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Cobalt-Catalyzed Regioselective Borylation of Arenes: *N*-Heterocyclic Silylene as Electron Donors in Metal-Mediated Activation of C–H Bonds

Hailong Ren,[a] Yu-Peng Zhou,[b] Yunping Bai,[a] Chunming Cui*,[a,c] and Matthias Driess[b]

Abstract: *C-H Borylation of arenes has been a subject of great current interest because of its atom-economy and the wide applicability of borylated products in value-added synthesis. A new bis(silylene)cobalt(II) complex bearing a bis(N-heterocyclic silylene)–pyridine pincer ligand (SiNSi) has been synthesized and structurally characterized. It enabled the regioselective catalytic C–H borylation of pyridines, furans and fluorinated arenes. Notably, it exhibited the complementary regioselectivity for the borylation of fluorinated arenes compared to previously known catalytic systems, demonstrating that N-heterocyclic silylene donors have enormous potential in metal-catalyzed catalytic applications.*

Selective C–H functionalization of organic compounds is an important and long–standing goal in synthetic chemistry.[1] A vast number of C–H functionalization reactions are currently available, whereas C–H borylation is often preferred due to the versatility of the organoboron compounds in synthesis.[2-3] In comparison to the precious–metal based catalysts such as Rh, Pt and Ir,[2,4-6] cheap and nontoxic metals are of great current interest. Recently, iron-, nickel-, cobalt- and copper-based catalysis for C–H borylation have been developed.[7-9] In this context, cobalt pincer complexes have attracted a great deal attention.[10-13] Remarkably, C–H borylation of arenes has recently been reported by Chirik et al. using PNP cobalt pincer complexes.[13] However, cheap metal-catalyzed C–H borylation is still in its infancy, and the selective metal catalysts are still highly desirable.

To modulate the reactivity and selectivity of metal catalysts, the electron donors on suitable ligand frameworks play important roles. While σ-donors based on phosphines and N-heterocyclic carbenes have been extensively studied. Recent surge in the development of silylene chemistry has shown that silylenes, isoelectronic with singlet carbenes, are potential σ-donors for catalysis. Although a large number of stable silylenes could be isolated and their coordination ability toward transition-metals has been studied as well,[14,15] the application of silylenes in catalysis remains largely unexplored. Nevertheless, Fürstner and Roesky et al. have shown that palladium the complexes supported by the NHSi ligand **I** (Chart 1) were active for Suzuki and Heck reactions.[16,17] Reduction of amides to amines mediated by rhodium and iridium-NHSi complexes with the ligand **II** (Chart 1) complexes has been reported by Driess and co-workers.[18] The latter group has recently developed new pincer-type ligands with two NHSi arms such as **III** and **IV**, which have been successfully employed for the preparation of Ir, Co, Ni and Fe complexes.[19-21] Interestingly, the Ir complexes enabled catalytic C–H borylation of arenes. These results demonstrated that NHSis can act as very useful electron-donors in metal-mediated catalytic transformations and current studies are aiming at widen the scope of applications of such ligands in catalysis.

Encouraged by the advances of NHSi ligands and cobalt-mediated catalysis, we became interested in the investigation of cobalt complexes supported by the pyridine-based pincer ligand **IV** modified with two NHSi donor arms (SiNSi, Chart 1) and its catalytic ability. Herein, we report the synthesis of the $CoBr_2$ complex **1** supported by the SiNSi pincer ligand **IV** (Chart 1) and its application in catalytic C-H borylation of arenes. Notably, this system enabled highly regioselective borylation of fluorinated arenes distinct from the known cobalt PNP system.

