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Cobalt Pincer Complexes in Catalytic C-H Borylation: The Pincer Ligand Flips Rather Than Dearomatizes

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Abstract

The mechanism for the borylation of an aromatic substrate by a cobalt pincer complex was investigated by density functional theory calculations. Experimental observations identified *trans*-(ⁱPrPNP)CoH₂(BPin) as the resting state in the borylation of five-membered heteroarenes, and 4-BPin-(ⁱPrPNP)Co(N₂)BPin as the resting state in the catalytic borylation of arene substrates. The active species, 4-R-(ⁱPrPNP)CoBPin (R=H, BPin), were generated by reductive elimination of H₂ in the former, through Berry pseudorotation to the *cis* isomer, and N₂ loss in the latter. The catalytic mechanism of the resulting Co(I) complex was computed to involve three main steps: C-H oxidative addition of the aromatic substrate (C₆H₆), reductive elimination of PhBPin, and regeneration of the active complex. The oxidative addition product formed through the most favorable pathway, where the breaking C-H bond of C₆H₆ is parallel to a line between the two phosphine atoms, leaves the complex with a distorted PNP ligand, which rearranges to a more stable complex via dissociation and re-association of HBPin. Alternative pathways, σ -bond metathesis and the oxidative addition in which the breaking C-H bond is parallel to the Co-B bond, are predicted to be unlikely for this Co(I) complex. The thermodynamically favorable formation of the product PhBPin via reductive elimination drives the reaction forward. The active species regenerates through the oxidative addition of B₂Pin₂ and reductive elimination of HBPin. *In the overall reaction, the flipping (refolding) of the five-membered phosphine rings, which connects the species with two phosphine rings folded in the same direction and that with them folded in different directions, is found to play an important role in the catalytic process, as it relieves steric crowding within the PNP ligand and opens Co coordination space.* Metal-ligand cooperation based on the ligand's aromatization/dearomatization, a common mechanism for heavy-metal pincer complexes, and the dissociation of one phosphine ligand, do not apply in this system. This study

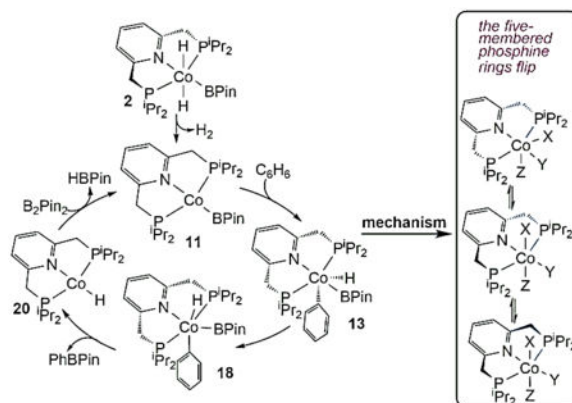
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SUPPORTING INFORMATION AVAILABLE:

Verification of ground states of four-coordinate cobalt species; optimized geometries of some species involved in Figure 2; the superimposed structures of the optimized geometry of **2** and its X-ray crystal structure; an alternative pathway for the formation of **4** from **2**; formation of the isomer of **9**; isomerization of **4** to its isomer; results for the release of H₂ from the *trans*-dihydride Co-complex with model systems; verification of ω B97XD/Def2TZVP(SMD)// ω B97XD/BS4; optimized geometries of transition states for the release of H₂ from **2Ir**, **2Ph**, **2Ir-Ph**, and **2Ir-Ph-tBu**; a possible pathway for the formation of the active species from the catalyst precursor with model systems; alternative pathways for the addition of C₆H₆ to the cobalt boryl species with model systems; comparisons of transition state **TS11-13** and that for the formation of **15** and its isomer; addition of C₆H₆ to corresponding Rh and Ir complexes; optimized geometries for the species in Figure 6 in the text; results for the reductive elimination of the B-C bond with model systems; optimized geometries of the species in Figure 7; results for the regeneration of the active species with model systems; Cartesian coordinates and energies of the species involved in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

provides guidance for understanding important features of pincer ligands with first-transition-row metals that differ from those in heavier metal complexes.

Graphical Abstract



Keywords

cobalt pincer complex; catalytic C-H borylation; the flipping of the five-membered phosphine rings; DFT calculations; mechanistic studies

1. Introduction

Catalytic C-H borylation is one of the most attractive methods for C-H functionalization, as the C-B products are versatile synthetic reagents for constructing new carbon-carbon and carbon-heteroatom bonds.¹ Efforts by many researchers have developed catalytic borylations for C(sp³)-H, C(sp²)-H,¹⁻⁶ C(sp)-H bonds,⁷⁻¹¹ and chemo-, regio-, and stereo-selective C-H borylations.^{1-4,9-11} Among them, catalytic C-H borylation of arenes and heteroarenes is a particularly attractive approach to synthesize organoboronate esters, which are key synthetic intermediates for Suzuki-Miyaura cross-coupling reactions.¹⁻⁶

Transition-metal complexes have been widely applied to catalyze the C-H borylations, for which the iridium-based complexes are most common.^{1-5,8} Furthermore, some iridium complexes have been reported to catalyze methane borylations,^{12,13} a major challenge. However, widespread applications for iridium and other noble metal catalysis suffer from their many disadvantages: expense, toxicity, scarcity, and difficulty in separation. These limitations have motivated researchers to develop catalysts with earth abundant first transition-row metals,^{14,15} paving the way for sustainable and environmentally friendly synthesis. Although Hartwig and coworkers reported several C-H borylations with CpFe(CO)₂Bcat (Cp = η⁵-C₅H₅; cat = O₂C₆H₄) under photochemical conditions in 1995, catalytic reactions were not observed in their systems.¹⁶ Significant progress in developing catalytic C-H borylations with first transition-row metal complexes has only been made recently. Although catalytic C-H borylations has been reported by using metal-free systems based on the concept of “Frustrated Lewis Pairs”,¹⁷⁻²¹ most of the work has involved

bimetallic copper-iron,^{22–24} zinc-iron complexes,^{22,23} monometallic iron complexes,^{25–27} and recently a series of cobalt^{28–35} and nickel complexes.^{36,37}

Important applications of C-H borylations in synthetic chemistry need new efficient catalysts, whose development can benefit from fully understanding the catalytic mechanism. Such mechanisms at various level of detail have been reported from both experiments and computations.^{20,23,33,34,38–45} Furthermore, efforts to elucidate the origin of chemo-, regio-, and stereo-selectivity have also had some success.^{4,46–54} Generally, catalytic borylations involve C-H bond cleavage by oxidative addition and C-B bond formation by reductive elimination, routes that utilize the inherent two-electron redox property of heavier transition metals. However, metal-assisted σ -bond metathesis mechanism has been suggested for the C-H bond cleavage and H transfer,^{39,42,45,47,49} a route that avoids the formation of higher oxidation-state intermediates. In addition, both steric and electronic effects, together with weak interactions between ligands and substrates, were found to govern the selectivity of some reactions.^{47,49,50,54}

In spite of these studies, detailed mechanistic investigations of C-H borylations with first transition-row metals are still scarce.^{20,43} Unlike heavier transition metals with two-electron redox chemistry, the first-row metals usually demonstrate one-electron redox processes,^{14,15} a difference that suggest some new mechanistic pathways may be involved. Furthermore, variable coordination geometries and multiple spin states of the first transition-row metal complexes, especially those with weak field ligands, challenge characterizations of their electronic structures and catalytic reactivity. Thus, metal-metal cooperativity has been recognized to facilitate the catalytic photochemical C-H borylation with bimetallic Cu-Fe and Zn-Fe complexes, which may mimic heavier transition metal complexes.^{22–24} Herein, we are interested in understanding the catalytic mechanism for the C-H borylations of heterocycles and arenes with several pincer-ligated cobalt complexes reported by Chirik and coworkers.²⁸ Among their tested cobalt complexes, the pyridine-based PNP pincer complex, (*i*PrPNP)Co(CH₂SiMe₃) (*i*PrPNP = 2,6-bis(di-iso-propyl)phosphinomethyl)pyridine, **1** in Scheme 1), was observed to perform best. With the catalyst **1**, the borylation of methyl furan-2-carboxylate has achieved up to 5000 turnovers at 23 °C (eq 1 in Scheme 1), and the borylation of benzene has also been realized with excess benzene (benzene: B₂Pin₂ = 20:1, Pin = O₂C₂Me₄) at 80 °C (eq 2 in Scheme 1). The *trans*-dihydride cobalt complex, *trans*-(*i*PrPNP)CoH₂(BPin) (Pin = O₂C₂Me₄, complex **2** in Figure 1), synthesized separately by adding two equivalents of HBPIn to the cobalt alkyl compound **1** and releasing one equivalent of Me₃SiCH₂BPin, was identified as the resting state in the borylation of 2-methylfuran with HBPIn. According to their proposed mechanism (Figure 1), complex **2** first isomerizes to a *cis*-dihydride cobalt complex, which then releases H₂ to generate the active species (*i*PrPNP)CoBPin, followed by the oxidative addition of a C-H bond and the subsequent reductive elimination of the B-C bond to form the borylated product. Finally, addition of HBPIn to (*i*PrPNP)CoH regenerates complex **2**. Although several experiments have been conducted to explore the catalytic mechanism and the structures of cobalt intermediates,^{28–34,55} a complete catalytic cycle has not been established yet. Furthermore, related PNP pincer ligated metal complexes synthesized by Milstein and coworkers are well known to show a mode of metal-ligand cooperation based on the ligand's aromatization/

dearomatization.^{56–58} This gives rise to an interesting question that whether the *trans*-(ⁱPrPNP)CoH₂(BPin) complex shows similar reactivity or not during its catalytic cycle. Building on our previous mechanistic studies of the borylation with transition metal complexes,^{39,42,48} and studies of Milstein's systems,^{58,59} we herein employed density functional theory (DFT) calculations to fully understand the catalytic mechanism by computing the detailed reaction pathways for the proposed mechanism as shown in Figure 1.

