



Thiocarbonyl-enabled ferrocene C–H nitrogenation by cobalt(III) catalysis: thermal and mechanochemical

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Full Research Paper

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Abstract

Versatile C–H amidations of synthetically useful ferrocenes were accomplished by weakly-coordinating thiocarbonyl-assisted cobalt catalysis. Thus, carboxylates enabled ferrocene C–H nitrogenations with dioxazolones, featuring ample substrate scope and robust functional group tolerance. Mechanistic studies provided strong support for a facile organometallic C–H activation manifold.

Introduction

C–H activation has surfaced as a transformative tool in molecular sciences [1–9]. While major advances have been accomplished with precious 4d transition metals, recent focus has shifted towards more sustainable base metals [10–17], with considerable progress by earth-abundant cobalt catalysts [18–22]. In this context, well-defined cyclopentadienyl-derived cobalt(III) complexes have proven instrumental for enabling a wealth of C–H transformations [23–41], prominently featuring transformative C–H nitrogenations [42,43] in an atom- and step-economical fashion [44–59]. Within our program on cobalt-catalyzed C–H activation [60–68], we have now devised

C–H nitrogenations assisted by weakly-coordinating [69] thiocarbonyls [70,71], allowing the direct C–H activation on substituted ferrocenes [72–93] – key structural motifs of powerful transition metal catalyst ligands and organocatalysts (Figure 1) [94–97]. During the preparation of this article, the use of strongly-coordinating, difficult to remove directing groups has been reported [70,71]. In sharp contrast, notable features of our approach include (i) cobalt-catalyzed C–H amidations of thiocarbonylferrocenes by weak coordination, (ii) thermal and mechanochemical [98–100] cobalt-catalyzed ferrocene C–H nitrogenations, (iii) versatile access to synthetically useful

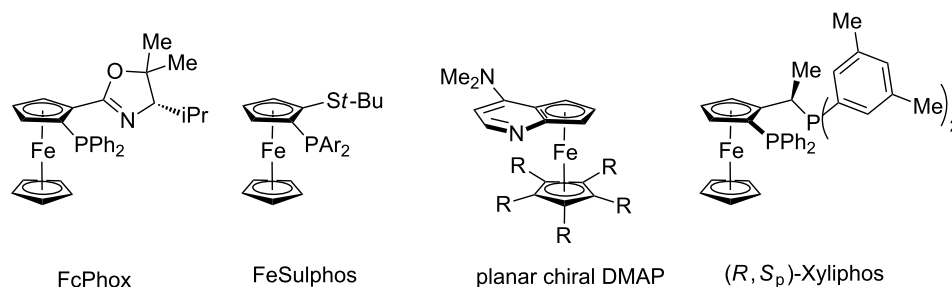


Figure 1: Selected ferrocene-based ligands and organocatalysts.

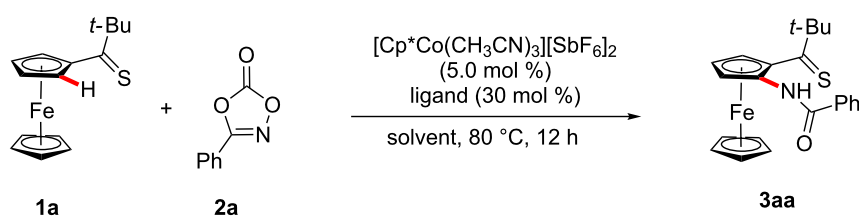
aminoketones, and (iv) key mechanistic insights on facile C–H cobaltation.

Results and Discussion

We initiated our studies by probing various reaction conditions for the envisioned C–H amidation of ferrocene **1a** (Table 1). Among a variety of ligands, N-heterocyclic carbenes and phosphines provided unsatisfactory results (Table 1, entries 1–3),

while the product **3aa** was formed when using amino acid derivatives, albeit as of yet in a racemic fashion (Table 1, entries 4–7). Yet, optimal catalytic performance was realized with 1-AdCO₂H (Table 1, entries 8 and 9) [101–104], particularly when using DCE as the solvent (Table 1, entries 9–12). A control experiment verified the essential nature of the cobalt catalyst (Table 1, entry 13). In contrast to the thiocarbonyl-assisted C–H amidation, the corresponding ketone failed thus