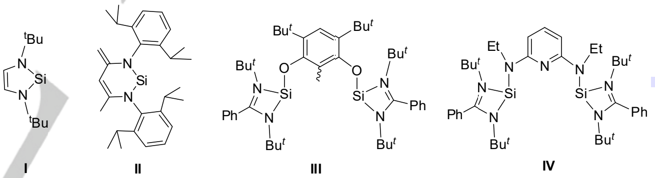
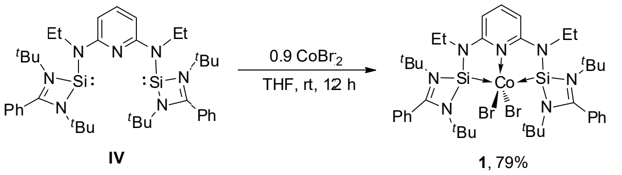


Chart 1. N-Heterocyclic silylenes applied as electron donors in metal-catalyzed reactions.



Scheme 1. Synthesis of $(SiNSi)CoBr_2$ **1**.

The cobalt complex $(SiNSi)CoBr_2$ **1** was obtained as dark crystals in 79% yield by the reaction of **IV** with $CoBr_2$ in THF (Scheme 1). The structure of the paramagnetic complex **1** has been elucidated by a single-crystal X–ray diffraction analysis (Figure 1, Tables S1-S2 in the SI). The SiNSi ligand acts as a tridentate pincer ligand to cobalt. The N5–Co1 bond distance of 2.026(3) Å is short compared to those observed in related bis(imino)- and bis(phosphino)pyridine cobalt halides (2.051(3)-2.102(5) Å).[22] The Si–Co bond lengths of 2.1949 and 2.2244(11) Å are close to those found in $(\mathbf{L}SiCl)_2CoBr_2$ (L = $PhC(N\mathit{t}Bu)_2$, 2.1949(5) and 2.1793(5) Å).[23] Magnetic susceptibility

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Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate)) measurements of **1** (μeff = 2.12 μB) revealed a low–spin d^7-Co center, comparable with a bis(carbene)pyridine dibromido cobalt(II) complex (μeff = 2.00 μB).[24] On the basis of the previous studies applying the strongly electron-donating properties of NHSis, we reasoned that **1** could be a potentially useful precatalyst for the selective C−H functionalization which are otherwise difficult to achieve.

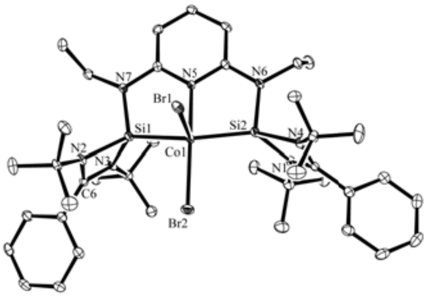
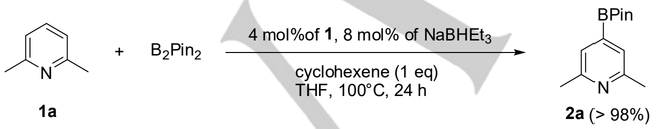


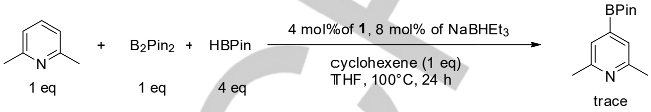
Figure 1. The ORTEP representation of complex **1** in the solid state. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen and solvent atoms are omitted for clarity.

At first we probed the borylation of 2,6–lutidine **1a** with bis(pinacolato)diboron B_2Pin_2 as a model reaction (Scheme 2). The reaction was initially conducted with 4.0 mol% loading of **1** and 8.0 mol% loading of $NaBHEt_3$ (0.1 M in THF) as the reductant. Although the borylation of 2,6–lutidine with B_2Pin_2 at 100 °C yielded the expected product, the lutidine cannot be completely converted to the desired borylated product even after prolonged reaction time (Table S3 in the SI). We reasoned that the side product HBpin may suppress the C−H borylation. Indeed, upon addition of one equivalent of cyclohexene, the borylation at 100 °C for 24 h led to a complete conversion with the selective formation of the 4-substituted product **2a** (Table S3 in the SI), along with the formation of $C_6H_{11}BPin$ and cyclohexane as the side products. Furthermore, the borylation reaction in the presence of four molar equivalents of HBPin and cyclohexene only led to the formation of trace borylated product **2a**, and cyclohexene was completely consumed as indicated by the proton NMR spectroscopy (Scheme 3). These results indicated that HBpin was generated in the course of borylation and could be consumed by the addition of cyclohexene.



