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Catalytic Dehydrogenative Borylation of Terminal Alkynes by a SiNN Pincer Complex of Iridium

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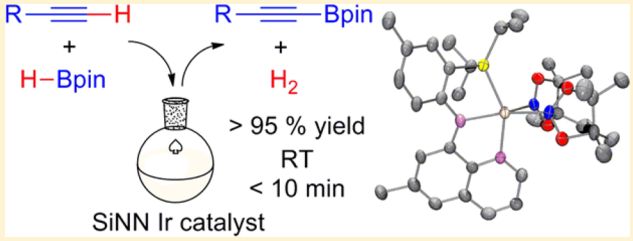
Supporting Information

ABSTRACT: Compounds with carbon−boron bonds are versatile intermediates for building more complex molecules via the elaboration of the carbon−boron bonds into other carbon−element bonds. The synthesis of carbon−boron bonds by catalytic dehydrogenative borylation of carbon−hydrogen bonds with dialkoxyboranes $(RO)_2BH$ is particularly attractive. It has been demonstrated for a variety of carbon−hydrogen bond types but not for the C(sp)−H bonds of terminal alkynes, for which hydroboration of the triple bond is a competing process. We report a new iridium catalyst that is strictly chemoselective for C−H borylation of terminal alkynes. The key to the success of this catalyst appears to be the new ancillary SiNN pincer ligand that combines amido, quinoline, and silyl donors and gives rise to structurally unusual Ir complexes. A variety of terminal alkynes (RC≡C—H) can be converted to their alkynylboronates (RC≡C—Bpin, where pin = pinacolate) in high yield and purity within minutes at ambient temperature.



INTRODUCTION

Conversion of hydrocarbon carbon−hydrogen bonds into carbon−boron bonds has progressed over the last two decades from initial reports[1,2] to a prominent and widely used synthetic method.[3−5] Dehydrogenative borylation of aromatic C−H bonds has been brought to particularly impressive heights with the advent of highly active iridium catalysts of Hartwig et al.[6] and Smith et al.[7] with supporting bipyridine and bidentate phosphine ligands. Multiple examples of catalytic conversion of unactivated C−H bonds in alkanes,[8−10] benzylic[11] and allylic $C(sp^3)$−H bonds,[12] as well as $C(sp^2)$−H bonds in alkenes[13,14] have been reported (see Figure 1).

Conspicuously absent from this list are the C(sp)−H bonds of terminal alkynes. C(sp)−H bonds are quite strong thermodynamically but possess substantially higher acidity than $C(sp^2)$−H and $C(sp^3)$−H bonds in hydrocarbons without strongly electron-withdrawing groups. Thus, activation of C(sp)−H bonds is often not viewed as a challenge because they can be fairly reliably "activated" by deprotonation. In spite of this, catalytic dehydrogenative C(sp)−H borylation of terminal alkynes (referred to as DHBTA from here on) has not yet been reported. The products, alkynylboronic esters (alkynylboronates), are valuable building blocks in organic synthesis. A very recent review summarized the use of alkynylboron compounds (alkynylboronates, dialkylalkynylboranes, and others) in organic synthesis.[15] Alkynylboronates can be viewed as potentially convenient coupling partners in the alkynyl version of the Suzuki coupling, similar to the most common use of aryl- and alkenyl-boronic esters, but their convenience is severely diminished by sensitivity to moisture.[16,17] Even more attractive are their reactions that utilize the boryl-substituted C≡C functionality "simply" as a substituted alkyne: cyclotrimerization,[18] [3 + 2] cycloaddition,[19] cyclopentenone synthesis,[20] hydrozirconation,[21] enyne metathesis,[22] and others.[23−26] These reactions produce new organic structures containing C−B bonds that would be difficult or impossible to introduce by late-stage C−H or C−X borylation and that themselves could be used for C−C bond forming Suzuki-type coupling or C−B oxidation reactions. Currently, the attractiveness of alkynylboronic esters is limited by the three-step conventional synthesis that involves treatment of the deprotonated alkyne with a boric ester, followed by carefully controlled protonation with dry Brønsted acids.[27] Dehydrogenative C−H borylation would clearly be a much more attractive route that would help unleash the full synthetic promise of alkynylboronic esters. It seems to us that the challenge in discovering a method for catalytic DHBTA to alkynylboronates lies not "merely" in the finding of a catalyst that would convert a C−H bond of the terminal alkyne to a C−B bond but rather in the finding of such a catalyst that does not more rapidly catalyze addition of a B−H bond across the triple bond. Traditionally, terminal alkynes react with dialkylboranes to yield alkenylboranes.[28] Catalysis of hydroboration of alkynes with the less reactive dialkoxyboranes (e.g., pinacolborane and catecholborane) has also been reported with various levels of regioselectivity.[29,30]