2. Computational methods

Detailed DFT calculations of the catalytic mechanism were conducted by using benzene and B₂Pin₂ as representative substrates with catalyst **1** (eq 1 in Scheme 1), as all its C-H bonds are equal, benzene simplifies our explorations on the mechanism. With the ωB97XD functional,⁶⁰ geometries of all intermediates and transition states were optimized in gas phase by employing the basis set BS1, where atoms of the ⁱPrPNP ligand except N and P use cc-pVDZ⁶¹ and the others (including the Co) use Def2TZVP.⁶² On the basis of gas-phase optimized geometries, single point calculations were conducted in C₆H₆ solvent with the SMD solvent model⁶³ at the level of ωB97XD/Def2TZVP, where all the atoms use Def2TZVP. In addition, an 'ultrafine' grid was used to make optimizations of large molecules with many soft modes such as methyl rotations more reliable. Furthermore, '5D' option was used for all d functions in these calculations. Unless noted otherwise, free energies and enthalpies in C₆H₆ solvent together with the free energies in gas phase, which are represented by $G_{C_6H_6}[H_{C_6H_6}](G_{gas})$, respectively, are reported in this work.

In addition to calculating the experimentally reported system, we also computed a simplified model system to explore various alternative reaction pathways. In the simplified model system, we replaced all the ⁱPr substituents of the ⁱPrPNP ligand with Me, and further replaced B₂Pin₂ with B₂eg₂ (eg = ethyleneglycolato) to save computation time. The ωB97XD functional was also used to calculate the model system. Geometries of all intermediates and transition states were optimized in gas phase at the level of BS2, where Co employs LANL2DZ ECP-basis set⁶⁴ and the others use cc-pVDZ. With the optimized geometries in gas phase, the energetic results were refined by single point calculations with the SMD solvent model at the level of ωB97XD/BS3, where Co employs SDD ECP-basis set⁶⁵ and the others use cc-pVTZ. The THF solvent, which was used in the catalytic borylation of some substituted pyridines in experiments, was selected in the SMD single point calculations. Free energies and enthalpies in THF and the free energies in gas phase, which are represented by $G_{THF}[H_{THF}](G_{gas})$, were reported. Results for the model system are presented mainly in the Supporting Information.

Results reported in this work are based on optimized geometries for closed shell singlet states. However, triplet states or open shell singlet states may also be possible for cobalt complexes, especially for four-coordinate cobalt species. For example, the solid-state structure of the cobalt alkyl complex **1** was confirmed to be diamagnetic with a four-coordinate Co in a square-planar geometry, while its ¹H NMR spectra appears to be somewhat paramagnetically shifted at high temperature, implying a low-lying triplet state.²⁸ To verify this observation, several DFT functionals involving hybrid functionals (ωB97XD, M06,⁶⁶ TPSSh⁶⁷) and non-hybrid functionals (TPSS,⁶⁷ TPSS-D3 (with D3 = Empirical

Dispersion = GD3BJ,⁶⁸ M06L,⁶⁹ PBE⁷⁰) were selected to calculate its possible structures. As expected, the relative energies between singlet and triplet states depend strongly on the functionals, where TPSS gives square-planar, singlet ground states and ω B97XD over stabilizes tetrahedral triplet states (SI1). To further confirm this, several experimentally isolated species, (ⁱPrPNP)CoCl, (^tBuPNP)CoCl, and (^tBuPNP)CoH,⁵⁵ were investigated by using TPSS and ω B97XD. Similarly, TPSS predicts singlet ground states consistent with experiment, while ω B97XD over stabilizes triplet states (SI1). Comparisons of the optimized geometries at TPSS and ω B97XD show that ω B97XD predicts longer Co-X bonds (X any coordinated atom) than TPSS, and these differences are larger for triplet states than for singlet states (SI1). With TPSS, singlet and triplet states of selected stationary points, especially the four-coordinate cobalt species involved in the reaction, such as (ⁱPrPNP)CoBPin (**11**), (ⁱPrPNP)CoPh (**16**), and (ⁱPrPNP)CoH (**20**), were recalculated, and all are predicted to be singlet ground states (SI1). Thus, the singlet states are reported for the mechanism. The geometries and the energies reported for the reaction mechanism are from the ω B97XD calculations, as their predicted rate-determining barriers (around 25 kcal/mol) are more consistent with the experimental conditions at 80°C than the barriers of over 34 kcal/mol predicted by using the TPSS functional (see the following discussions). However, using TPSS to recalculate the rate-determining transition states and thermodynamics of key steps did not change the conclusions.

All the DFT calculations were performed with the Gaussian 09 program.⁷¹ The three-dimensional molecular structures reported in this work were drawn using the JIMP2 molecular visualizing and manipulating program.^{72–74}

3. Results and discussion

Following the proposed mechanism of catalytic borylation of 2-methylfuran with HBPIn from the *trans*-(ⁱPrPNP)CoH₂(BPIn) complex (**2**, a resting state in the reaction) as in Figure 1,^{28,34} the active species (ⁱPrPNP)CoBPin was generated from the *trans*-(ⁱPrPNP)CoH₂(BPIn) complex by releasing H₂. Furthermore, in the catalytic borylation of arene substrates, the 4-BPin-(ⁱPrPNP)Co(N₂)BPIn complex (BPIn substituted the 4-position of the pincer ligand) was identified as the resting state, which was proposed to form the related active species 4-BPin-(ⁱPrPNP)CoBPin through the dissociation of N₂.³⁰ From the active species, the catalytic borylation mechanism involves similar steps: oxidative addition of the C-H bond, reductive elimination of B-C bond, and regeneration of the active species. We first examined the mechanism for the generation of the active species (ⁱPrPNP)CoBPin from the *trans*-(ⁱPrPNP)CoH₂(BPIn) complex to determine if aromatization/dearomatization of the pincer ligand is operative in this system or not. Then, we calculated the following three steps from the active species (ⁱPrPNP)CoBPin by using C₆H₆ and B₂Pin₂ as substrates to reduce the computational cost: oxidative addition of C₆H₆, reductive elimination of B-C bond to form PhBPIn, and regeneration of (ⁱPrPNP)CoBPin. Considering that 4-BPin-(ⁱPrPNP)CoBPin is the active species in the catalytic borylation of arene substrates, some selected transition states and intermediates involved in the oxidative addition and reductive elimination steps were recalculated by using the 4-BPin-(ⁱPrPNP)CoBPin complex. Details for these steps will be reported separately in the following sections.

3.1 Generation of (iPrPNP)CoBPin from *trans*-(iPrPNP)CoH₂(BPin)

In the experiments, the *trans*-(iPrPNP)CoH₂(BPin) complex **2** was observed as a resting state in the catalytic reaction, and was proposed to release H₂ to generate an active species (iPrPNP)CoBPin.^{28,34} However, direct release of H₂ from **2** is unlikely as the two H atoms on Co are *trans*. Thus, an isomerization process from **2** to a *cis*-(iPrPNP)CoH₂(BPin) complex was suggested.²⁸ Our calculations support this suggestion, and the detailed pathway for this process is shown in Figure 2 with optimized geometries of some species in Figure 3.

The optimized geometry of complex **2** is close to its X-ray crystal structure, as the differences of bond lengths and angles between them are no more than 0.03 Å and 3.2°, respectively (see Figure 3 and their superimposed structures in SI3), an agreement that supports the methodology used here. In **2**, two five-membered phosphine rings of the pincer ligand are folded in different directions; one sp³-C of the ring tips down (in blue), while the other tips up (in black). Via transition state **TS**₂₋₃, the sp³-C of the phosphine ring in blue flips up, and a new complex **3** was formed. This ring-flipping process is clear from their optimized geometries and is especially obvious from the alternative perspective in Figure 3. The two hydrides at Co are *trans* in **3**, and then move simultaneously towards the B atom via transition state **TS**₃₋₄ where the Co-H¹ bond lengthens and both B-H distances shorten, generating complex **4** with two unequally bridging H atoms (Co-H-B) (see its optimized geometry in Figure 3). In contrast, the stepwise pathway where the two hydrides move separately is unlikely; as optimizations of corresponding intermediates formed after moving one hydride repeatedly converge to **3** again. Complex **4** is higher than **2** by only 1.7 kcal/mol, and the formation of **4** from **2** is calculated to proceed via two low-barrier transition states, **TS**₂₋₃ and **TS**₃₋₄. In addition, an alternative pathway for the formation of **4** from **2**, where the two hydrides at Co in **2** firstly move simultaneously toward the B atom and then the sp³-C of the phosphine ring in blue flips up to generate **4**, was calculated to compete with the path in Figure 2 (see SI4). Furthermore, a dynamic process was suggested by experiments, which show a broad cobalt hydride signal in ¹H NMR spectrum.²⁸ Thus, this experimental observation can be ascribed to the rapidly transformation between **2** and **4** which represent a *mer* isomer and a *fac* isomer, respectively, the latter also displaying semibridging Hs.