Scheme 2. Borylation of 2,6-lutidine **1a** with B_2Pin_2.

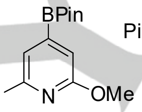
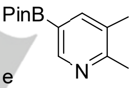
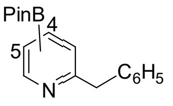
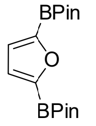
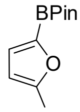
In order to clarify the role of cyclohexene, hydroboration of cyclohexene with one equivalent of HBPin under the similar catalytic conditions was conducted. The reaction yielded ca. 19% $C_6H_{11}BPin$, 23% cyclohexane and ca 29% B_2Pin_2 as estimated by the GCMS and ^1H NMR spectroscopy (Figures S1 and S2 in the SI). B_2Pin_2 cannot be separated in pure form and has been detected in the mixture by the ^{11}B NMR spectrum (Figure S1). In contrast, the reaction of cyclohexene with B_2Pin_2 under the similar conditions only yielded trace of $C_6H_{11}BPin$ and $C_6H_{10}Bpin$. The results indicated that cyclohexene does not consume B_2Pin_2 noticeably.



Scheme 3. Borylation of 2,6-lutidine in presence of excess HBPin.

Next we investigated the C−H borylation of various arenes; we found that **1** can catalyze the borylation of benzene derivatives with electron-donating groups but only very low conversions. This indicates the pronounced electronic effects of the catalytic borylation. We then focussed on heteroarenes such as pyridines and furans and benzene derivatives with electron-withdrawing groups.

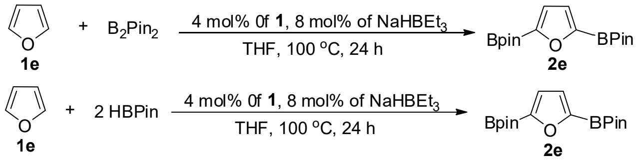
Table 1. Co-catalyzed borylation of *N*-and *O*-heteroarenes.

				
2b	**2c**	**2d**	**2e**	**2f**
[a]71 (50%)	>98 (77%)	>98 (90%) 49:51 (4:5)	[b]100 (85%)	[b]>99 (87%)

Reaction conditions: pyridines (0.5 mmol), B_2Pin_2 (0.5 mmol) and cyclohexene (0.5 mmol); furan (0.5 mmol) and B_2Pin_2 (0.5 mmol); 2-methylfuran (0.5 mmol) and B_2Pin_2 (0.25 mmol), in 0.4 mL THF at 100°C for 24 h with precatalyst 1 (4 mol%) and $NaBHEt_3$ (8 mol%). Reported values are % conversions with respect to the arenes as determined by ^1H NMR spectroscopy, the ratios of the product were determined by NMR spectroscopy, and the values in parentheses are isolated yield. [a]with precatalyst **1** (8 mol%) and $NaBHEt_3$ (16 mol%); [b] without cyclohexene.

We first investigated the borylation of substituted pyridines and furans. The results are summarized in Table 1. The borylation of 2-methoxy–6–methyl pyridine is much slower than that of lutidine **1a** and required 8 mol% loading of precatalyst **1** for an acceptable conversion, selectively yielding the 4-substituted product in ca 71% yield in 24 h based on NMR analysis. The borylation of 2,3–lutidine **1c** with 4 mol% of **1** selectively borylated the 5-position of the ring (**2c**), whereas borylation of 2–benzylpyridine **1d** furnished a mixture containing almost the same amount of 4– and 5–borylated regioisomers **2d**.

In contrast to the borylation of pyridines, the borylation of furan did not require cyclohexene. The borylation of furan **1e** led to the bis-borylation of 2- and 5-positions (Scheme 4 and Table 1, **2e**) of the ring with one molar equiv of B_2Pin_2, while 2–methylfuran **1f** selectively occurred at the 5-position with 0.5 molar equiv of B_2Pin_2 to give **2f**. This indicated that the borylation of furan can be performed with HBPin. Indeed, the borylation of both furan and 2–methylfuran with HBPin yielded the expected borylated products in good yields.