Table 1: Thiocarbonyl-assisted C–H nitrogenation of ferrocene **1a**.^a



Entry	Solvent	Ligand	Yield (%)
1	DCE	–	–
2	DCE	IMes·HCl	–
3	DCE	PPh ₃	–
4	DCE	Boc-Leu-OH	40
5	DCE	Boc-Val-OH	55
6	DCE	Boc-Pro-OH	30
7	DCE	Boc-Ala-OH	62
8	DCE	MesCO ₂ H	80
9	DCE	1-AdCO₂H	84
10	1,4-dioxane	1-AdCO ₂ H	75
11	toluene	1-AdCO ₂ H	79
12	GVL	1-AdCO ₂ H	35
13	DCE	1-AdCO ₂ H	– ^b

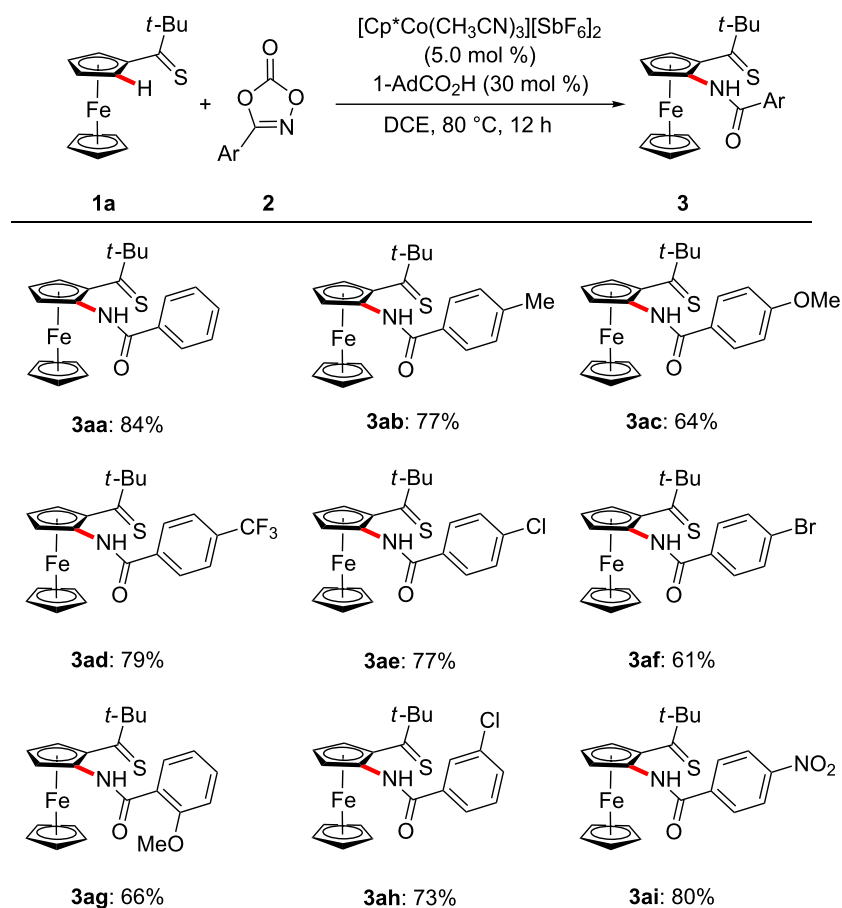
^aReaction conditions: **1a** (0.13 mmol), **2a** (0.15 mmol), ligand (30 mol %), [Co] (5.0 mol %), solvent (1.0 mL). ^bReaction performed in the absence of [Cp*Co(CH₃CN)₃][SbF₆]₂. Yields of isolated product.

far to deliver the desired product, under otherwise identical reaction conditions.

