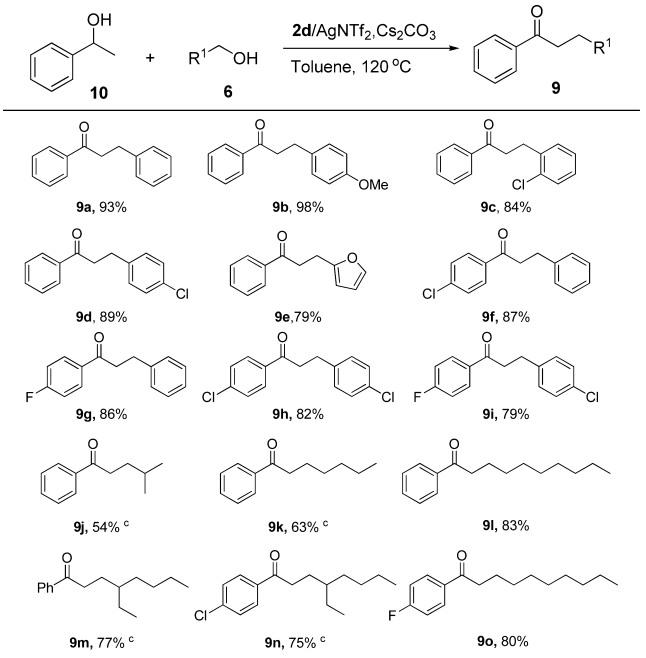
In 2012, Shi and co-workers revealed a long-overlooked "silver effect" in gold catalysis, which led to the revision of silver-involved reactions.[41] They found that many reactions involving silver (AgCl or silver nanoparticle, in most cases) actually comprised bimetallic catalysis or silver-assisted 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.

As indicated in Table 8, the test of silver salts was conducted. The complex $[(bo)_2Ir(PBu_3)]NTf_2$, 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 $AgSbF_6$ as additives. So, silver does not play a role in this reaction, and the effective catalyst is iridium.

CONCLUSION

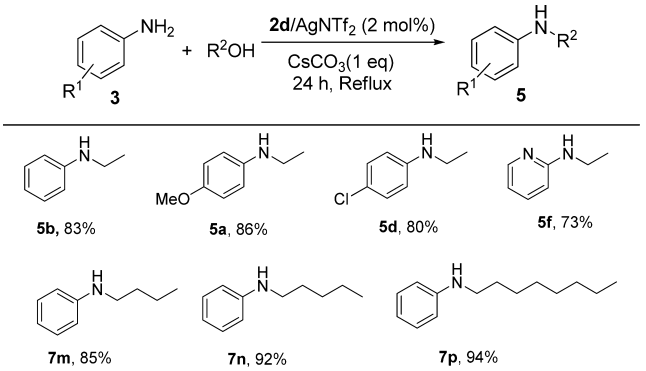
In conclusion, several new types of bisbenzoxazolyl iridium(III) complexes have been synthesized and characterized through X-ray crystallography. The experiments showed that these complexes exhibit good catalytic activity in borrowing hydrogen for C−C or C−N bond formation under mild conditions. Moreover, these iridium(III) complexes are effective catalysts for the alkylation of amine with alcohol and ketone with alcohol

Table 5. Alkylation of Two Alcohols[a,b]



[a]Reagents and conditions: **8** (1.0 mmol), **6** (1.1 mmol), **2d** (2 mol %, 0.02 mmol), $AgNTf_2$ (2 mol %, 0.02 mmol), Cs_2CO_3 (1.1 mmol), toluene (2 mL), 120 °C, 16 h. [b]Isolated yield. [c]**6** (3 mmol).

Table 6. Alkylation of Amine with Alcohol under Solvent-Free Conditions[a,b]



[a]Reagents and conditions: **3** (1.0 mmol), R^2OH (1 mL), **2d** (2 mol %, 0.02 mmol), $AgNTf_2$ (2 mol %, 0.02 mmol), Cs_2CO_3 (1 mmol); reflux, 24 h. [b]Isolated yield.

under solvent-free conditions. The catalytic activity of these complexes is greatly enhanced by noncoordinating anions, while the experiments have excluded the possibility of a "silver effect" (bimetallic catalysis or silver-assisted metal catalysis) from the experiments.

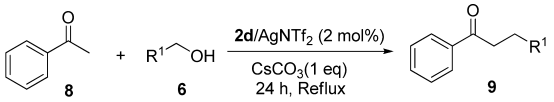
EXPERIMENTAL DETAILS

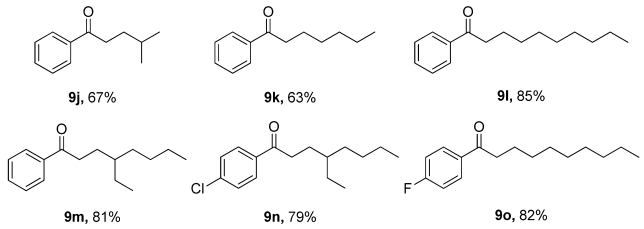
Materials. $IrCl_3·3H_2O$ and other chemicals were obtained from commercial sources and used without further purification. Chloro-bridged dimer $(bo)_2Ir(\mu\text{-}Cl)_2Ir(bo)_2$ was prepared according to the reported literature procedures. All solvents were dried by standard methods.

