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Cobalt-Catalyzed α-Alkylation of Ketones with Primary Alcohols

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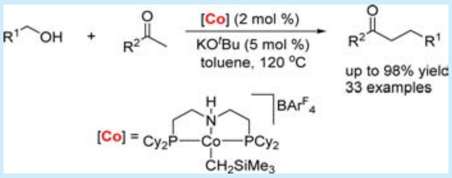
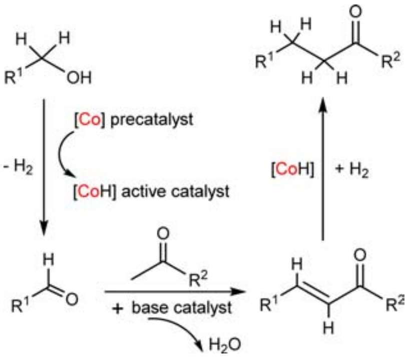
Supporting Information

ABSTRACT: An ionic cobalt−PNP complex is developed for the efficient α-alkylation of ketones with primary alcohols for the first time. A broad range of ketone and alcohol substrates were employed, leading to the isolation of alkylated ketones with yields up to 98%. The method was successfully applied to the greener synthesis of quinoline derivatives while using 2-aminobenzyl alcohol as an alkylating reagent.



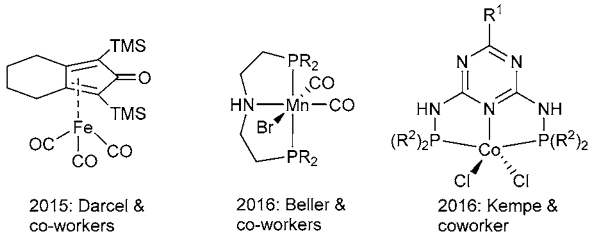
The α-alkylation of carbonyl compounds toward the construction of a C−C bond is a fundamental method in synthetic chemistry.[1] While halides have been traditionally utilized as alkylating reagents in the presence of a stoichiometric amount of base, some drawbacks such as the formation of toxic waste and high cost have limited their sustainable applications.[2] Recently, alcohols have emerged as inexpensive and "greener" alternative alkylation reagents when a catalytic method was introduced. A metal-catalyzed hydrogen-borrowing strategy, also known as hydrogen autotransfer, is, therefore, attracting significant attention as a result of its high efficiency, low cost, and waste-free feature.[3] In this process, an alcohol is first dehydrogenated (release of H_2 gas) to generate an aldehyde or ketone which experiences an in situ condensation reaction with an amine or enolate to form an imine or α,β-unsaturated ketone, which is finally reduced to form a new C−N or C−C single bond by H_2 (Scheme 1). Thus, the hydrogen-borrowing strategy involving the use of an active metal catalyst has been widely applied to the formation of both C−N and C−C bonds through the reactions of alcohols with amines or C-nucleophiles, respectively,[4,5a−h] as well as the Guerbet process for the conversion of methanol or ethanol into butanol.[5i,j] However, most of the catalysts developed thus far constitute noble metals, such as ruthenium and iridium. The replacement of noble metal catalysts with nonprecious ones is highly desirable.

Scheme 1. "Hydrogen-Borrowing" Strategy as a Model for the Cobalt-Catalyzed α-Alkylation of Ketones with Alcohols



Nonprecious metals (such as Fe, Co, or Mn) have received increasing attention in sustainable chemistry, as they are more earth-abundant, eco-friendly, and inexpensive in addition to their different reactivity compared with noble metals.[6−8] Encouraging results have been reported very recently on the nonprecious-metal-catalyzed hydrogen-borrowing C−N or C−C bond-forming reactions[9] following the observation of remarkably active nonprecious metal catalysts mainly involving Fe, Co, and Mn for hydrogenation and "acceptorless" dehydrogenation reactions.[6−8] The first Knölker-type Fe-catalyzed alkylation of ketones with primary alcohols through a hydrogen-borrowing process was reported by Darcel and co-workers in 2015 (Scheme 2).[10a] Notably, the Beller group recently introduced a Mn^{I} pincer complex that is effective for the α-alkylation of a range of valuable ketone substrates with alcohols.[10b] In addition, Co^{II} catalysts with N-rich ligands were observed to catalyze the C-alkylation of unactivated amides and esters with alcohols,[10c] whereas cobalt-catalyzed α-alkylation of ketones remains unknown.

