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Cobalt-Catalyzed C–H Borylation of Alkyl Arenes and Heteroarenes Including the First Selective Borylations of Secondary Benzylic C–H Bonds

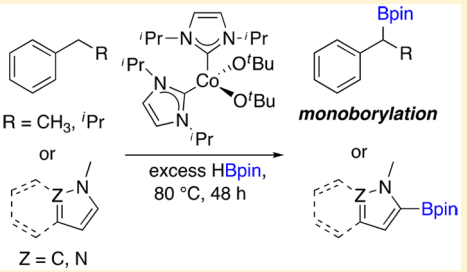
Chathurika R. K. Jayasundara,[†] Dmitrijs Sabasovs,[†] Richard J. Staples,[†] Jossian Oppenheimer,*[,‡] Milton R. Smith, III,*[,†] and Robert E. Maleczka, Jr.*[,†]

[†]Department of Chemistry, Michigan State University, 578 South Shaw Lane, East Lansing, Michigan 48824, United States

[‡]The Dow Chemical Company, Process Chemistry & Development, Core R&D, Midland, Michigan 48674, United States

Supporting Information

ABSTRACT: A cobalt di-*tert*-butoxide complex bearing N-heterocyclic carbene (NHC) ligands has been synthesized and characterized. This complex is effective at catalyzing the selective monoborylation of the benzylic position of alkyl arenes using pinacolborane (HBpin) as the boron source. This same cobalt complex enables selective monoborylation of *N*-methylpyrrole, *N*-methylpyrazole, and *N*-methylindole. Catalysis can be achieved with as little as 2–3 mol % of the cobalt precatalyst at 80 °C.



INTRODUCTION

Catalytic C–H borylation (CHB) is a proven method for making organoboron compounds.[1] Precious metal catalysts based on Ir,[1] Pt,[2] and Rh[1] are among those known to promote CHBs. Recently, multiple efforts have focused on developing earth-abundant catalysts for CHBs. Fe-,[3] Co-,[4] Ni-,[5] and Fe–Cu-catalyzed[6] as well as metal-free C–H[7] functionalizations have been described. Most catalysts functionalize C(sp^2)–H bonds, while CHBs of unactivated C(sp^3)–H bonds usually require directing groups,[8] highly active substrates,[9] and/or high temperatures.[10] A handful of nondirected methods have been reported for selective functionalization of benzylic C–H bonds.[8]

Chirik and co-workers have recently synthesized geminal diboronates and polyboronate compounds, via CHBs of both benzylic and unactivated C(sp^3)–H bonds using 5–20 mol % of an air-stable α-diimine cobalt bis(carboxylate) catalyst (Scheme 1a).[11] They subsequently showed that an α-diimine nickel compounds can catalyze chemoselective triborylation of benzylic C(sp^3)–H bonds by B_2pin_2.[12] Huang and co-workers have reported that 1,1,1-tris(boronates) substituted at homobenzylic carbons can be efficiently and selectively prepared from styrenes and B_2pin_2 with Co(I) precatalysts (Scheme 1b).[13] These reactions proceed via Co-catalyzed double dehydrogenative borylation of vinylarenes and subsequent hydroboration of 1,1-diborylalkene intermediates with in situ generated HBpin. Benzylic CHBs have also been described by Lin and co-workers using a metal–organic framework (MOF) with catalytically active cobalt nodes (Scheme 1c).[14] In this case, reaction times at 103 °C with 0.20 mol % of Co ranged from 48 to 144 h.

Herein, we report a new and complementary Co precatalyst (**A**) that mediates mono- and diborylations of benzylic C(sp^3)–H bonds with ∼3 mol % Co precatalyst loadings in neat substrates at 80 °C (Scheme 1d). Notably, in addition to the monoborylation of benzylic C–H bonds, this precatalyst was effective for monoborylation of nitrogen-containing heterocycles such as *N*-methylpyrrole, *N*-methylpyrazole, and *N*-methylindole. This is the first report of Co-catalyzed CHBs of *N*-methylpyrrole and *N*-methylpyrazole.

RESULTS AND DISCUSSION

Our choice of Co complex **A** to explore catalytic CHBs was motivated by Herrmann's Rh and Ir N-heterocyclic carbene complexes that facilitate CHBs of arene C(sp^2)–H bonds.[15] Given this precedent, we wondered if NHC complexes of Co, the lightest group 9 element, would behave like Herrmann's catalysts.

Cobalt complex **A** was synthesized by reacting $CoCl_2$ with potassium *tert*-butoxide and 1,3-diisopropyl-1*H*-imidazol-3-ium chloride in THF (Scheme 2). Recrystallization from pentane afforded single crystals suitable for X-ray diffraction studies (Figure 1). There are three broad resonances (41.70, 39.00, 8.76, 2.31 ppm) in the ^{1}H NMR spectrum (C_6D_6) of **A**. Assignments for the O-*t*-Bu and NHC ligand methyl protons can be made on the basis of integrations. The lowest intensity resonances (δ 41.70 and δ 39.00) are due to the NHC ligand's isopropyl methine and imidazolyl ring protons. Application of the Evans method yields μ_{eff} = 4.20 μ_B for **A**. Although **A** is air-