The C−H activation step of the state-of-the-art iridium catalysts for aromatic C−H borylation apparently involves a concerted hydrogen transfer from a coordinated arene to a boryl ligand on trivalent iridium. This hydrogen transfer has significant proton transfer character, and the basic character of

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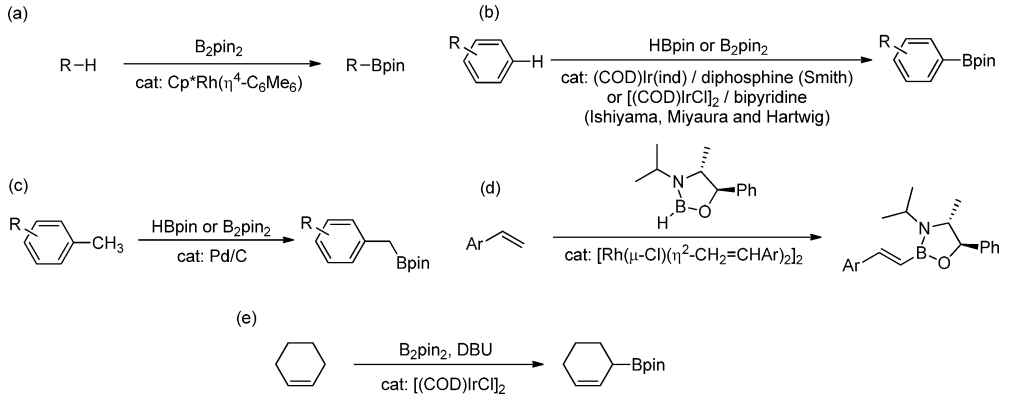

Figure 1. Representative examples of dehydrogenative borylation: (a) alkane borylation by Hartwig et al.;[8] (b) arene borylation by Hartwig et al.[6] and Smith et al.;[7] (c) benzylic borylation by Ishiyama et al.;[11] (d) alkene borylation by Brown and Lloyd-Jones;[13] and (e) allylic borylation by Szabó and Olsson.[12].

