

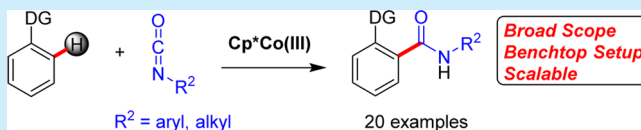
## Cobalt(III)-Catalyzed C–H Bond Amidation with Isocyanates

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## S Supporting Information

**ABSTRACT:** The first examples of cobalt(III)-catalyzed C–H bond addition to isocyanates are described, providing a convergent strategy for arene and heteroarene amidation. Using a robust air- and moisture-stable catalyst, this transformation demonstrates a broad isocyanate scope and good functional-group compatibility and has been performed on gram scale.



In recent years, many elegant strategies employing transition-metal-catalyzed C–H bond functionalization have emerged for the synthesis of amines and nitrogen heterocycles.<sup>1</sup> Among the rich array of metal complexes that mediate C–H functionalization, Rh(III)-catalysts have proven to be exceptionally versatile due to their unique reactivity and high functional-group compatibility,<sup>2</sup> with additions of C(sp<sup>2</sup>)–H bonds to polarized  $\pi$ -bonds providing for convergent introduction of heteroatom functionality.<sup>3–9</sup> In this regard, we reported direct C(sp<sup>2</sup>)–H bond addition to isocyanates as a particularly step- and atom-economic strategy for the preparation of aromatic, heterocyclic, and alkenyl amides.<sup>6f</sup> Direct C(sp<sup>2</sup>)–H bond additions to isocyanates have also been accomplished with Re<sup>10</sup> and Ru<sup>11</sup> catalysts.<sup>12</sup> In contrast, catalytic C–H bond functionalization with earth-abundant first-row transition metals has emerged only recently,<sup>13</sup> and to our knowledge, additions to isocyanates have not been described. Herein we report the first examples of cobalt-catalyzed C–H bond amidation with isocyanates.<sup>14,15</sup> This convenient benchtop procedure is effective for multiple heterocycle directing groups, shows good functional group compatibility and a broad scope for aromatic and alkyl isocyanates, and is readily scalable.

For initial evaluation of Co(III)-catalyzed C–H bond additions to isocyanates, we chose 1-phenyl-1H-pyrazole (**1a**) and phenyl isocyanate (**2a**) as the coupling partners. First developed by Kanai, Matsunaga, and co-workers for additions to sulfonyl imines<sup>14p</sup> we anticipated that the cationic preformed catalyst [Cp\*Co(C<sub>6</sub>H<sub>6</sub>)](PF<sub>6</sub>)<sub>2</sub> (**4a**) might also facilitate C–H bond amidation with isocyanates (Figure 1). Indeed, the desired reactivity was achieved when catalyst **4a** was utilized in the presence of catalytic potassium acetate at 80 °C, providing

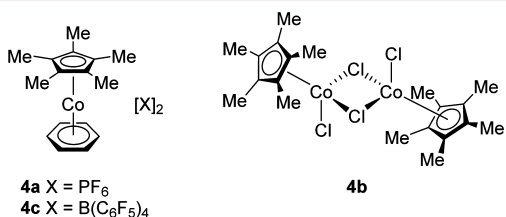
product **3a** in 74% yield (Table 1, entry 1). Given that solvent effects have been observed to play a key role in obtaining

**Table 1. Optimization of Reaction Conditions for Co(III)-Catalyzed Amidation with Phenyl Isocyanate<sup>a</sup>**

entry	Co(III)-catalyst (mol %)	KOAc (mol %)	temp (°C)	solvent	yield (%) <sup>b</sup>
1	<b>4a</b> (10)	20	80	1,4-dioxane	74
2	<b>4a</b> (10)	20	80	THF	62
3	<b>4a</b> (10)	20	80	DCE	66
4	<b>4a</b> (10)	20	80	toluene	8
5	<b>4a</b> (10)	20	120	1,4-dioxane	84 (84) <sup>c,d</sup>
6 <sup>e</sup>	<b>4a</b> (2.5)	5	120	1,4-dioxane	80 (79) <sup>d</sup>
7	<b>4a</b> (1)	2	120	1,4-dioxane	66
8 <sup>e</sup>	<b>4a</b> (10)	20	120	1,4-dioxane	84
9 <sup>f</sup>	<b>4a</b> (10)	20	120	1,4-dioxane	84
10	<b>4a</b> (2.5)	5	100	1,4-dioxane	60
11	<b>4b</b> (5)	20	120	1,4-dioxane	5
12	<b>4c</b> (2.5)	5	100	1,4-dioxane	57
13	<b>4a</b> (10)	–	120	1,4-dioxane	7
14	–	20	120	1,4-dioxane	–

<sup>a</sup>Conditions: **2a** (1.0 equiv), **1a** (2.0 equiv) in 1,4-dioxane (2.0 M) for 20 h. <sup>b</sup>Determined by GC analysis relative to tetradecane as an external standard. <sup>c</sup>Reaction run on the benchtop under nitrogen.