Preparation of Complex 2a. A solution of $[\{(bo)_2Ir(\mu\text{-}Cl)\}_2]$ (0.1 mmol) and tributylphosphine (0.22 mmol) in CH_2Cl_2 (10 mL) was stirred at temperature overnight under a nitrogen atmosphere. The mixture was filtered off and the

dx.doi.org/10.1021/cs5009909 | ACS Catal. 2014, 4, 3910−3918

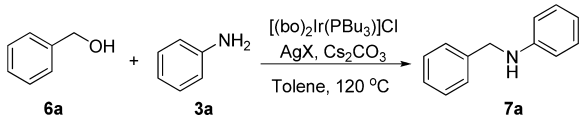
Table 7. Alkylation of Acetophenone with Alcohol under Solvent-Free Conditions[a,b]





[a]Reagents and conditions: **8** (1.0 mmol), R^2OH (1 mL), **2d** (2 mol %, 0.02 mmol), $AgNTf_2$ (2 mol %, 0.02 mmol), Cs_2CO_3 (1 mmol); reflux, 24 h. [b]Isolated yield.

Table 8. Verification Test of Silver Effect[a,b]



entry	catalyst	conditions	yield [%][b]
1	$[(bo)_2Ir(PBu_3)]Cl$ (**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), Cs_2CO_3 (1.1 mmol), toluene (2 mL), 120 °C, 16 h. The filtration was conducted to remove AgCl through Celite. [b]Isolated yield.

solvent removed under a vacuum. The crude product was further recrystallized in CH_2Cl_2/hexane, and a desired product, **2a**, was obtained (yield: 84%). ^1H NMR (400 MHz, $CDCl_3$): 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). ^{13}C NMR (101 MHz, $CDCl_3$): 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. ^{31}P NMR (162 MHz, $CDCl_3$): δ −9.24; Anal. Calcd for $C_{44}H_{31}ClIrN_2O_2P$: 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), $AgNTf_2$ (2 mol %, 0.02 mmol), and xylene (1 mL) was stirred in a Schlenk tube under N_2 at room temperature for a moment. Subsequently, aromatic amine (1.0 mmol), aliphatic amine (1.0 mL), and cesium 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 an 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), $AgNTf_2$ (2 mol %, 0.02 mmol), and toluene (1 mL) was stirred in a Schlenk tube uder N_2 at room temperature for a moment. Subsequently, aromatic amine (1.1 mmol), primary alcohol (1.0 mmol), and cesium 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 an 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), $AgNTf_2$ (2 mol %, 0.02 mmol), and toluene (1 mL) was stirred in a Schlenk tube uder N_2 at room temperature for a moment. Subsequently, secondary alcohol (1.1 mmol), primary alcohol (1.0 mmol), and cesium 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 an 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), $AgNTf_2$ (2 mol %, 0.02 mmol), and alcohol (1 mL) was stirred in a Schlenk tube under N_2 at room temperature for a moment. Subsequently, aromatic amine (1 mmol), and cesium carbonate (1 mmol) were 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 an 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), $AgNTf_2$ (2 mol %, 0.02 mmol), and alcohol (1 mL) was stirred in a Schlenk tube uder N_2 at room temperature for a moment. Subsequently, acetophone (1 mmol), and cesium carbonate (1 mmol) were 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 an eluent to give the desired product.

■ ASSOCIATED CONTENT

Supporting Information

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

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: wangdw@jiangnan.edu.cn.
*E-mail: yding@jiangnan.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge financial support of this work by the National Natural Science Foundation of China (21401080, 21371080), the Natural Science Foundation of Jiangsu Province of China (BK20130125), and MOE & SAFEA for the 111 Project (B13025).

■ REFERENCES

(1) For recent reviews, see: (a) Beccalli, E. M.; Broggini, G.; Martinelli, M.; Sottocornola, S. *Chem. Rev.* **2007**, *107*, 5318−5365. (b) Birkholz, M.-N.; Freixa, Z.; van Leeuwen, P. W. N. M. *Chem. Soc. Rev.* **2009**, *38*, 1099−1118. (c) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *Chem. Rev.* **2010**, *110*, 624−655. (d) Mkhalid, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. *Chem. Rev.* **2010**, *110*, 890−931. (e) Beletskaya, I. P.; Ananikov, V. P. *Chem. Rev.* **2011**, *111*, 1596−1636. (f) Li, B. J.; Shi, Z. J. *Chem. Soc. Rev.* **2012**, *41*, 5588−5598. (g) Gulevich, A. V.; Dudnik, A. S.; Chernyak, N.; Gevorgyan, V. *Chem. Rev.* **2013**, *113*, 3084−3213.