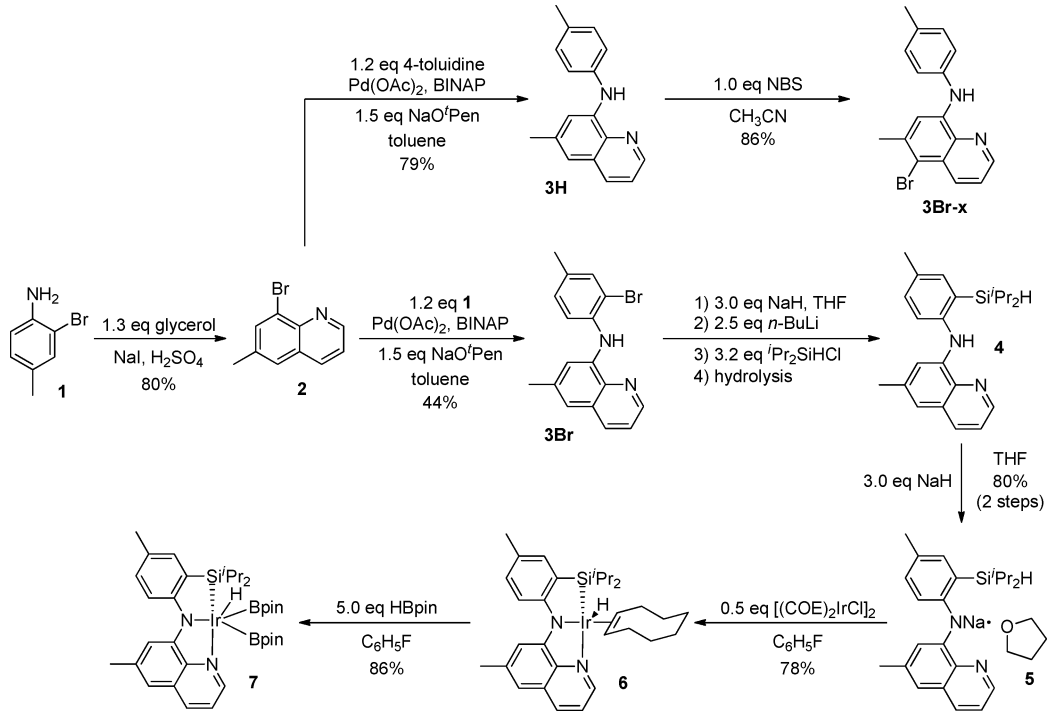

Figure 2. Synthesis of the SiNN ligand and its iridium complexes.

the Ir–boryl bond is boosted by two other, strongly donating spectator boryl ligands attached to Ir.[31] Our group's interest in transition-metal complexes of pincer ligands (typically defined as tridentate, meridionally, or T-shaped binding ligands)[32,33] led us to wonder whether this step is adaptable to a pincer-derived framework. Without pursuing a precise structural analogy to the Hartwig/Smith Ir catalysts, we envisioned that a tridentate, dianionic pincer ligand carrying a strong donor comparable to a boryl might provide an operationally related environment. Incorporating boryl donors into pincer ligands remains somewhat of a challenge, and we focused on silyl as another ligand of strong σ-donating ability. We conceived of a ligand combining a central amido site for ease of attachment to a metal, a side silyl donor, and another neutral side donor opposite the silyl. We now report our success in synthesizing such a ligand, characterizing its iridium complexes that contain unusual structural features, and their successful use in catalysis. Although our original expectations of broad-scope C–H borylation catalysis have not come to pass, the catalytic system we arrived at is very active and selective in C–H borylation of terminal alkynes.

RESULTS AND DISCUSSION

Synthesis of the SiNN Ligand. The synthesis of the proto-pincer ligand (**4**) is depicted in Figure 2. 4-Toluidine served as the precursor for both "halves" of the ligand. Selective bromination of 4-toluidine with NBS gave 2-bromo-4-toluidine (**1**) in excellent yield. We then employed a variation of the Skraup reaction[34] to synthesize 8-bromo-6-methylquinoline (**2**). This reaction produced a mixture of **2** and 6-methylquinoline, but optimization of the conditions enabled us to obtain a 96:4 mixture with **2** as the major component, in 80% isolated yield on a greater than 10 g scale. The mixture was successfully used directly in the subsequent syntheses of **3Br** and **3H**. 8-Bromoquinoline has been used in ligand synthesis before,[35−38] but it is relatively expensive or needs to be made from 8-