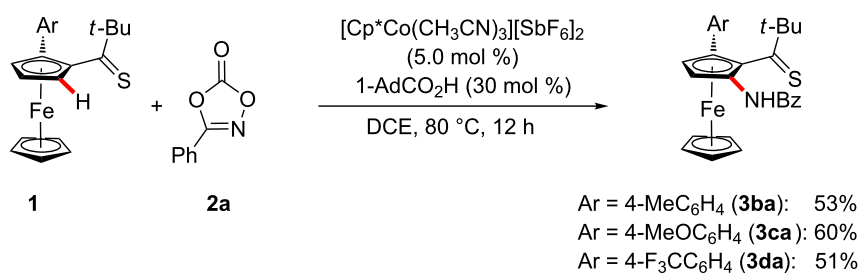
With the optimized reaction conditions in hand, we explored the robustness of the cobalt-catalyzed ferrocene C–H amidation with a variety of 1,4,2-dioxazol-5-ones **2** (Scheme 1). Hence, the chemoselectivity of the cobalt catalyst

was reflected by fully tolerating sensitive electrophilic functional groups, including amido, chloro, bromo and nitro substituents in the *para*-, *meta*- and even the more congested *ortho*-position.

The versatile cobalt-catalyzed C–H amidation was not limited to mono-substituted ferrocenes **1** (Scheme 2). Indeed, the



Scheme 1: Scope of substituted dioxazolones **2**.



Scheme 2: C–H Amidation of arylated ferrocenes **1**.

arylated ferrocenes **1b–d** were identified as viable substrates likewise.

Moreover, differently substituted thiocarbonyls **1** were found to be amenable within the cobalt-catalyzed C–H amidation manifold by weak-coordination (Scheme 3).

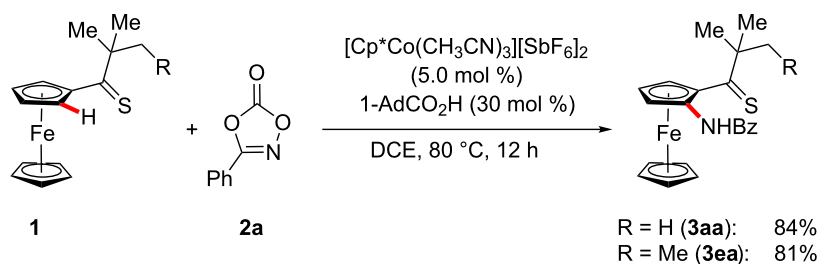
Given the versatility of the cobalt-catalyzed C–H nitrogenation, we became intrigued to delineating its mode of action. To this end, C–H amidations in the presence of isotopically labelled co-solvents led to a significant H/D scrambling in proximity to the thiocarbonyl group. These findings are indicative of a reversible, thus facile organometallic C–H cobaltation regime (Scheme 4).

Next, intermolecular competition experiments revealed that electron-rich arylated thiocarbonylferrocene **1** reacted preferen-

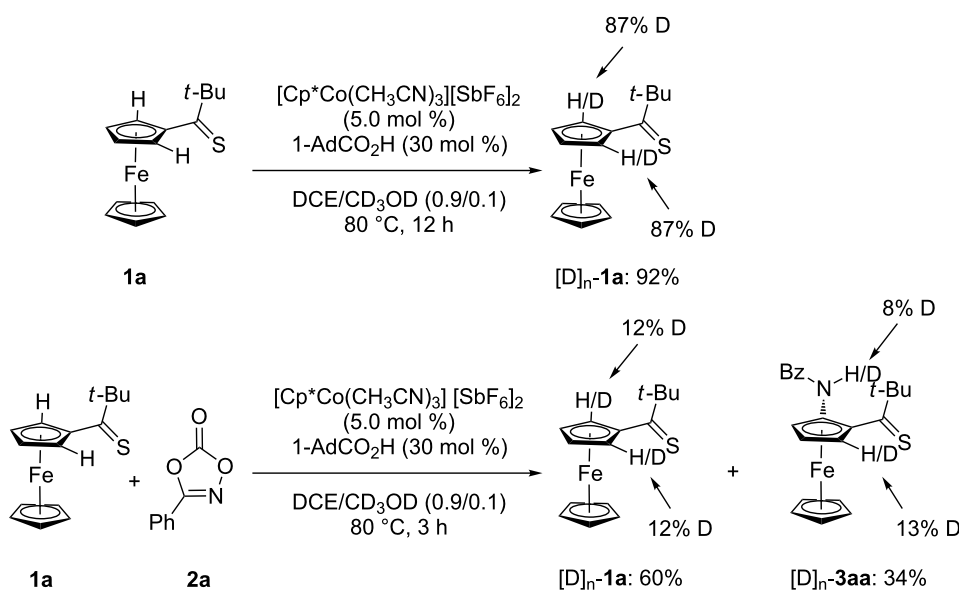
tially, which can be rationalized with a base-assisted internal electrophilic substitution (BIES) [24,105] C–H cobaltation mechanism. In addition, the electron-rich amidating reagent **2c** was found to be inherently more reactive (Scheme 5).

