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Cp*Co(III)-Catalyzed C−H Acylmethylation of Arenes by Employing Sulfoxonium Ylides as Carbene Precursors

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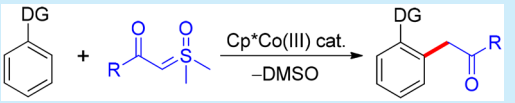
Supporting Information

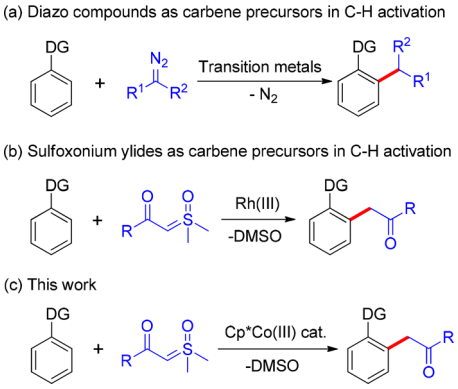
ABSTRACT: A Cp*Co(III)-catalyzed C−H bond functionalization of a range of arenes by employing sulfoxonium ylides as carbene precursors instead of diazo compounds and other carbene precursors has been established. This reaction is highly efficient without any additive, possesses high step and atom economies, and tolerates a range of functional groups.



In the past decades, the directed transition-metal-catalyzed C−H bond functionalization has flourished as a powerful and atom- and step-economical method to construct a range of complex molecules without preactivated substrates. Specifically, a nitrogen-containing directing-group-assisted C−H functionalization catalyzed by numerous noble metals (such as Ru, Rh, Pd, Ir) has been significantly developed.[1] However, these noble metals are low abundance and high cost, pressuring scientists to seek more abundant, more affordable, and less toxic first-row transition metals as the catalysts to take the place of noble metals. In recent years, Cp*Co(III) (Cp* = pentamethylcyclopentadienyl) catalyst systems have received extensive attention as catalysts for C−H functionalization, because of their higher Lewis acidity, smaller ionic radius, and low cost, compared to precious metals.[2] Since 2013, when Kanai and Matsunaga[3] first reported Cp*Co(III)-catalyzed directed addition reactions of aryl C−H bonds to polar electrophiles, many research groups such as those led by Glorius,[4] Ackermann,[5] Ellman,[6] Chang,[7] Li,[8] Cheng,[9] Jiao,[10] and others[11] subsequently expanded the application of Cp*Co(III) catalysts in C−H bond functionalization.

Recently, transition-metal-catalyzed C−H functionalization based on metal carbene migratory insertion has been significantly developed. α-Diazo carbonyls as carbene precursors and coupling partners were extensively employed in transition-metal-catalyzed C−H functionalization (Scheme 1a).[12,13] Despite this significant progress, there are still many limitations in the use of diazo compounds, such as the potential danger of exothermic linked to the liberate of nitrogen and inconvenience for reserve. In addition to diazo compounds, other carbene precursors, such as hydrazones,[14] triazoles,[15] cyclopropenes,[16] and ketone-functionalized enynes,[17] can also be used as coupling partners in C−H functionalization reactions, but it is still necessary to develop new reactants as surrogates of these carbene precursors. Significantly, transition-metal-catalyzed X−H insertions of sulfoxonium ylides were used industrially to form C−N and C−O bonds as safe alternatives to diazo compounds.[18] However, transition-metal-catalyzed C−H insertion reactions of sulfoxonium ylides are rarely studied. Only very recently, Aïssa, Li, and others reported the Cp*Rh(III)-catalyzed C−H functionalization of arenes with sulfoxonium ylides as carbene precursors and coupling partners (Scheme 1b).[19]

Scheme 1. Transition-Metal-Catalyzed C−H Functionalization Based on Metal Carbene Migratory Insertion



Based on our previous study of transition-metal-catalyzed C−H/diazo compounds coupling reactions,[20] we commenced our investigation by probing the reaction conditions for the envisioned C−H bond acylmethylation of 2-phenylpyridine **1a** and α-benzoyl sulfur ylide **2a** with Cp*Co(III) as catalyst (see Table 1). First, reactions of **1a** (0.2 mmol) with **2a** (0.3 mmol) in the presence of Cp*Co(CO)I_2 (10 mol %) and $AgSbF_6$ (20 mol %) in a variety of solvents at 100 °C under argon atmosphere for 12 h were studied, and 1,2-dichloroethane (DCE) (Table 1, entry 1) was demonstrated to be the most