<sup>d</sup>Isolated yield at 0.20 mmol scale. <sup>e</sup>Reverse stoichiometry: **2a** (2.0 equiv), **1a** (1.0 equiv). <sup>f</sup>Reaction conducted in 1,4-dioxane (0.5 M).



**Figure 1.** Cobalt(III)-catalysts used for C–H functionalization.

optimal yield in Ru(II)-<sup>11</sup> and Rh(III)-catalyzed C–H amidations,<sup>6</sup> different solvents were evaluated. While the use of the ethereal solvents 1,4-dioxane and tetrahydrofuran (entries 1 and 2) as well as 1,2-dichloroethane (entry 3) provided comparable yields, the nonpolar and noncoordinating

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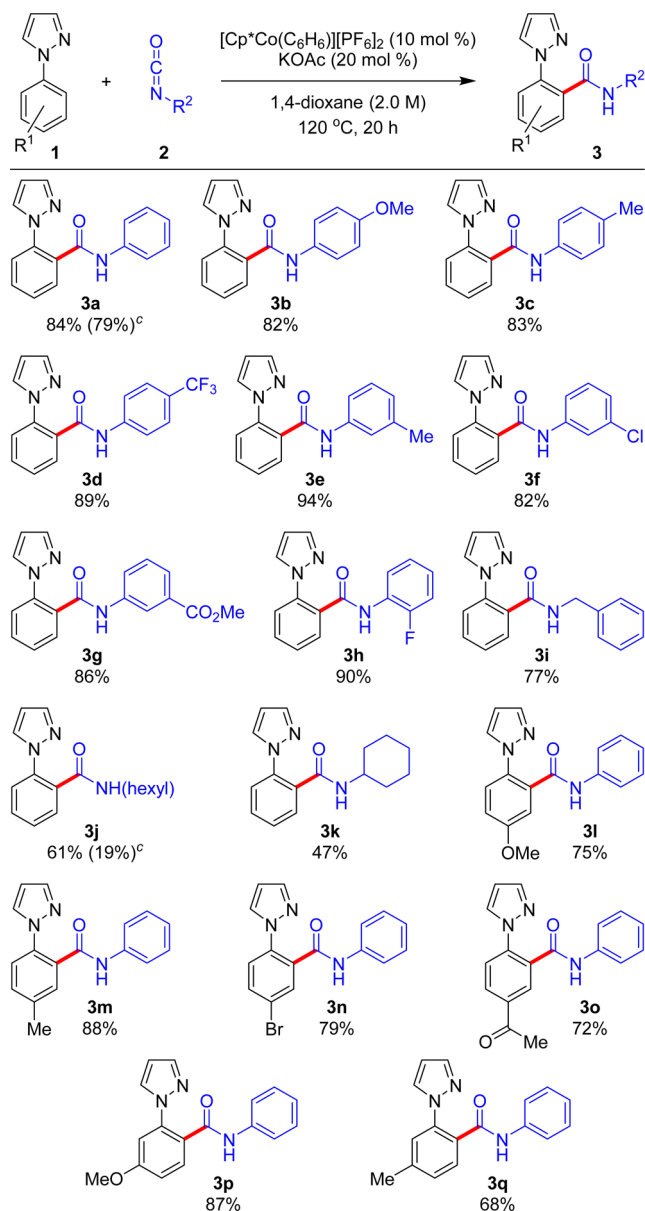
solvent toluene resulted in a low yield (entry 4). Ultimately, the higher boiling solvent 1,4-dioxane was selected for further reaction optimization because it allowed reactions to be conducted at higher temperatures.