Scheme 2. Recent Examples of Fe, Mn, and Co Catalysts for Hydrogen-Autotransfer C−C Bond Formation



Our research efforts have been dedicated to the development of active well-defined nonprecious metal cobalt and manganese catalysts for hydrogenation, hydrofunctionalization, as well as

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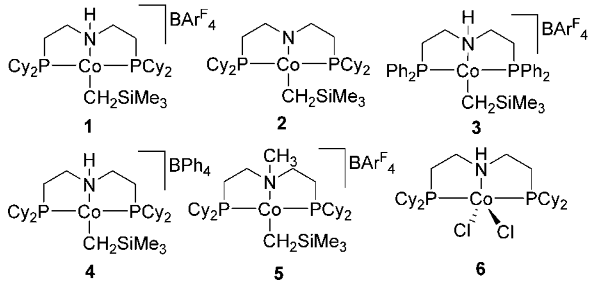
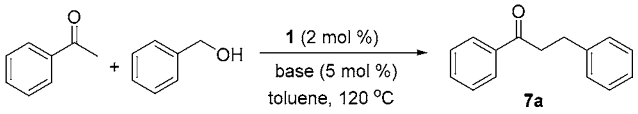
dehydrogenative coupling reactions.[9a,b,11] During the course of our continuing work on a Co^{II}−PNP pincer complex [(PNHPCy)Co(CH$_2$SiMe$_3$)][BArF$_4$] (**1**, Scheme 3) originally developed by Hanson and Zhang[11a] as a highly active catalyst for the hydrogenation of alkenes, aldehydes, ketone, and imines under mild conditions as well as the acceptorless dehydrogenation of alcohols and amines,[12] we have recently reported the applications of this catalyst in efficient *N*-alkylation of amines with alcohols[9b] or amines[9a] using the hydrogen-borrowing strategy. Herein, we reveal the activity of the same Co^{II} pincer catalyst toward the α-alkylation of ketones with primary alcohols. To the best of our knowledge, this represents the first example of cobalt-catalyzed ketone alkylation by alcohols via the hydrogen-borrowing pathway.

Scheme 3. Cobalt(II) Complexes 1−6 Studied in This Work



Preliminary reactivity tests were conducted using benzyl alcohol and acetophenone as substrates and **1** or its derivatives as a catalyst (Scheme 3). The results are summarized in Table 1. Initially, the reaction was carried out in toluene at 120 °C in the presence of **1** (2 mol %) without a base additive. However, only a trace amount of the desired product **7a** was detected, along with the formation of benzaldehyde in 62% GC yield (entry 1, Table 1). After addition of a strong base, KO^{t}Bu (5 mol %), into the same reaction system, highly selective conversion of the ketone and alcohol into **7a** was detected on GC after 24 h, and a 93% yield of **7a** was obtained after flash column chromatography purification (entry 2). According to these findings, the use of the base is critical for the promoted catalytic activity of **1**. We, therefore, examined other inorganic and organic bases under the same conditions using **1** as a catalyst, yet the results were much inferior, although cesium carbonate has been proven to be an excellent base additive for manganese-catalyzed ketone alkylation (entries 3−7).[10b] The solvent screening indicates that toluene behaves as the best solvent for the current reaction (entries 8−10). Furthermore, several catalyst analogues of **1** were tested for the same reaction. Whereas the neutral complex **2** was less effective, as confirmed in previously reported dehydrogenative coupling processes,[9a,b,11c] ionic complexes **3**−**5** modified from **1** on the PNP ligand and counteranion were found to be suitable catalysts, affording **7a** in good yields (entries 11−14). Additionally, air-stable complex **6** also catalyzed the reaction with moderate yield (55%, entry 15). In contrast, the reaction performed without a cobalt catalyst showed only trace conversion under the standard conditions (entry 16). The volume of the reaction vessel was also important for the optimal yield, and the reaction in a 50 mL reaction tube gave **7a** in only 70% yield (entry 17). Finally, the reaction conducted in the presence of 1 atm H$_2$ atmosphere was less efficient as well (entry 18). It is worth noting that the reaction under optimal conditions shows good selectivity toward the alkylated product and the byproduct formation was completely inhibited, unlike the Fe-catalyzed reactions reported previously.[10a]