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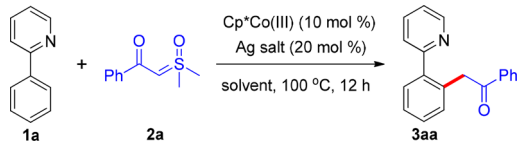
Table 1. Optimization of Reaction Conditions[a]



entry	catalyst/Ag salt	solvent	yield[b]
1	$Cp^*Co(CO)I_2/AgSbF_6$	DCE	67
2	$Cp^*Co(CO)I_2/AgSbF_6$	TFE	21
3	$Cp^*Co(CO)I_2/AgSbF_6$	toluene	14
4	$Cp^*Co(CO)I_2/AgSbF_6$	dioxane	21
5	$Cp^*Co(CO)I_2/AgSbF_6$	DCM	39
6	$Cp^*Co(CO)I_2/AgSbF_6$	CH_3CN	0
7	$Cp^*Co(CO)I_2/AgBF_4$	DCE	43
8	$Cp^*Co(CO)I_2/AgOTf$	DCE	43
9	$Cp^*Co(CO)I_2/AgNTf_2$	DCE	50
10	$Cp^*Co(CO)I_2$/-	DCE	0
11	$[Cp^*Co(CH_3CN)_3](SbF_6)_2$	DCE	89
12	$[Cp^*Co(CH_3CN)_3](SbF_6)_2$	DCE	96 (91)[c,d]
13	$[Cp^*Co(CH_3CN)_3](SbF_6)_2$	DCE	54[e]
14		DCE	0

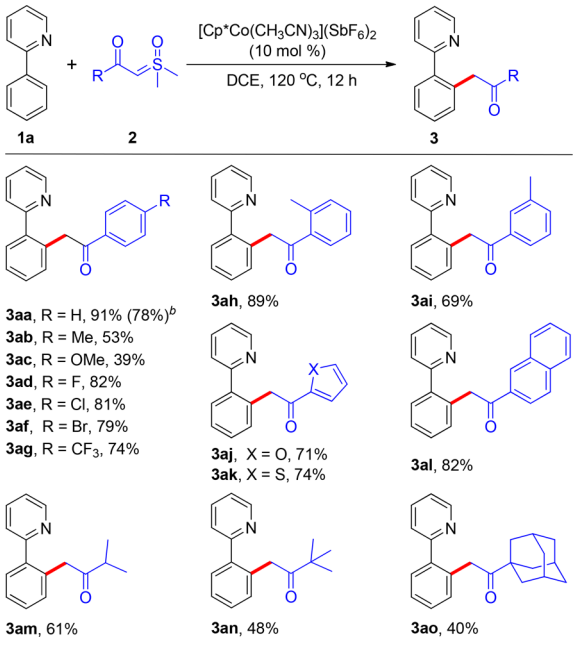
[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), and $Cp^*Co(CO)I_2$ (0.02 mmol)/Ag salt (0.04 mmol) or $[Cp^*Co(MeCN)_3](SbF_6)_2$ (0.02 mmol) were stirred in solvent (1.5 mL) at 100 °C for 12 h under Ar. [b]Yields were determined by ^1H NMR using 1,1,2,2-tetrachloroethane as an internal standard. [c]At 120 °C. [d]Isolated yield is shown in brackets. [e]Under an air atmosphere.

effective, affording the desired product **3aa** in 67% yield. When other solvents such as 2,2,2-trifluoroethanol (TFE), toluene, dioxane, CH_3CN, dichloromethane (DCM) were used for this reaction, the yields were only 0−39% (Table 1, entries 2−6). Co-catalytic amounts of a silver(I) salt were momentous for the C−H acylmethylation reaction, and $AgSbF_6$ gained the best performance (Table 1, entries 1 and 7−10). Delightfully, the use of cationic $[Cp^*Co(MeCN)_3](SbF_6)_2$ dramatically improved the yield of **3aa** to 89% (Table 1, entry 11). Moreover, **3aa** was formed in 96% yield (91% isolated yield) when the temperature was increased to 120 °C (Table 1, entry 12). When the reaction was proceeded under air, it still afforded **3aa** in 54% yield (Table 1, entry 13). No reaction was observed in the absence of the cobalt catalyst (Table 1, entry 14).

With the establishment of the optimized conditions, the substrate scope was further investigated. Initially, this acylmethylation protocol was applied to a variety of *α*-benzoyl sulfur ylides (see Scheme 2). Benzoyl-substituted sulfoxonium ylides bearing a variety of important functional groups, such as electron-donating groups (CH_3, OMe), the halogens (F, Cl, Br), and electron-withdrawing group (CF_3) at the *para*, *ortho*, and *meta* positions of the phenyl ring reacted smoothly with **1a** to afford the corresponding products (**3ab**−**3ai**) in moderate to high yields (39%−89%). Delightfully, the reactants could contain a thiophene/furan ring or naphthalene and the corresponding products (**3aj**−**3al**) were obtained in 71%−82% yields. The sulfoxonium ylides were not limited to (hetero)aryl-substituted substrates, several alkyl substrates were also suitable and the corresponding products were isolated in moderate yields (**3am**−**3ao**, 40%−61%).

