C–H Activation

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A Cationic High-Valent Cp*Co^{III} Complex for the Catalytic Generation of Nucleophilic Organometallic Species: Directed C–H Bond Activation**

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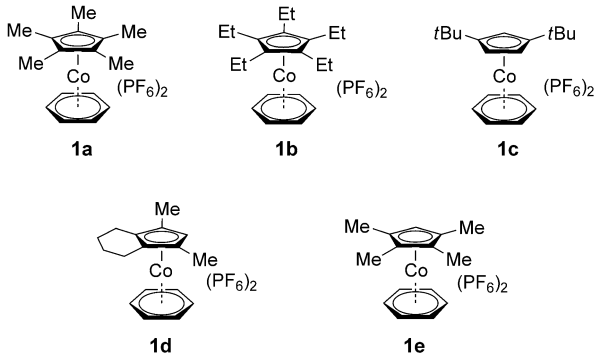
The nucleophilic addition of organometallic reagents to polar electrophiles, such as aldehydes, imines, and Michael acceptors, is a fundamental C–C bond-forming reaction in organic synthesis. The generation of nucleophilic organometallic reagents, however, generally requires stoichiometric amounts of strong bases and/or reducing metals, such as Mg and Li, and stoichiometric salt waste is therefore inevitably produced. Thus, the development of atom-economical processes[1] involving the catalytic generation of nucleophilic organometallic species and their addition to polar electrophiles without additional activating reagents is highly desirable. Transition-metal-catalyzed C–H bond functionalization could be an attractive method for addressing these issues,[2] but addition reactions of C–H bonds to polar C–X multiple bonds (X = N, O, or C) have been investigated much less[3] than related reactions with nonpolar alkenes and alkynes.[2] Quite recently, it was disclosed that Cp*Rh^{III} complexes (Cp* = pentamethylcyclopentadienyl)[4] catalyze addition reactions of arene C–H bonds to imines,[5] aldehydes,[6] Michael acceptors,[7] and other polar electrophiles.[8] Although Cp*Rh^{III}-catalyzed processes are useful and versatile, the need for expensive and precious rhodium sources is economically and environmentally disadvantageous. Therefore, studies are needed for the development of an inexpensive base metal catalyst as an alternative to the cationic Cp*Rh^{III} complexes.[9] Herein, we describe the utility of a cationic high-valent cobalt complex and the structure–activity relationship of various Cp*Co^{III} complexes (Scheme 1) for the catalytic generation of nucleophilic organometallic species. We found that the [Cp*Co^{III}(arene)](PF$_6$)$_2$ complex **1a** (5–10 mol%) promoted the addition of 2-aryl pyridines to imines, enones, and α,β-unsaturated *N*-acyl pyrroles as ester and amide surrogates.



Scheme 1. Cationic high-valent cobalt(III) complexes synthesized and investigated in this study.

We selected cobalt,[10] which is homologous with rhodium but a more abundant first-row transition metal,[11] and investigated the ability of high-valent cobalt catalysts to promote C–H bond functionalization. Optimization studies with 2-phenylpyridine (**2a**) and the sulfonyl imine **3a**[12–14] as model substrates are summarized in Table 1. Several commercially available Co^{II} and Co^{III} salts showed no catalytic activity at 100 °C in 1,2-dichloroethane (Table 1, entries 1 and 3–5). Even the addition of a silver salt to $CoCl_2$ to afford a cationic Co species resulted in no reaction (Table 1, entry 2). By analogy with Cp*Rh^{III} catalysis, we expected that the cyclopentadienyl–cobalt^{III} structure would be an appropriate catalyst core for the present reaction. The use of a dimeric [{Cp*CoCl$_2$}$_2$] complex, however, resulted in no reaction (Table 1, entry 6). The addition of $AgPF_6$ was effective, and a cationic Cp*Co^{III} complex generated in situ afforded **4aa** in 48% yield (Table 1, entry 7).