Table 1. Reactivity Tests for Cobalt-Catalyzed α-Alkylation of Acetophenone with Benzyl Alcohol[a]



entry	catalyst	base	solvent	yield[b] (%)
1	**1**		toluene	<2[c]
2	**1**	KO^{t}Bu	toluene	93
3	**1**	NaOH	toluene	8[c]
4	**1**	K$_2$CO$_3$	toluene	20[c]
5	**1**	Cs$_2$CO$_3$	toluene	24[c]
6	**1**	piperazine	toluene	10[c]
7	**1**	TEA	toluene	3[c]
8	**1**	KO^{t}Bu	THF	64
9	**1**	KO^{t}Bu	benzene	82
10	**1**	KO^{t}Bu	1,4-dioxane	57
11	**2**	KO^{t}Bu	toluene	25[c]
12	**3**	KO^{t}Bu	toluene	85
13	**4**	KO^{t}Bu	toluene	72
14	**5**	KO^{t}Bu	toluene	89
15	**6**	KO^{t}Bu	toluene	55
16		KO^{t}Bu	toluene	<2[c]
17[d]	**1**	KO^{t}Bu	toluene	70
18[e]	**1**	KO^{t}Bu	toluene	82

[a] Conditions: benzyl alcohol (0.6 mmol), acetophenone (0.5 mmol), cobalt **1** (2 mol %, formed in situ by mixing **2** and H[BAr$^F_4$]·(Et$_2$O)$_2$)), and solvent (4 mL) are heated to 120 °C in a 100 mL Schlenk tube, 24 h. [b] Yield of the isolated product. [c] Yield determined by GC analysis. [d] Reaction was run in a 50 mL Schlenk tube. [e] Reaction was run at 1 atm H$_2$ atmosphere. TEA: triethylamine.

To explore the applicability of our cobalt(II) pincer catalyst for a broader range of substrates, we next employed the optimized reaction conditions (entry 2, Table 1) for the coupling between a variety of alcohols and ketones. First, a series of aromatic and aliphatic primary alcohols were chosen to react with acetophenone, and the results are summarized in Scheme 4. Differently substituted benzylic alcohols are suitable substrates for the indicated reactions under the standard conditions, and in most cases, using benzylic alcohols bearing electron-withdrawing or -donating groups, the desired ketone products **7a**−**h** were isolated with good to excellent yields, except that a lower yield (46%) was obtained for 2-methylbenzyl alcohol, possibly owing to the steric effect that suppressed the C−C coupling process. However, this is not the case when the 2-methoxybenzyl alcohol was utilized as a substrate. Unfortunately, reaction with 4-nitrobenzyl alcohol gave a complicated mixture, and the products were inseparable by column chromatography with the desired **7i** being detected by GC in only 21% yield. Aliphatic alcohols including cyclohexylmethanol, 1-hexanol, and 1-octanol are subjected to the reactions with acetophenone, and 42−64% yields of the corresponding products were isolated. Gratifyingly, the reactions with challenging substrates such as cinnamyl alcohol or 4-pyridinemethanol also proceeded well, leading to the isolation of **7m** and **7n** in 66% and 74% yields, respectively.

