

# Co(III)-Catalyzed C–H Activation/Formal S<sub>N</sub>-Type Reactions: Selective and Efficient Cyanation, Halogenation, and Allylation

Da-Gang Yu, Tobias Gensch, Francisco de Azambuja, Suhelen Vásquez-Céspedes, and Frank Glorius\*

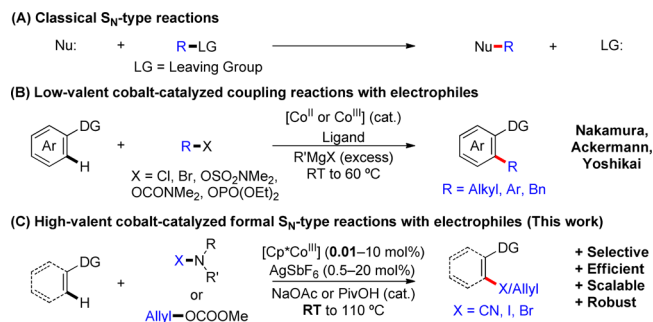
Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster, Corrensstrasse 40, 48149 Münster, Germany

**S** Supporting Information

**ABSTRACT:** The first cobalt-catalyzed cyanation, halogenation, and allylation via C–H activation have been realized. These formal S<sub>N</sub>-type reactions generate valuable (hetero)aryl/alkenyl nitriles, iodides, and bromides as well as allylated indoles using a bench-stable Co(III) catalyst. High regio- and mono-selectivity were achieved for these reactions. Additionally, allylation proceeded efficiently with a turnover number of 2200 at room temperature, which is unprecedented for this Co(III) catalyst. Alkenyl substrates and amides have been successfully utilized in Cp\*Co(III)-catalyzed C–H activation for the first time.

Nucleophilic substitution (S<sub>N</sub>) is a fundamental reaction class in chemistry (Figure 1A).<sup>1</sup> Various kinds of stoichiometric organometallic reagents have been applied as nucleophiles in S<sub>N</sub>-type reactions, but many of them are expensive, sensitive, or difficult to prepare and handle. An alternative is to generate nucleophilic organometallic species in situ under catalytic conditions with a suitable transition metal catalyst. Due to its high atom- and step-economy, the most attractive method to access such species is C–H activation.<sup>2</sup> Organometallic species generated in this way have been successfully employed in cross-couplings and nucleophilic addition or substitution with different electrophiles.<sup>2</sup>

Compared to noble metals, first-row transition metals are more earth-abundant, easily available, and inexpensive. As such, their use as catalysts attracts increasing attention, especially for C–H activation reactions.<sup>3,4</sup> For example, various kinds of C–C and C–heteroatom bond-forming reactions have been developed via cobalt-catalyzed C–H activation.<sup>4–6</sup> Among these transformations, a few examples of coupling reactions with electrophiles have been reported recently (Figure 1B).<sup>5</sup> Pioneered by Nakamura, Ackermann, and Yoshikai, Co-catalyzed efficient and selective C–H activation/coupling reactions have been realized with alkyl/aryl halides, phenol, and benzyl alcohol derivatives under mild reaction conditions. Grignard reagents were used as bases and reductants to generate reactive low-valent Co catalysts from precatalysts. Although many functional groups could be tolerated, reactive Grignard reagents induced some undesirable coupling reactions or dehydrohalogenation of the electrophiles. Thus, it is appealing to develop other catalytic systems without using Grignard reagents. Here we report the first Co-catalyzed cyanation, halogenation, and allylation reactions via C–H activation (Figure 1C). These Cp\*Co(III)-catalyzed formal S<sub>N</sub>-type reactions do not require the use of reactive Grignard reagents and are highly



**Figure 1.** Cobalt-catalyzed coupling and formal S<sub>N</sub>-type reactions with electrophiles via C–H activation. DG = directing group.

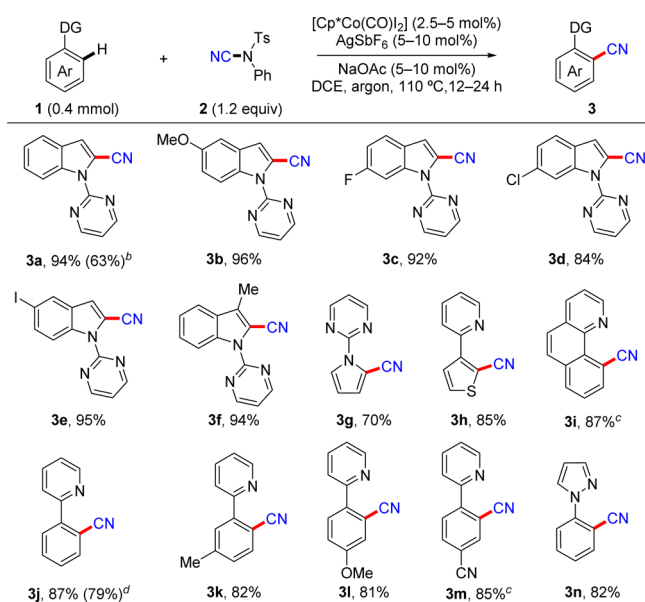
selective, efficient (with a turnover number (TON) of 2200), scalable, and robust. We also report the first Cp\*Co(III)-catalyzed C–H activation proceeding at room temperature (rt).<sup>7</sup>