The results in entries 6 and 7 of Table 1 prompted us to examine cationic Co^{III} complexes with thermally labile ligands. Although the synthesis, structure, and electrochemical properties of some cationic cyclopentadienyl–cobalt^{III} complexes with arene ligands have been reported,[15] the application of these complexes for synthetic organic transformations has not been investigated. Therefore, several

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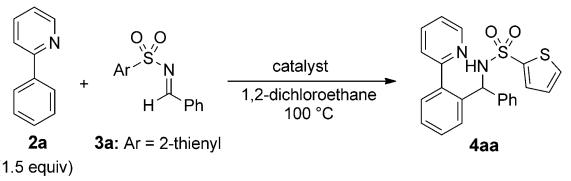
Table 1: Optimization of the reaction conditions for the arylation of imine **3a**.



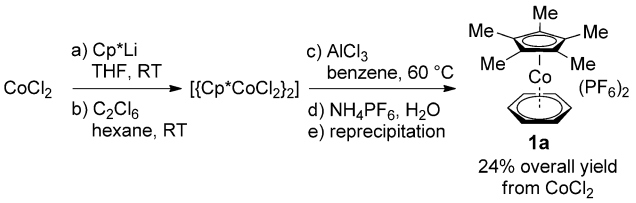
Entry	Catalyst (mol%)	*t* [h]	Yield [%][a]
1	$CoCl_2$ (10)	12	0
2	$CoCl_2$ (10) + $AgPF_6$ (20)	12	0
3	$Co(OTf)_2$	13	0
4	$[Co(acac)_3]$	12	0
5	$[Co(NH_3)_6Cl_3]$	13	0
6	$[\{Cp^*CoCl_2\}_2]$ (5)	13	0
7	$[\{Cp^*CoCl_2\}_2]$ (5) + $AgPF_6$ (20)	12	48
8	**1a** (10)	12	80[b]
9	**1b** (10)	20	39
10	**1c** (10)	20	11
11	**1d** (10)	20	trace
12	**1e** (10)	20	22

[a] The yield was determined by ^{1}H NMR spectroscopic analysis of the crude reaction mixture with dibenzyl ether as an internal standard. [b] Yield of the isolated product after purification by column chromatography on silica gel. acac = acetylacetonate, Tf = trifluoromethanesulfonyl.

cationic $[Cp\,Co^{III}(arene)]$ complexes with different Cp-type ligands were synthesized to evaluate the catalyst structure–activity relationship in detail (Scheme 1). The [Cp*Co(benzene)] complex (**1a**)[15] showed higher reactivity than the cationic catalyst generated in situ, and the yield of **4aa** was improved to 80% (Table 1, entry 8). This improved catalytic activity is probably due to the more efficient generation of an active catalytic species through thermal arene dissociation than through chloride abstraction with a silver salt. The sterically more hindered Co^{III} complexes **1b**–**1d**[16] were much less active than **1a** (Table 1, entries 9–11). Attempts to improve the catalytic activity with the sterically less crowded complex **1e** failed (Table 1, entry 12), because complex **1e** seemed to be unstable under the reaction conditions. The $[Cp^*Co^{III}(arene)](PF_6)_2$ complex **1a** showed the best balance between reactivity and stability. In contrast to the related catalysis of low-valent Co for the addition of C–H bonds to imines,[3e] the present system requires no additional reagents; a catalytic amount of the high-valent Co complex **1a** alone promoted the desired reaction in an atom-economical manner.

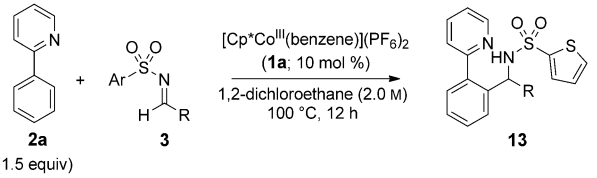
The optimal complex **1a** was readily synthesized from $CoCl_2$ in gram quantities without the use of any expensive reagents (Scheme 2).[15c,17] The reaction with Cp*Li, oxidation, and counterion exchange gave **1a** as an air- and moisture-stable solid in 24% overall yield after purification by reprecipitation.

