# Selective Double Hydroboration and Dihydroborylsilylation of Organonitriles by an Iron–indium Cooperative Catalytic System

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# Selective double hydroboration and dihydroborylsilylation of organonitriles by an iron-indium cooperative catalytic system

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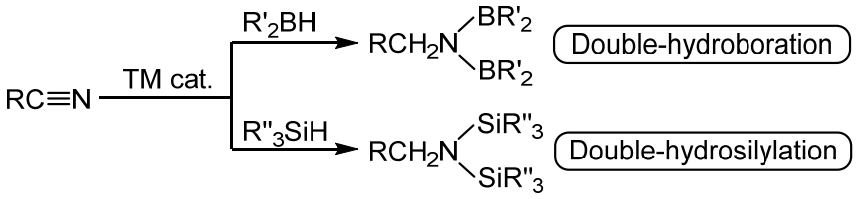
Double hydroboration, Dihydroborylsilylation, iron catalyst, indium, nitrile

**ABSTRACT:** Organonitriles (RC≡N) were selectively converted into the corresponding diborylamines ($RCH_2N(Bpin)_2$) in reactions with pinacolborane (pinBH) in the presence of a catalytic amount of iron-indium complex $[Fe(MeCN)_6][cis\text{-}Fe(CO)_4(InCl_3)_2]$. The catalytic reaction mechanism was tentatively proposed. In addition, this catalytic system was found to be applicable for the synthesis of borylsilylamine in high yield when organonitrile was treated with hydroborane and hydrosilane simultaneously.

## ■ INTRODUCTION

Selective bond formation among heteroatoms (E−E') is becoming important from the point of synthetic chemistry. In particular, the addition reaction of an E−H bond to an unsaturated bond between two elements involving at least one heteroatom is one of the most atom-economical synthetic methods to create an E−E' bond because it does not involve any by-products such as unnecessary inorganic salts or $H_2$ gas.[1] Among unsaturated bonds, the carbon-nitrogen triple bond in organonitrile is thought to be extremely stable because of its relatively high bond dissociation energy.[2] The inertness of the C ≡ N triple bond toward hydroboration and hydrosilylation under typical reaction conditions was reported.[3,4] However, it is expected that RC ≡ N would be converted into double hydroboration product, $RCH_2N(BR'_2)_2$, and double hydrosilylation product, $RCH_2N(SiR'_3)_2$, with the help of an appropriate catalyst. Recently, some double hydroboration reactions[5] and double hydrosilylations[6] at the C≡N triple bond were achieved by using a transition metal catalyst (Scheme 1).

**Scheme 1.** Double hydroboration and double hydrosilylation of organonitriles.




Those compounds bearing an N−B or N−Si bond are expected to exhibit an unusual function not displayed by organic compounds composed of carbon and hydrogen. For example, borylamine has a unique reactivity as an iminium ion generator.[7] Although the examples are few,

it has already been reported that disilylamines are useful as precursors for the production of Si/N-containing polymers,[8] new types of amine ligands in organometallic chemistry,[9] and silylating agents for the syntheses of silicon compound.[10] Moreover, hydroboration and hydrosilylation of C≡N bonds are effective methods to reduce organonitriles.[11] In addition, it was found that borylsilylamines are advantageous precursors to obtain the B/Si/N/C ceramics which has highly heat-resistant property.[12]

We previously demonstrated an unprecedented double hydrosilylation of organonitriles catalyzed by an ionic iron-indium complex ([$Fe(MeCN)_6$][*cis*-$Fe(CO)_4(InCl_3)_2$] (**$FeIn_{Cl}$**)), prepared by the reaction of $Fe_3(CO)_{12}$ with $InCl_3$.[13,14] Herein, we pursued the possibility of selective double hydroboration using the Fe/In catalyst. In addition, we challenged to achieve single-step synthesis of borylsilylamine by an unprecedented dihydroborylsilylation of organonitrile using **$FeIn_{Cl}$** catalyst.

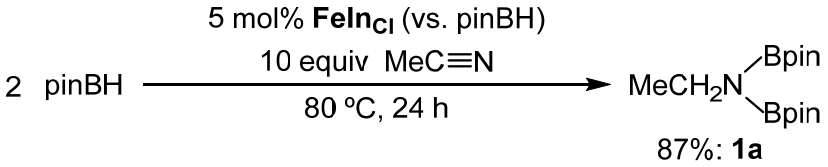
## ■ RESULTS AND DISCUSSION

### Selective double hydroboration of organonitriles catalyzed by $FeIn_{Cl}$.

Our previous report that **$FeIn_{Cl}$** exhibited a catalytic activity for the double hydrosilylation of a C≡N bond inspired us to examine the double hydroboration. A reaction of pinacolborane (pinBH) with an excess amount (5 equiv) of acetonitrile (MeCN) in the presence of 5 mol% of **$FeIn_{Cl}$** with respect to pinBH was examined at 80 °C for 24 h under a dry argon atmosphere (Scheme 2). Quantitative conversion of pinBH into diborylamine $EtN(Bpin)_2$ took place according to the $^1$H NMR spectrum of the reaction mixture. No signals corresponding to the borylimine (mono hydroboration compound) were observed. The reaction mixture obtained was distilled using a Kugelrohr apparatus in a glove box to afford the corresponding diborylamine as

colorless crystals in 87% yield. The double hydroboration reaction did not proceed when the reaction mixture was not heated at 80 °C, when only $InCl_3$ or only $Fe_3(CO)_{12}$ was used as a catalyst.