Next, we investigated the substrate scope of ketones while using benzyl alcohol or pyrdinemethanols as the alkylating reagents. As shown in Scheme 5, acetophenones containing halo groups on the benzene ring were well converted to the new

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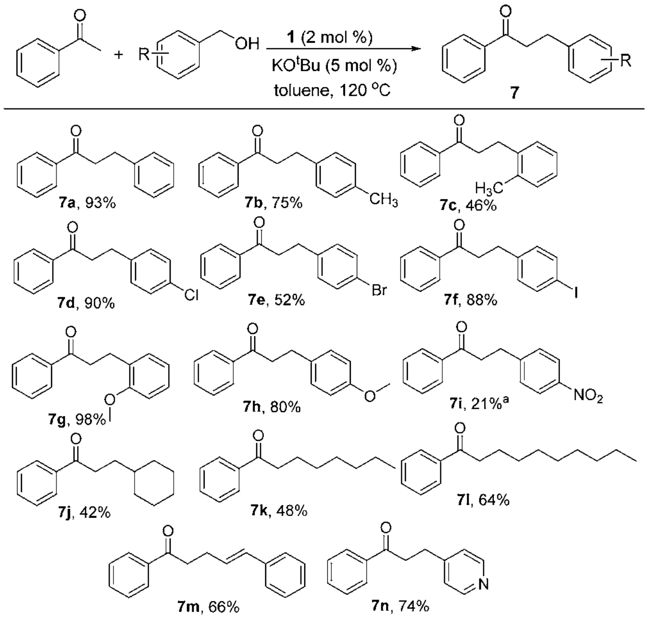
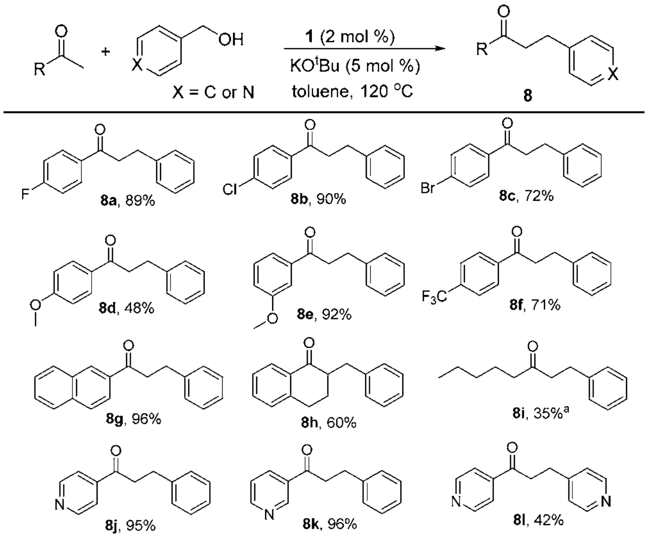
Scheme 4. α-Alkylation of Acetophenone with Various Alcohols[a]



[a]Conditions: primary alcohol (0.6 mmol), acetophenone (0.5 mmol), cobalt **1** (2 mol %), KOtBu (5 mol %), and toluene (4 mL) are heated to 120 °C in a 100 mL Schlenk tube, 24 h. Yields are of isolated products. Yield determined by GC analysis.

Scheme 5. α-Alkylation of Various Ketones with Benzyl Alcohol or 4-Pyridinemethanol[a]

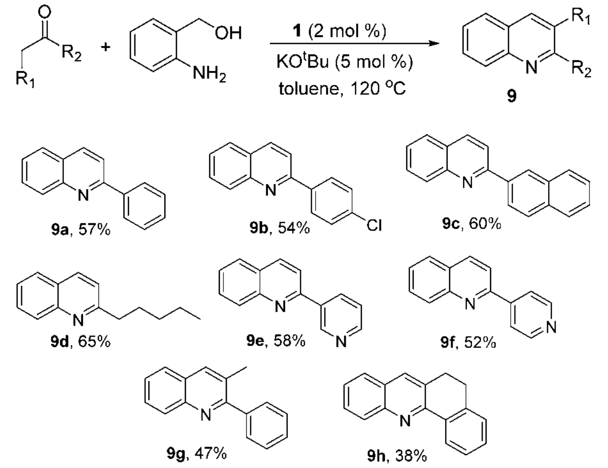


[a]Conditions: benzyl alcohol or 4-pyridinemethanol (0.6 mmol), ketone (0.5 mmol), cobalt **1** (2 mol %), KO^{t}Bu (5 mol %), and toluene (4 mL) are heated to 120 °C in a 100 mL Schlenk tube, 24 h. Yields are of isolated products. Yield determined by GC analysis.