In the optimized geometry of **4** (Figure 3), the N, Co, and B atoms are not in line with the BPin group bending upwards. In addition, the B-H¹ bond is shorter than the B-H² bond by 0.10 Å, implying that the B atom is bound to H¹ more tightly than to H². Correspondingly, the Co-H¹ bond is longer than the Co-H² bond by 0.19 Å. Furthermore, the B-H¹ bond at 1.31 Å and the Co-H² bond at 1.55 Å are in the normal range for these bonds. Thus, complex **4** could be considered the product formed by coordinating H¹BPin to a cobalt-hydride complex (i.e., **20** in the following sections). Consistent with this proposal, a process for the dissociation of HBPin from an isomer of complex **4**, where two five-membered phosphine rings of the pincer ligand are folded in different directions, has been located with a barrier of 12.4 kcal/mol higher than **4**. Therefore, the H¹BPin group in **4** is able to rotate in a counterclockwise direction along the B-Co axis towards P¹ and simultaneously H² moves far from B, as is described by **TS**₄₋₅, to form complex **5**, which adopts a distorted trigonal

bipyramidal geometry in which H¹BPIn and phosphine ligands occupy the equatorial positions with H² and pyridine ligands in the axial positions. Subsequently, the H¹BPIn group of **5** continues to rotate in an anticlockwise direction along the B-Co axis towards H², and concurrently H² moves downwards (i.e., far from the B atom) via transition state **TS₅₋₆**, giving complex **6**, which adopts a distorted trigonal bipyramidal geometry in which H², H¹BPIn, and pyridine ligands occupy the equatorial positions with phosphine ligands lying almost in the axial positions. Here, we are considering H¹BPIn as a single σ -bonded ligand with H¹-B bond occupying one coordination site, although both H¹ and B are shown as coordinated to Co in Figure 3. Thus, the isomerization process from **4** to **6** via **5** proceeds like a Berry pseudorotation,⁷⁵ which occurs widely in trigonal bipyramidal structures. Compared to **4**, the B-H² distance is longer and the P¹-Co-P² angle is smaller in **5** (Figure 3), thus, **5** is higher in energy due to the loss of the B-H² bonding interaction and the steric effects of two phosphine ligands in **5**. Furthermore, **6** is higher than **5** because of additional steric effects between H², H¹BPIn, and pyridine ligands in the same plane. For the same reasons, the barrier of **TS₅₋₆** is also higher than that of **TS₄₋₅**.

The two hydrides, which in **6** are cis with H¹ bridging Co and B atoms, then simultaneously move away from B (via **TS₆₋₇**) to generate **7**. Complex **7** adopts an octahedral geometry with one H trans to N and the other trans to B, and the two five-membered phosphine rings in **7** are folded in the same direction. Next, one sp³-C of the phosphine ring (in blue) flips down via **TS₇₋₈** to form complex **8**, *cis*-(ⁱPrPNP)CoH₂(BPIn), which is more stable than **7** but less stable than the *trans*-(ⁱPrPNP)CoH₂(BPIn) complex **2** by 7.8 kcal/mol. Then in **TS₈₋₉** the other phosphine ring (in black) is also flipping down to form **9**, in which the BPIn group is bending towards the trans position of the pyridine ligand because of steric clashes with the P substituents. The movement of BPIn drives the H atoms closer and the H₂-formation transition state, **TS₉₋₁₀**, leads to an H₂ σ -complex, **10**, which then releases H₂ to generate a four-coordinated Co(I) complex **11** with a planar geometry around Co. The formation of **11** has been confirmed in experiments by capturing it as a CO adduct, **11(CO)**, with CO occupying a vacant position on Co.³⁰ It should be noted that the five-membered ring plane of BPIn is perpendicular to the plane of the pyridine ring in the optimized geometry of **11**. In contrast, the two planes are parallel to each other in the crystal structure of **11(CO)**. Comparisons of the Co-X bonds (X any coordinated atom) in the optimized geometry and crystal structure of **11(CO)** show that the largest difference (0.023 Å) corresponds to the Co-N bond. When CO is added to the structure of **11**, BPIn rotates toward being planar, but there is a barrier to overcome to form the planar **11(CO)**; however, the planar structure is more stable than this intermediate structure. Furthermore, optimizations of the structure generated by removing CO from **11(CO)** converge back to the geometry of **11** in Figure 3. In the process for the release of H₂ from **2** (Figure 2), the rate-determining transition state is **TS₉₋₁₀** with a barrier of 18.5[19.8](17.6) kcal/mol, and the formation of **11** and H₂ is uphill by 11.3[21.4](9.9) kcal/mol relative to complex **2**. The TPSS functional predicts a more favorable process, where the barrier for **TS₉₋₁₀** and the products **11** and H₂ are 15.2[16.2] (16.2) and 6.5[16.8](16.2) kcal/mol, respectively.

In the reverse reaction complex **9** can be considered an H₂-activation product that is formed from **11** and H₂ via **TS₉₋₁₀**, where the H₂ bond-breaking H atoms are moving towards BPIn

and pyridine ligands, respectively. Alternatively, H₂ can be also cleaved along a direction parallel to the line between two phosphine atoms to form an isomer of **9**, which adopts an octahedral geometry in which two H atoms and two phosphine ligands occupy the equatorial positions, and the pyridine ligands and BPin occupy the axial positions. As shown in SI5, this isomer of **9** could be formed reversibly, which then releases H₂ to regenerate complex **11**.

For each species in Figure 2, several different geometries are possible by rotating iPr groups of the phosphine ligands, and the geometries shown in Figure 3 and SI2 correspond to the most stable ones. In addition, these geometries are considered to isomerize between each other very easily by rotating the iPr groups separately (see SI6 for an example of the isomerization process from **4** to its isomer). Thus, species with different orientations of iPr groups may exist, but that would not change the results obtained in the following discussions.

The mechanism shown in Figure 2 is generally similar to that for the model systems (SI7), in which all the iPr substituents of the ^{iPr}PNP ligand were replaced with Me and B₂Pin₂ was replaced with B₂eg₂ (superscript “m” is added to the reported complex’s number to denote their corresponding model complex). Due to less steric clashing between the substituents on the phosphine ligands in the model systems, the barriers for the ring “flipping” transition states **TS**₂₋₃^m, **TS**₇₋₈^m, and **TS**₈₋₉^m are 2.6, 8.0, and 16.5 kcal/mol relative to **2**^m (Figure S5 and S6), which are lower than the corresponding (full system) transition states **TS**₂₋₃, **TS**₇₋₈, and **TS**₈₋₉ in Figure 2. By using the model systems, other possibilities were checked. For example, the isomerization between **11**^m and its isomer in which two five-membered phosphine rings are folded in different directions was calculated to occur very easily (Figure S6). Furthermore, isomers of **5**^m, **6**^m, and **10**^m in which two five-membered phosphine rings are folded in different directions are found to be unlikely, as optimizations of these isomers repeatedly converge to **5**^m, **6**^m, and **10**^m, respectively. In addition, other possible pathways are calculated to be unlikely or less favorable, which include the direct release of H₂ from the cis-dihydride cobalt complex **8**^m, the formation of **8**^m from the trans-dihydride cobalt complex **2**^m via the dissociation and association of HBeg (Figure S7), the formation of **8**^m from **2**^m through dissociation of one phosphine (Figure S8), and the release of H₂ via the dearomatization of the pyridine ligand (Figure S9). Our results, which involve reductive elimination (RE) of H₂ from a Co(III) pincer complex, differ from a previous study of the C-C bond formation via RE from a cobalt(III) dimethyl complex, where dissociation of a phosphine ligand was required prior to RE.⁷⁶ Maybe for future work, it is also interesting to compare the PNP system with all of this flexibility to terpyridine ones that also borylate but are more rigid.