**Scheme 2.** Double hydroboration of MeCN in the presence of $\mathbf{FeIn_{Cl}}$.

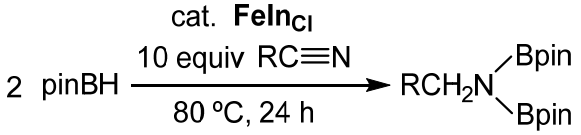


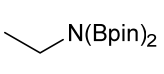
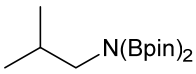
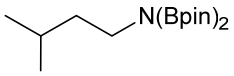
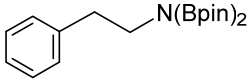
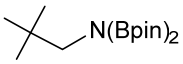
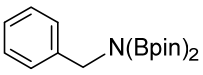
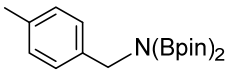
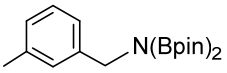
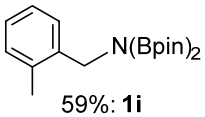
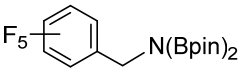
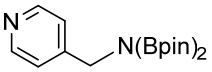
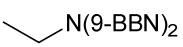
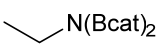
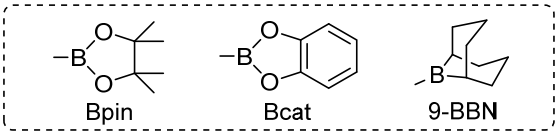

The results of the reactions of pinacolborane (pinBH) with several organonitriles in the presence of $\mathbf{FeIn_{Cl}}$ catalyst are shown in Table 1. Various aliphatic and aromatic nitriles (RC≡N, for which R = Me, $^i$Pr, $^i$Bu, $^t$Bu, Ph, Bzl, *p*-Tol, *m*-Tol or *o*-Tol) were converted into the corresponding double hydroboration products; pure diborylamines $RCH_2N(Bpin)_2$ **1a**–**1i** were obtained in good to excellent yields by distillation using a Kugelrohr apparatus in a glove box. Some organonitriles with electron-withdrawing substituents, such as $CCl_3$ and $C_6F_5$ groups, were not converted into the corresponding hydroboration products. Although the tendency of the double hydroboration was similar to that of the double hydrosilylation, the following differences were observed: (i) $^t$BuCN was reactive in the double hydroboration but not in the double hydrosilylation, (ii) 4-PyCN did not react in the double hydroboration but reacted in the double hydrosilylation.

Regarding hydroborane used in double hydroboration of organonitriles, most of the reports are research on pinBH. Quite recently, the double hydroboration with catechol borane (catBH) have been reported using Mo catalyst[5c,e] and Ni catalyst.[5f] In both catalytic systems, the double

hydroboration proceeds at room temperature within 18 h. Therefore, we examined the reaction of MeCN with catBH in the presence of **FeIn$_{Cl}$** at room temperature for 18 h, and found that the double hydroboration product EtN(Bcat)$_2$ **2** was obtained in 81% yield. Therefore, it was found that **FeIn$_{Cl}$** serves as a catalyst for both pinBH and catBH. To our best knowledge, **FeIn$_{Cl}$** is the first transition metal complex showing catalytic activity in the double hydroboration of organonitirle with both pinBH and catBH. We also examined the catalytic activity of **FeIn$_{Cl}$** toward 9-borabicyclo[3.3.1]nonane (9-BBN), and found that no catalytic activity was observed in this case.

**Table 1.** Double hydroboration of organonitriles in the presence of **FeIn$_{Cl}$**.[a,b]




| | | | |
|---|---|---|---|
|  87%: **1a** |  71%: **1b** |  58%: **1c** |  58%: **1d** |
|  51%: **1e** |  65% (81%)[c]: **1f** |  64%: **1g** |  47%: **1h** |
|  59%: **1i** |  0% |  0% |  0% |
|  0% |  81%[d]: **2** |  Bpin Bcat 9-BBN | |

[a]See the experimental section for details of the reaction conditions. [b]Isolated yield. [c]10 mol% **FeIn$_{Cl}$** was used. [d]Catechol borane was used at room temperature for 18 h.