(2) For some examples, see: (a) Schaub, T.; Backes, M.; Radius, U. *J. Am. Chem. Soc.* **2006**, *128*, 15964−15965. (b) Nicolaou, K. C.; Li, H.; Nold, A. L.; Pappo, D.; Lenzen, A. *J. Am. Chem. Soc.* **2007**, *129*, 10356−10357. (c) Anderson, D. J.; McDonald, R.; Cowie, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 3741−3744. (d) Erhardt, S.; Macgregor, S. A. *J. Am. Chem. Soc.* **2008**, *130*, 15490−15498. (e) Boebel, T. A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2008**, *130*, 7534−7535. (f) He, H.; Liu, W.-B.; Dai, L.-X.; You, S.-L. *J. Am. Chem. Soc.* **2009**, *131*, 8346−8347. (g) Meier, G.; Braun, T. *Angew. Chem., Int. Ed.* **2009**, *48*, 1546−1548. (h) Jana, A.; Samuel, P. P.; Tavcar, G.; Roesky, H. W.; Schulzke, C. *J. Am. Chem. Soc.* **2010**, *132*, 10164−10170. (i) Robbins, D. W.; Boebel, T. A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2010**, *132*, 4068−4069. (j) Yuan, B.; Pan, Y.; Li, Y.; Yin, B.; Jiang, H. *Angew. Chem., Int. Ed.* **2010**, *49*, 4054−4058. (k) Ueda, S.; Su, M.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2011**, *50*, 8944−8947. (l) Dugan, T. R.; Sun, X.; Rybak-Akimova, E. V.; Olatunji-Ojo, O.; Cundari, T. R.; Holland, P. L. *J. Am. Chem. Soc.* **2011**, *133*, 12418−12421. (m) Ciana, C.-L.; Phipps, R. J.; Brandt, J. R.; Meyer, F.-M.; Gaunt, M. J. *Angew. Chem., Int. Ed.* **2011**, *50*, 458−462. (n) Ge, S.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **2012**, *51*, 12837−12841.

(3) (a) Liskey, C. W.; Hartwig, J. F. *J. Am. Chem. Soc.* **2012**, *134*, 12422−12425. (b) Ohmura, T.; Torigoe, T.; Suginome, M. *J. Am. Chem. Soc.* **2012**, *134*, 17416−17419. (c) Lv, H.; Zhan, J.-H.; Cai, Y.-B.; Yu, Y.; Wang, B.; Zhang, J.-L. *J. Am. Chem. Soc.* **2012**, *134*, 16216−16227. (d) He, Z.; Kirchberg, S.; Fröhlich, R.; Studer, A. *Angew. Chem., Int. Ed.* **2012**, *51*, 3699−3702. (e) DeAngelis, A.; Wang, D. H.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2013**, *52*, 3434−3437. (f) Frei, R.; Waser, J. *J. Am. Chem. Soc.* **2013**, *135*, 9620−9623. (g) Giannerini, M.; Hornillos, V.; Vila, C.; Fañanás-Mastral, M.; Feringa, B. L. *Angew. Chem., Int. Ed.* **2013**, *52*, 13329−13333. (h) McInturff, E. L.; Nguyen, K. D.; Krische, M. J. *Angew. Chem., Int. Ed.* **2014**, *53*, 3232−3235. (i) Morofuji, T.; Shimizu, A.; Yoshida, J.-i. *J. Am. Chem. Soc.* **2014**, *136*, 4496−4499. (j) Neely, J. M.; Rovis, T. *J. Am. Chem. Soc.* **2014**, *136*, 2735−2738. (k) Pérez-Temprano, M. H.; Racowski, J. M.; Kampf, J. W.; Sanford, M. S. *J. Am. Chem. Soc.* **2014**, *136*, 4097−4100.

(4) For recent reviews, see: (a) Hamid, M. H. S. A.; Slatford, P. A.; Williams, J. M. J. *Adv. Synth. Catal.* **2007**, *349*, 1555−1575. (b) Díez-González, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612−3676. (c) Guillena, G. J.; Ramón, D.; Yus, M. *Chem. Rev.* **2010**, *110*, 1611−1641. (d) Suzuki, T. *Chem. Rev.* **2011**, *111*, 1825−1845. (e) Stratakis, M.; Garcia, H. *Chem. Rev.* **2012**, *112*, 4469−4506. (f) Allen, S. E.; Walvoord, R. R.; Padilla-Salinas, R.; Kozlowski, M. C. *Chem. Rev.* **2013**, *113*, 6234−6458.