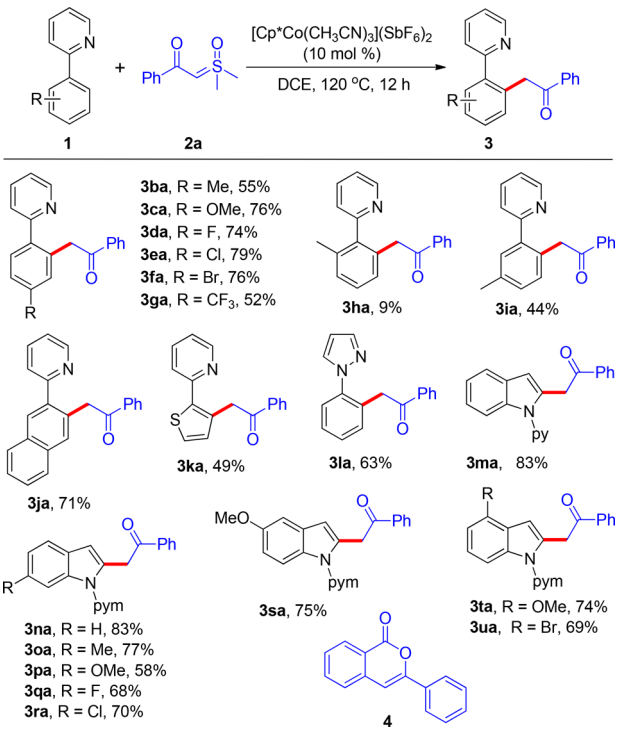
Then, the substrate scope of 2-arylpyridines was extended (Scheme 3). Interestingly, the electronic effect of various functional groups at 2-phenylpyridine was different from that

Scheme 2. Substrate Scope of Sulfoxonium Ylides[a]



[a]Reaction conditions: **1a** (0.2 mmol), **2** (0.3 mmol) $Cp^*Co(CH_3CN)_3(SbF_6)_2$ (10 mol %), DCE (1.5 mL), 120 °C, under Ar, 12 h, isolated yield. [b]1.0 mmol scale.

Scheme 3. Substrate Scope of 2-Arylpyridines[a]



[a]Reaction conditions: **1a** (0.2 mmol), **2** (0.3 mmol), $Cp^*Co(CH_3CN)_3(SbF_6)_2$ (10 mol %), DCE (1.5 mL), 120 °C, under Ar, 12 h, isolated yield. py = pyridyl, pym = pyrimidyl.

of sulfoxonium ylides. The substrate with an electron-donating group (OMe) at the *para* position of the phenyl ring performed better (**3ca**, 76%) than that with an electron-withdrawing group (CF_3) (**3ga**, 52%). The halogen substituted

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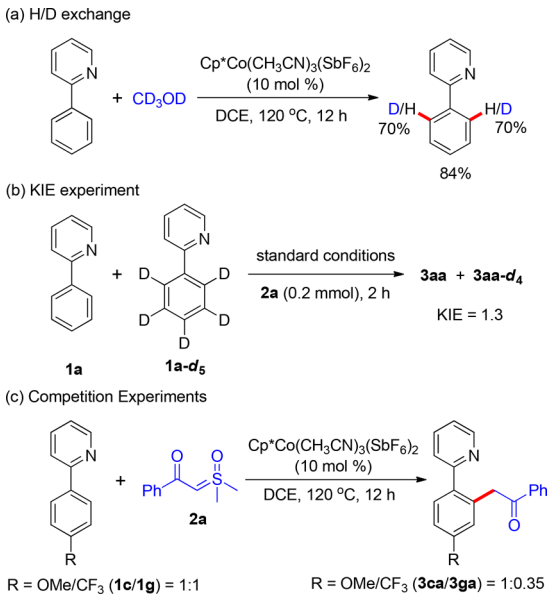
2-phenylpyridines afforded the expected products (**3da**−**3fa**) in good yields (74%−79%). It was noteworthy that **3ha** was only obtained in 9% yield. One possible reason is that the steric hindrance of methyl group at the *ortho* position of phenyl ring makes it difficult to form cyclo-cobalt intermediate. When **1i** was employed as coupling partner, selective C−H acylmethylation occurred only at the C6 position to give the desired product **3ia** in 44% yield. Moreover, polycyclic and heterocyclic arenes were also suitable for the acylmethylation reaction, to give the corresponding products **3ja** and **3ka** in moderate yields (71% and 49%). When *N*-phenylpyrazole was used as a substrate, the acylmethylation product **3la** was obtained in 63% yield. Encouraged by these initial findings, the scope of the substrate was further extended to *N*-pyridyl- or *N*-pyrimidyl-indoles, in which the pyridyl or pyrimidyl group can act as a removable directing group, the corresponding products (**3ma**−**3ua**) were obtained in 58%−83% yields.