The molecular structures of $EtN(Bpin)_2$ **1a** and $PhCH_2N(Bpin)_2$ **1f** were confirmed by X-ray analysis. The ORTEP drawings of these compounds are depicted in Figure 1 with the atomic numbering scheme. The selected bond lengths and angles are listed in Table 2. The B–N bond lengths of **1a** (1.423(3) and 1.425(3) Å) and **1f** (1.4246(18) and 1.4291(19) Å) resemble those of previously reported compounds (1.407(6)–1.436(2) Å) and the B–N–B bond angle of **1a** (126.93(18)°) and **1f** (126.29(12)°) are slightly broader than those of previously reported compounds (122.97(14)–125.51(10)°) because of steric repulsion between two Bpin groups and less bulky substituent on the N atom.[5f, 15]

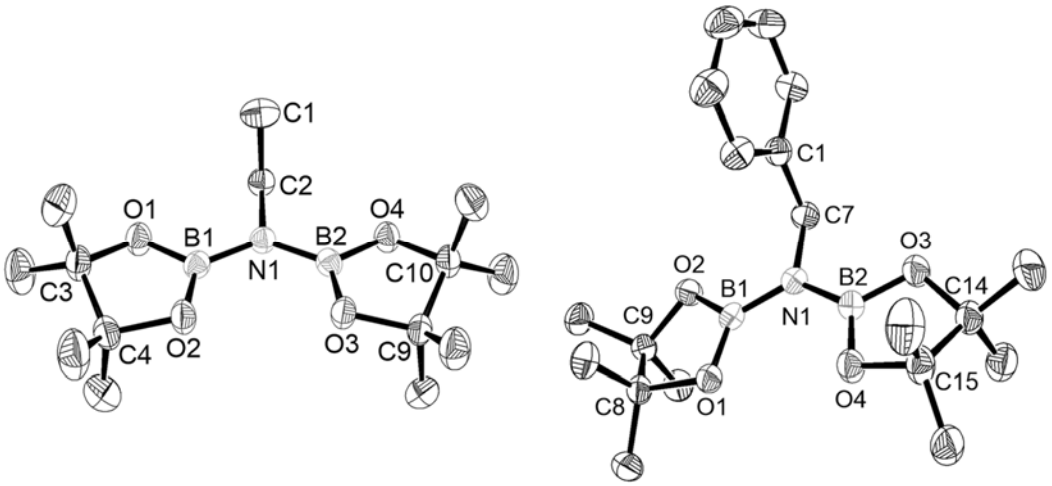


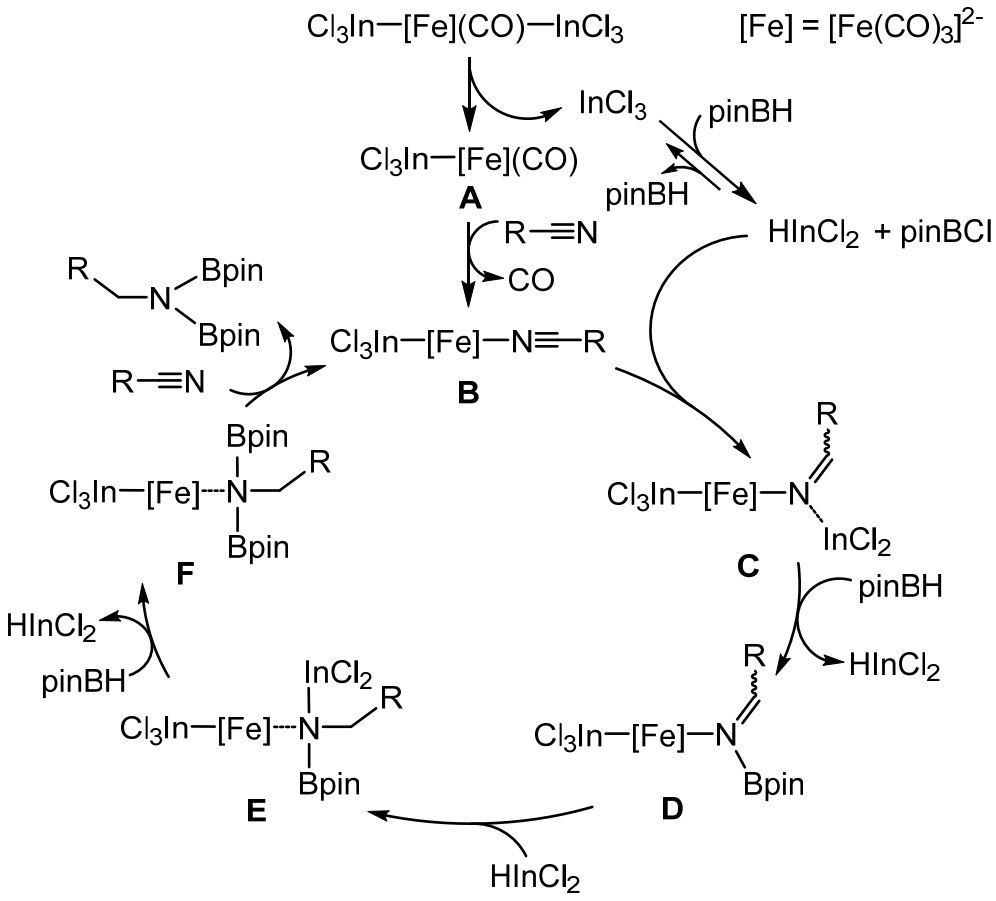

**Figure 1.** ORTEP drawings of $EtN(Bpin)_2$ **1a** (left) and $PhCH_2N(Bpin)_2$ **1f** (right) with 50% thermal ellipsoidal plots. All hydrogen atoms are omitted for clarity.

**Table 2.** Selected bond lengths (Å) and bond angles (°) for **1a** and **1f**

| | **1a** | **1f** |
|---|---|---|
| N1–B1 | 1.425(3) | 1.4246(18) |
| N1–B2 | 1.423(3) | 1.4291(19) |
| N1–C2(C7 for **1f**) | 1.484(3) | 1.4765(18) |
| | | |
| B1–N1–B2 | 126.93(18) | 126.29(12) |
| B1–N1–C2(C7 for **1f**) | 116.01(18) | 117.03(11) |
| B2–N1–C2(C7 for **1f**) | 116.83(18) | 116.56(11) |

A tentative catalytic cycle for the double hydroboration of organonitriles promoted by **FeIn$_{Cl}$** was proposed (Scheme 3). First, one $InCl_3$ of **FeIn$_{Cl}$** dissociates to give the mono-indium iron complex **A**, and then a CO ligand in **A** is substituted by the organonitrile to give **B**. The reaction was examined in which 5 equiv of $InCl_3$ to **FeIn$_{Cl}$** was added under same conditions in Scheme 2, and it was found that no double hydroboration product was generated. This result suggests that the reaction mechanism involves the dissociation of $InCl_3$ from the iron center in **FeIn$_{Cl}$**. We also examined the reaction of pinBH with $InCl_3$ in acetnitrile-$d_3$ and confirmed the formation of pinBCl[16] by the NMR measurement of the reaction mixture. These experimental results support the process where the released $InCl_3$ reacts with pinBH to give $HInCl_2$[17] and pinBCl. $HInCl_2$ thus formed reacts with RCN in **B**, which is more reactive than free RCN,[18] to produce indylimine