With the optimized catalyst **1a** in hand, we investigated the scope of the reaction with various polar electrophiles, including imines (Table 2), enones (Scheme 3), and α,β-unsaturated *N*-acyl pyrroles as ester surrogates (Scheme 4). Aryl imines with either an electron-donating or an electron-



Scheme 2. Gram-scale synthesis of **1a**.

Table 2: Substrate generality in the arylation of imines **3**.[a]

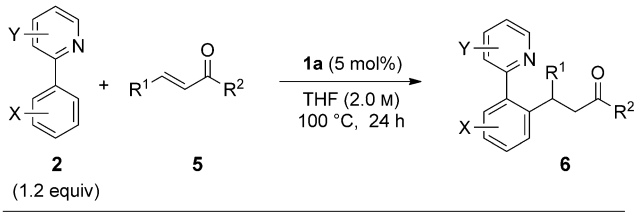


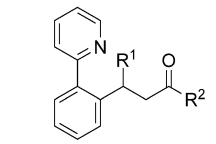
Entry	R: imine **3**		Product	Yield [%][b]
1	Ph	**3a**	**4aa**	80
2	2-naphthyl	**3b**	**4ab**	79
3	*p*-Cl-C_6H_4	**3c**	**4ac**	83
4	*p*-Br-C_6H_4	**3d**	**4ad**	72
5	*p*-CF_3-C_6H_4	**3e**	**4ae**	64
6	*m*-Cl-C_6H_4	**3f**	**4af**	76
7	*p*-Me-C_6H_4	**3g**	**4ag**	76
8	*p*-MeO-C_6H_4	**3h**	**4ah**	57
9	*o*-Me-C_6H_4	**3i**	**4ai**	71
10	2-thienyl	**3j**	**4aj**	69
11	2-furyl	**3k**	**4ak**	66

[a] Reaction conditions: **1a** (0.04 mmol), **2a** (0.60 mmol), **3** (0.40 mmol), 1,2-dichloroethane (0.2 mL), Ar atmosphere. [b] Yield of the isolated product after purification by column chromatography on silica gel.

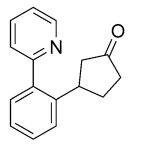
withdrawing substituent at the *para* or *meta* position showed good reactivity (Table 2, entries 3–7), whereas an imine with a strongly electron donating methoxy substituent showed slightly lower reactivity (Table 2, entry 8). The reaction also proceeded with the sterically hindered *ortho*-substituted imine **3i** (Table 2, entry 9) and other heteroaryl imines (Table 2, entries 10 and 11).[18]

THF was the best solvent for conjugate addition to α,β-unsaturated carbonyl compounds, and the catalyst loading was successfully reduced to 5 mol% in most cases. As shown in Scheme 3, a broad range of enone substrates were applicable. Chalcone and its derivatives containing either electron-donating or electron-withdrawing substituents were converted into the desired products in 67–80% yield. Other acyclic alkyl-substituted enones and cyclic enones were transformed into products **6af**–**6aj** in 76–90% yield. The reaction was also successfully carried out on a preparative scale (5.0 mmol) to give **6ai** without significant loss of yield. With 2-cyclopenten-1-one as the electrophile, we also investigated the scope of the reaction with respect to the donor (Scheme 3). The reaction of donors with either an electron-withdrawing or an electron-donating group at the *para* position to the directing 2-pyridyl group afforded the desired products **6bi**–**6di** in good yield. Notably, the present