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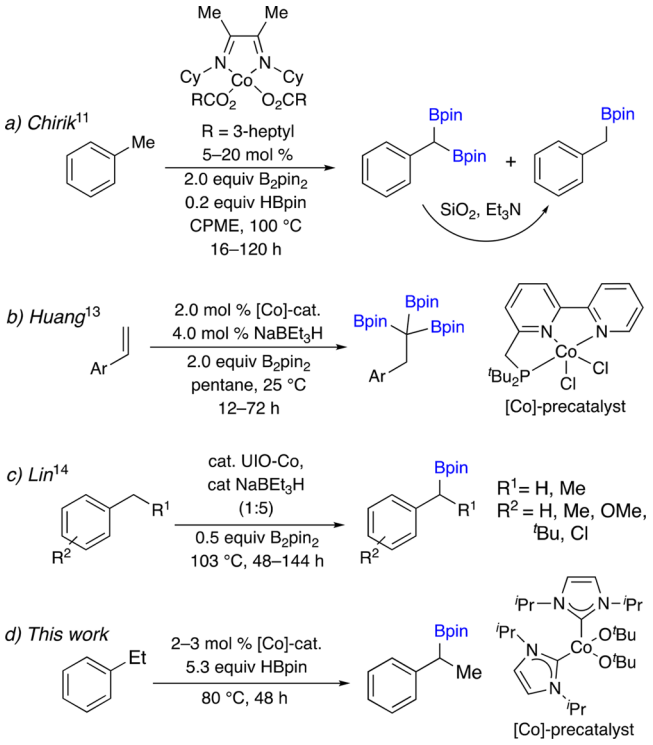
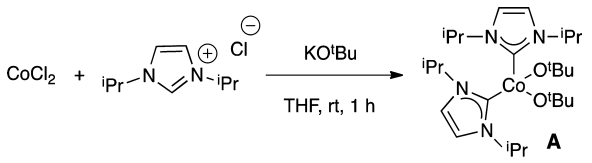
Scheme 1. Cobalt-Mediated Syntheses of Polyborylated sp^3 Carbon Centers



Scheme 2. Synthesis of Cobalt Complex A



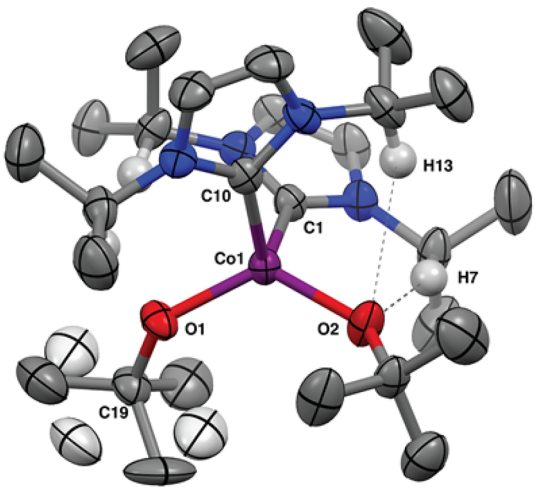


Figure 1. X-ray structure for Co complex **A** (CCDC 1535519) with thermal ellipsoids calculated at 50% probability levels. Selected bond distances (Å) and angles (deg): Co1–O1 1.899(2), Co1–O2 1.888(2), Co1–C1 2.076(3), Co1–C10 2.076(3); O1–Co1–C1 111.2(1), O1–Co1–C10 102.6(1), O2–Co1–O1 123.4(1), O2–Co1–C1 102.6(1), O2–Co1–C10 110.1(1), C1–Co1–C10 106.0(1).

sensitive, it has remained active for more than 1 year when stored at −35 °C.

The structure of **A**, shown in Figure 1, reveals a distorted-tetrahedral geometry with rotational disorder of the methyl group about the O1–C19 vector in one O-*t*-Bu ligand. The bond angles with Co at the vertex range from 102.6° for ∠O1–Co1–C10 and ∠O2–Co1–C1 to 123.4° for ∠O2–Co1–O1. There are close contacts between the O-*t*-Bu O atoms and the methine H atoms of the NHC isopropyl groups, as represented by H13–O2 and H7–O2 distances of 2.698 and 2.112 Å, respectively. The latter O–H distance is typical for structures with O···H hydrogen bonding. However, the short O···H distances in **A** could simply be geometric consequences of the sterically most favored orientation of bulky *i*-Pr and *t*-Bu groups.

With Co complex **A** in hand, we explored its proclivity for CHBs. A sealed-tube reaction of toluene with 2 mol % of Co precatalyst **A** and 2.6 equiv of HBpin in THF at 80 °C for 48 h gave a 63% conversion (GC) of the starting material to a 2:3 mixture of mono (**1a**)- and dibenzylic (**1b**) CHB products. When it is activated with 0.05 equiv of HBpin, B_2pin_2 could be used as the boron source, but the conversion was nearly identical with that obtained with HBpin. B_2pin_2 was less practical for isolating diborylated products, since chromatographic separation with silica gel of unreacted B_2pin_2 promotes the aforementioned protodeboronation of $PhCH(Bpin)_2$.[11] Since HBpin is a liquid, we explored CHBs in neat HBpin (2.6 equiv). This gave a modest improvement in conversion (70%). Increasing the reaction temperature to 150 °C decreased conversion (52% at 4 h), with no further conversion at longer reaction times. As depicted in entry 1 of Table 1, an excellent isolated yield with high selectivity for the $PhCH(Bpin)_2$ was obtained at 80 °C with 5.3 equiv of HBpin and 3 mol % of **A** (97% conversion, mono:di = 1:9). These optimized conditions established an efficiency for Co precatalyst **A** that was on par with Chirik's best conditions for the diborylation of toluene.[11]

CHBs of *m*-xylene, *p*-xylene, and cymene were examined in neat HBpin (5.3 equiv per arene) with 2 mol % of **A**. All three compounds were selectively borylated at benzylic positions. Nonetheless, there were differences between substrates. *m*-Xylene afforded a 1:1 mixture of the monoborylated (**2a**) and geminally diborylated (**2b**) products (74% conversion). Increasing the HBpin stoichiometry to 6.7 equiv improved conversion and selectivity for **2b** (81% conversion, **2a**:**2b** = 1:2). The borylated products were isolated as a mixture in 78% yield after workup, and the diborylated (**2b**) material could be separated by column chromatography with recovery of only 38% of **2b** that was present in the mixture, presumably due to protodeboronation. Surprisingly, CHB of *p*-xylene with 6.7 equiv of HBpin ceased after 40% conversion, giving a 33% isolated yield of a 1:1 mixture of monosubstituted (**3a**) to geminally substituted diborylation (**3b**) products. Cymene was the least reactive substrate, giving only 33% conversion and 21% isolated yield of the monosubstituted (**4a**) and geminally substituted diborylation (**4b**) products in a 1:1 ratio.