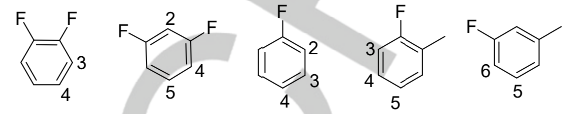
Scheme 4. Borylation of furan with B_2Pin_2 and HBPin.

As fluorinated arylboronic esters are highly valuable building blocks in pharmaceutical and material chemistry,[25] catalytic borylation of fluoro- and trifluoromethylarenes has been probed as well. The results are summarized in Table 2. Disubstituted benzenes with at least one trifluoromethyl substituent undergo selective borylation at the least hindered positions (Table 2, **2g**-**2k**), indicating that the selectivity is controlled by steric effects of the ring. Borylation of 1–methyl–2–(trifluoromethyl)- and 1-methoxyl-2(trifluoromethyl)benzenes (**2j** and **2k**) led to the formation of a mixture containing two regioisomers. However, the regioselectivity for the two substrates was observed to some extend at the para-position to the CF_3 group in the ring. It has been reported that similar selectivity could be achieved for **2j** and **2k** with iridium catalysts.[4d, 6f]

Borylation of 1,2–difluorobenzene (Table 2, **2l**) proceeded smoothly under the similar reaction conditions to yield the corresponding 4-borylated product as a major regioisomer (24:76). Notably, 1,3–difluorobenzene predominantly gave the 5-borylated product **2m** in 97% yield as determined by ^{19}F NMR spectroscopy. To the best of our knowledge, there has been no catalyst reported reaching such a high level of regioselectivity for this substrate. It was shown that iridium–catalyzed borylation of 1,3–difluorobenzene yielded 2-, 4- and 5-positional regioisomers in the molar ratio of 17:33:50.[6c] Chatani and Iwasawa et al. reported that the platinum–catalyzed borylation of 1,3–difluorobenzene occurred preferentially at the 2–position.[5] Borylation of 2–substituted 1,3–difluorobenzenes proceeded at the 5–position selectively in good yields (**2n** and **2o**), whereas 1,2,3-trifluorobezene led to a relatively low selectivity at the 5-position with the contamination of 4-borylated product in ca 22% yield (**2p**). Fluorobenzene underwent smooth borylation, yielding the 3-borylated regioisomer (**2q**) as the major product with high efficiency. This regioselectivity is opposite and complementary to that catalyzed by PNP cobalt pincer complexes.[12a] Similarly, borylation of 2–methylfluorobenzene preferably occurred at the 4–position (**2r**) with 2- and 5-borylated products as side products. 1-Fluoro-3-methylbenzene selectively borylated at the meta position of the fluorine atom (Table 2, 2**s**), and the borylation of 1-fluoro-3-(trifluoromethyl)benzene yielded the single borylated product 2**t**.

It can be seen from Chart 2, this cobalt-catalyzed borylation of selected fluorinated arenes exhibited good regioselectivity at the meta-position to the fluorine atom(s). It appeared to be more regioselective compared to iridium catalysts,[4d, 6] whereas it exhibited opposite regioselectivity to platinum and cobalt pincer precatalysts.[5, 13] This regioselectivity could be attributed to the combination of the electronic and steric factors afforded by the [NSiN] donor ligand. However, the deep understanding of these factors has yet to be investigated.