(5) For some examples, see: (a) Hollmann, D.; Bahn, S.; Tillack, A.; Beller, M. *Chem. Commun.* **2008**, 3199−201. (b) Shimizu, K.-i.; Sato, R.; Satsuma, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 3982−3986. (c) Yamaguchi, K.; He, J.; Oishi, T.; Mizuno, N. *Chem.—Eur. J.* **2010**, *16*, 7199−7207. (d) Kumar, A.; Sharma, S.; Maurya, R. A. *Adv. Synth. Catal.* **2010**, *352*, 2227−2232. (e) Ghosh, R.; Sarkar, A. *J. Org. Chem.* **2011**, *76*, 8508−8512. (f) Gowrisankar, S.; Neumann, H.; Beller, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 5139−5143. (g) Miura, T.; Kose, O.; Li, F.; Kai, S.; Saito, S. *Chem.—Eur. J.* **2011**, *17*, 11146−11151. (h) Ghosh, R.; Sarkar, A. *J. Org. Chem.* **2011**, *76*, 8508−8512. (I) He, W.; Wang, L.; Sun, C.; Wu, K.; He, S.; Chen, J.; Wu, P.; Yu, Z. *Chem.—Eur. J.* **2011**, *17*, 13308−13317. (j) Agrawal, S.; Lenormand, M.; Martín-Matute, B. *Org. Lett.* **2012**, *14*, 1456−1459. (k) Bartoszewicz, A.; Marcos, R.; Sahoo, S.; Inge, A. K.; Zou, X.; Martín-Matute, B. *Chem.—Eur. J.* **2012**, *18*, 14510−14519. (l) Liu, H.; Chuah, G.-K.; Jaenicke, S. *J. Catal.* **2012**, *292*, 130−137. (m) Bartoszewicz, A.; Marcos, R.; Sahoo, S.; Inge, A. K.; Zou, X.; Martín-Matute, B. *Chem.—Eur. J.* **2012**, *18*, 14510−14519. (n) Baumann, W.; Spannenberg, A.; Pfeffer, J.; Haas, T.; Kockritz, A.; Martin, A.; Deutsch, J. *Chem.—Eur. J.* **2013**, *19*, 17702−17706.

(6) (a) Quintard, A.; Constantieux, T.; Rodriguez, J. *Angew. Chem., Int. Ed.* **2013**, *52*, 12883−12887. (b) Zhang, M.; Neumann, H.; Beller, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 597−601. (c) Zhang, M.; Fang, X.; Neumann, H.; Beller, M. *J. Am. Chem. Soc.* **2013**, *135*, 11384−11388. (d) Soule, J. F.; Miyamura, H.; Kobayashi, S. *Chem. Commun.* **2013**, *49*, 355−357. (e) Quintard, A.; Constantieux, T.; Rodriguez, J. *Chem.—Eur. J.* **2013**, *19*, 14030−14033. (f) Gunanathan, C.; Milstein, D. *Science.* **2013**, *341*, 249−249. (g) Wang, D.; Guo, X.-Q.; Wang, C.-X.; Wang, Y.-N.; Zhong, R.; Zhu, X.-H.; Cai, L.-H.; Gao, Z.-W.; Hou, X.-F. *Adv. Synth. Catal.* **2013**, *355*, 1117−1125. (h) Weickmann, D.; Frey, W.; Plietker, B. *Chem.—Eur. J.* **2013**, *19*, 2741−2748. (i) Wetzel, A.; Wöckel, S.; Schelwies, M.; Brinks, M. K.; Rominger, F.; Hofmann, P.; Limbach, M. *Org. Lett.* **2013**, *15*, 266−269. (j) Chan, L. K.; Poole, D. L.; Shen, D.; Healy, M. P. *Angew. Chem., Int. Ed.* **2014**, *53*, 761−765. (k) Yan, F.-X.; Zhang, M.; Wang, X.-T.; Xie, F.; Chen, M.-M.; Jiang, H. *Tetrahedron* **2014**, *70*, 1193−1198. (l) Xie, F.; Chen, M.; Wang, X.; Jiang, H.; Zhang, M. *Org. Biomol. Chem.* **2014**, *12*, 2761−2768.

(7) (a) Kwon, M. S.; Kim, N.; Seo, S. H.; Park, I. S.; Cheedrala, R. K.; Park, J. *Angew. Chem., Int. Ed.* **2005**, *44*, 6913−6915. (b) Zhang, Y.; Qi, X.; Cui, X.; Shi, F.; Deng, Y. *Tetrahedron Lett.* **2011**, *52*, 1334−1338. (c) Corma, A.; Navas, J.; Rodenas, T.; Sabater, M. J. *Chem.—Eur. J.* **2013**, *19*, 17464−17471. (d) Hikawa, H.; Matsuda, N.; Suzuki, H.; Yokoyama, Y.; Azumaya, I. *Adv. Synth. Catal.* **2013**, *355*, 2308−2320.

(8) (a) Wang, Y.; Zhu, D.; Tang, L.; Wang, S.; Wang, Z. *Angew. Chem., Int. Ed.* **2011**, *50*, 8917−8921. (b) Tang, C.-H.; He, L.; Liu, Y.-M.; Cao, Y.; He, H.-Y.; Fan, K.-N. *Chem.—Eur. J.* **2011**, *17*, 7172−7177. (c) Sabater, S.; Mata, J. A.; Peris, E. *Chem.—Eur. J.* **2012**, *18*, 6380−6385. (d) Soule, J. F.; Miyamura, H.; Kobayashi, S. *Chem. Commun.* **2013**, *49*, 355−357.

(9) (a) Shimizu, K.-I.; Sato, R.; Satsuma, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 3982−3986. (b) Cui, X.; Zhang, Y.; Shi, F.; Deng, Y. *Chem.—Eur. J.* **2011**, *17*, 1021−1028. (c) Chen, C.; Hong, S. H. *Org. Biomol. Chem.* **2011**, *9*, 20−26.