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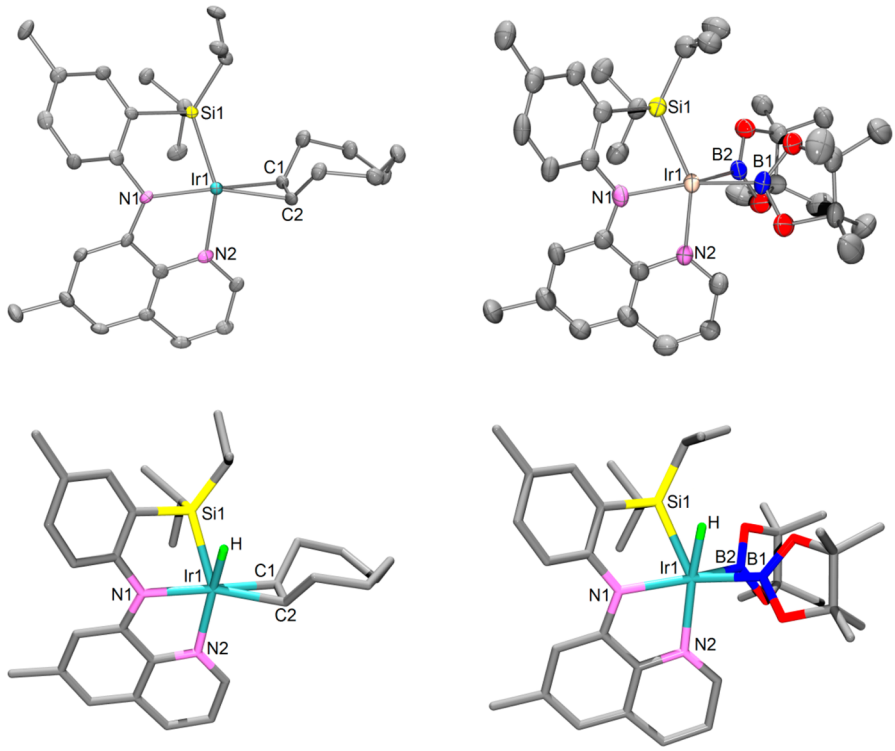

Figure 3. ORTEP drawings[49] (50% probability ellipsoids) of **6** (top left) and **7** (top right) showing selected atom labeling, and drawings of the DFT-calculated structures of **6** (bottom left) and **7** (bottom right). Hydrogen atoms are omitted for clarity, except for the hydride on the Ir atom. Selected bond distances (Å) and angles (deg) for **6**, with DFT-derived metrics in square brackets: Ir1−Si1, 2.3573(15) [2.391]; Ir1−H, [1.596]; Si1−H, [2.007]; C1−C2, 1.423(9) [1.413]; Si1−Ir1−H, [56.3]. For **7**: Ir1−Si1, 2.4130(14) [2.452]; Ir1−H, [1.609]; Si1−H, [1.889]; Ir1−B1, 2.069(5) [2.064]; Ir1−B2, 2.062(6) [2.055]; Si1−Ir1−H, [50.4]; B1−Ir1−B2, 66.5(2), [64.4].

aminoquinoline via diazotization.[39] Our simple and scalable synthesis of **2** can be quite useful for constructing other polydentate ligands with a quinoline unit. We originally envisioned Buchwald−Hartwig coupling of **2** with 4-toluidine to give **3H**, followed by bromination to obtain **3Br**. Unfortunately, bromination of **3H** led to a different isomer **3Br−x**.[40] We were thus forced to use 2-bromo-4-toluidine (**1**) in the coupling with **2**. This was not ideal because both substrates possessed an aryl bromide functionality, but we were nonetheless able to isolate **3Br** in 44% yield.

Installation of the silyl group was accomplished by deprotonation of the NH in **3Br** with NaH, followed by addition of *n*-BuLi,[41] quenching with 3.2 equiv of $^{i}Pr_2SiHCl$, and hydrolysis. The material obtained from this reaction was an oil that contained approximately 90% of **4** and proved very difficult to purify. However, the Na derivative **5** could be isolated in a pure form in 80% yield (based on **3Br**) by recrystallization. Pure samples of **4** could then be obtained via hydrolysis of **5**. The NMR spectroscopic features of **4** and **5** were unsurprising, including the $^{1}J_{Si-H}$ = 183 Hz for **4**, a typical value for triorganosilanes.[42]

Synthesis of the SiNN Complexes of Ir. Compound **5** reacted smoothly with $[(COE)_2IrCl]_2$ (Figure 2, COE = cyclooctene) to produce complex **6** in 78% yield after workup and recrystallization. One of the COE ligands was retained in the Ir coordination sphere in **6**. Crucially, the iridium center inserted into the Si−H bond, resulting in a silyl/hydride functionality. Complex **6** displayed a hydridic resonance at −21.1 ppm in the ^{1}H NMR spectrum with a small J_{Si-H} (8 Hz) and a resonance at 28.4 ppm in the ^{29}Si NMR spectrum.