Performing the reaction at 120 °C rather than 80 °C moderately increased the yield (entry 1 vs 5). This reaction is amenable to a benchtop setup, providing an isolated yield of 84%, identical to that achieved with a glovebox setup (entry 5). Reducing the catalyst loading from 10 to 2.5 mol % did not significantly influence the reaction outcome for this substrate combination (entry 5 vs 6), although at a 1 mol % catalyst loading the yield dropped to 66% (entry 7). Using the reverse stoichiometry with **1a** as the limiting reagent provided an identical yield to that achieved under standard conditions (entry 5 vs 8), although isolation of pure product was more challenging due to byproduct formation. Conducting the reaction at a concentration of 0.5 M did not affect the reaction yield (entries 5 vs 9); however, the higher concentration of 2.0 M was selected to provide conditions that minimize solvent waste. Lowering the reaction temperature to 100 °C to operate below the boiling point of 1,4-dioxane resulted in a moderate drop in yield to 60% when 2.5 mol % of **4a** was employed (entries 6 vs 10). The noncationic dimeric complex  $[\text{Cp}^*\text{CoCl}_2]_2$  (**4b**) provided only a 5% yield even at a higher catalyst loading and an elevated temperature (entry 11). When operating below the solvent boiling point, a comparable yield was observed with preformed cationic catalyst **4c** relative to **4a** (entry 10 vs 12). This result indicates that, for Co(III)-catalyzed C–H bond additions to isocyanates, a completely noncoordinating counterion provides no rate enhancement relative to  $\text{PF}_6^-$ .<sup>16</sup> Removal of potassium acetate dramatically reduced the yield of desired product (entry 13). Moreover, no product was observed when catalyst **4a** was excluded (entry 14), demonstrating that a Co(III)-catalyst is required for this C–H functionalization. Due to the lower cost of the  $\text{PF}_6^-$  counterion, cobalt catalyst **4a** was selected for evaluating the substrate scope. A catalyst loading of 10 mol % was used to achieve higher conversion for less reactive substrates (see Scheme 1). Finally, given that C–H bond amidation with isocyanates has been reported for Re, Ru, and Rh, ICP-MS analysis of Co(III)-catalyst **4a** was performed to detect the levels of several second and third row metals known to mediate C–H functionalization. Complex **4a** showed less than 1 ppm of Re, Ru, Rh, Ir, and Pt, and Pd at 1 ppm (see Supporting Information for details).

The substrate scope was first evaluated with a series of functionalized isocyanates **2** and *N*-aryl-1*H*-pyrazoles **1** (Scheme 1). For aromatic isocyanates, electron-rich (**3b**), electron-neutral (**3c**, **3e**), and electron-deficient (**3d**, **3f–h**) derivatives all coupled in high yield. Additionally, high yields were maintained when substituents were placed at the para (**3b–d**), meta (**3e–g**), and ortho (**3h**) positions. Linear alkyl isocyanates coupled to provide the *N*-benzyl amide **3i** and *N*-hexyl amide **3j** in good yields, while a branched alkyl isocyanate gave the *N*-cyclohexyl amide **3k** in moderate yield. A higher 10 mol % catalyst loading was necessary for some of the isocyanates. For example, while a good yield was obtained when employing 2.5 mol % of catalyst **4a** in the synthesis of **3a**, a dramatically lower 19% yield of **3j** was observed at this lower loading for hexyl isocyanate.

A series of substituted *N*-aryl-1*H*-pyrazoles **1** were then evaluated and provided amide products **3** in good yields for electron-rich (**3l**, **3p**), electron-neutral (**3m–n**, **3q**), and

**Scheme 1. Substrate Scope for Amidation of *N*-Aryl-1*H*-Pyrazoles with Isocyanates<sup>a,b</sup>**

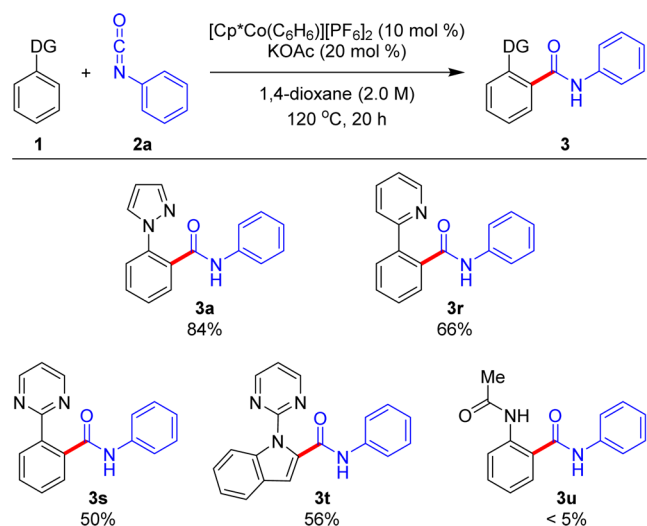


<sup>a</sup>Conditions: isocyanate **2** (0.20 mmol), *N*-aryl-1*H*-pyrazole **1** (0.40 mmol) in 1,4-dioxane (2.0 M) at 120 °C for 20 h. <sup>b</sup>Isolated yields after chromatography. <sup>c</sup>Reaction conducted using 2.5 mol % of catalyst **4a** and 5 mol % of KOAc.