Among these unfavorable pathways, the dearomatization of the pyridine ligand is quite interesting, as a series of PNP pincer ligated Ru complexes that are similar to complex **2** have been synthesized by Milstein and coworkers and reported to show a mode of metal-ligand cooperation based on the ligand’s aromatization/dearomatization.⁵⁶⁻⁵⁸ Pincer ligand benzylic deprotonations and hydrogen abstractions in related Co(I) complexes suggest that the metal-ligand cooperation in the Rh complexes may involve deprotonation at the benzylic site,⁵⁵ consistent with calculations on the Ru mechanism.⁵⁶⁻⁵⁸ To confirm the conclusions

obtained with model systems, we recalculated this pathway by using complex **2** with the full ligand (*i*PrPNP). Considering that the pyridine ligand and other atoms use different basis sets in the optimizations (see SI1 in Computational Details), we employed another basis set BS4 (LANL2DZ for Co and 6-31G* for the others) to optimize the species involved in this pathway. The rest of the methodology was the same (see Computational Details). Thus, the results for this pathway used in the following discussions are obtained at the level of ω B97XD/Def2TZVP(SMD)// ω B97XD/BS4. At this level, the barrier for **TS**₉₋₁₀ and the product complex **11** with the release of H₂ are 18.2[19.5] and 10.7[21.3] kcal/mol ($G_{C_6H_6}$ [$H_{C_6H_6}$]), respectively, relative to **2**. As shown in SI8, the level of ω B97XD/Def2TZVP(SMD)// ω B97XD/BS4 is suitable in the calculations of this system by giving reasonable optimized geometries and the results close to that at the level of ω B97XD/Def2TZVP(SMD)// ω B97XD/BS1.

With ω B97XD/BS4, the optimized geometries for transition state **TS**₂₋₁₂ and the product complex **12** involved in the pathway via the dearomatization of the pyridine ligand are shown in Figure 4. **TS**₂₋₁₂ corresponds to the formation of H₂ by eliminating a hydride at Co and a proton from the sp³-C of the pyridine ligand. In contrast to the reductive elimination pathway to form the Co(I) complex **11** via **TS**₉₋₁₀, complex **12** remains a Co(III) complex due to the dearomatization of the pyridine ligand. In addition, the hydride at Co is close to B, which could indicate an interaction between the hydride and the vacant orbital on B. At the level of ω B97XD/Def2TZVP(SMD)// ω B97XD/BS4, **TS**₂₋₁₂ and complex **12** with the release of H₂ are 31.5[32.4] and 6.1[17.1] kcal/mol ($G_{C_6H_6}$ [$H_{C_6H_6}$]), respectively, relative to **2**. In addition, the dissociation of HBPIn from **12** is unfavorable, as this process is endothermic by 13.1[27.4] kcal/mol. The origin of the higher barrier for **TS**₂₋₁₂ can be seen in the distance between two eliminating H atoms in their optimized geometries. The distance between the hydride at Co and the hydrogen atom at sp³-C of the pyridine ligand) decreases by 2.02 Å in forming **TS**₂₋₁₂, the corresponding distance between the two eliminating H atoms decreases by only 0.82 Å in forming **TS**₉₋₁₀. Thus, changing geometries from **2** to **TS**₂₋₁₂ requires more energy. Moreover, the dearomatization of the pyridine ligand further destabilizes transition state **TS**₂₋₁₂. Therefore, the mechanism for the release of H₂ via the dearomatization of the pyridine ligand is less favorable than that via the reductive elimination mechanism shown in Figure 2. Furthermore, the mechanism via the reversible ligand dearomatization-aromatization was also ruled out based on the experimental observations.³⁰

To understand the effect of the metal, we investigated the release of H₂ from the corresponding iridium complex **2**^{Ir} (*trans*-(*i*PrPNP)IrH₂(BPIn)) formed by replacing Co in **2** with Ir. The barriers for H₂ formation in the iridium analogues are higher than those in the cobalt systems: **TS**₉₋₁₀^{Ir} and **TS**₂₋₁₂^{Ir} are higher than **TS**₉₋₁₀ and **TS**₂₋₁₂ by 14.3 and 5.3 kcal/mol, respectively (Table 1). To understand the effect of the ligand, we also calculated the release of H₂ from their phenyl analogues (**2**^{Ph} = *trans*-(*i*PrPNP)CoH₂(Ph) and **2**^{Ir-Ph} = *trans*-(*i*PrPNP)IrH₂(Ph)), which are generated by using Ph to replace BPIn in **2** and **2**^{Ir}, respectively. The barriers for H₂ formation for **2** and **2**^{Ir} are close to those for their phenyl analogues (**2**^{Ph} and **2**^{Ir-Ph}) with the variations of less than 3 kcal/mol (Table 1). Thus, the choice of the metal affects the reactivity to a greater degree than the choice of the ligand. In

particular, the barriers for H₂ formation via the reductive elimination mechanism for iridium analogues (**TS**₉₋₁₀^{Ir} and **TS**₉₋₁₀^{Ir-Ph}) are higher by more than 14 kcal/mol than those for cobalt systems (**TS**₉₋₁₀ and **TS**₉₋₁₀^{Ph}, respectively). In contrast, H₂ formation via the dearomatization of the pyridine ligand for the iridium analogues (**TS**₂₋₁₂^{Ir} and **TS**₂₋₁₂^{Ir-Ph}) are higher by only 5.3 kcal/mol than those for the cobalt systems (**TS**₂₋₁₂ and **TS**₂₋₁₂^{Ph}, respectively). Relative to **2**^{Ir}, the barriers for the H₂ formation, **TS**₉₋₁₀^{Ir} and **TS**₂₋₁₂^{Ir}, are over 32 kcal/mol (Table 1). Consistent with these results, Chirik and coworkers observed that the iridium congener with a pyrrolidinyl substituent in 4-position of the pincer ligand is very stable under catalytic conditions, which can be ascribed to a more difficult reductive elimination from Ir(III) to Ir(I) than from Co(III) to Co(I), as proposed by Chirik and coworkers.³⁰ Furthermore, Milstein and coworkers did not observe the release of H₂ from an iridium complex **2**^{Ir-Ph-tBu} (*trans*-(^tBuPNP)IrH₂(Ph)),⁷⁷ for which the predicted barriers for H₂ formation are over 33 kcal/mol (Table 1). In addition, **TS**₂₋₁₂^{Ir-Ph-tBu} is very close to **TS**₂₋₁₂^{Ir-Ph}, while **TS**₉₋₁₀^{Ir-Ph-tBu} is much higher than **TS**₉₋₁₀^{Ir-Ph}, which can be ascribed to the steric effects between tBu groups in **TS**₉₋₁₀^{Ir-Ph-tBu} (see their optimized geometries in SI9).

3.2 Oxidative addition of C₆H₆

The cobalt boryl complex (ⁱPrPNP)CoBPin (**11**), which is generated from complex **2** via the H₂ release mechanism (Figure 2), is the active species that catalyzes the borylation reactions of five-membered heteroarenes. This active species can also be formed in the presence of B₂Pin₂ directly from the catalyst precursor (ⁱPrPNP)Co(CH₂SiMe₃) (**1**) by releasing Me₃SiCH₂BPin, as observed in experiments.²⁸ This reaction was calculated to be thermodynamically very favorable ($\Delta G_{C_6H_6}[\text{H}_{C_6H_6}](\text{G}_{\text{gas}}) = -25.1[-24.6](-27.3)$ kcal/mol), and a possible pathway with reasonable barriers was located by using the model systems (SI10). The calculated energy profiles for the oxidative addition of C₆H₆ by **11** together with their optimized geometries are shown in Figure 5. A search along the backward direction of the imaginary frequency from **TS**₁₁₋₁₃ toward **11** failed to find either a Co σ -complex or a Co π -complex. In the forward direction of the oxidative-addition transition state **TS**₁₁₋₁₃, the breaking C-H bond of C₆H₆ is parallel to a line between the two phosphine atoms. Thus, **TS**₁₁₋₁₃ and the product complex **13** adopt a distorted octahedral geometry in which C₆H₅, H, and phosphine ligands occupy the equatorial positions, and the pyridine ligands and BPin occupy the axial positions. In this geometry, the pyridine ligand occupies one face of the octahedron around Co, i.e., the N and P atoms of the pyridine ligand are cis to each other, a facial isomeric form. Therefore, due to the distorted backbone of pyridine ligands and the steric effects between the substituents of phosphine ligands, complex **13** is very high in energy, 23.0 kcal/mol relative to separated **11** and C₆H₆. This step is also unfavorable under the TPSS functional, where **TS**₁₁₋₁₃ and **13** are 34.8[18.9] (19.5) and 33.6[18.2](18.8) kcal/mol, respectively. However, the next process, the reductive elimination of B-C bond to form PhBPin, can drive the overall reaction forward.

In addition to the pathway shown in Figure 5, alternative pathways for the oxidative addition of C₆H₆ to the cobalt boryl complex in the model systems were explored (SI11): (1) an oxidative-addition pathway to form another facial isomer of **13**^m in which C₆H₅ and Bg are switched (Figure S13(B) in SI11), (2) oxidative-addition pathways directly forming

meridional complex **15^m** (see Figure 6 and Figure S13(C) in SI11) and its meridional isomer in which C₆H₅ and H are switched (Figure S13(D) in SI11), (3) σ -bond metathesis pathways, and (4) a pathway for the oxidative-addition of C₆H₆ to the cobalt complex with one phosphine ligand dissociated (Figure S14 in SI11). However, these alternative pathways were calculated to be unlikely or less favorable than that in Figure 5.