Our group has been working in the area of Rh(III)-catalyzed C–H activation for several years.<sup>8</sup> Although much progress has been made, the relatively high price of Rh catalysts and curiosity about the reactivity and selectivity of its lighter congener led us to investigate Co(III) catalysis. Recently, Kanai and Matsunaga pioneered and contributed greatly to this field.<sup>6</sup> With well-defined Cp\*Co(III) catalyst precursors, they developed reactions to insert unsaturated moieties (imines, enones, and alkynes) and nitrogen (with azides as N source) into aryl C–H bonds. They also developed an unprecedented indole C2-alkenylation/intramolecular addition to generate pyrrolo-indolones. We were interested in the behavior of the Cp\*Co(III) catalyst in *intermolecular formal S<sub>N</sub>-type reactions*<sup>2o</sup> with electrophilic cyanation, halogenation, and allylation reagents, which might be not compatible with Grignard reagents in the low-valent Co catalysis.<sup>5</sup> Moreover, valuable organo nitriles and halides as well as allylated arenes could be generated, common motifs in bioactive molecules<sup>9</sup> and organic synthesis.<sup>10</sup>

We first tested cyanation due to its high value and the ease of derivatization of organo nitriles.<sup>11</sup> Direct functionalization of the indole motif is highly important and thus attracts much attention. Due to its inherent nucleophilicity at the C3 position, there are several reports on electrophilic C3-cyanation.<sup>12</sup> We expected to overcome this reactivity to achieve selective directed C2-cyanation using the bench-stable complex [Cp\*Co(CO)I<sub>2</sub>] as the catalyst.<sup>6d</sup> For its low toxicity, ease of handling, and stability,<sup>13</sup> N-cyano-N-phenyl-p-toluenesulfonamide (NCTS, 2) was chosen as the reaction partner. To our delight, after

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Scheme 1. Cobalt-Catalyzed C–H Cyanation<sup>a</sup>

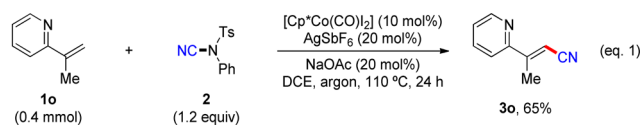
extensive screen, we successfully realized a highly selective and efficient C2-cyanation of *N*-(2-pyrimidinyl)indole (**1a**) to give **3a** in the presence of catalytic amounts of AgSbF<sub>6</sub> and NaOAc (Scheme 1). No reaction was observed in the absence of the Co(III) catalyst or using 1-cyanopyrrolidine as the CN source, but 63% yield was obtained using only 0.5 mol% of the Co(III) catalyst.

Under the optimized reaction conditions, other indoles were tested (Scheme 1). Many functional groups, including methoxy (**3b**), fluoro (**3c**), chloro (**3d**), and iodo (**3e**), were tolerated, which provides great opportunities for further functionalizations. To our delight, substrate **1f** gave the desired product **3f** in an excellent yield despite the steric hindrance.

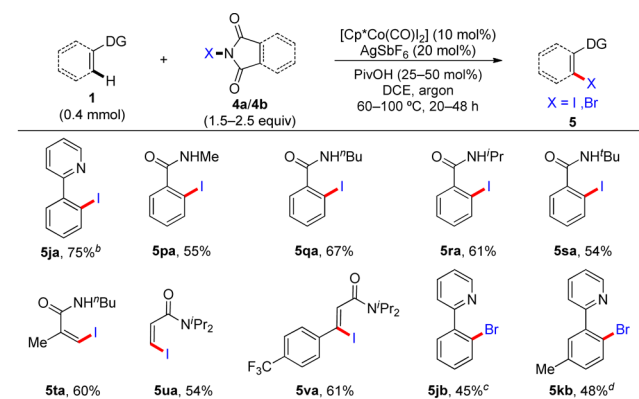
Other kinds of arenes and heteroarenes with different directing groups (DGs) were explored. *N*-(2-Pyrimidinyl)pyrrole (**1g**) underwent selective and clean transformation to generate **3g**, albeit with a slightly lower efficiency. 2-Arylpyridines showed good reactivity and selectivity for mono-cyanation. For these compounds, the reaction was sensitive to steric hindrance and the substrate electronics. For example, C–H cyanation of 2-(*m*-tolyl)pyridine (**1k**) occurred selectively at the position with lower steric hindrance.<sup>14</sup> Compared to the electron-poor **1m**, the more electron-rich **1l** showed higher reactivity, which was also demonstrated by a competition experiment (products **3l** and **3m** formed in a ratio of 29:1; see the SI for details). Both steric and electronic effects might contribute to the high regio- and chemoselectivity of this transformation. A gram-scale reaction of 2-phenylpyridine (**1j**) proceeded with similar efficiency. Another heterocycle, the thiophene derivative **1h**, underwent highly selective C2-cyanation in 85% yield with pyridyl as DG. Benzo[*h*]quinoline (**1i**) and *N*-phenylpyrazole (**1n**) also showed good reactivity and selectivity in this transformation. Further, a robustness screen was done to demonstrate the good functional group tolerance.<sup>15</sup>