Reaction of **6** with HBpin (Figure 2, HBpin = pinacolborane) resulted in the clean formation of the new product **7**, concurrent with the liberation of cyclooctane that displayed a singlet at 1.5 ppm in the ^{1}H NMR spectrum. The hydridic resonance of complex **7** was at −14.7 ppm in the ^{1}H NMR spectrum with a larger J_{Si-H} (32 Hz) than that in **6** and a ^{29}Si resonance at 35.2 ppm in the ^{29}Si NMR spectrum. In the ^{11}B NMR spectrum, the Bpin resonances were accidentally degenerate with a signal at 28.9 ppm.

X-ray Diffraction and Density Functional Theory Studies of the SiNN Complexes of Ir. X-ray diffraction (XRD) studies on the single crystals of **6** and **7** allowed the determination of their structures in the solid state (Figure 3, top). In order to augment the X-ray studies, particularly with respect to the location of the Ir-bound hydrogen in each complex, we also carried out density functional theory (DFT) calculations on the molecules of **6** and **7** in the gas phase using the M06 functional (Figure 3, bottom). The calculated structures closely reproduced the positions of the non-hydrogen atoms from the experimental XRD determination. The longer calculated Si−H distance in **6** (2.007 Å) versus **7** (1.889 Å) is consistent with the observed J_{Si-H} values of 8 and 32 Hz, respectively. The Ir−Si distance in **7** is approximately 0.05 Å longer than in **6** and approximately 0.08 Å longer than Tilley's Ir(V) complexes with $SiPh_3$ ligands.[43] Nonclassical Si−H interactions in metal complexes have received a significant amount of attention.[42,44,45] The values for **7** are borderline for the presence of an Si−H bonding interaction, but the values for **6** are rather outside of that range. Thus, **6** should be viewed as containing trivalent iridium with classical silyl and hydride ligands, whereas **7** could be considered an Ir^{V} silyl/hydride or

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an Ir^{III} Si−H complex depending on the rather arbitrary divide based on the Si−H metrics.

The B−H interactions in **7** can be conclusively ruled out. The two Ir−boryl fragments feature essentially the same metrics, there is no apparent B−H coupling, and the calculated B−H distances are far outside of the B−H bonding range. The Ir−B distances in **7** are similar to the analogous Ir−Bpin and Ir−Bcat* distances reported in the literature (1.97−2.08 Å).[6,46]

The structure of **7** can be described as Y-shaped five-coordinate, with $N_{quinoline}$, Si, and H forming the "Y" about the Ir atom (Figure 4). Y-shaped structures are common for five-

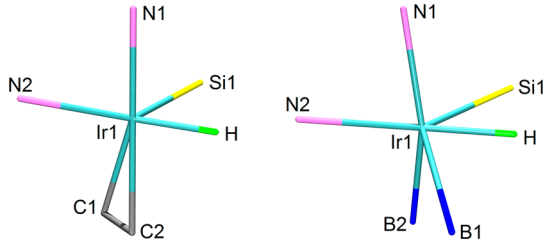

Figure 4. Drawings showing the immediate coordination environment about Ir in **6** (left) and **7** (right) based on the DFT-calculated structures.

coordinate d^6 complexes, but the stem of the Y is almost invariably a π-donor ligand.[47] The fact that the stem of the Y in **7** is occupied by $N_{quinoline}$ (not a π donor) is unusual. The coordination environment about Ir in **7** can be viewed as two Y's in different planes with a common Ir node (Figure 4). One of the Y's in **7** is the same as in **6**; the other is defined by N_{amido} (π donor at the stem) and the two boryl ligands. The B−Ir−B angle in **7** is quite acute at 66.5°, but this is a common feature of the Y-type geometry, particularly when it involves boryl ligands.[48] The B···B distance of approximately 2.26 Å is too long to contemplate boron−boron bonding.