(10) (a) Miura, T.; Kose, O.; Li, F.; Kai, S.; Saito, S. *Chem.—Eur. J.* **2011**, *17*, 11146−11151. (b) Dixit, M.; Mishra, M.; Joshi, P. A.; Shah, D. O. *Catal. Commun.* **2013**, *33*, 80−83. (c) Santoro, F.; Psaro, R.; Ravasio, N.; Zaccheria, F. *RSC Adv.* **2014**, *4*, 2596−2600.

(11) (a) Cui, X.; Shi, F.; Zhang, Y.; Deng, Y. *Tetrahedron Lett.* **2010**, *51*, 2048−2051. (b) Wu, M.; Hu, X.; Liu, J.; Liao, Y.; Deng, G.-J. *Org. Lett.* **2012**, *14*, 2722−2725. (c) Bala, M.; Verma, P. K.; Sharma, U.; Kumar, N.; Singh, B. *Green Chem.* **2013**, *15*, 1687−1693.

(12) (a) Cui, X.; Dai, X.; Deng, Y.; Shi, F. *Chem.—Eur. J.* **2013**, *19*, 3665−3675. (b) Shimizu, K.-i.; Imaiida, N.; Kon, K.; Siddiki, S. M. A. H.; Satsuma, A. *ACS Catal.* **2013**, *3*, 998−1005.

(13) (a) Bertoli, M.; Choualeb, A.; Lough, A. J.; Moore, B.; Spasyuk, D.; Gusev, D. G. *Organometallics* **2011**, *30*, 3479−3482. (b) Buil, M. L.; Esteruelas, M. A.; Herrero, J.; Izquierdo, S.; Pastor, I. M.; Yus, M. *ACS Catal.* **2013**, *3*, 2072−2075.

(14) (a) Padwa, A. *Chem. Soc. Rev.* **2009**, *38*, 3072−3081. (b) Satyanarayana, P.; Reddy, G. M.; Maheswaran, H.; Kantam, M. L. *Adv. Synth. Catal.* **2013**, *355*, 1859−1867.

(15) (a) Hamid, M. H. S. A.; Allen, C. L.; Lamb, G. W.; Maxwell, A. C.; Maytum, H. C.; Watson, A. J. A.; Williams, J. M. J. *J. Am. Chem. Soc.* **2009**, *131*, 1766−1774. (b) Cano, R.; Ramón, D. J.; Yus, M. *J. Org. Chem.* **2011**, *76*, 5547−5557. (c) Agrawal, S.; Lenormand, M.;