iron complex **C**, which then reacts with pinBH to yield borylimine iron complex **D**. Complex **D** undergoes a similar reaction to **B** and **C** to produce diborylamine iron complex **F** through **E**. Finally, dissociation of the diborylamine from the iron center in **F** and recoordination of an organonitrile to the iron center takes place to regenerate the catalytic intermediate **B**. As the diborylamine is selectively formed over borylimine, we believe that **D** reacts with $HInCl_2$ to give **E** faster than the dissociation of the borylimine ligand from **D**.

**Scheme 3.** Presumed catalytic cycle for the double hydroboration of organonitriles in the presence of **FeIn$_{Cl}$**.

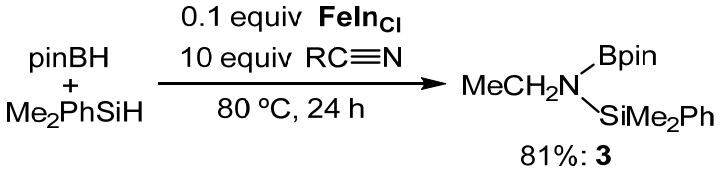



**Selective dihydroborylsilylation of organonitrile catalyzed by FeIn$_{Cl}$.**

We have described the double hydrosilylation of organonitriles using the Fe/In catalyst in the previous paper[13] and the double hydroboration in this paper. As the extension of these reactions using Fe/In cooperative catalytic system, we examined the reaction of organonitrile with both of hydroborane and hydrosilane in the presence of **FeIn$_{Cl}$** catalyst with the hope of the formation of borylsilylamine. Several combinations of organonitrile, hydroborane, and hydrosilane were examined, and it was found that the reaction of $CH_3CN$ with both of pinBH and $Me_2PhSiH$ in the presence of **FeIn$_{Cl}$** catalyst showed excellent results: the corresponding

ethylborylsilylamine, EtN(Bpin)($SiMe_2Ph$) was the main product (Scheme 4), and that $EtN(Bpin)_2$ was formed in only 6% yield (according to NMR). Purification of the product by distillation using a Kugelrohr apparatus in a globe box afforded pure EtN(Bpin)($SiMe_2Ph$) **3** in 81% yield. This reaction is the first single-step synthesis of a borylsilylamine *via* the catalytic hydroboration and hydrosilylation of an organonitrile.[19]

**Scheme 4.** Dihydroborylsilylation of MeCN in the presence of $\mathbf{FeIn_{Cl}}$.




## ■ CONCLUSION

We have developed selective double hydroboration and dihydroborylsilylation of organonitriles catalyzed by an iron-indium cooperative complex. The iron-indium cooperative reaction is an unprecedented catalytic system in double hydroboration. It should be noted that we have achieved the first single-step synthesis of a borylsilylamine.