Catalytic DHBTA Studies. The summary of optimization of the DHBTA reactions (Figure 5) is given in Table 1.

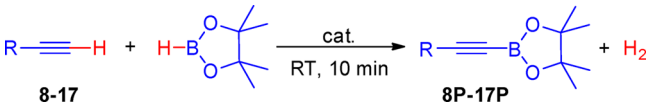

Figure 5. Catalytic DHBTA reaction (details in Tables 1 and 2).

Addition of HBpin to 1 mol % **6** in C_6D_6 followed by addition of equimolar (vs HBpin) amount of PhCCH all at once led to vigorous H_2 gas evolution. Analysis of the mixture by NMR spectroscopy after approximately 10 min revealed formation of approximately 50% of the alkynylboronate product, along with approximately 50% of unreacted HBpin and PhCCH (Table 1, entry 5). This composition remained virtually unchanged when monitored further at room temperature (RT). These observations are consistent with the presence of an active and selective but short-lived catalyst. Performing analogous experiments with a higher loading of **6** allowed us to achieve higher conversion and yield (entry 6), but that did not seem to be an ideal solution. Performing experiments with 1% catalyst loading but using different molar ratios of HBpin to PhCCH (entries 9 and 10) pointed to the apparent detrimental effect of the higher alkyne concentration or the higher alkyne/HBpin ratio. We surmised that rationed addition of the alkyne to the HBpin reagent solution containing the catalyst should give improved

Table 1. Optimization of DHBTA (Reaction in Figure 5)

entry[a]	R-	alkyne/HBpin	solvent	catalyst	yield[b]
1[c]	phenyl- (**8**)	1:1	C_6D_6	no catalyst	0%[d]
2[e]	phenyl- (**8**)	1:1	C_6D_6	2.5 mol % $[(COE)_2IrCl]_2$	0%[f]
3[e]	phenyl- (**8**)	1:1	C_6D_6	20 mol % PCy_3 + 5 mol % $[(COE)_2IrCl]_2$	0%[f]
4[e]	phenyl- (**8**)	1:1	C_6D_6	20 mol % PPh_3 + 5 mol % $[(COE)_2IrCl]_2$	0%[f]
5	phenyl- (**8**)	1:1	C_6D_6	1 mol % **6**	46%
6	phenyl- (**8**)	1:1	C_6D_6	5 mol % **6**	>95%
7	phenyl- (**8**)	1:1	C_6H_5F	1 mol % **6**	57%
8	phenyl- (**8**)	1:1	THF	1 mol % **6**	48%
9	phenyl- (**8**)	5:1	C_6D_6	1 mol % **6**	15%[g]
10	phenyl- (**8**)	1:5	C_6D_6	1 mol % **6**	>95%
11	phenyl- (**8**)	1:2	C_6D_6	1 mol % **6**	76%
12	phenyl- (**8**)	1:2	C_6D_6	1 mol % **6**	>95%
13	4-Me-C_6H_4- (**9**)	1:2	C_6D_6	1 mol % **7**	99%
14	4-Me-C_6H_4- (**9**)	1:2	C_6D_6	1 mol % **5** + 0.5 mol % $[(COE)_2IrCl]_2$	99%

[a]The catalyst and HBpin were dissolved in specific solvent in a J. Young tube. Alkyne was then added in once (entries 1−11) or added in four portions with 1 min intervals (entries 12−14), and the mixture was allowed to stand at ambient temperature for 10 min, see the Supporting Information for details. [b]NMR yield. [c]70 °C, 24 h. [d]Only unreacted HBpin and phenylacetylene were present. [e]RT, 30 min. [f]Multiple products, including alkenylboronates, were observed but not alkynylboronate (**8P**). [g]Based on HBpin.