Some conclusions obtained from the model systems remain the same for the experimentally reported systems (SI12). For example, alternative σ -bond metathesis pathways remain unlikely relative to oxidative addition, because the Co(I) in **11** is easily oxidized to Co(III) via the oxidative addition. In contrast, previously reported σ -bond metathesis pathways are proposed for the reactions of complexes in high oxidation states, such as W(III),^{39,45} Rh(III),⁴² and Ir(III)^{47,49} complexes. In addition, alternative oxidative-addition pathways to form meridional complex **15** and its meridional isomer are still less favorable than that via **TS₁₁₋₁₃** in Figure 5 (Figure S15 in SI12). The lower barrier of **TS₁₁₋₁₃** can be ascribed to lower distortion energy of the Co catalyst and the more negative interaction energy (Table S6 in SI12).

Using model complexes, pathways for adding C₆H₆ to the corresponding Rh and Ir complexes (**Rh11^m** and **Ir11^m**) obtained by replacing Co in **11^m** with Rh and Ir, respectively, were examined (SI13). Like the Co complex, σ -bond metathesis pathways for the Rh and Ir complexes are still unlikely because of their low oxidation state. In addition, the oxidative-addition pathways via **RhTS_{11-13^m}** and **IrTS_{11-13^m}** (corresponding Rh and Ir transition states of **TS_{11-13^m}**) are still more favorable than that for directly forming **Rh15^m** and **Ir15^m** (corresponding Rh and Ir complexes of **15^m**) and their isomers.

With the active species 4-BPin-(ⁱPrPNP)CoBPIn, we calculated this process by optimizing corresponding species **TS_{11-13^{BPIn}}** and **13^{BPIn}** with ω B97XD/BS4 (LANL2DZ for Co and 6-31G* for the others). The same method was employed to recalculate **TS₁₁₋₁₃** and **13** for consistency. At the level of ω B97XD/Def2TZVP(SMD)// ω B97XD/BS4, **TS₁₁₋₁₃**, **13**, **TS_{11-13^{BPIn}}**, and **13^{BPIn}** are 24.2[8.2](23.0), 21.9[6.9](22.0), 23.8[8.2](22.8), and 21.6[7.1] (21.7) kcal/mol, respectively. Although the barrier for **TS_{11-13^{BPIn}}** is slightly lower than that for **TS₁₁₋₁₃** in free energy, they are the same in enthalpy, and the former is slightly higher than the latter by 0.05 kcal/mol in SCF energy. Furthermore, as shown by Table 2 and corresponding discussions in the following section, the relative energies of **TS_{11-13^{BPIn}}** and **TS₁₁₋₁₃** depend on selected calculation methods. The experimental observations that the C-H oxidative addition with 4-BPin-(ⁱPrPNP)CoBPIn is slower than that with (ⁱPrPNP)CoBPIn³⁰ may be explained by these differences.

3.3 Reductive elimination of B-C bond to form PhBPIn

From the C₆H₆ addition product **13**, the calculated energy profiles for the reductive elimination of the B-C bond to generate the borylation product PhBPIn are shown in Figure 6. By beginning at complex **13**, where the pincer is folded and C₆H₅, H, and BPIn are in the opposite *fac* site, the H and BPIn groups rotate via transition state **TS₁₃₋₁₄** to form complex **14**, which adopts a distorted octahedral geometry where C₆H₅, H, BPIn, and the pyridine ligands are in the same plane, and the P-Co-P angle begins to open. Then, the P arm in blue

tips up and the pincer unfolds into its *mer* site to form **15**, where the Ph and BPin groups are *trans*. Subsequently, the HBPin group dissociates from **15** to form a four-coordinated Co-phenyl complex **16**, followed by the re-association of HBPin to generate complex **17** where the Ph and BPin groups are in *cis* positions (alternative dissociation/re-association route are possible but were not investigated). For the vibrational modes of transition states **TS₁₅₋₁₆** and **TS₁₆₋₁₇**, in addition to the oxidation and reductive elimination of HBPin, the Ph groups are also rotating around Co towards or away from the *trans* position of the N atom. From complex **17** where the two five-membered phosphine rings of the pincer ligand are folded in different directions, the P arm in blue then flips down to afford complex **18**. In **18**, the Ph and BPin groups are in *cis* positions, from which they proceed through a reductive elimination transition state **TS₁₈₋₁₉** to form complex **19**, followed by the release of the product PhBPin to generate a Co-hydride complex **20**. The transition state **TS₁₈₋₁₉** corresponds to the reductive elimination of PhBPin and the rotation of H atom around Co.

Due to the release of steric effects between the ligands, complex **14** is more stable than **13** by 3.1 kcal/mol, and complex **15** is more stable than **14** by 2.0 kcal/mol. Moreover, complex **17** is more stable than **15** by 6.8 kcal/mol. According to Figure 6, the reductive elimination processes are very favorable. The formations of Co(I) complexes **16** and **20** from their corresponding Co(III) complexes **15** and **18**, respectively, are favorable by releasing more than 9 kcal/mol. Overall, the generated PhBPin and complex **20** are lower than complex **13** by 26.5 kcal/mol, and they are also lower than separate reactants (C₆H₆ and **11**) by 3.5 kcal/mol. Thus, the reductive elimination process is thermodynamically favorable, which drives the reaction to produce PhBPin.

In comparison with the oxidative addition process in Figure 5, the reductive elimination process in Figure 6 appears to have the rate-determining step, as several transition states involved in Figure 6 (**TS₁₃₋₁₄**, **TS₁₄₋₁₅**, **TS₁₅₋₁₆**, **TS₁₆₋₁₇**, and **TS₁₈₋₁₉**) are a little higher than the C-H oxidative-addition transition state **TS₁₁₋₁₃**. The same conclusion was also obtained by using the experimentally proposed active species 4-BPin-(*i*PrPNP)CoBPin, as the barrier of **TS₁₁₋₁₃^{BPin}** (23.8[8.2](22.8) kcal/mol) for the C-H oxidative addition is still lower than that of **TS₁₈₋₁₉^{BPin}** (25.7[9.7](23.0) kcal/mol) for the reductive elimination at the level of ω B97XD/Def2TZVP(SMD)// ω B97XD/BS4. These results appear to be inconsistent with the experimental observations that the C-H oxidative addition was indicated to be the rate-determining step for the borylation of 2,6-lutidine with B₂Pin₂.³⁰ Of course, the differences between these barriers are small and the transition states involved in Figure 6 could adopt other lower-barrier conformations due to the flexibility of ligands, in particular the rotations of *i*Pr groups and the orientations of phosphine ligands. Here, we hesitate to try to find all possible conformations because of the large computation cost and because we could not trust such small differences. To support this postulation, a similar reductive elimination pathway was calculated by using model systems (Figure S17 in SI15). The results show that the reductive elimination transition state **TS₁₈₋₁₉^m** (corresponding to **TS₁₈₋₁₉**) is the highest one among these transition states. However, **TS₁₈₋₁₉^m** is slightly lower by 0.5 kcal/mol than the C-H oxidative addition transition state **TS₁₁₋₁₃^m**. Thus, for the model system, the oxidative addition step is the rate-determining step. To further explore the effects of functionals and basis sets, calculations were conducted for these two important

transition states **TS**_{11–13} (the oxidative addition transition state) and **TS**_{18–19} (the reductive elimination transition state) by employing several different DFT functionals and basis sets (Table 2). Although the barriers for **TS**_{18–19} are predicted to be slightly higher than that for **TS**_{11–13} with most of these tested methods, **TS**_{18–19} is lower than **TS**_{11–13} with M06L. In addition, the results at the level of M06/Def2TZVP(SMD)//M06/BS1 are very close with a difference of only 0.6 kcal/mol. Thus, the choice of functional could be a source of this small inconsistency. Considering that the C-H oxidative addition is the rate-determining step, the overall barrier for the reaction is 24.2 kcal/mol from **11** to **TS**_{11–13}. Consistent with the calculated barrier, the reaction was observed to occur at 80°C for 24 h with the isolated yield of 87% by employing a 20:1 ration of arene to B₂Pin₂ in the reported experiments.²⁸

From complex **13**, the barriers for the reductive elimination of the C-H bond via **TS**_{11–13}, the reductive elimination of the B-H bond via **TS**_{15–16}, and the reductive elimination of the B-C bond via **TS**_{18–19} are 1.2, 5.8, and 2.2 kcal/mol, respectively. Furthermore, their corresponding thermodynamics are –23.0, –14.7, and –26.5 kcal/mol for the formations of **11** and C₆H₆, the formations of **16** and HBPin, and the formations of **20** and PhBPin. Thus, the reductive elimination of the B-C bond is the most favorable process, which drives the reaction forward to produce PhBPin, while the reductive eliminations of the C-H and B-H bond are considered to be reversible.