Martín-Matute, B. *Org. Lett.* **2012**, *14*, 1456−1459. (d) Nakajima, Y.; Okamoto, Y.; Chang, Y.-H.; Ozawa, F. *Organometallics* **2013**, *32*, 2918−2925.
(16) (a) Iuchi, Y.; Obora, Y.; Ishii, Y. *J. Am. Chem. Soc.* **2010**, *132*, 2536−2537. (b) Blank, B.; Kempe, R. *J. Am. Chem. Soc.* **2010**, *132*, 924−925. (c) Kuo, H.-Y.; Liu, Y.-H.; Peng, S.-M.; Liu, S.-T. *Organometallics* **2012**, *31*, 7248−7255. (d) Michlik, S.; Hille, T.; Kempe, R. *Adv. Synth. Catal.* **2012**, *354*, 847−862. (e) Li, F.; Sun, C.; Shan, H.; Zou, X.; Xie, J. *ChemCatChem.* **2013**, *5*, 1543−1552.
(17) (a) Guillena, G.; Ramon, D. J.; Yus, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 2358−2364. (b) Mata, J. A.; Hahn, F. E.; Peris, E. *Chem. Sci.* **2014**, *5*, 1723−1732. (c) Nixon, T. D.; Whittlesey, M. K.; Williams, J. M. *Dalton Trans.* **2009**, 753−762.
(18) (a) Kawahara, R.; Fujita, k.-I.; Yamaguchi, R. *J. Am. Chem. Soc.* **2010**, *132*, 15108−15111. (b) Kawahara, R.; Fujita, K.-i.; Yamaguchi, R. *Adv. Synth. Catal.* **2011**, *353*, 1161−1168. (c) Fujita, k.-I.; Yamamoto, K.; Yamaguchi, R. *Org. Lett.* **2002**, *4*, 2691−2694. (d) Fujita, k.-I.; Fujii, T.; Yamaguchi, R. *Org. Lett.* **2004**, *6*, 3525−3528. (e) Fujita, k.-I.; Asai, C.; Yamaguchi, T.; Hanasaka, F.; Yamaguchi, R. *Org. Lett.* **2005**, *7*, 4017−4019. (f) Yamaguchi, R.; Kawagoe, S.; Asai, C.; Fujita, k.-I. *Org. Lett.* **2008**, *10*, 181−184.
(19) (a) Saidi, O.; Blacker, A. J.; Farah, M. M.; Marsdenb, S. P.; Williams, J. M. J. *Chem. Commun.* **2010**, *46*, 1541−1543. (b) Black, P. J.; Edwards, M. G.; Williams, J. M. J. *Eur. J. Org. Chem.* **2006**, 4367−4378. (c) Black, P. J.; Cami-Kobeci, G.; Edwards, M. G.; Slatford, P. A.; Whittlesey, M. K.; Williams, J. M. *Org. Biomol. Chem.* **2006**, *4*, 116−125. (d) Saidi, O.; Blacker, A. J.; Lamb, G. W.; Marsden, S. P.; Taylor, J. E.; Williams, J. M. J. *Org. Process Res. Dev.* **2010**, *14*, 1046−1049.
(20) (a) Blank, B.; Madalska, M.; Kempe, R. *Adv. Synth. Catal.* **2008**, *350*, 749−758. (b) Blank, B. t.; Michlik, S.; Kempe, R. *Adv. Synth. Catal.* **2009**, *351*, 2903−2911. (c) Blank, B.; Michlik, S.; Kempe, R. *Chem.—Eur. J.* **2009**, *15*, 3790−3799. (d) Michlik, S.; Kempe, R. *Chem.—Eur. J.* **2010**, *16*, 13193−13198. (e) Hille, T.; Irrgang, T.; Kempe, R. *Chem.—Eur. J.* **2014**, *20*, 5569−5572.
(21) (a) Cumpstey, I.; Agrawal, S.; Borbasa, K. E.; Martín-Matute, B. *Chem. Commun.* **2011**, *47*, 7827−7829. (b) Agrawal, S.; Lenormand, M.; Martín-Matute, B. *Org. Lett.* **2012**, *14*, 1456−1459.
(22) (a) Prades, A.; Corberan, R.; Poyatos, M.; Peris, E. *Chem.—Eur. J.* **2008**, *14*, 11474−11479. (b) da Costa, A. P.; Viciano, M.; Sanaú, M.; Sonia, M.; Tejeda, J.; Peris, E.; Royo, B. *Organometallics* **2008**, *27*, 1305−1309.
(23) (a) Gnanamgari, D.; Sauer, E. L. O.; Schley, N. D.; Butler, C.; Incarvito, C. D.; Crabtree, R. H. *Organometallics* **2009**, *28*, 321−325. (b) Balcells, D.; Nova, A.; Clot, E.; Gnanamgari, D.; Crabtree, R. H.; Eisenstein, O. *Organometallics* **2008**, *27*, 2529−2535.
(24) (a) Morita, M.; Obora, Y.; Ishii, Y. *Chem. Commun.* **2007**, 2850−2852. (b) Mizuta, T.; Sakaguchi, S.; Ishii, Y. *J. Org. Chem.* **2005**, *70*, 2195−2199.
(25) (a) Nordstrøm, L. U.; Madsen, R. *Chem. Commun.* **2007**, 5034−5036. (b) Lorentz-Petersen, L. L. R.; Nordstrøm, L. U.; Madsen, R. *Eur. J. Org. Chem.* **2012**, 6752−6759. (c) Tursky, M.; Lorentz-Petersen, L. L.; Olsen, L. B.; Madsen, R. *Org. Biomol. Chem.* **2010**, *8*, 5576−5582. (d) Fristrup, P.; Tursky, M.; Madsen, R. *Org. Biomol. Chem.* **2012**, *10*, 2569−2577.
(26) (a) Qu, P.; Sun, C.; Ma, J.; Li, F. *Adv. Synth. Catal.* **2014**, *356*, 447−459. (b) Li, F.; Shan, H.; Chen, L.; Kang, Q.; Zou, P. *Chem. Commun.* **2012**, *48*, 603−605. (c) Li, F.; Qu, P.; Ma, J.; Zou, X.; Sun, C. *ChemCatChem.* **2013**, *5*, 2178−2182.
(27) Zhang, Y.; Lim, C. S.; Sim, D. S.; Pan, H. J.; Zhao, Y. *Angew. Chem., Int. Ed.* **2014**, *53*, 1399−1403.
(28) (a) Ogawa, S.; Obora, Y. *Chem. Commun.* **2014**, *50*, 2491−2493. (b) Obora, Y.; Ogawa, S.; Yamamoto, N. *J. Org. Chem.* **2012**, *77*, 9429−9433.
(29) Guo, l.; Liu, Y.; Yao, W.; Leng, X.; Huang, Z. *Org. Lett.* **2013**, *15*, 1144−1147.
(30) (a) Wöckel, S.; Plessow, P.; Schelwies, M.; Brinks, M. K.; Rominger, F.; Hofmann, P.; Limbach, M. *ACS Catal.* **2014**, *4*, 152−161. (b) Wetzel, A.; Wöckel, S.; Schelwies, M.; Brinks, M. K.; Rominger, F.; Hofmann, P.; Limbach, M. *Org. Lett.* **2013**, *15*, 266−269.