results and that indeed turned out to be the case (entries 11 and 12). Even simply spreading the addition of the alkyne over 30 s (1 mmol scale) allowed yields and conversion in excess of 90%. Table 2 details the substrate scope of our investigations and shows that this methodology is readily applicable to aryl-, alkyl-, and silyl-substituted alkynes. By NMR spectroscopy, the reaction resulted in nearly quantitative yields of the alkynylboronic esters. The crude products appear to be greater than 95% pure but are significantly darkened by the highly colored Ir complexes (catalyst residue and decomposition products). The alkynylboronate products that are solids at RT (Table 2, entries 1−4 and 9) were isolated in the pure, colorless form in 88−95% yield by sublimation from the crude reaction mixture after the removal of solvent and excess HBpin in vacuo. Even the liquid alkynylboronate product (Table 2, entry 10) could be isolated in 85% yield by using a modified sublimation apparatus.[50] Trimethylsilyl propargyl ether (Table 2, entry 8) gave only a very poor yield of the product. Given that DHBTA can be run in THF as the solvent, there is no reason to think that coordination of an ether via oxygen to Ir is a problem. It seems more likely that propargylic C−O cleavage is possible and leads to catalyst deactivation. This notion is supported by that the homopropargyl ether (Table 2, entry 10) undergoes DHBTA in high yield and that the bulkier propargylic substrate

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Table 2. DHBTA of Various Alkynes Catalyzed by 6

Entry[a]	R-	Yield[b,c]
1	(8)	96% (90%)
2	(9)	99% (95%)
3	(10)	99% (88%)
4	(11)	98%[d] (90%[d])
5	(12)	99%
6	(13)	99%
7	(14)	99%
8	(15)	9%[e]
9	(16)	99% (92%)
10	(17)	98% (85%)

[a]The catalyst **6** (0.0010 mmol) and HBpin (0.20 mmol) were dissolved in C_6D_6 in a J. Young tube. Alkyne (0.10 mmol for monoynes [0.050 mmol for 1,7-octadiyne]) was then added in four portions with 1 min intervals, and the mixture was allowed to stand at ambient temperature for 10 min, see the Supporting Information for details. [b]NMR yield. [c]Yields in parentheses are isolated yields in preparative-scale reactions that used toluene as the solvent instead of C_6D_6. [d]Yield of diborylated product. [e]The remaining is unreacted alkyne and pinacolborane.

$Me_3SiOCMe_2CCH$ (Table 2, entry 9) also works fine in this reaction.

When **6** was treated with excess HBpin, purple **7** is rapidly formed prior to the addition of alkyne, and this color turns blue gradually during the addition of the alkyne in successful reactions. Not surprisingly, analogous catalytic turnover was observed when isolated **7** was used in place of **6** (Table 1, entry 13). In addition, the active catalyst could also be generated in situ from **5** and $[(COE)_2IrCl]_2$ with the same reaction outcome (Table 1, entry 14). On the other hand, HBpin reacted with 1-hexene, styrene, or 3,4-dihydro-2*H*-pyran only slowly in the presence of 1 mol % **6**, with less than 40% conversion (to hydroboration products) at RT for 24 h. No reaction was detected between HBpin and furan or thiophene (arguably the most reactive substrates in aromatic C−H borylation)[3−5] in the presence of 1 mol % **6** at 70 °C for 24 h.

No reaction was observed between HBpin and phenylacetylene in C_6D_6 at 70 °C for 24 h (Table 1, entry 1). Interestingly, this is in contrast to the previous report uncatalyzed hydroboration of alkynes with in situ prepared HBpin in CH_2Cl_2.[51] Using $[(COE)_2IrCl]_2$ or $[(COE)_2IrCl]_2$/R_3P as catalysts led to the formation of multiple products at RT (primarily hydroboration) but no alkynylboronate (Table1, entries 2−4).