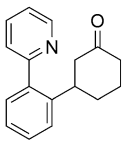




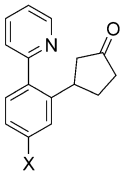
R^1 = Ph, R^2 = Ph, **6aa**, 80%
R^1 = *p*-Cl-C_6H_4, R^2 = Ph, **6ab**, 75%
R^1 = *p*-MeO-C_6H_4, R^2 = Ph, **6ac**, 67%
R^1 = Ph, R^2 = *p*-Br-C_6H_4, **6ad**, 75%
R^1 = Ph, R^2 = *m*-MeO-C_6H_4, **6ae**, 76%
R^1 = Ph, R^2 = Me, **6af**, 78%
R^1 = Me, R^2 = Ph, **6ag**, 84%
R^1 = Me, R^2 = Et, **6ah**, 84%



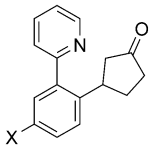
6ai, 90% (85%[a])



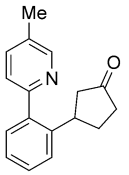
6aj, 76%[b]



X = Me, **6bi**, 80%
X = OMe, **6ci**, 87%
X = Br, **6di**, 74%
X = Ac, **6ei**, 78%
X = OH, **6fi**, 80%
X = NMe_2, **6gi**, 73%



X = Me, **6hi**, 67%[b]
X = OMe, **6ii**, 70%
X = Cl, **6ji**, 76%

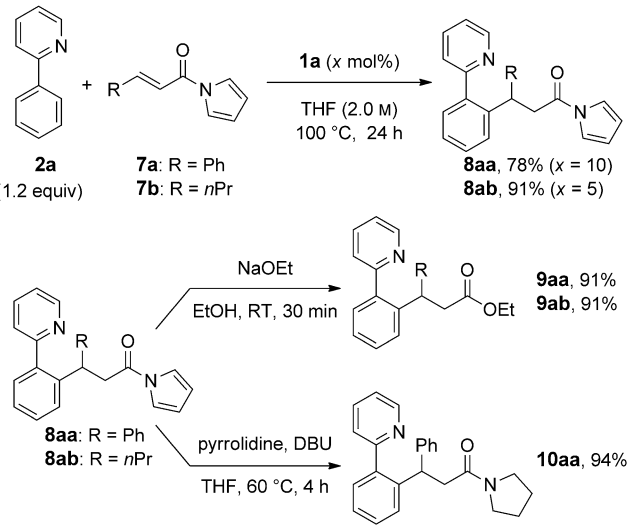


6ki, 83%

Scheme 3. Scope of the arylation of α,β-unsaturated ketones. Reaction conditions: **1a** (0.02 mmol, 5 mol%), **2** (0.48 mmol), **5** (0.40 mmol), THF (0.2 mL), Ar atmosphere. The yield of **6** after purification by column chromatography on silica gel is shown for each reaction. [a] The reaction was carried out on a 5.0 mmol scale (quantity of **5**). [b] The reaction was carried out with 10 mol% of **1a**.

$[Cp^*Co^{III}(arene)](PF_6)_2$ complex showed good functional-group compatibility: an acetyl group (in product **6ei**), a free phenolic hydroxy group (in **6fi**), and a tertiary amino group (in **6gi**) did not interfere with the desired reactions. Furthermore, *meta*-substituted donors showed modest reactivity with the predominant formation of products **6hi**–**6ji**.