The barriers for the ring “flipping” transition states **TS**_{14–15^m and **TS**_{17–18^m, relative to separate C₆H₆ and **11^m**, are 12.7 and –2.3 kcal/mol (Figure S17), which are lower than the corresponding (full system) transition states **TS**_{14–15} and **TS**_{17–18} in Figure 6, as there is less steric clashing between the substituents on the phosphine ligands in the model systems. In addition to the pathway shown in Figure 6, several other possibilities were considered by using model systems and found to be less favorable (see SI15): direct reductive elimination of the B-C bond from the oxidative addition product **13^m** (Figure S18), reductive elimination through an isomer of the **TS**_{18–19^m with two phosphine ligands in different directions (Figure S19(A)), reductive elimination with the assist of HBeg (Figure S19(B)), reductive elimination from the C₆H₆ oxidative addition product where the cleaved C₆H₅ and H are in cis positions (Figure S19(C)), reductive elimination via the dissociation of one phosphine ligand (Figure S19(D)), and reductive elimination from the oxidative addition product from B₂eg₂ and the Co(I)-Ph complex (Figure S20). With the experimentally reported systems, the process for the reductive elimination of the B-C bond to generate the borylated product PhBPin through the direct reductive elimination from **13** was further calculated to be unlikely, as the barrier for **TS**_{13–20} is very high, 38.4[23.6](36.3) kcal/mol relative to separated C₆H₆ and **11** (Figure S21). In addition, another possible pathway for the oxidative addition of C₆H₆ to the Co(I)-H complex **20^m** was also considered (Figure S22), but it was less favorable thermodynamically and kinetically than the oxidative addition of B₂eg₂ to regenerate the active species (Figure S24 in SI17).}}}

At the level of ωB97XD/Def2TZVP(SMD)//ωB97XD/BS4, **TS**_{18–19}, **20**, **TS**_{18–19^{BPin}, and **20^{BPin}** are 26.0[9.7](23.3), –3.2[–0.8](2.2), 25.7[9.7](23.0), and –5.2[–1.0](0.2) kcal/mol, respectively, where **20^{BPin}** and **TS**_{18–19^{BPin} are the active species 4-BPin-(ⁱPrPNP)CoBPin and its corresponding transition state. Accordingly, the reductive elimination process with 4-}}

BPin-(ⁱPrPNP)CoBPin is more favorable than that with (ⁱPrPNP)CoBPin both kinetically and thermodynamically.

3.4 Regeneration of (ⁱPrPNP)CoBPin

In the presence of B₂Pin₂, the active species (ⁱPrPNP)CoBPin (**11**) can be regenerated from (ⁱPrPNP)CoH (**20**) by following the pathway shown in Figure 7. Coordination of B₂Pin₂ to **20** gives complex **21**, in which the B-B bond is parallel with N-Co-H axis, is followed by transition state **TS**₂₁₋₂₂ corresponding to simultaneous cleavage of B-B bond and rotation of Co-H bond to generate an octahedral complex **22**. Subsequently, the sp³-C of the phosphine ring in blue flips up via transition state **TS**₂₂₋₂₃ to form complex **23**. Like the dihydride cobalt complexes in Figure 2, complex **23**, where the two five-membered rings are folded in different directions, is slightly more stable than complex **22** where the two five-membered rings are folded in the same direction. Then, through transition state **TS**₂₃₋₂₄, in which the H and BPin on Co are moving towards each other, and transition state **TS**₂₄₋₂₅, in which BPin rotated and forms the new H-B bond. Finally, HBPin dissociates from **25** via transition state **TS**₂₅₋₁₁ to regenerate the active species **11**. An alternative pathway for the generation of **11** from **25** via an intermediate that is formed from **25** by flipping up the sp³-C of the phosphine ring in blue is slightly less favorable, and the transition state for the dissociation of HBPin from this intermediate is higher than **TS**₂₅₋₁₁ by 0.7 kcal/mol. As shown in Figure 7, the formation of **11** with releasing HBPin from **20** and B₂Pin₂ is favorable thermodynamically and kinetically; the rate-determining barrier for this process is only 14.1 kcal/mol (**TS**₂₄₋₂₅ relative to **23**).

The pathways discussed above are consistent with those for the model systems (SI17). In the model system several less favorable alternative paths were explored: formation of an isomer of **21**, in which the B-B bond is parallel with the P-Co-P axis, formation of **24** from **22**, in which the H and Beg on Co firstly move towards each other, followed by the sp³-C of one phosphine ring flips up, formation of **25** from **24**, in which the sp³-C of one phosphine ring firstly flips up to generate an intermediate with two phosphine rings bending in the same direction, and the pathway with one phosphine ligand dissociated (Figure S25 in SI17).

4. Conclusions

Density functional theory (DFT) calculations on C-H borylation catalyzed by cobalt pincer complexes with C₆H₆ and B₂Pin₂ as substrates predict a mechanism involving three distinct steps: oxidative addition of C₆H₆, reductive elimination PhBPin, and regeneration of (ⁱPrPNP)CoBPin. The *trans*-(ⁱPrPNP)CoH₂(BPin) complex was experimentally observed as a resting state in the borylation of five-membered heteroarenes. Starting from this complex, the active species, (ⁱPrPNP)CoBPin, is generated by rearrangement to the *cis* isomer and reductive elimination of H₂. The isomerization pathway is similar to the well-known Berry pseudorotation mechanism with the H¹BPin group acting as a unit in a 5-coordinate Co. The metal-ligand cooperative mechanism based on the ligand's aromatization/dearomatization, which is widely proposed to explain the catalytic reactions by the PNP pincer ligated to heavier metals, is computed to be less favorable for this system. Additionally, the 4-BPin-(ⁱPrPNP)Co(N₂)BPin complex, which can easily release N₂ to form the active species, was

identified as the resting state in the catalytic borylation of arene substrates. The lowest barrier for oxidative addition of C₆H₆ forms a complex with a distorted PNP ligand, which rearranges to a more stable complex via dissociation and re-association of HBPin. Possible σ -bond metathesis pathways are predicted to be unlikely for this Co(I) complex. Reductive elimination of PhBPin is thermodynamically favorable and drives the reaction forward. The regeneration of the active species was found to proceed through the oxidative addition of B₂Pin₂ and reductive elimination of HBPin. In the overall reaction, the flipping up and down of the sp³-C of the five-membered phosphine rings, which connects the species with two phosphine rings folded in the same direction and that with them folded in different directions, is found to play important roles in the catalytic process, as this motion releases steric crowding within the PNP ligand and opens Co coordination space. This investigation provides some guidance for further understanding of important features of pincer ligands with first-transition-row metals that differ from those in heavier metal complexes.

Supplementary Material

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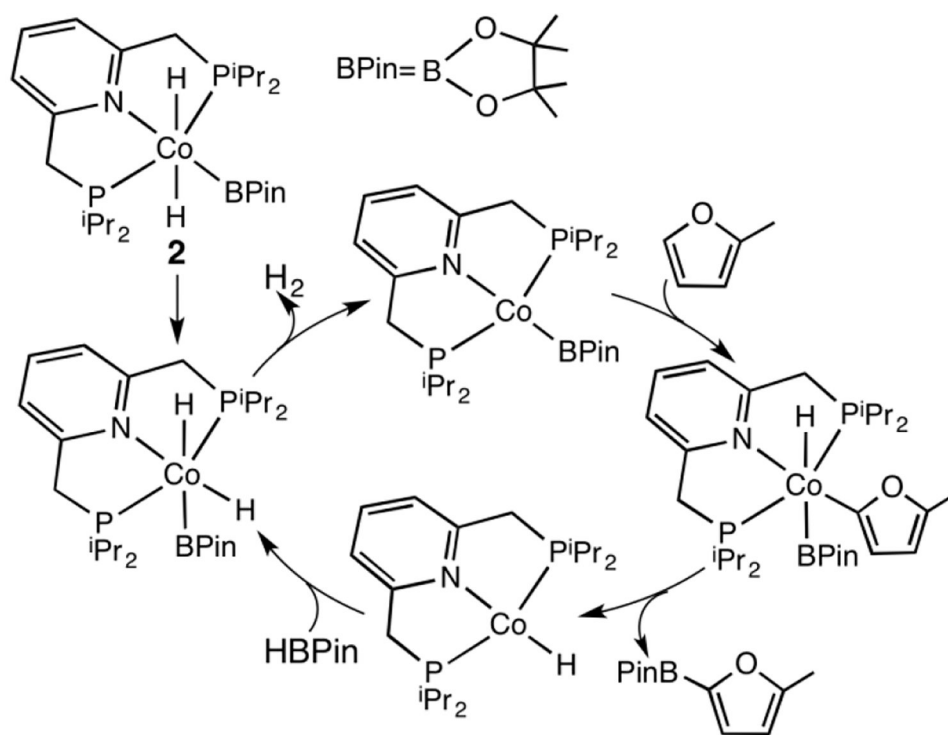


Figure 1. A proposed mechanism for the catalytic borylation of 2-methylfuran with HBPin from the resting-state complex **2** in ref. 28.