We do not have enough evidence to construct a detailed mechanistic picture. However, the generic sequence depicted in Figure 6 seems logical to propose and is analogous to the

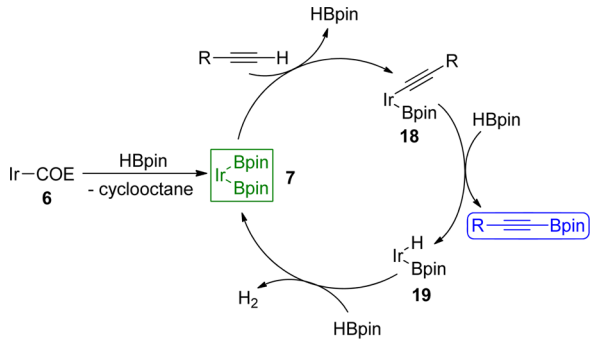

Figure 6. Plausible DHBTA mechanism.

mechanisms put forth for the aromatic C−H borylation. We have established the formation of the diboryl complex **7**. It can likely react with a terminal alkyne to give intermediate **18** followed by C−B reductive elimination and yield borylhydride complex **19**. Finally, **19** would react with pinacolborane to release H_2 and reformation of **7**. Smith et al. highlighted the correlation of C−H acidity with the ease of activation in aromatic borylation reactions.[31] The reason C−H borylation in our system proceeds so readily for alkynes but not for arenes or alkenes is probably related to (1) the significantly higher acidity of alkynyl C−H bonds and (2) terminal alkynes being compact ligands that are typically more readily coordinating than alkenes and especially arenes. The reaction of **7** with the alkyne is probably initiated by alkyne coordination to this 16-electron Ir center and facile proton transfer from C to B. The decomposition of the catalyst appears to derive from a reaction with an alkyne. The alkyne substrate is required in the cycle for forming the product, but ostensibly, another side reaction exists, in which one of the Ir intermediates in the productive catalytic cycle is "derailed" by another molecule of alkyne. The nature of this side reaction is not clear at this point. There is also not enough information yet to determine whether the SiH/Ir moiety is merely a spectator fragment of the supporting ligand (as our Figure 6 implies) or the hydride is involved in the main catalysis or catalyst-destroying reactions.

■ CONCLUSION

In this work, we are reporting iridium complexes featuring a new silyl−amido−quinoline tridentate SiNN pincer ligand. The silyl moiety of this ligand results from the insertion of the iridium center into the Si−H bond of the parent proto-ligand. The geometry and presumably the electronic interactions in the Ir/Si/H triangle appear to be able to adapt in response to the changes in the metal coordination sphere. This mechanism of electronic adaptability is rather unexplored for a spectator donor site in a polydentate ancillary ligand.

The new iridium SiNN complexes give rise to an active catalyst for selective conversion of terminal alkynes into alkynylboronic esters via dehydrogenative C−H borylation (DHBTA) with pinacolborane. This is a new and significantly advantageous method of synthesis of alkynylboronates. Optimization of the reactions conditions allowed us to achieve approximately 100 turnovers at ambient temperature in less than 10 min with aryl-, alkyl-, and silyl-substituted terminal

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alkynes. The catalyst is remarkably chemoselective, performing DHBTA but no other catalytic alkyne transformation under the same conditions. Moreover, the catalyst showed low or no activity toward heteroarenes and alkenes. The reactivity of the catalyst is limited by a decomposition pathway that apparently stems from a side reaction with the alkyne substrate.

The origins of the high reactivity selectively toward terminal alkynes and the origins of the decomposition reaction are not yet clear. In particular, it is not obvious whether all elements of the rather specific ligand design executed here are critical for the success of alkyne C−H borylation. The great variety of accessible pincer ligands promises exciting directions for exploring this new reaction further.

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic information in the form of CIF files; general considerations; computational details; X-ray structural determination details; ligand synthesis; synthesis of iridium complexes; optimization of catalytic reactions and control experiments; optimized catalytic reactions; NMR spectra; and movie of the hydrogen evolution from the addition of 1-hexyne to a mixture of (SiNN)IrH(COE) and HBpin in toluene. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic information in the form of CIF files is available free of charge from the Cambridge Crystallographic Data Centre (CCDC 900440 and CCDC 900441).

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Notes

The authors declare no competing financial interests.

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