Despite *m*-xylene being more reactive than *p*-xylene, the Co precatalyst system appears to be very sensitive to sterics at the benzylic position, as indicated by the borylation of methyl vs isopropyl substituents on cymene. The inert nature of the isopropyl group was studied further through the attempted borylations of isopropylbenzene, as well as 1,3-di- and 1,3,4-triisopropylbenzene. All three compounds failed to borylate at

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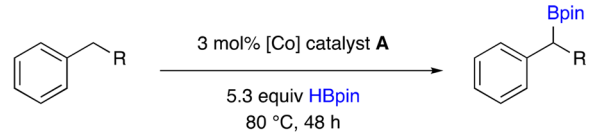
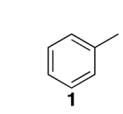
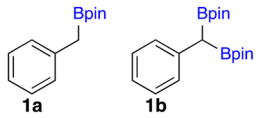
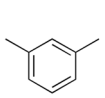
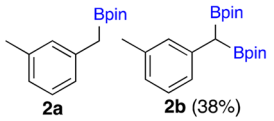
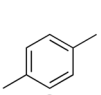
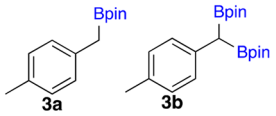
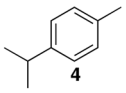
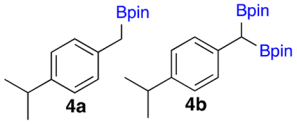
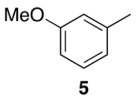
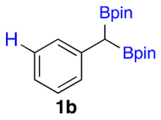
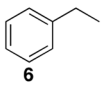
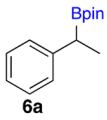
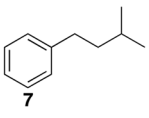
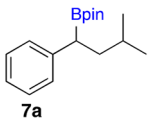
Table 1. Cobalt-Catalyzed CHBs[a]



Entry	Starting material	Products	Ratio/isolated yield
1			**1a**:**1b** = 1:9 **1a**+**1b** = 80%
2			**2a**:**2b** = 1:1.9 **2a**+**2b** = 78%
3			**3a**:**3b** = 1:1 **3a**+**3b** = 33%
4			**4a**:**4b** = 1:1 **4a**+**4b** = 21% (36%[b])
5			**1b** = 30%
6			**6a** = 49% (74%[b])
7			**7a** = 35%

[a]Isolated yields. [b]Borylation with 20 mol % of **A**.

any position, including the benzylic and C(sp^2)−H bonds. Chirik and co-workers showed that the isopropyl methyl groups of cymene (**4**) can be borylated, albeit more slowly than for the aryl methyl site.[11] Empirically, the more reactive the substrate, the more likely it undergoes diborylation.

The methyl vs isopropyl results raised an interesting question: Can the direct[16] selective monoborylation of secondary benzylic positions be achieved? Thus, we tested this with CHBs of ethylbenzene and isopentylbenzene (Table 1, entries 6 and 7).

Under our standard conditions using 2 mol % of **A**, ethylbenzene gave the monoborylated benzyl-Bpin product (**6a**) as the exclusive product, but with a modest 42% conversion. Interestingly, reducing HBpin to 2.6 equiv gave 51% conversion and **6a** was isolated in 49% yield. Increasing the loading of **A** to 20 mol % and HBpin to 3.3 equiv improved the yield of **6a** to 74% (77% conversion). CHB of isopentylbenzene using 2 mol % of **A** and 5.3 equiv of HBin gave **7a** exclusively (35% isolated yield, 44% conversion).

The ability of solutions of HBpin and **A** to catalyze the selective production of monoborylated **6a** from ethylbenzene stands in contrast to the use of Chirik's Co catalyst and conditions, which in our hands afforded a mixture of polyborylated products. Furthermore, Lin's Co-MOF catalysts gave a 4:1 mixture of benzylic and aryl borylation products.[17] While Ni(cod)$_2$/Icy-catalyzed (Icy = 1,3-bis(cyclohexyl)-imidazolium-2-ylidene) CHBs of arenes (arene:HBpin = (9−7.5):1) can generate monoborylated products at primary and secondary benzylic positions, functionalization of C(sp^2)−H sites is favored.[5a] Monoborylations of toluene and *m*-xylene have been reported using the UiO-Co MOF catalysts in Scheme 1.[14] For these substrates the selectivity for C(sp^3)−H borylation is high, but the use of excess arene ([substrate]:[B_2pin_2] ≥ 90) potentially biases selectivities for monoborylation in comparison to our chemistry, where the arene is the limiting reagent. For substrates with secondary and tertiary C−H bonds, the selectivity for C(sp^3)−H vs C(sp^2)−H borylation drops to 4:1 with the UiO-Co MOF catalysts.[14] Entries 6 and 7 of Table 1 indicate that selective monoborylation for substrates that exhibit poor selectivity with other catalysts is achievable with precatalyst **A**.