## ■ EXPERIMENTAL SECTION

### General considerations

All manipulations were performed using standard Schlenk techniques or in a glove box under a dry argon atmosphere. The iron-indium complexes $[Fe(CH_3CN)_6][cis\text{-}Fe(CO)_4(InCl_3)_2]$ ($\mathbf{FeIn_{Cl}}$) was prepared according to the literature methods.[14] The other chemicals were commercially available. Solvents were purified employing a two-column solid-state purification system or were distilled from appropriate drying agents under nitrogen. NMR spectra ($^1$H,

$^{11}B\{^1H\}$, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$) were recorded at ambient temperature using a JEOL JNM AL-400 spectrometer. $^1H$ and $^{13}C\{^1H\}$ NMR data were referred to residual peaks of solvent as an internal standard. Peak positions of the $^{11}B\{^1H\}$ and $^{29}Si\{^1H\}$ NMR spectra were referenced to an external $BF_3 \cdot Et_2O$ ($\delta$ = 0 ppm) and $Me_4Si$ ($\delta$ = 0 ppm), respectively. Elemental analysis data were obtained on a Perkin-Elmer 2400 CHN elemental analyzer. GC/MS analyses were carried out by SIMADZU-QP2010 Plus, equipped with a Rtx-5MS capillary column and an ion trap detector. ESI-MS imaging experiments were performed on a 7.0 T solariX FT-ICR MS (Bruker Daltonics) in positive-ion mode.

**General method for synthesis of diborylamines**

Organonitrile (4.0 mmol) was treated with pinBH (0.80 mmol) in the presence of **$FeIn_{Cl}$** (36.5 mg, 0.040 mmol) at 80 °C for 24 h. The reaction mixture was distilled using a Kugelrohr apparatus in a glove box to obtain the corresponding diborylamine.

**Spectroscopic data of 1a**

$^1H$ NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 1.02 (t, $J_{H\text{-}H}$ = 7.2 Hz, 3H, $CH_2C\underline{H}_3$), 1.22 (s, 24H, Bpin), 3.05 (q, $J_{H\text{-}H}$ = 7.1 Hz, 2H, $NC\underline{H}_2CH_3$). $^{11}B\{^1H\}$ NMR (79.3 MHz, $CDCl_3$, ppm): $\delta$ 25.49 (br). $^{13}C\{^1H\}$ NMR (100.4 MHz, $CDCl_3$, ppm): $\delta$ 18.79 (s, $NCH_2\underline{C}H_3$), 24.65 (s, Bpin-$\underline{C}H_3$), 38.73 (s, $N\underline{C}H_2CH_3$), 82.14 (s, Bpin-*ipso*). Elemental analysis (%) calcd for $C_{14}H_{29}B_2NO_4$: C, 56.62; H,9.84; N, 4.72; found: C, 56.27; H, 9.80; N, 4.66%. GC/MS (EI) *m/z* (% relative intensity): $[M]^+$ 297 (2), $[M\text{-}CH_3]^+$ 282 (100), 254 (1), 240 (9), 182 (14), 156 (24), 112 (67).

**Spectroscopic data of 1b**

$^{1}$H NMR (400 MHz, $C_6D_6$, ppm): δ 0.82 (d, 6H, *J* = 6.8 Hz, $NCH_2CH(C\underline{H}_3)_2$), 1.21 (s, 24H, Bpin), 1.62 (tsep., 1H, *J* = 6.8 Hz, $NCH_2C\underline{H}(CH_3)_2$), 2.84 (d, 2H, *J* = 7.0 Hz, $NC\underline{H}_2CH(CH_3)_2$). $^{11}$B{$^{1}$H} NMR (79.3 MHz, $CDCl_3$, ppm): δ 25.51 (br). $^{13}$C{$^{1}$H} NMR (100.4 MHz, $C_6D_6$, ppm): δ 20.05 (s, $NCH_2CH(\underline{C}H_3)_2$), 24.62 (s, Bpin-$\underline{C}H_3$), 30.91 (s, $NCH_2\underline{C}H(CH_3)_2$), 51.16 (s, $N\underline{C}H_2CH(CH_3)_2$), 82.16 (s, Bpin-*ipso*). Elemental analysis (%) calcd for $C_{16}H_{33}B_2NO_4$: C, 59.12; H, 10.23; N, 4.31; found: C, 58.47; H, 10.26; N, 3.83%. HRMS (ESI) *m/z* (% relative intensity): $[M+Na]^+$ Calcd. for $C_{16}H_{33}B_2NNaO_4$: 348.2493; Found: 348.2486.