(31) (a) Bhat, S.; Sridharan, V. *Chem. Commun.* **2012**, *48*, 4701−4703.
(32) (a) Cano, R.; Yus, M.; Ramón, D. J. *Chem. Commun.* **2012**, *48*, 7628−7630.
(33) (a) Schranck, J.; Tlili, A.; Beller, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 7642−7644. (b) Lia, J.-Q.; Andersson, P. G. *Chem. Commun.* **2013**, *49*, 6131−6133. (c) Andrushko, N.; Andrushko, V.; Roose, P.; Moonen, K.; Borner, A. *ChemCatChem.* **2010**, *2*, 640−643. (d) Chaudhari, C.; Siddiki, S. M. A. H.; Kon, K.; Tomita, A.; Tai, Y.; Shimizu, K.-I. *Catal. Sci. Technol.* **2014**, *4*, 1064−1069. (e) Chang, Y. H.; Fu, C. F.; Liu, Y. H.; Peng, S. M.; Chen, J. T.; Liu, S. T. *Dalton Trans.* **2009**, 861−867. (f) Anxionnat, B.; Gomez Pardo, D.; Ricci, G.; Cossy, J. *Eur. J. Org. Chem.* **2012**, 4453−4456. (g) Huang, J.-L.; Dai, X.-J.; Li, C.-J. *Eur. J. Org. Chem.* **2013**, 6496−6500. (h) Pintado-Sierra, M.; Rasero-Almansa, A. M.; Corma, A.; Iglesias, M.; Sánchez, F. *J. Catal.* **2013**, *299*, 137−145. (i) Crotti, C.; Farnetti, E.; Licen, S.; Barbieri, P.; Pitacco, G. *J. Mol. Catal. A: Chem.* **2014**, *382*, 64−70. (j) Xu, C.; Dong, X.-M.; Wang, Z.-Q.; Hao, X.-Q.; Li, Z.; Duan, L.-M.; Ji, B.-M.; Song, M.-P. *J. Organomet. Chem.* **2012**, *700*, 214−218. (k) Pouy, M. J.; Leitner, A.; Weix, D. J.; Ueno, S.; Hartwig, J. F. *Org. Lett.* **2007**, *9*, 3949−3952. (l) Zhang, W.; Dong, X.; Zhao, W. *Org. Lett.* **2011**, *13*, 5386−5389. (m) Chang, Y.-H.; Nakajima, Y.; Ozawa, F. *Organometallics* **2013**, *32*, 2210−2215. (n) Nie, S.-Z.; Sun, X.; Wei, W.-T.; Zhang, X.-J.; Yan, M.; Xiao, J.-L. *Org. Lett.* **2013**, *15*, 2394−2397. (o) Anxionnat, B.; Gomez Pardo, D.; Ricci, G.; Rossen, K.; Cossy, J. *Org. Lett.* **2013**, *15*, 3876−3879.
(34) For recent examples, see: (a) Saidi, O.; Blacker, A. J.; Farah, M. M.; Marsden, S. P.; Williams, J. M. *Angew. Chem., Int. Ed.* **2009**, *48*, 7375−7378. (b) Shimizu, K.-i.; Shimura, K.; Ohshima, K.; Tamura, M.; Satsuma, A. *Green Chem.* **2011**, *13*, 3096−3100. (c) Shimizu, K.-i.; Ohshima, K.; Tai, Y.; Tamura, M.; Satsuma, A. *Catal. Sci. Technol.* **2012**, *2*, 730−738. (d) Tan, X.; Li, B.; Xu, S.; Song, H.; Wang, B. *Organometallics* **2013**, *32*, 3253−3261.
(35) (a) Yang, W.; Fu, H.; Song, Q.; Zhang, M.; Ding, Y. *Organometallics* **2011**, *30*, 77−83. (b) Yang, W.; Wang, D.; Song, Q.; Zhang, S.; Wang, Q.; Ding, Y. *Organometallics* **2013**, *32*, 4130−4135. (c) Ge, B.; Wang, D.; Dong, W.; Ma, P.; Li, Y.; Ding, Y. *Tetrahedron Lett.* **2014**, *55*, 5443−5446. (d) Wang, D.; Yu, X.; Zhao, K.; Ding, Y. *Tetrahedron Lett.* **2014**, *55*, 5739−5741.
(36) For selected recent papers in our group, see: (a) Li, L.; Wu, F.; Zhang, S.; Wang, D.; Ding, Y.; Zhu, Z. *Dalton Trans.* **2013**, *42*, 4539−4543. (b) Liu, X.; Zhang, S.; Ding, Y. *Dalton Trans.* **2012**, *41*, 5897−5902. (c) Zhang, S.; Ding, Y. *Organometallics* **2011**, *30*, 633−641. (d) Zhang, S.; Shi, L.; Ding, Y. *J. Am. Chem. Soc.* **2011**, *133*, 20218−20229. (e) Yang, W.; Zhang, S.; Ding, Y.; Shi, L.; Song, Q. *Chem. Commun.* **2011**, *47*, 5310−5312. (f) Zhao, K.; Wang, D.; Wang, H.; Zhu, Z.; Ding, Y. *Inorg. Chem. Commun.* **2014**, *47*, 131−133.
(37) (a) Lamansky, S.; Djurovich, P.; Murphy, D.; Abdel-Razzaq, F.; Kwong, R.; Tsyba, I.; Bortz, M.; Mui, B.; Bau, R.; Thompson, M. E. *Inorg. Chem.* **2001**, *40*, 1704−1711. (b) Ostrowski, J. C.; Robinson, M. R.; Heeger, A. J.; Bazan, G. C. *Chem. Commun.* **2002**, *7*, 784−785. (c) Tsuboyama, A.; Iwawaki, H.; Furugori, M.; Mukaide, T.; Kamatani, J.; Igawa, S.; Moriyama, T.; Miura, S.; Takiguchi, T.; Okada, S.; Hoshino, M.; Ueno, K. *J. Am. Chem. Soc.* **2003**, *125*, 12971−12979. (d) Coppo, P.; Plummer, E. A.; Cola, L. D. *Chem. Commun.* **2004**, *15*, 1774−1775. (e) Li, C.; Su, Y.; Tao, Y.; Chou, P.; Chien, C.; Cheng, C.; Liu, R. *Adv. Funct. Mater.* **2005**, *15*, 387−395. (f) Babgi, B.; Rigamonti, L.; Cifuentes, M. P.; Corkery, C.; Randles, M. D.; Schwich, T.; Petrie, S.; Stranger, R.; Teshome, A.; Asselberghs, I.; Clays, K.; Samoc, M.; Humphrey, M. G. *J. Am. Chem. Soc.* **2009**, *131*, 10293−10307. (g) Grelaud, G.; Cador, O.; Roisnel, T.; Argouarch, G.; Cifuentes, M. P.; Humphrey, M. G.; Paul, F. *Organometallics* **2012**, *31*, 1635−1642. (h) Randles, M. D.; Dewhurst, R. D.; Cifuentes, M. P.; Humphrey, M. G. *Organometallics* **2012**, *31*, 2582−2588. (i) Jo, J.; Olasz, A.; Chen, C.-H.; Lee, D. *J. Am. Chem. Soc.* **2013**, *135*, 3620−3632. (j) Li, Y.; Wang, J.; Wu, Y.; Zhu, H.; Samuel, P. P.; Roesky, H. W. *Dalton Trans.*