electron-deficient (**3o**) substituents. For meta-substituted derivatives, C–H functionalization occurred exclusively at the less hindered position to give amides **3p** and **3q**, thereby demonstrating that regioselectivity can be controlled by steric effects.<sup>17</sup> Notably, incorporation of both bromo (**3n**) and methyl ketone (**3o**) groups proceeded in good yield, highlighting the functional-group compatibility of  $\text{Cp}^*\text{Co(III)}$  catalysis, which consequently enables subsequent transformations for late stage introduction of molecular complexity.

The directing group scope of this reaction was also investigated (Scheme 2). In addition to the amidation of *N*-aryl-1*H*-pyrazoles, the 2-pyridyl (**3r**) and 2-pyrimidinyl (**3s**) directing groups also provided amide products albeit in modestly diminished yields. The 2-pyrimidinyl directing group

### Scheme 2. Directing Group Scope for C–H Bond Amidation<sup>a,b</sup>

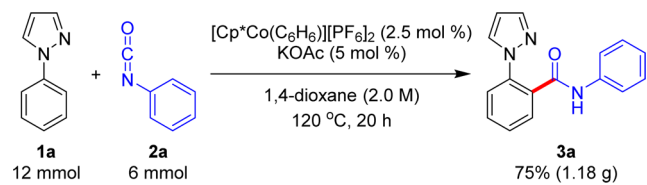


<sup>a</sup>Conditions: **2a** (0.20 mmol), directing group **1** (0.40 mmol) in 1,4-dioxane (2.0 M) at 120 °C for 20 h. <sup>b</sup>Isolated yields after chromatography.

was also further successfully applied to indole functionalization (**3t**).<sup>18</sup> Given that both 2-phenylpyrimidine and 1-(pyrimidin-2-yl)-1*H*-indole contain two potential nitrogen directing groups, we were pleased to find that only monoamidation products **3s** and **3t** were obtained without any double addition products. We also evaluated acetanilide, which we had previously determined to be an effective substrate for Rh(III)-catalyzed isocyanate additions.<sup>6f</sup> However, this substrate was not effective for Co(III)-catalyzed isocyanate addition because the KOAc additive resulted in competitive *N*-acylation rather than providing the desired C–H bond addition product **3u**.

A gram scale reaction was conducted to assess the scalability of this Co(III)-catalyzed C–H bond amidation with isocyanates (Scheme 3). Employing only 2.5 mol % of

### Scheme 3. Gram Scale Synthesis of Pyrazole **3a**



preformed catalyst **4a** and 5 mol % of KOAc under the optimized reaction conditions, pyrazole **3a** was furnished in 75% yield (1.18 g), which was a similar yield to that obtained on a smaller scale.

In summary, the cationic preformed cobalt complex  $[\text{Cp}^*\text{Co}(\text{C}_6\text{H}_6)][\text{PF}_6]_2$  (**4a**) efficiently catalyzes C–H bond additions to isocyanates and represents the first example of earth-abundant metal catalysis of this type of transformation. In addition to the *N*-aryl-1*H*-pyrazole directing group, this process has been achieved with other nitrogen heterocycle directing groups. Using an air- and moisture-stable catalyst, this transformation is amenable to a benchtop setup and has been performed on gram scale with a low catalyst loading. The broad scope and high functional-group compatibility of this method

showcase the ability of earth-abundant  $\text{Cp}^*\text{Co}(\text{III})$  catalysis to mediate practical synthetic transformations.

### ■ ASSOCIATED CONTENT

#### Supporting Information

Experimental details, gram scale synthesis, and characterization data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b00910.

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#### Notes

The authors declare no competing financial interest.

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(16) For Co(III)-catalyzed C–H bond additions to aldehydes to provide indazoles and furans, we found that the use of the noncoordinating B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> counterion was highly beneficial. See ref 14g for details.

(17) Reaction at the site of lower steric hindrance to provide a single regioisomer is consistent with other reports of Co(III)-catalyzed C–H bond additions to polarized  $\pi$ -bonds. For examples of aldehyde additions and cyanations, see refs 14g, 14b, 14h, and 14i, respectively.

(18) When phenyl(pyrrolidin-1-yl)methanone was also tested as a directing group under the optimized reaction conditions, amidation was not observed. For a Ru(II)-catalyzed amidation of secondary benzamides leading to phthalimides, see ref 11a.