**Spectroscopic data of 1c**

$^{1}$H NMR (400 MHz, $CDCl_3$, ppm): δ 0.86 (d, 6H, *J* = 6.8 Hz, $NCH_2CH_2CH(C\underline{H}_3)_2$), 1.21 (s, 24H, Bpin), 1.25-1.29 (m, 2H, $NCH_2C\underline{H}_2CH(CH_3)_2$), 1.56 (tsep., 1H, *J* = 6.8 Hz, $NCH_2CH_2C\underline{H}(CH_3)_2$), 3.03 (t, 2H, *J* = 7.0 Hz, $NC\underline{H}_2CH_2CH(CH_3)_2$). $^{11}$B{$^{1}$H} NMR (79.3 MHz, $CDCl_3$, ppm): δ 25.49 (br). $^{13}$C{$^{1}$H} NMR (100.4 MHz, $CDCl_3$, ppm): δ 22.95 (s, $NCH_2CH_2CH(\underline{C}H_3)_2$), 24.62 (s, Bpin-$\underline{C}H_3$), 25.20 (s, $NCH_2CH_2\underline{C}H(CH_3)_2$), 41.85 (s, $NCH_2\underline{C}H_2CH(CH_3)_2$), 42.50 (s, $N\underline{C}H_2CH_2CH(CH_3)_2$), 82.11 (s, Bpin-*ipso*). Elemental analysis (%) calcd for $C_{17}H_{35}B_2NO_4$: C, 60.22; H, 10.40; N, 4.13; found: C, 59.65; H, 10.53; N, 3.72%. HRMS (ESI) *m/z* (% relative intensity): $[M+Na]^+$ Calcd. for $C_{17}H_{35}B_2NNaO_4$: 362.2650; Found: 362.2655.

**Spectroscopic data of 1d**

$^{1}$H NMR (400 MHz, $CDCl_3$, ppm): δ 1.17 (s, 24H, Bpin), 2.70 (t, *J* = 7.0 Hz, 2H, $NC\underline{H}_2CH_2$), 3.29 (t, *J* = 7.0 Hz, 2H, $NCH_2C\underline{H}_2$) 7.12-7.19 (m, 3H, Ph), 7.22-7.26 (m, 2H, Ph). $^{11}$B{$^{1}$H} NMR (79.3 MHz, $CDCl_3$, ppm): δ 25.40 (br). $^{13}$C{$^{1}$H} NMR (100.4 MHz, $CDCl_3$, ppm): δ 24.62 (s,

Bpin-$\underline{C}H_3$), 39.56 (s, $NCH_2\underline{C}H_2$), 45.31 (s, $N\underline{C}H_2CH_2$), 82.21 (s, Bpin-*ipso*), 125.78 (s, Ph), 128.21 (s, Ph), 129.42 (s, Ph), 140.62 (s, Ph-*ipso*). Elemental analysis (%) calcd for $C_{20}H_{33}B_2NO_4$: C, 64.38; H, 8.92; N, 3.75; found: C, 64.03; H, 9.04; N, 3.75%. HRMS (ESI) *m/z* (% relative intensity): $[M+Na+CH_3CN]^+$ Calcd. for $C_{20}H_{33}B_2NO_4$: 396.24934; Found: 396.24975.

**Spectroscopic data of 1e**

$^1H$ NMR (400 MHz, $CDCl_3$, ppm): δ 0.81 (s, 9H, $NCH_2C(C\underline{H}_3)_3$), 1.21 (s, 24H, Bpin), 2.87 (s, 2H, $NC\underline{H}_2C(CH_3)_3$). $^{11}B\{^1H\}$ NMR (79.3 MHz, $CDCl_3$, ppm): δ 25.45 (br). $^{13}C\{^1H\}$ NMR (100.4 MHz, $CDCl_3$, ppm): δ 24.59 (s, Bpin-$\underline{C}H_3$), 27.41 (s, $NCH_2C(\underline{C}H_3)_3$), 33.30 (s, $NCH_2\underline{C}(CH_3)_3$), 54.58 (s, $N\underline{C}H_2C(CH_3)_3$), 82.27 (s, Bpin-*ipso*). Elemental analysis (%) calcd for $C_{17}H_{35}B_2NO_4$: C, 60.22; H, 10.40; N, 4.13; found: C, 60.02; H, 10.55; N, 3.88%. HRMS (ESI) *m/z* (% relative intensity): $[M+Na]^+$ Calcd. for $C_{17}H_{35}B_2NNaO_4$: 362.2650; Found: 362.2649.