2013, *42*, 13715−13722. (k) Zhang, G.; Zhang, H.; Gao, Y.; Tao, R.; Xin, L.; Yi, J.; Li, F.; Liu, W.; Qiao, J. *Organometallics* **2014**, *33*, 61−68.
(38) For selected examples, see: (a) Yang, Y.; Zhao, Q.; Li, F. *Chem. Rev.* **2013**, *113*, 192−270. (b) Liu, Q.; Yin, B.; Yang, T.; Yang, Y.; Shen, Z.; Yao, P.; Li, F. *J. Am. Chem. Soc.* **2013**, *135*, 5029−5037. (c) Liu, Q.; Yang, T.; Feng, W.; Li, F. *J. Am. Chem. Soc.* **2012**, *134*, 5390−5397. (d) Liu, Q.; Sun, Y.; Feng, W.; Li, C.; Li, Y. *J. Am. Chem. Soc.* **2011**, *133*, 17122−17125. (e) Wu, W.; Yao, L.; Yang, T.; Yin, R.; Li, F.; Yu, Y. *J. Am. Chem. Soc.* **2011**, *133*, 15810−15803. (f) Liu, J.; Liu, Y.; Liu, Q.; Li, C.; Sun, L.; Li, F. *J. Am. Chem. Soc.* **2011**, *133*, 15276−15279. (g) Li, C.; Yu, M.; Sun, Y.; Wu, Y.; Huang, C.; Li, F. *J. Am. Chem. Soc.* **2011**, *133*, 11231−11239.
(39) For selected examples, see: (a) Zhang, X.; Tang, X.; Yang, J.; Li, Y.; Yan, H.; Bregadze, V. I. *Organometallics* **2013**, *32*, 2014−2018. (b) Zhang, R.; Zhu, L.; Liu, G.; Dai, H.; Lu, Z.; Zhao, J.; Yan, H. *J. Am. Chem. Soc.* **2012**, *134*, 10341−10344. (c) Zhong, W.; Yang, Q.; Shang, Y.; Liu, G.; Zhao, H.; Li, Y.; Yan, H. *Organometallics* **2012**, *31*, 6658−6668. (d) Zhao, N.; Zhang, J.; Yang, Y.; Chen, G.; Zhu, H.; Roesky, H. W. *Organometallics* **2013**, *32*, 762−769. (e) Zhao, N.; Zhang, J.; Yang, Y.; Zhu, H.; Li, Y.; Fu, G. *Inorg. Chem.* **2012**, *51*, 8710−8718. (f) Tan, G.; Zhu, H. *Inorg. Chem.* **2011**, *50*, 6979−6986. (g) Tan, G.; Yang, Y.; Chu, C.; Zhu, H.; Roesky, H. W. *J. Am. Chem. Soc.* **2010**, *132*, 12231−12233.
(40) (a) Sprouse, S.; King, K.; Spellane, P.; Watts, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 6647−6653. (b) Garces, F.; King, K.; Watts, R. *Inorg. Chem.* **1988**, *27*, 3464−3471.
(41) Wang, D.; Cai, R.; Sharma, S.; Jirak, J.; Thummanapelli, S. K.; Akhmedov, N. G.; Zhang, H.; Liu, X.; Petersen, J.; Shi, X. *J. Am. Chem. Soc.* **2012**, *134*, 9012−9019.