Seeking to expand the scope of this Co precatalyst system to more functionalized arenes, we subjected 1-methoxy-3-methylbenzene (entry 5) to the CHB conditions in Table 1. Unfortunately, the OMe substituent was cleaved, giving diborylated toluene **1b** in 30% isolated yield. Chirik saw minor amounts (13%) of C−OMe cleavage with his cobalt catalyst,[11] but methoxy substituents were tolerated in his benzylic borylations catalyzed by (^{ipc}ADI)Ni(OPiv)$_2$ (^{ipc}ADI = *N*,*N*′-di-(−)-isopinocampheyl)butane-2,3-diimine).[12] Chatani did observe PhBpin as a byproduct of C−OMe cleavage in Ni(cod)$_2$/Icy-catalyzed borylations of anisole, where C(sp^2)−H borylation predominated to produce a mixture of monoborylated anisoles.[5a]

m-Fluorotoluene defluorinated in CHBs with precatalyst **A**, as judged from ^{19}F-NMR and ^{11}B-NMR.[18] The NMR data pointed to trace amounts of unidentified species where C−B or B−F bond formation had occurred. When 1-methyl-4-(trifluoromethyl)benzene (**11**) was subjected to our standard CHB conditions, only 6% conversion of **11** was observed.[18] GCMS indicated the formation of compound **11a**, defluorinated **11a**′ (**11a**:**11a**′ = 5:1), and two additional unidentified compounds both with *m*/*z* = 277. The reduction of C(sp^2)−F and C(sp^3)−F bonds by precatalyst **A** contrasts C(sp^2)−F compatibility for 5-fluoro-*N*-methylindole[5a] and C(sp^3)−F compatibility for trifluoromethylbenzene[5b] in Ni-catalyzed CHBs. It should be noted that C−F bonds were problematic when CHBs of arenes containing C(sp^2)−F bonds or CF_3 groups were attempted using Ni(cod)$_2$/Icy catalysts.[5a] The UiO-Co MOF catalysts tolerate Cl and OMe groups, in contrast to CHBs catalyzed by precatalyst **A**.[14]

We were pleased to learn that the reaction scope for Co precatalyst **A** can be extended to certain heteroarenes (Table 2). *N*-Methylpyrrole was exceptionally reactive and formed the 2-borylated product **8a** and its 2,5-diborylated counterpart, **8b**. Although **8a** is prone to protodeboronation during purification, we managed to obtain a crystal structure of the product, which confirmed the assigned regiochemistry (SI). With HBpin as the limiting reagent, good yields of **8a** have been reported with the Ni(cod)$_2$/Icy CHB catalyst.[5a]

Both *N*-methylpyrazole and *N*-methylindole also borylate primarily at the position α to the formally sp^3 N, affording **9a**

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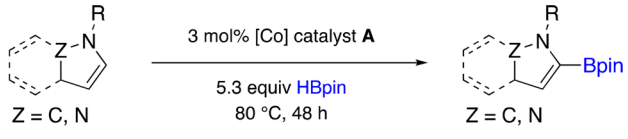
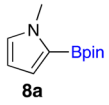
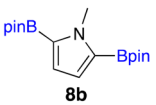
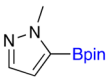
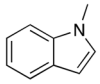
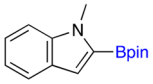
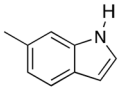
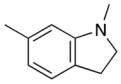
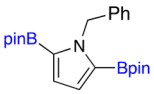
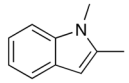
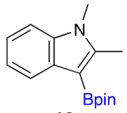
Table 2. Cobalt-Catalyzed CHBs of N-Heterocycles[a]



Entry	Starting material	Products	Ratio/isolated yield
8	 **8**	 **8a**  **8b**	**8a**:**8b** = 2:1 **8a**+**8b** = 88%
9	 **9**	 **9a**	**9a** = 90%
10	 **10**	 **10a**	**10a** = 53%[b]
11	 **11**	 **11c**	**11c** = 54%[c]
12	 **12**	 **12b**	**12b** = 51%[d]
13	 **13**	 **13a**	**13a** = 6%

[a]Isolated yields. [b]88% isolated material with the monoborylated, diborylated, and hydrogenated products present in a 5:2:1 ratio. The monoborylated product was isolated in 53% yield. [c]Based on NMR yield. [d]After 48 h another 3 mol % of **A** and 0.4 equiv of HBpin were added and the mixture was heated at 80 °C for 24 h.

and **10a**, respectively. *N*-Methylpyrazole is efficiently borylated under these conditions, giving 5-borylated pyrazole (**9a**) in 90% yield, representing the first CHB of *N*-methylpyrazole catalyzed by a 3d metal.[19] For *N*-methylindole, minor amounts of diborylated indole and *N*-methyl-4,5,6,7-tetrahydro-1*H*-indole were also detected in addition to **10a**. It is noteworthy that 6-methyl-1*H*-indole (**11**) itself undergoes C2−C3 hydrogenation under these conditions to give 6-methylindoline (**11c**) as the major product (54% conversion). Quantitative yields of **10a** have been reported for CHBs mediated by the $Ni(OAc)_2$/Icy precatalyst/ligand combination, with *N*-methylindole being the limiting reagent.[5a]