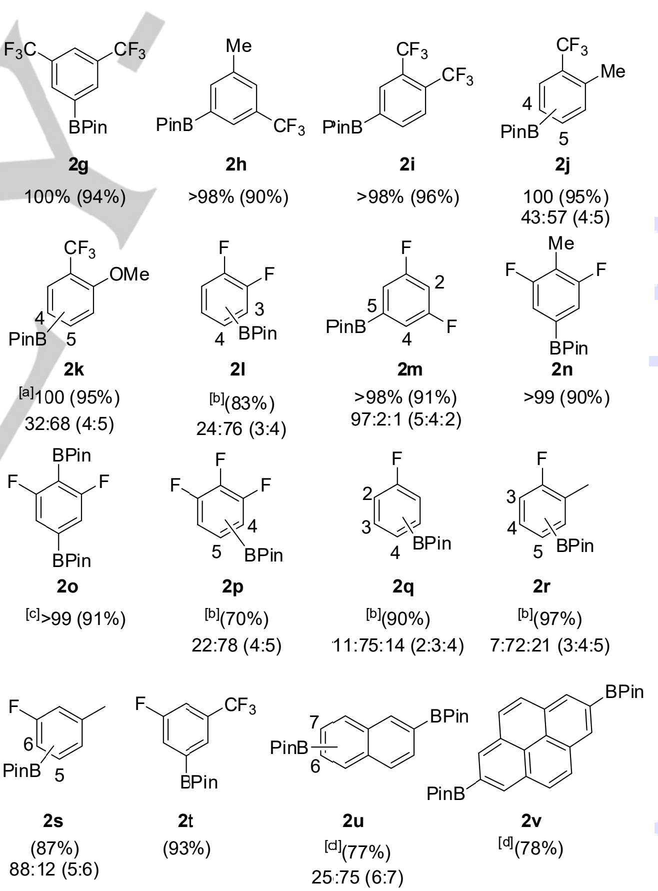
Chart 2. Comparison of **1** with iridium, platinum and PNP cobalt precatalysts for the C–H borylation of fluorinated arenes.



	3:4	2:4:5	2:3:4	3:4:5	5:6
This work	24:76	1:2:97	11:75:14	7:72:21	88:12
Ir	33:67[a]	17:33:50[b]	15:55:28[c]		49:41[d]
[PSiN]Pt[e]	91:9	78:18:4	84:13:3	71:16:4:6	
[NHC]Pt[f]	99:1	82:18	73:20:7		
[PNP]Co[g]			89:11		

[a] Ref 6c; [b] Ref 6d; [c] Ref 6e; [d] Ref 4d; [e] Ref 5b; [f] Ref 5a; [g] Ref 13a.

Table 2. Catalytic borylation of fluorine-containing arenes and polyarenes.



2g 100% (94%)

2h >98% (90%)

2i >98% (96%)

2j 100 (95%) 43:57 (4:5)

2k [a]100 (95%) 32:68 (4:5)

2l [b](83%) 24:76 (3:4)

2m >98% (91%) 97:2:1 (5:4:2)

2n >99 (90%)

2o [c]>99 (91%)

2p [b](70%) 22:78 (4:5)

2q [b](90%) 11:75:14 (2:3:4)

2r [b](97%) 7:72:21 (3:4:5)

2s (87%) 88:12 (5:6)

2t (93%)

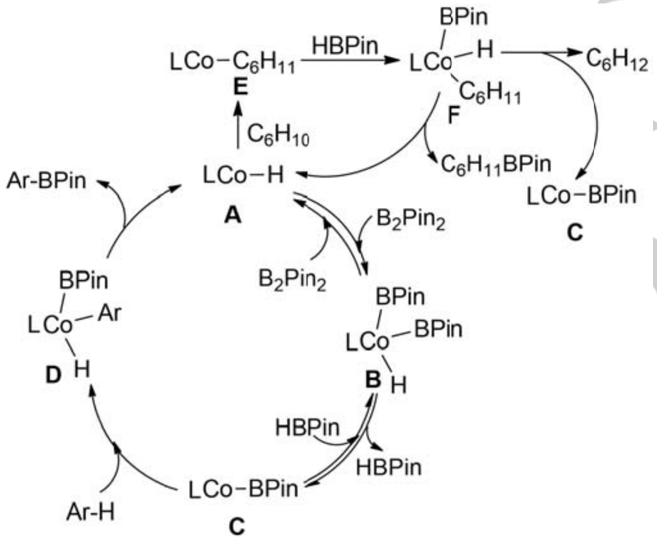
2u [d](77%) 25:75 (6:7)