ketones **8a−c** in 72−90% isolated yields. Whereas 4′-methoxyacetophenone was a less effective substrate (48% yield of **8d**), 3′-methoxyacetophenone and 4′-trifluoromethylacetophenone reacted smoothly with benzyl alcohol to provide the desired products in 92% and 71% yield, respectively. In addition, 2-acetylnaphthalene was found to be an excellent substrate for this reaction, and **8g** was isolated in 96% yield. Interestingly, the cyclic ketone substrate, α-tetralone, was also alkylated, giving **8h** as the only product in good yield. An aliphatic ketone, 2-heptanone, was examined for the alkylation with benzyl alcohol, but an inseparable product mixture containing the coupling product **8i** in 35% GC yield was observed. In addition, heterocyclic ketones such as 4- or 3-acetylpyridine furnished the reactions with high yields (95 and 96%, respectively), although when 4-pyridinemethanol was subjected to react with 4-acetylpyridine, a low 42% yield was obtained for **8l**.

The good applicability of our cobalt pincer catalyst for ketone alkylation was further established through the catalytic one-pot synthesis of quinoline derivatives. Although quinoline derivatives have been previously prepared by the classic Friedländer annulation reaction from 2-aminobenzaldehyde and various ketones, the poor product selectivity due to some side reactions was often the problem.[13] The utilization of 2-aminobenzyl alcohol as a more stable starting material for the annulation via the hydrogen-borrowing concept is attractive and has been first carried out using the Knölker-type catalyst.[10a] We were pleased to find that using the standard catalytic conditions for α-alkylation of ketones cobalt **1** also promoted the reaction of 2-aminobenzyl alcohol with 1 equiv of acetophenone, providing the corresponding quinoline derivative **9a** in 57% isolated yield, comparable to the results obtained by using the iron catalyst at higher temperature. The results presented in Scheme 6 reveal that our method could apply to a broader range of ketone substrates than those reported.[10a] For example, 4′-chloroacetophenone and 2-acetylnaphthalene reacted with 2-aminobenzyl alcohol to afford the desired quinoline derivatives **9b** and **9c** in 45% and 60% yields, respectively. Aliphatic 2-heptanone was found to be effective for the formation of **9d**, which was readily isolated in 65% yield. As stated above in the ketone alkylations, heterocyclic ketones were also tolerated for new quinolines bearing an additional pyridine ring. Thus, 3- and 4-acetylpyridines were employed, and the corresponding quinoline products were isolated in reasonable yields. In addition, propiophenone and α-tetralone were proven reactive under the optimal conditions, although relatively lower yields of the isolated products were obtained for both substrates.

Scheme 6. Cobalt-Catalyzed Modified Friedländer Annulation Reaction[a]



[a]Conditions: 2-aminobenzyl alcohol (0.5 mmol), ketone (0.5 mmol), cobalt **1** (2 mol %), KO^{t}Bu (5 mol %), and toluene (6 mL) are heated to 120 °C in a 100 mL Schlenk tube, 24 h. Yields are of isolated products.

In summary, we have reported the first cobalt-catalyzed α-alkylation of ketones with primary alcohols through a hydrogen-borrowing method. The cobalt catalyst proved to be not only effective for the C−C bond-forming between a variety of ketones and a range of alcohols as alkylating reagents but also applicable in the catalytic Friedländer annulation reactions of 2-aminobenzyl alcohol with ketones. This method further expands the applications of cobalt pincer catalysts in synthetic chemistry regarding the C−C bond-forming process.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b00106.

Detailed experimental procedures and characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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