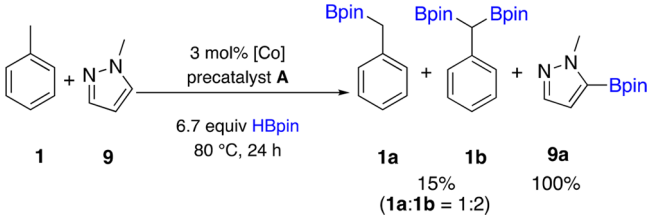
To compare C(sp^3)−H vs C(sp^2)−H CHB selectivities between arenes and heteroarenes, we examined the CHB of *N*-benzylpyrrole (**12**) with precatalyst **A**. Exclusive C(sp^2)−H CHB occurred at the 2-position. The general borylation conditions with 6.7 equiv of HBpin gave 95% conversion, affording a mixture of mono- and diborylated products (mono:di = 1.3:1). After 48 h, more precatalyst **A** (3 mol %) and HBpin (2.7 equiv) were added to the reaction mixture, which was heated at 80 °C for an additional 24 h. **12b** was isolated as a white solid in 51% yield (X-ray crystal structure CCDC 1576846).

To test whether alkyl groups attached to heteroarenes are similarly disposed toward C(sp^3)−H CHBs with precatalyst **A** like arenes are, we subjected indole **13** to identical borylation conditions using precatalyst **A**. Since the 2-position of indole preferentially borylates with Ir and other Co CHB catalysts, we selected a 2-methyl substrate to favor C(sp^3)−H CHB. Only 9% of **13** was converted (based on NMR) with borylation exclusively at the 3-position, affording **13a**.

Although the bond dissociation enthalpies of methyl C−H bonds in propene and toluene are identical,[20] the electron in the benzylic radical is delocalized over more atoms than in the allyl radical. Given that pyrrole, furan, and thiophene are more aromatic than their benzo-fused counterparts (indole etc.), we examined the CHB of 2-methylfuran, since ESR spectra of the radical formed from the formal abstraction of H from the 2-methyl position indicate extensive delocalization, as judged from hyperfine coupling constants of the radical with C(sp^2)−H atoms of the five-membered ring,[21] which are similar to those measured for the benzyl radical.[22] Furthermore, high-level calculations predict that the methyl C−H BDE is 86 ± 1 kcal/mol, which is comparable to the methyl C−H BDE of toluene.[23] CHB of 2-methylfuran with precatalyst **A** afforded a complex mixture that prevented the isolation of pure products. A single borylated species was identified in the GC/MS spectra of the crude reaction mixture. Its retention time and fragmentation pattern matched that of an authentic sample of the compound obtained from borylation of 2-methylfuran at the 5-position. In a sample prepared from the crude reaction mixture, the aromatic region of the ^{1}H NMR spectrum revealed major resonances for this isomer.[3b] There were two additional, sharp resonances of lower intensity. Their chemical shifts do not match those reported for the isomer where 2-methylfuran is borylated at the 4-position.[3b] If significant CHB had occurred at the methyl C−H bonds, three additional resonances would have been expected in the aromatic region. Thus, we see no evidence for CHB of C(sp^3)−H bonds when Cα is bound to a heterocycle.

All the above data suggest that precatalyst **A** favors CHBs of C(sp^2)−H of heteroarenes over Cα(sp^3)−H bonds of alkyl groups attached to heteroarenes. To investigate the speed of CHB of C(sp^2)−H of heteroarenes vs C(sp^2)−H and C(sp^3)−H bonds of alkylated arenes, the CHB of a toluene/*N*-methylpyrazole mixture was performed (Scheme 3). The

Scheme 3. CHB of Toluene vs *N*-Methylpyrazole



preference for C(sp^2)−H CHB at C5 of *N*-methylpyrazole further validates that CHBs of heterocycle C(sp^2)−H bonds with precatalyst **A** are favored over Cα(sp^3)−H CHBs of alkyl groups in substituted arenes and heteroarenes.

As with arenes, Co precatalyst **A** appears to be narrowly tuned to certain classes of heterocycles. Thiophenes, pyridines, and their benzo-fused derivatives were not borylated under

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these conditions. When borylation of equimolar amounts of *m*-xylene and 2-methylthiophene was attempted under the standard conditions, no reaction proceeded, presumably due to poisoning of the Co precatalyst by thiophene.

The identity of the catalytically active species is presently unknown. When HBpin is added to solutions of **A**, the chemical shifts for the paramagnetically shifted proton resonances assigned to **A** remain constant, but the intensities for decrease and vanish when $[HBpin]_0 \approx 3[\mathbf{A}]_0$ (page S14 in the Supporting Information). The ^{11}B NMR spectra initially show one sharp resonance at δ 22.5. The chemical shift and line width are virtually identical with those reported for *t*-BuOBpin.[24] When $[HBpin]_0 > 3[\mathbf{A}]_0$, a broader resonance appears at δ 29.5, which is close to the chemical shift for HBpin ($^{11}B\{^1H\}$ NMR, C_6D_6: δ 28.5, $^1J_{H-B}$ = 179 Hz). In the ^{11}B NMR spectrum when $[\mathbf{A}]_0$ = 0.03 M and $[HBpin]_0$ = 0.27 M, the full width at half-maximum (fwhm) is 450 Hz for the resonance at δ 29.5. In the $^{11}B\{^1H\}$ spectrum of the same sample, this resonance has fwhm = 298 Hz. The difference in fwhm between ^{11}B and $^{11}B\{^1H\}$, Δfwhm = 152 Hz (page S15 in the Supporting Information), is close to the $^1J_{H-B}$ value for HBpin. This observation, combined with the fact that the fwhm in the $^{11}B\{^1H\}$ spectrum is smaller than that in the proton-coupled spectrum, confirms the assignment of the resonance at δ 29.5 to HBpin. In the ^{11}B and $^{11}B\{^1H\}$ spectra of the same sample, fwhm = 92 Hz for the resonance at δ 22.5.