**Spectroscopic data of 1f**

$^1H$ NMR (400 MHz, $CDCl_3$, ppm): δ 1.20 (s, 24H, Bpin), 4.23 (s, 2H, $NCH_2$), 7.13-7.18 (m, 1H, Ph), 7.22-7.25 (m, 2H, Ph), 7.29-7.31 (m, 2H, Ph). $^{11}B\{^1H\}$ NMR (79.3 MHz, $CDCl_3$, ppm): δ 25.51 (br). $^{13}C\{^1H\}$ NMR (100.4 MHz, $CDCl_3$, ppm): δ 24.65 (s, Bpin-$\underline{C}H_3$), 47.39 (s, $NCH_2$), 82.46 (s, Bpin-*ipso*), 126.18 (s, Ph), 127.64 (s, Ph), 127.92 (s, Ph), 143.20 (s, Ph-*ipso*). Elemental analysis (%) calcd for $C_{19}H_{31}B_2NO_4$: C, 63.55; H, 8.70; N, 3.90; found: C, 63.26; H, 8.80; N, 3.85%. HRMS (ESI) *m/z* (% relative intensity): $[M+Na+CH_3CN]^+$ Calcd. for $C_{21}H_{34}B_2N_2NaO_4$: 423.2602; Found: 423.2602.

**Spectroscopic data of 1g**

$^{1}$H NMR (400 MHz, $CDCl_3$, ppm): δ 1.20 (s, 24H, Bpin), 2.30 (s, 3H, *p*-($C\underline{H}_3$)$C_6H_4$), 4.19 (s, 2H, $NCH_2$), 7.05 (d, 2H, $J_{H\text{-}H}$ = 8.0 Hz, *p*-($CH_3$)$C_6\underline{H}_4$), 7.19 (d, $J_{H\text{-}H}$ = 8.0 Hz, 2H, *p*-($CH_3$)$C_6\underline{H}_4$). $^{11}$B{$^{1}$H} NMR (79.3 MHz, $CDCl_3$, ppm): δ 25.65 (br). $^{13}$C{$^{1}$H} NMR (100.4 MHz, $CDCl_3$, ppm): δ 21.20 (s, *p*-($\underline{C}H_3$)$C_6H_4$), 24.65 (s, Bpin-$\underline{C}H_3$), 47.03 (s, $NCH_2$) , 82.41 (s, Bpin-*ipso*), 127.57 (s, *p*-Tol), 128.60 (s, *p*-Tol), 135.52 (s, *p*-Tol-*ipso*), 140.19 (s, *p*-Tol-*ipso*). Elemental analysis (%) calcd for $C_{20}H_{33}B_2NO_4$: C, 64.38; H, 8.92; N, 3.75; found: C, 64.12; H, 9.02; N, 3.59%. HRMS (ESI) *m/z* (% relative intensity): $[M+Na+CH_3CN]^+$ Calcd. for $C_{22}H_{36}B_2N_2NaO_4$: 437.2756; Found: 437.2755.

**Spectroscopic data of 1h**

$^{1}$H NMR (400 MHz, $CDCl_3$, ppm): δ 1.20 (s, 24H, Bpin), 2.30 (s, 3H, *m*-($C\underline{H}_3$)$C_6H_4$), 4.20 (s, 2H, $NCH_2$), 6.96-7.15 (m, 4H, *m*-($CH_3$)$C_6\underline{H}_4$). $^{11}$B{$^{1}$H} NMR (79.3 MHz, $CDCl_3$, ppm): δ 25.53 (br). $^{13}$C{$^{1}$H} NMR (100.4 MHz, $CDCl_3$, ppm): δ 21.54 (s, *p*-($\underline{C}H_3$)$C_6H_4$), 24.65 (s, Bpin-$\underline{C}H_3$), 47.26 (s, $NCH_2$) , 82.44 (s, Bpin-*ipso*), 124.63 (s, *m*-Tol), 126.86 (s, *m*-Tol), 127.82 (s, *m*-Tol), 128.42 (s, *m*-Tol), 137.35 (s, *m*-Tol-*ipso*), 143.08 (s, *m*-Tol-*ipso*). Elemental analysis (%) calcd for $C_{20}H_{33}B_2NO_4$: C, 64.38; H, 8.92; N, 3.75; found: C, 64.13; H, 9.05; N, 3.46%. HRMS (ESI) *m/z* (% relative intensity): $[M+Na]^+$ Calcd. for $C_{20}H_{33}B_2NNaO_4$: 396.2493; Found: 396.2483.