Gratifyingly, the cyanation happened not only on (hetero)arenes but also on olefins via alkenyl C–H activation. 2-(Prop-1-en-2-yl)pyridine (**1o**) showed good reactivity in this reaction,

and subsequent isomerization generated **3o** as the thermodynamically favored product (eq 1; see SI for details). To the best of our knowledge, this is the first reported example of Cp\*Co(III)-catalyzed alkenyl C–H activation.



The success of the cyanation reaction led us to extend the method developed to other electrophiles containing N-based leaving groups. Since organo-halides are powerful substrates, the selective halogenation of C–H bonds is an important transformation,<sup>16</sup> especially when using commercially available and less toxic halogen sources such as *N*-iodosuccinimide (NIS, **4a**) and *N*-bromophthalimide (NBP, **4b**). We proposed selective halogenation could be possible with Cp\*Co(III) catalysis. Indeed, under reaction conditions similar to those of the cyanation reaction, **1j** underwent selective mono-iodination at 70 °C to give **5ja** in good yield (Scheme 2).<sup>17</sup>

Scheme 2. Cobalt-Catalyzed C–H Halogenation<sup>a</sup>

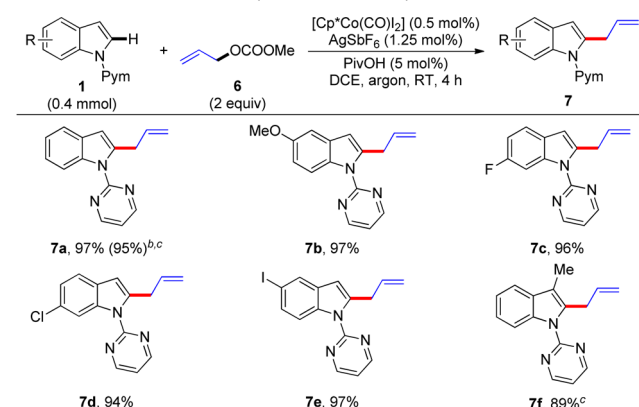
<sup>a</sup>Reaction conditions: see the SI. <sup>b</sup>NaOAc (20 mol%) was used instead of PivOH. <sup>c</sup>3.0 equiv of **1j**, NMR yield. <sup>d</sup>2.0 equiv of **1k**.

When moving to other substrates with different DGs, pivalic acid was found to promote the iodination, and higher conversions were achieved than with sodium acetate. The role of the acid might be to activate NIS through protonation, increasing its electrophilicity, or to generate a highly reactive Co catalyst with a vacant site for coordination.<sup>18</sup> Under the slightly modified reaction conditions, *N*-alkylbenzamides **1p**, **1q**, **1r**, and **1s**, which have not yet been successfully applied in Cp\*Co(III)-catalyzed C–H activation,<sup>19</sup> showed moderate to good reactivity to generate mono-iodinated products **5pa**, **5qa**, **5ra**, and **5sa**.<sup>20</sup> Selective mono-iodination was also observed for olefins via alkenyl C–H activation. Thus, acrylamides **1t**, **1u**, and **1v** reacted under these reaction conditions to selectively generate **5ta**, **5ua**, and **5va** in moderate yields. No desired product was detected in the absence of the Co(III) catalyst. Selective mono-bromination of **1j** and **1k** occurred with moderate yields using NBP as the bromination reagent.<sup>21</sup>

Based on the success of S<sub>N</sub>2-type reactions, related S<sub>N</sub>2'-type transformations were considered. Due to the importance of the allyl motif in bioactive compounds and the ease of subsequent functionalization, allylation reactions attract much attention,<sup>22</sup> especially the aryl C–H bond allylation,<sup>23</sup> yet there is no report

of allylation via Co-catalyzed C–H activation. Thus, the high value of C2-allylated indole structures<sup>9b</sup> made us wonder if Cp\*Co(III)-catalyzed formal S<sub>N</sub>-type reactions with readily available allyl carbonate **6** could generate 2-allylindoles **7** (Scheme 3).<sup>24</sup> Gratifyingly, the reaction proceeded selectively,