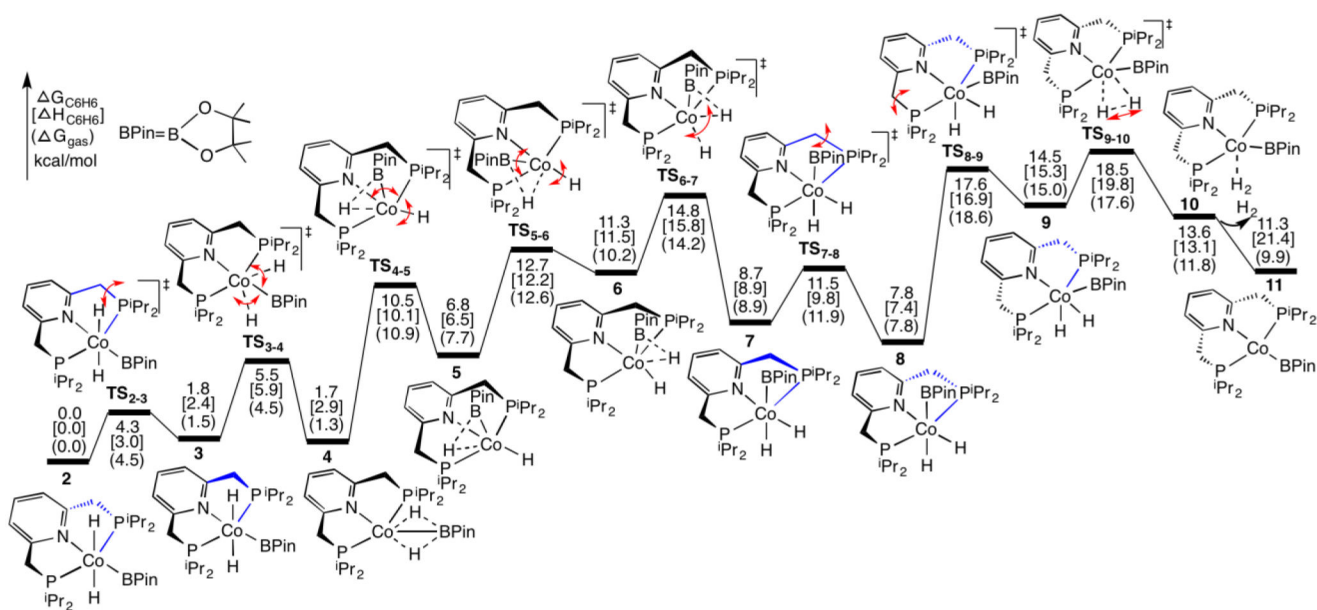


Figure 2. Calculated energy profiles for the release of H₂ from *trans*-(*i*PrPNP)CoH₂(BPin) complex **2**, which isomerizes to *cis*-(*i*PrPNP)CoH₂(BPin) before the rate determining reductive elimination.

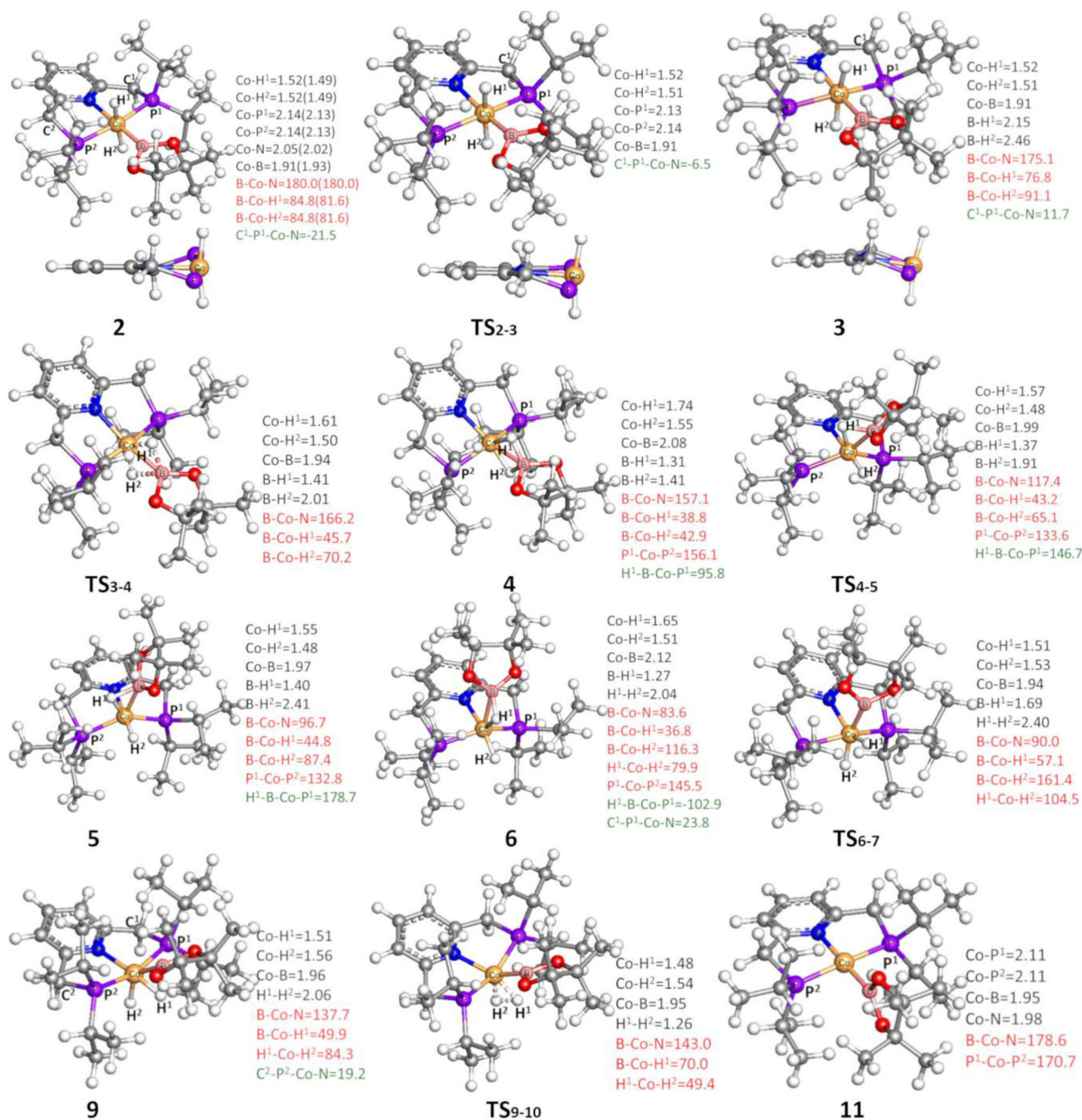


Figure 3. Optimized geometries of key species involved in the mechanism in Figure 2 (other species are in SI2). Some bond distances in Å, angles in °, and dihedral angles in ° are given in black, red, and green colors, respectively. Values in the parentheses in complex **2** are from its crystal structure. Geometries of **2**, **TS₂₋₃**, and **3** drawn in another perspective are also shown here, where *i*Pr groups on P and BPin on Co are omitted for clarity.

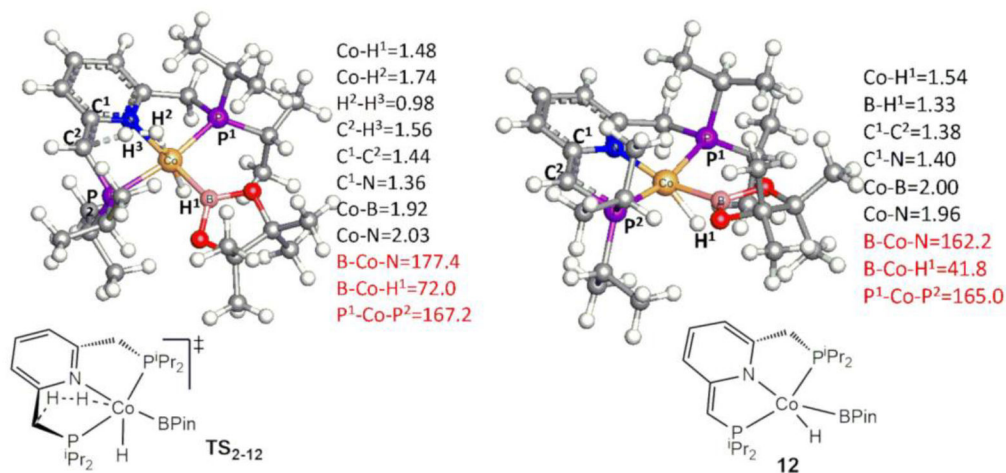


Figure 4. Optimized geometries of transition state TS_{2-12} and complex **12**. Some bond distances in Å and angles in ° are given in black and red colors, respectively.