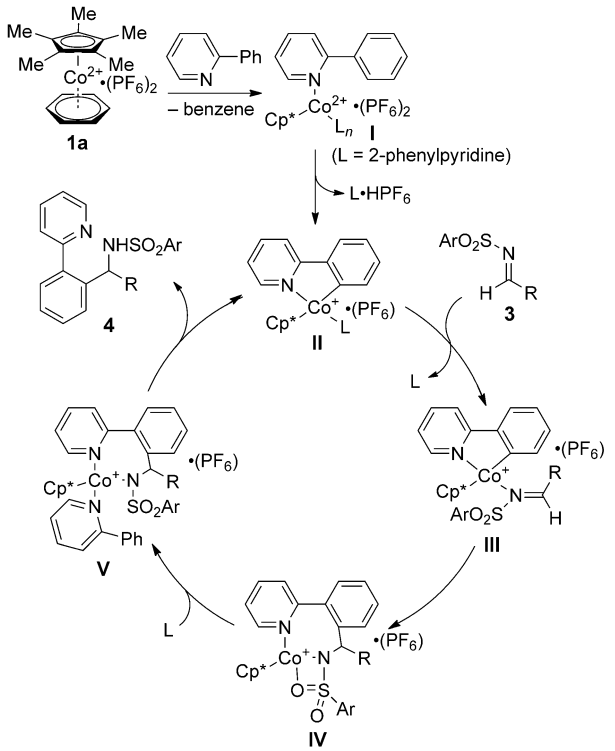
In contrast to enones, α,β-unsaturated esters and amides did not afford the desired Michael adducts, possibly owing to their low electrophilicity. Therefore, α,β-unsaturated *N*-acyl pyrroles **7** were used as ester and amide surrogates[19,20] to expand the utility of the present system. As shown in Scheme 4, the desired products **8aa** and **8ab** were obtained from the corresponding β-aryl and β-alkyl α,β-unsaturated *N*-acyl pyrroles in 78 and 91% yield, respectively. The *N*-acyl pyrrole unit was readily converted into an ester group (**9aa**, **9ab**: 91%) by treatment with NaOEt at room temperature or into an amide (**10aa**: 94%) with an amine and DBU. Because β-substituted α,β-unsaturated esters and amides have not been used successfully in the corresponding direct addition of



Scheme 4. Addition to α,β-unsaturated *N*-acyl pyrroles and transformation of the products into esters and an amide. DBU = 1,8-diazabicyclo-[5.4.0]undec-7-ene.

a C–H bond with Cp^*Rh^{III} complexes, the results in Scheme 4 are synthetically useful.

A plausible catalytic cycle based on related Rh^{III} catalysis[5c,d] is shown in Scheme 5. Initially, the coordinating benzene ring in **1a** would dissociate upon heating to generate the 2-phenylpyridine complex **I**. The process of C–H activation is assumed to proceed through electrophilic aromatic substitution or a concerted metalation–deprotonation mechanism to form the cyclometalated intermediate **II**. After



Scheme 5. Proposed catalytic cycle for the arylation of imines.

ligand exchange to give **III** and the insertion of the electrophile to give **IV**, proto-demetalation from **V** with another molecule of 2-phenylpyridine (or with the acidic hydrogen atom captured at the step from **I** to **II**) would lead to dissociation of the products and regenerate the key intermediate **II**.

In summary, we have demonstrated the utility of a cationic, high-valent Co complex for atom-economical directed addition reactions of aryl C–H bonds to polar electrophiles. Studies of the catalyst structure–activity/stability relationship revealed that the $[Cp^*Co^{III}(arene)](PF_6)_2$ complex **1a** was the most suitable catalyst. The Cp^*Co^{III} complex **1a** catalytically generated the nucleophilic species in situ without any additional reagents and enabled the directed C–H bond addition of 2-aryl pyridines to imines, enones, and α,β-unsaturated *N*-acyl pyrroles as ester and amide surrogates. Cp^*Co^{III} complexes, which have not attracted much attention in the field of synthetic organic chemistry, are thus promising catalysts for cost- and atom-efficient C–H bond-functionalization processes. Further studies on the application of the Cp^*Co^{III} complexes to other catalytic transformations, including the development of asymmetric variants,[21] are ongoing in our research group.

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[16] For the preparation of the new cationic Co complexes **1b**–**1e**, see the Supporting Information. We did not utilize the corresponding cationic Co^{III} catalyst with a simple Cp ligand because it was rather unstable.
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[18] These reaction conditions were not applicable to imines derived from aliphatic aldehydes, possibly as a result of fast isomerization to the corresponding enamides.
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