As to further late-stage manipulation of the thus-obtained products, the amidated thiocarbonylferrocene **3aa** could be easily transformed into the corresponding synthetically useful aminoketone **4aa** (Scheme 6), illustrating the unique synthetic utility of our strategy.

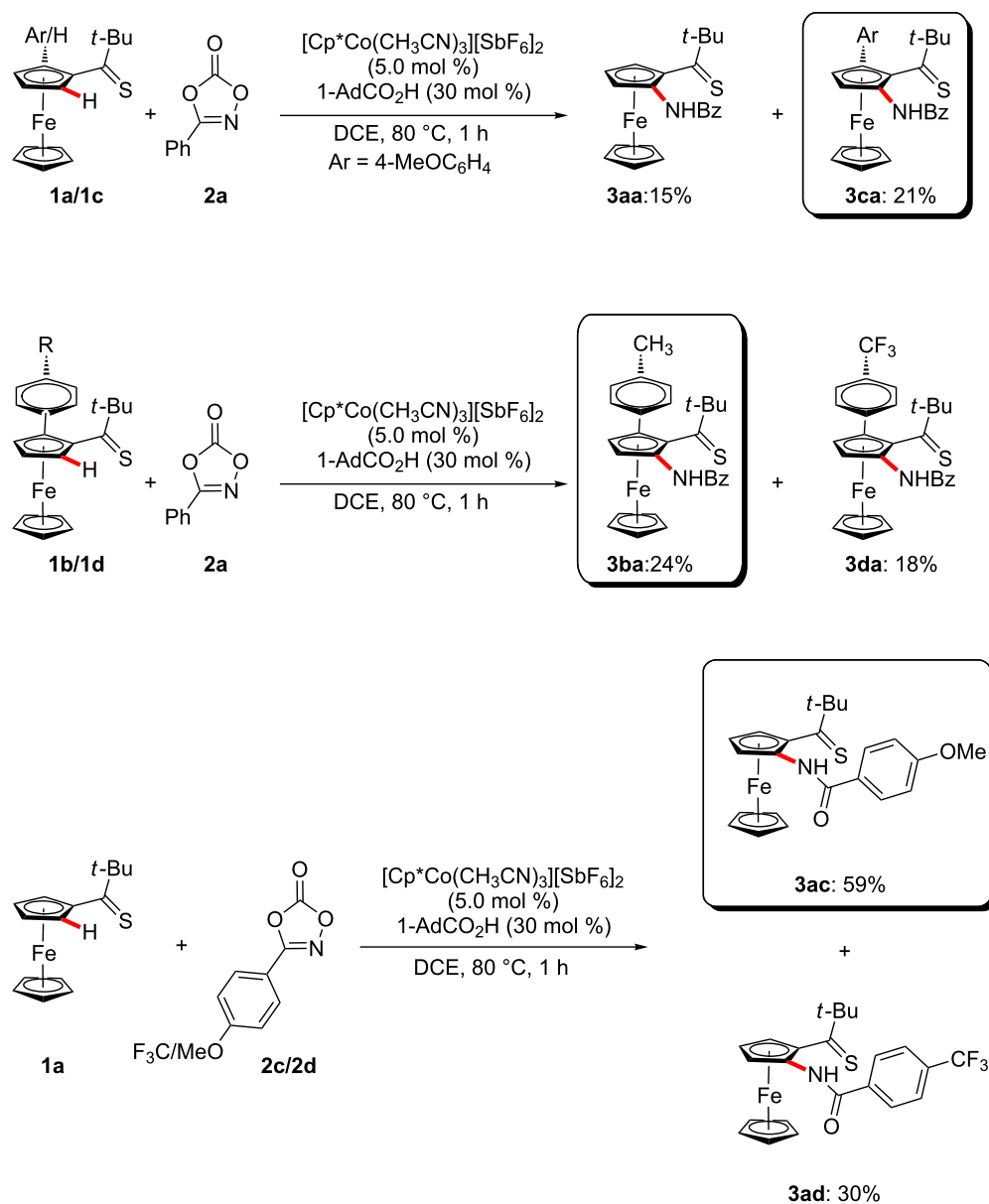
Mechanochemical molecular synthesis has attracted recent renewed attention as an attractive alternative for facilitating sustainable organic syntheses [106]. Thus, we were delighted to observe that the mechanochemical C–H nitrogenations proved likewise viable by thiocarbonyl assistance in an effective manner (Scheme 7).