### Scheme 3. Cobalt-Catalyzed C–H Allylation<sup>a</sup>

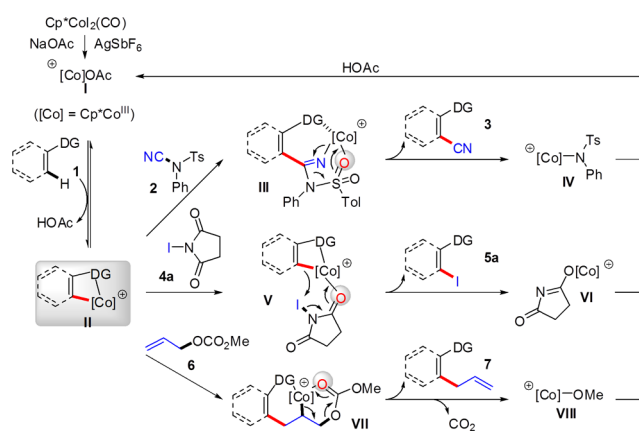


<sup>a</sup>Reaction conditions: see the SI. <sup>b</sup>**1** (1 mmol), [Cp\*Co(CO)<sub>2</sub>] (0.2 mol%), AgSbF<sub>6</sub> (0.5 mol%), PivOH (2 mol%), DCE (5 mL). <sup>c</sup>8 h. Pym = 2-pyrimidinyl.

with negligible amount of the alternative isomer resulting from double bond migration (<1% yield). To our delight, this transformation took place efficiently even at rt, which is unprecedented for Cp\*Co(III)-catalyzed C–H activation. No reaction occurred when Co or Ag was omitted, but an excellent yield was obtained for the allylation of **1a** with as low as 0.2 mol% catalyst loading with a TON of 474. We found that, if given time, the TON can reach an impressive 2200 at rt (see SI for details). Reported TONs of this level are rare in the field of C–H activation/C–C bond formation.

Preliminary mechanistic experiments indicated that the C–H activation was reversible in the presence or absence of NCTS, even at rt (see SI for details). Based on previous reports<sup>6</sup> and our results, we propose the following mechanism (Scheme 4). First, the active Cp\*Co(III) catalyst **I** is generated in situ in the presence of AgSbF<sub>6</sub> and a carboxylate source (NaOAc or PivOH) with release of the CO ligand.<sup>21</sup> Coordination of the Co(III) catalyst to the DG (**1**) promotes C–H activation and generates the cobaltacycle **II**. For the cyanation, coordination of the

### Scheme 4. Proposed Mechanisms



sulfonamide or cyano groups of NCTS to the Co(III) center may assist the insertion of the C≡N group into the C–Co bond to generate **III**. This assertion is supported by the fact that 1-cyanopyrrolidine, which does not possess a sulfonamide group, showed no reactivity. This is followed by release of the desired product **3** and regeneration of **I** from **IV** by ligand exchange. For halogenation with NIS, nucleophilic attack of the C–Co bond to the I–N bond (**V**) is proposed to generate the C–I bond in **5a**, which is similarly promoted by the interaction of Co with one carbonyl group (**V**). For the allylation, a similar coordination of the carbonyl group to Co is proposed to direct the selective insertion, facilitate the β-O elimination, and suppress the unproductive β-H elimination.

In conclusion, we have developed the first cobalt-catalyzed C–H cyanation, halogenation, and allylation reactions. Various arenes, heteroarenes, and alkenes directly undergo such regio- and chemoselective formal S<sub>N</sub>-type reactions with good functional group tolerance. Alkenyl substrates and amides were successfully utilized in Cp\*Co(III)-catalyzed C–H activation for the first time. This C–H activation occurred efficiently at room temperature using 0.01–0.5 mol% of a bench-stable Co(III) catalyst. A TON of 2200 was obtained. Valuable organo nitriles, iodides, and bromides as well as allylated indoles were generated from easily available starting materials. The coordination of oxygen in the leaving group toward Co is proposed to play a vital role in ensuring selectivity and reactivity in these transformations.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental details and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

glorius@uni-muenster.de

### Notes

The authors declare no competing financial interest.

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- (21) Using the preformed cationic Co(III) complex [Cp\*Co(MeCN)<sub>3</sub>(SbF<sub>6</sub>)<sub>2</sub>] instead of [Cp\*Co(CO)I<sub>2</sub>] and AgSbF<sub>6</sub>, similar reactivity is observed in the halogenation reactions, e.g., 50% isolated yield for the substrate **1k**, supporting the intermediacy of **I**.
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