The substrates with other directing groups such as amide, ketone, oxime, azobenzene, imine, and 2-phenyl imidazole have been also tested under the standard conditions. Unfortunately, they all failed to give the desired products. In some cases, a byproduct **4** was isolated in 18%−38% yields (see the Supporting Information). In contrast to the formation of **4** by Cp*Rh(III)-catalyzed C−H/**2a** coupling and tandem cyclization,[19c] for our Cp*Co(III) catalyst system, compound **4** should be formed via the self-coupling of **2a**. These results show the different reactivities of the cobalt catalyst, in comparison with that of a rhodium catalyst.[19]

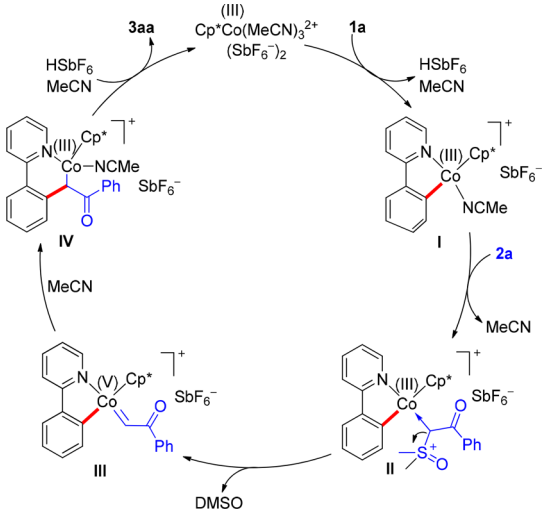
To gain more insight in the mechanism of this reaction, some experiments have been conducted. First, an H/D exchange experiment was performed, when 2-phenylpyridine (**1a**) was subjected to the optimized reaction conditions using $[Cp^*Co(MeCN)_3](SbF_6)_2$ in the presence of CD_3OD. 2-Phenylpyridine was recovered in 84% yield and the NMR analysis disclosed H/D exchange occurred at the *ortho* position (70% D) of the phenyl ring (see Scheme 4a), suggesting that the Cp*Co(III)-catalyzed C−H activation was reversible. The kinetic isotope effect (KIE) experiment was implemented, and a deuterium competition experiment between substrate **1a** and d_5-**1a** illustrated a KIE of k_H/k_D = 1.3 (see Scheme 4b). The result shows that the cleavage of the C−H bond may not be included in the rate-determining step. A intermolecular competition reaction between 2-(4-methoxyphenyl)pyridine (**1c**) and 2-(4-(trifluoromethyl)phenyl)pyridine (**1g**) with **2a** was performed in a one-pot fashion. The NMR yield of **3ca** was higher than that of **3ga**, indicating a higher reactivity for the electron-rich substrate (see Scheme 4c).

Scheme 4. Mechanism Study Experiments



Based on the above experimental results and the literature reports,[19,21] a rational mechanism was proposed (Scheme 5).

Scheme 5. Proposed Mechanistic Pathway



The first step is likely the coordination of pyridine with cobalt to replace a CH_3CN of $[Cp^*Co(MeCN)_3](SbF_6)_2$ and subsequent *ortho* C−H bond activation process to form the cobaltacycle intermediate **I**. The ligand exchange between **2a** and **I** affords intermediate **II**, which undergoes elimination of DMSO to acquire a cobalt carbene intermediate **III**. Migratory insertion of the cobalt-carbene into the Co−C bond leads to intermediate **IV**. Finally, protonation of **IV** delivers the final product **3aa** and releases the active catalyst.

In conclusion, we have achieved the Cp*Co(III)-catalyzed C−H bond functionalization with sulfoxonium ylides as carbene precursors and coupling partners. The reaction conditions are simpler without additional additives, in comparison with the rhodium catalyst systems. This catalyst systems may be used industrially for the synthesis of related complex compounds instead of diazo compounds in the future.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b02796.

Full experimental procedures, characterization and ^1H, ^{13}C, and ^{19}F NMR spectra of products (PDF)

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Notes

The authors declare no competing financial interest.

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