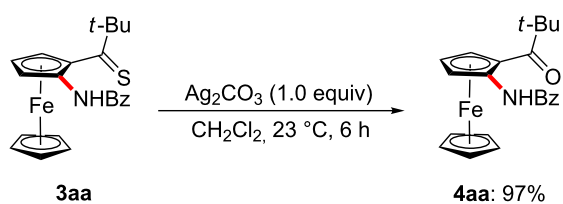
Scheme 3: Thiocarbonyl-assisted C–H amidation.



Scheme 4: H/D Exchange reactions.

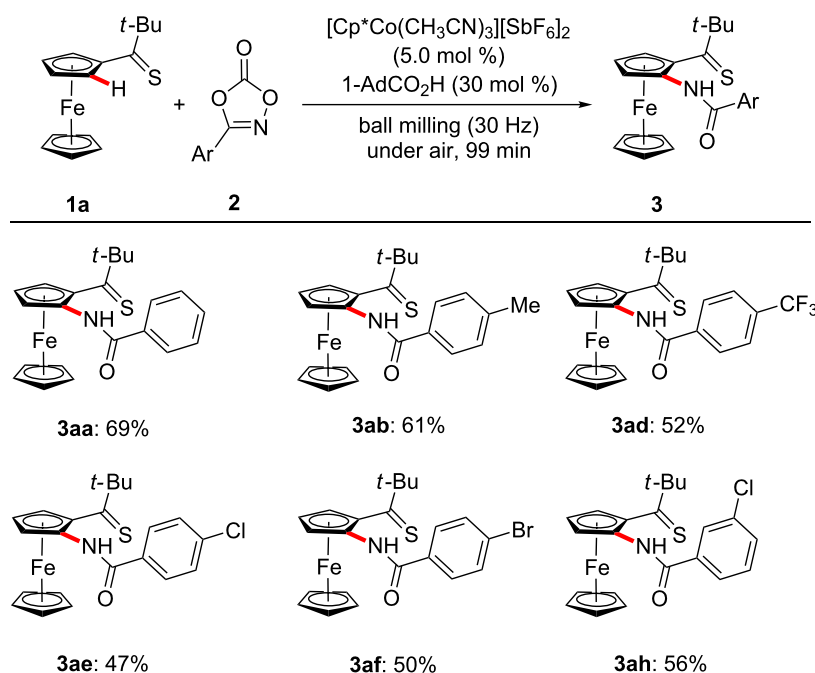


Scheme 5: Intermolecular competition experiments.

Scheme 6: Synthesis of aminoketone **4aa**.

Conclusion

In conclusion, we have reported on the unprecedented cobalt-catalyzed C–H nitrogenation of ferrocenes by weakly-coordinating thiocarbonyls. The carboxylate-assisted cobalt catalysis was characterized by high functional group tolerance and ample substrate scope. Mechanistic studies provided evidence for a facile C–H activation. The C–H amidation was achieved in a thermal fashion as well as by means of mechanochemistry, providing access to synthetically meaningful aminoketones.



Scheme 7: Mechanochemical ferrocene C–H nitrogenation.

Supporting Information

Supporting Information File 1

Experimental procedures, characterization data, and NMR spectra for new compounds.

[<https://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-14-131-S1.pdf>]

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