**Spectroscopic data of 1i**

$^{1}$H NMR (400 MHz, $CDCl_3$, ppm): δ 1.21 (s, 24H, Bpin), 2.33 (s, 3H, *m*-($C\underline{H}_3$)$C_6H_4$), 4.25 (s, 2H, $NCH_2$), 7.09-7.16 (m, 3H, *o*-($CH_3$)$C_6\underline{H}_4$), 7.25-7.30 (m, 1H, *o*-($CH_3$)$C_6\underline{H}_4$). $^{11}$B{$^{1}$H} NMR (79.3 MHz, $CDCl_3$, ppm): δ 25.55 (br). $^{13}$C{$^{1}$H} NMR (100.4 MHz, $CDCl_3$, ppm): δ 19.53 (s, *o*-($\underline{C}H_3$)$C_6H_4$), 24.80 (s, Bpin-$\underline{C}H_3$), 45.17 (s, $NCH_2$), 82.68 (s, Bpin-*ipso*), 125.73 (s, *o*-Tol),

126.04 (s, *o*-Tol), 126.50 (s, *o*-Tol), 129.81 (s, *o*-Tol), 135.54 (s, *o*-Tol-*ipso*), 141.01 (s, *o*-Tol-*ipso*). Elemental analysis (%) calcd for $C_{20}H_{33}B_2NO_4$: C, 64.38; H, 8.92; N, 3.75; found: C, 63.63; H, 8.92; N, 3.51%. HRMS (ESI) *m/z* (% relative intensity): $[M+Na]^+$ Calcd. for $C_{20}H_{33}B_2NNaO_4$: 396.2493; Found: 396.2493.

**Synthesis of EtN(Bcat)$_2$ 2**

Acetonitrile (418 $\mu$L, 8.0 mmol) was treated with catBH (170 $\mu$L, 1.6 mmol) in the presence of **FeIn$_{Cl}$** (73 mg, 0.08 mmol) at room temparature for 18 h. The reaction mixture was dried under vacuo and then extracted with $C_6H_6$ (4 mL × 2). The solution was concentrated to dryness to give EtN(Bcat)$_2$ **2** (182 mg, 81%) as a white powder. Compound **2** was identified by comparing their $^1$H and $^{11}$B NMR data with those previously reported.[5c,h]

**Synthesis of silylborylamine EtN(Bpin)(SiMe$_2$Ph) 3**

Acetonitrile (209 $\mu$L, 4.0 mmol) was treated with pinBH (58 $\mu$L, 0.40 mmol) and $Me_2PhSiH$ (62 $\mu$L, 0.40 mmol) in the presence of **FeIn$_{Cl}$** (36.5 mg, 0.040 mmol) at 80 °C for 24 h. The reaction mixture was distilled using a Kugelrohr apparatus in a glove box to obtain the corresponding borylsilylamine (98.9 mg, 0.324 mmol, 81%) as a colorless oil. $^1$H NMR (400 MHz, $C_6D_6$, ppm): δ 0.56 (s, 6H, Si-$CH_3$), 1.06 (s, 12H, Bpin), 1.11 (t, $J_{H\text{-}H}$ = 7.2 Hz, 3H, $NCH_2C\underline{H}_3$), 3.11 (q, $J_{H\text{-}H}$ = 7.1 Hz, 2H, $NC\underline{H}_2CH_3$), 7.16-7.28 (m, 3H, Ph), 7.66-7.69 (m, 2H, Ph). $^{11}$B{$^1$H} NMR (79.3 MHz, $C_6D_6$, ppm): δ 25.68 (br). $^{13}$C{$^1$H} NMR (100.4 MHz, $C_6D_6$, ppm): δ -0.19 (s, Si-$CH_3$), 19.73 (s, $NCH_2\underline{C}H_3$), 24.64 (s, Bpin-$\underline{C}H_3$), 39.41 (s, $N\underline{C}H_2CH_3$), 81.78 (s, Bpin-*ipso*), 127.94 (s, Ph), 129.22 (s, Ph), 134.13 (s, Ph), 140.28 (s, Ph-*ipso*). $^{29}$Si{$^1$H} NMR (79.3 MHz, $C_6D_6$, ppm): δ 1.57 (s). GC/MS (EI) *m/z* (% relative intensity): $[M]^+$ 305 (5), $[M–CH_3]^+$ 290 (84), 232 (10),

208 (100). HRMS (DART) *m/z* (% relative intensity): $[M+H]^+$ Calcd. for $C_{16}H_{28}BNO_2Si$: 306.2061; Found: 306.2053. Elemental analysis was not obtained due to its incombustibility.

**X-ray crystallography measurements**

X-ray intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo-Kα radiation. Calculations were performed with the CrystalClear software package of Molecular Structure Corporation. The structures were solved by direct methods and expanded using Fourier techniques. The structures were refined by full matrix least-squares technique using the program ShelXL-97[20] or ShelXL-2014[21]. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions.

ASSOCIATED CONTENT

**Supporting Information**. The Supporting Information is available free of charge on the

ACS Publications website at DOI:

NMR spectra of the obtained compounds and crystal data for **1a** and **1f** are given in Supporting Information.

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**Notes**

The authors declare no competing financial interest.

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**BRIEFS:** Iron-indium complex, $[Fe(MeCN)_6][cis\text{-}Fe(CO)_4(InCl_3)_2]$, catalyzes double hydroboration selectively in the reaction of organonitrile with hydroborane to give diborylamine. The complex catalyzes also dihydroborylsilylation in the reaction of organonitrile with hydroborane and hydrosilane to give borylsilylamine.