The broadening and 1.1 ppm upfield shift for the HBpin ^{11}B resonances is due to interaction of HBpin with unidentified paramagnetic or diamagnetic species. For $[\mathbf{A}]_0$ = 0.03 M and $[HBpin]_0$ = 0.27 M, resonances for precatalyst **A** are undetected in ^1H NMR spectra, and no other ^{11}B resonances are observed, aside from those noted above. Thus, **A** is converted to unidentified species before catalysis ensues. The addition of 1 drop of mercury to a borylation reaction mixture completely inhibited the reaction. This likely indicates that the true catalysts generated from **A** are heterogeneous. Notably, similar mercury poisoning has been reported for CHBs catalyzed by species generated from combinations of N-heterocyclic carbene ligands and Ni precatalysts.[5a] While Hg poisoning of heterogeneous catalysts is well documented and is often offered as proof that the catalytically active species are *not* homogeneous,[25] there are examples where *homogeneous* catalysts are poisoned by Hg.[26,27] Thus, homogeneous catalysts cannot be definitively excluded at this juncture.

Ir-catalyzed CHBs of most $C(sp^2)$–H bonds in heterocyclic compounds are greatly favored over $C(sp^2)$–H CHBs of aromatic molecules. Except for examples where CHBs are directed by H-bonding[28] or electrostatic[29] interactions, computational models based on (i) the extent of negative charge on the aryl or heteroaryl group in the transition states or intermediates[30] or (ii) differences between $C(sp^2)$–H BDEs of substrates and $C(sp^2)$–Ir BDEs in the C–H cleaving transition states revealed in distortion analysis[31] are good predictors of for relative reactivities of $C(sp^2)$–H bonds. Whether this extends to Co catalysts has yet to be determined. The fact that the C5–H BDE has been shown by experiment,[32] and confirmed by theory,[23] to be 120 kcal/mol—7 kcal/mol stronger than the C–H BDE in benzene—is yet another example that debunks the notion that reactant BDEs are reliable predictors of their reactivities.

CONCLUSIONS

Co compound **A** is the first 3d transition-metal precatalyst that can monoborylate primary and secondary benzylic C–H bonds with high selectivity. Compound **A** is also the first Co precatalyst capable of borylating both $C(sp^3)$–H bonds of alkylbenzenes and $C(sp^2)$–H bonds in heterocycles.[33] For diborylations, Co precatalyst **A** is generally more selective for the geminally diborylated products than previously described Co catalysts. Like $Ni(cod)_2$/Icy-catalyzed CHBs, catalysis with compound **A** is completely inhibited by adding elemental Hg.

EXPERIMENTAL SECTION

General Procedures. In a nitrogen-filled glovebox, a 5 mL vial was charged with cobalt complex **A** (15.3 mg, 0.03 mmol, 3 mol %) followed by addition of HBpin (0.8 mL, 5.3 mmol). The reaction mixture was stirred at room temperature until its color changed from purple to brown (~5 min). Next, the substrate (1 mmol) was then introduced by syringe. The vial was capped, taken out of the glovebox, and placed in an oil bath that was preheated to 80 °C. The reaction was allowed to proceed at this temperature for 48 h. At that time, the mixture was cooled to room temperature and analyzed by GC and NMR. The crude mixture was transferred into a 20 mL vial, and any excess HBpin was removed by rotary evaporation. A black-blue residue was obtained. To that residue was added deionized water, and the resultant mixture was stirred until the black-blue color had disappeared. The aqueous layer was extracted with dichloromethane (2 × 5 mL). The combined organics were dried over $MgSO_4$, concentrated, and passed through a short silica plug with hexane or hexane/EtOAc (9/1) as eluent. This plug step removed boronate byproducts from the reaction mixture.

Hg Test.[18] In a nitrogen-filled glovebox, a 5 mL vial was charged with cobalt complex **A** (15.3 mg, 0.03 mmol, 3 mol %) followed by addition of HBpin (0.8 mL, 5.3 mmol). The reaction mixture was stirred at room temperature until its color changed from purple to brown (~5 min). Next, toluene (1 mmol) was introduced. Finally, 1 drop of Hg was placed in the vial (dark brown reaction mixture). The vial was capped, taken out of the glovebox, and placed in an oil bath that was preheated to 80 °C. The reaction was allowed to proceed at this temperature for 18 h. A transparent (green in color) reaction mixture was observed after 18 h. ^1H NMR confirmed no CHB.

Preparation of Precatalyst A. Inside a nitrogen-filled glovebox, an oven-dried flask was charged with $CoCl_2$ (344 mg, 2.65 mmol) and 1,3-diisopropyl-1*H*-imidazol-3-ium chloride (1.010 g, 5.3 mmol). THF (16 mL) was added followed by addition of KOtBu (1.19 g, 10.6 mmol) in one portion. The resulting mixture was stirred inside the glovebox for 1 h. Then, solvent was removed under vacuum. The residue was suspended in toluene and filtered through a pad of Celite. The filtrate was collected, and solvent was removed under vacuum, providing a dark purple crystalline material that was dried under vacuum. Recrystallization from pentane at −35 °C afforded 1.140 g (84%) of crystalline complex **A** (mp 165 °C dec). Single crystals suitable for X-ray diffraction studies were selected from the recrystallization, and such analysis confirmed the structure. ^1H NMR (500 MHz, C_6D_6, ppm): δ 41.70 (s, 4 H), 39.00 (br s, 4 H), 8.76 (br s, 18 H), 2.31 (br s, 24 H). Complex **A** is stable on storage in the glovebox at −35 °C but quickly decomposes on exposure to ambient atmospheric conditions. The effective magnetic moment for precatalyst **A** calculated by the Evans method is 4.29 μ_B.