2v [d](78%)

Reaction conditions: arenes (0.5 mmol), B_2Pin_2 (0.5 mmol) and cyclohexene (0.5 mmol) in 0.4 mL THF at 100°C for 24 h, with precatalyst **1** (4 mol%) and $NaBHEt_3$ (8 mol%); Reported values are % conversions with respect to the arenes as determined by ^1H NMR spectroscopy, product ratios were determined by NMR spectroscopy, and the values in parentheses are isolated yield. [a] 36 h; [b]10 molar equiv of arenes (5 mmol); [c] 2-(2,6-difluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane as substrate; [d] 8.0 mol% loading of **1** and 16 mol% of $NaBHEt_3$, 2 molar equiv of cyclohexene and B_2Pin_2 for 48 h.

The bis-borylation of naphthalene and pyrene was also examined (Table 2, **2u** and **2v**). These reactions led to the isolation of the corresponding products in 77 and 78% yields, respectively. The borylation of naphthalene yielded the 6- and 7-borylated products in the molar ratio of 1:3, whereas borylation of pyrene selectively gave the single product **2v**.

On the basis of the cobalt-catalyzed C−H borylation mechanism previously proposed[13] and our experiment results, the tentative mechanism for the borylation reaction is outlined in Scheme 5. It is reasoned that the cobalt(I) hydride **A** was generated in situ upon addition of $NaHBEt_3$ to precatalyst **1**. Unfortunately, many attempts to isolate and detect **A** were unsuccessful date. The oxidative-addition of B_2Pin_2 to **A** could lead to the intermediate **B**. Subsequently, the reductive elimination of HBPin from **B** yielded the active cobalt (I) boryl intermediate **C**. The C−H oxidative-addition of an arene to **C** followed by the reductive elimination of arylboronate ester regenerated the cobalt (I) hydride **A**. In the presence of cyclohexene, it reacted with the hydride **A** via coordinate-insertion to form the intermediate **E**. Subsequent reductive elimination yielded cyclohexane and $C_6H_{11}BPin$ with the generation of the cobalt boryl species **C** and hydride **A**, respectively. In the absence of cyclohexene, with the increase of the amounts of HBPin in the catalytic cycle the reductive elimination of **B** to form **C** could be suppressed, thus the catalytic cycle was interrupted.



Scheme 5. Proposed mechanism for [SiNSi]Co−catalyzed C−H borylation of arenes.

In summary, we reported the synthesis of the first bis(NHSi) pyridine cobalt complex. This well-defined complex enabled the facile and regioselective C–H borylation of fluorinated benzenes in high yields. In particular, the observed distinct regioselectivity from the known [PNP] cobalt catalyst suggested that NHSi ligands can be complementary to phosphine ligands and thus very promising for a wide scope of applications. Further studies to elucidate the differences of NHSi ligands from phosphine ligands are ongoing in our laboratories.

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Keywords: silylene • pincer ligand• cobalt • C−H borylation • silicon

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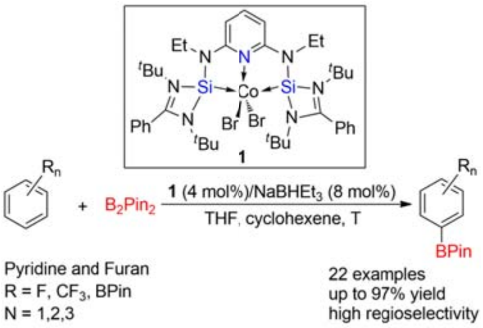
COMMUNICATION

Silylene in C-H Borylation. A new SiNSi cobalt pincer complex with two *N*-heterocyclic silylene (NHSi) arms enabled the direct and facile C-H borylation of heteroarenes and fluorinated arenes with complementary regioselectivity compared to previously reported transition-metal-based catalysts.



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Cobalt-Catalyzed Regioselective Borylation of Arenes: *N*-Heterocyclic Silylene as Electron Donors in Metal-Mediated Activation of C–H Bonds