Preparation of 2-Benzyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1a) and 2,2′-(Phenylmethylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1b).[11] The general borylation procedure was carried out on toluene to afford 0.265 g of the products as a white solid (**1a**:**1b** = 1:9) in 80% yield. Data for **1b**: ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 7.27 (d, J = 6.5 Hz, 2 H), 7.22 (t, J = 7.5 Hz, 2 H), 7.08 (t, J = 7.0 Hz, 1 H), 2.30 (s, 1 H), 1.23 (s, 12 H), 1.21 (s, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 139.49, 129.13, 127.92, 124.15, 83.34, 24.68, 24.59; ^{11}B NMR (160 MHz, $CDCl_3$, ppm) δ 33.3.[11]

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Preparation of 2-(3-Methylbenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2a) and 2,2′-(*m*-Tolylmethylene)bis-(4,4,5,5-tetramethyl-1,3,2 dioxaborolane) (2b).[11] The general borylation procedure was carried out on *m*-xylene using 1.0 mL of HBpin (6.7 equiv). This modified procedure afforded 0.248 g of the products (**2a**:**2b** = 1:1.9) in 78% yield. SiO_2 column chromatography, with hexane/EtOAc (5/1) as eluent, afforded 0.136 g of the diborylated product (**2b**) as a white sticky solid in 38% yield. Data for **2b**: ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.13−7.09 (m, 2 H),7.05 (s, 1 H), 6.89 (d, J = 6.5 Hz, 1 H), 2.29 (s, 3 H), 2.26 (s, 1 H), 1.23 (s, 12 H), 1.22 (s, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 139.26, 137.26, 129.94, 127.78, 126.23, 125.01, 83.30, 24.69, 24.60; ^{11}B NMR (160 MHz, $CDCl_3$, ppm) δ 32.9. Data for **2a**:[8g] ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.13 (t, J = 7.5 Hz, 1 H), 7.00 (s, 1 H), 6.98 (s, 1 H), 6.94 (d, J = 7.5 Hz, 1 H), 2.31 (s, 3 H), 2.26 (s, 2 H), 1.24 (s, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 138.46, 137.72, 129.86, 128.13, 125.96, 125.60, 83.37, 24.72, 21.52; ^{11}B NMR (160 MHz, $CDCl_3$, ppm) δ 33.1.

Preparation of 2-(4-Methylbenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3a)[34] **and 2,2′-(*p*-Tolylmethylene)bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3b).** The general borylation procedure was carried out on *p*-xylene using 1.0 mL of HBpin (6.7 equiv). This modified procedure afforded 0.098 g of the products as an oil (**3a**:**3b** = 1:1) in 33% yield. Data for diborylated product (**3b**):[11] ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.15 (d, J = 7.5 Hz, 2 H), 7.02 (d, J = 7.5 Hz, 2 H), 2.28 (s, 3 H), 2.25 (s, 1 H), 1.23−1.22 (overlapping peaks, 24 H); ^{11}B NMR (160 MHz, $CDCl_3$, ppm) δ 33.0. Data for monoborylated product (**3a**):[35] ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.07 (m, 4 H), 2.29 (s, 3 H), 2.25 (s, 2 H), 1.21 (s, 12 H).

Preparation of 2-(4-Isopropylbenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4a) and 2,2′-((4-Isopropylphenyl)-methylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4b).[11,8g] The general borylation procedure was carried out on cymene and afforded 0.091 g of the products as an oil mixture (**4a**:**4b** = 1:1) in 21% yield. Data for monoborylated product (**4a**): ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.11 (s, 4 H), 2.85 (m, 1 H), 2.27 (s, 2 H), 1.21 (s, 12 H). Data for diborylated product (**4b**): ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.19 (d, J = 8.5 Hz, 2 H), 7.07 (d, J = 8.5 Hz, 2 H), 2.85 (m, 1 H), 2.29 (s, 1 H), 1.24 (s, 12 H), 1.23 (s, 12 H).

Preparation of 2-(1-Phenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6a).[36] The general borylation procedure was carried out on ethylbenzene with 2 mol % of Co precatalyst (10.2 mg, 0.02 mmol) and HBpin (0.4 mL, 2.6 mmol). This modified procedure afforded 0.106 g of the product, was isolated as a colorless oil in 49% yield: ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.27−7.21 (m, 4 H), 7.14−7.12 (m, 1 H), 2.43 (q, J = 7.5 Hz, 1 H), 1.33 (d, J = 7.5 Hz, 3 H), 1.21 (s, 6 H), 1.20 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 144.95, 128.29, 127.78, 125.08, 83.27, 24.62, 24.58, 17.06; ^{11}B NMR (160 MHz, $CDCl_3$, ppm) δ 33.3.

Preparation of 2-(3-Methyl-1-phenylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7a).[34] The general borylation procedure was carried out on isopentylbenzene with 2 mol % of Co precatalyst (10.2 mg, 0.02 mmol). After workup 0.097 g of the product was isolated as a colorless oil in 35% yield: ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.27−7.21 (m, 4 H), 7.14−7.12 (m, 1 H), 2.43 (t, J = 8.0 Hz, 1 H), 1.72−1.58 (m, 2 H), 1.52−1.45 (m, 1 H), 1.20 (s, 6 H), 1.18 (s, 6 H), 0.90 (d, J = 7.0 Hz, 3 H), 0.88 (d, J = 6.5 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 143.45, 128.34, 128.23, 125.02, 83.19, 41.46, 29.72 (C−B), 26.87, 24.57, 22.99, 22.17; ^{11}B NMR (160 MHz, $CDCl_3$, ppm) δ 33.2.

Preparation of 1-Methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrrole (8a)[5a] **and 1-Methyl-2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrrole (8b).** The general borylation procedure was carried out on *N*-methylpyrrole with 2 mol % of Co precatalyst (10.2 mg, 0.02 mmol). This modified procedure afforded 0.211 g of the products as a solid mixture (**8a**:**8b** = 2:1) in 88% yield. 2-Borylated *N*-methylpyrrole is not stable and deboronates back to starting material. Data for monoborylated product (**8a**): ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 6.81−6.80 (m, 2 H), 6.15 (dd, J = 2.5, 3.5 Hz, 1 H), 3.85 (s, 3 H), 1.27 (s, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 128.2, 121.8, 108.3, 83.0, 36.6, 24.8; ^{11}B NMR (160 MHz, $CDCl_3$, ppm) δ 28.9. Data for diborylated product (**8b**): ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 6.77 (s, 2 H), 4.01 (s, 3 H), 1.30 (s, 24 H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 121.6, 108.1, 83.1, 24.5; ^{11}B NMR (160 MHz, $CDCl_3$, ppm) δ 28.9; HRMS (EI+) m/z 334.2349 [(M + H$^+$) calcd for $C_{17}H_{30}B_2NO_4$ 334.2360].

Preparation of 1-Methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrazole (9a).[37] The general borylation procedure was carried out on *N*-methylpyrazole with 2 mol % of Co precatalyst (10.2 mg, 0.02 mmol). This modified procedure afforded 0.185 g of the product as a white solid (mp 59−60 °C; lit.[19] mp 74−75 °C[38]) in 90% yield: ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.49 (d, J = 2.0 Hz, 1 H), 6.71 (d, J = 2.0 Hz, 1 H), 4.09 (s, 3 H), 1.34 (s, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 138.3, 115.8, 84.1, 39.3, 24.8; ^{11}B NMR (160 MHz, $CDCl_3$, ppm) δ 27.7.

Preparation of 1-Methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (10a).[5a] The general borylation procedure was carried out on *N*-methylindole and afforded 0.227 g of a mixture of products. SiO_2 column chromatography, with hexane/CH_2Cl_2 (3/1) as eluent, afforded 0.133 g of the 2-borylated product, which was isolated as a white solid (mp 82−84 °C) in 53% yield. Over time in a refrigerator **10a** developed a brownish color. Data for **10a**: ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.65 (d, J = 8.0 Hz, 1 H), 7.35 (d, J = 8.0 Hz, 1 H), 7.28−7.25 (m, 1 H), 7.13 (s, 1 H), 7.09 (t, J = 7.5 Hz, 1 H), 3.98 (s, 3 H), 1.37 (s, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 140.1,127.8, 123.2, 121.6, 119.3, 114.2, 109.7, 83.7, 32.2, 24.8; ^{11}B NMR (160 MHz, $CDCl_3$, ppm) δ 28.4.

Preparation of 1-Benzyl-2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrrole (12b). The general borylation procedure was carried out on 1-benzyl-1*H*-pyrrole, and after 48 h another 3 mol % of Co precatalyst and HBpin (0.4 mL) were added; this mixture was heated at 80 °C for another 48 h. This modified procedure afforded 0.207 g of the product as a white solid (mp 107−108 °C) in 51% yield: ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.23−7.16 (m, 2H), 7.16−7.11 (m, 1H), 7.04−6.99 (m, 2H), 6.85 (s, 2H), 5.73 (s, 2H), 1.22 (s, 24H); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 141.2, 127.8, 126.5, 126.3, 121.9, 83.3, 51.7, 24.6; ^{11}B NMR (160 MHz, $CDCl_3$, ppm) δ 27.8; HRMS (EI+) m/z 410.2708 [(M + H$^+$) calcd for $C_{23}H_{34}B_2NO_4$ 410.2674].

Preparation of 1,2-Dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (13a).[39] The general borylation procedure was carried out on 1,2-dimethylindole and afforded 0.016 g of product as a sticky white solid in 6% yield: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03−7.97 (m, 1H), 7.25 (dt, J = 8.0, 0.9 Hz, 1H), 7.18−7.04 (m, 2H), 3.67 (s, 3H), 2.64 (s, 3H), 1.36 (s, 12H); ^{13}C NMR (126 MHz, chloroform-*d*) δ 147.5, 137.9, 132.4, 121.8, 120.8, 120.1, 108.5, 82.3, 24.9.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00144.

Experimental details and product characterization data (PDF)

Accession Codes

CCDC 1535249, 1576846, and 1576850 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Authors

*J.O.: tel, 989-638-1438; e-mail, joppenheimer@dow.com.

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*M.R.S.: tel, 517-353-1071; e-mail, smithmil@msu.edu.
*R.E.M.: tel, 517-353-0834; e-mail, maleczka@chemistry.msu.edu.

ORCID

Chathurika R. K. Jayasundara: 0000-0003-2651-4344
Dmitrijs Sabasovs: 0000-0002-0484-1830
Jossian Oppenheimer: 0000-0003-4508-8651
Milton R. Smith III: 0000-0002-8036-4503
Robert E. Maleczka Jr.: 0000-0002-1119-5160

Notes

The authors declare the following competing financial interest(s): C.R.K.J., D.S., J.O., M.R.S., and R.E.M. are inventors on U.S. Patent Application 61/874,249. M.R.S. and R.E.M. acknowledge a financial interest in BoroPharm, Inc.

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