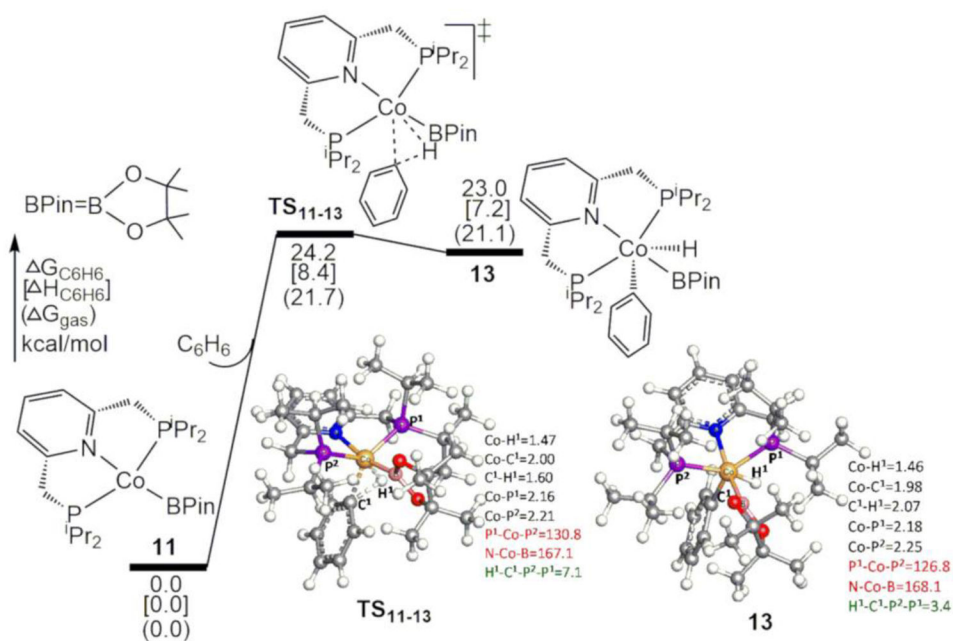


Figure 5. Calculated energy profiles for the oxidative addition of C_6H_6 to **11**. Some bond distances in Å, angles in $^\circ$, and dihedral angles in $^\circ$ are given in black, red, and green colors, respectively.

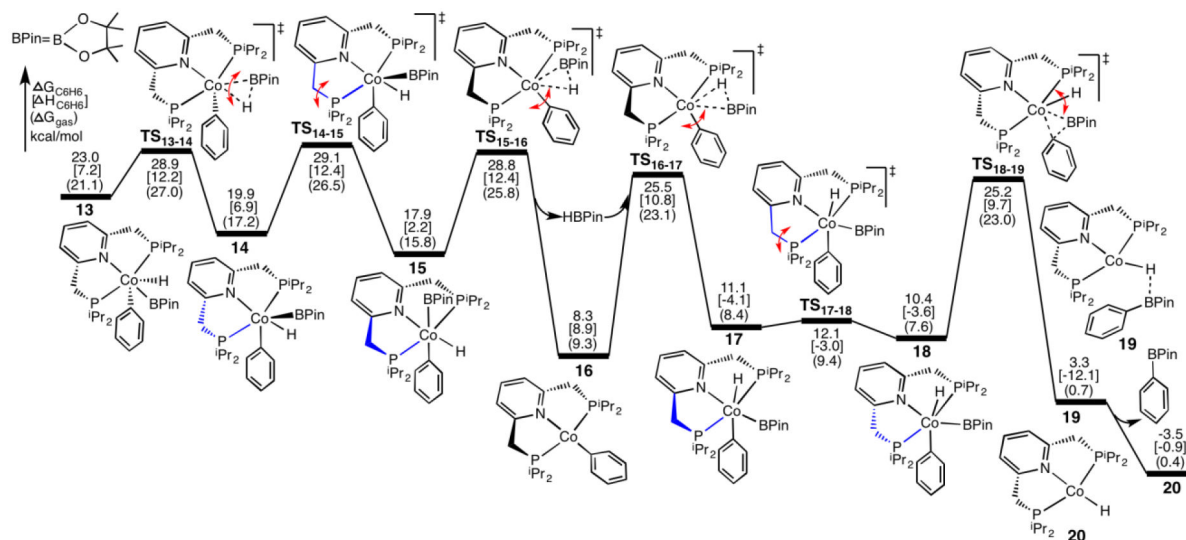


Figure 6. Calculated energy profiles for the reductive elimination of B-C bond to form PhBPIn. The energies for these species are relative to separate C₆H₆ and **11**, and their optimized geometries are shown in SI14.

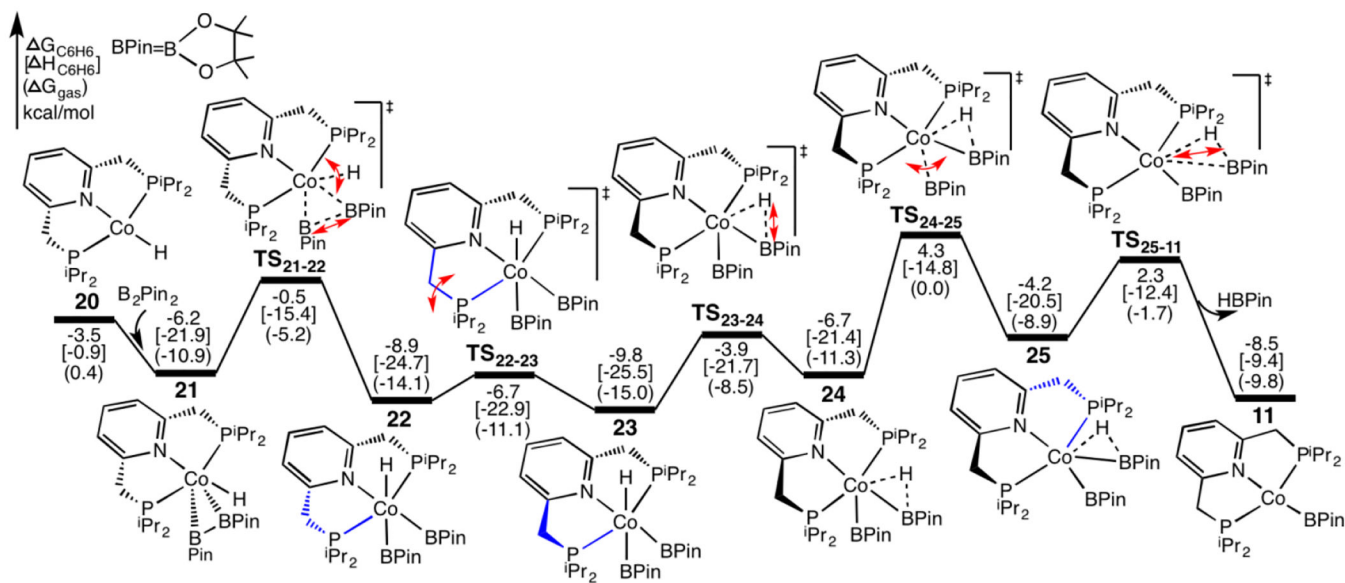
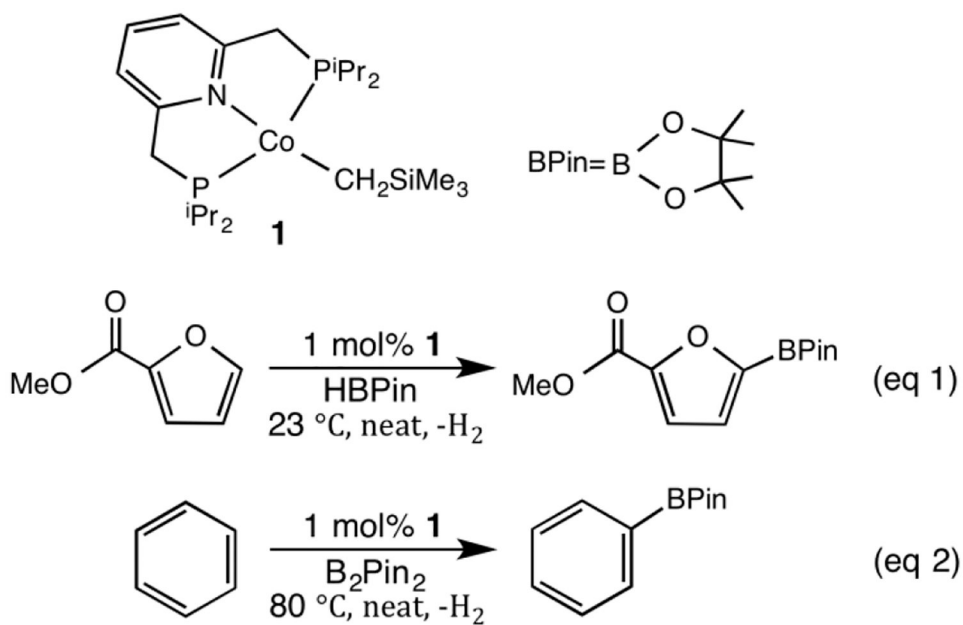


Figure 7. Calculated energy profiles for the regeneration of $(iPrPNP)CoBPin$ (**11**) from $(iPrPNP)CoH$ (**20**) and B_2Pin_2 . Optimized geometries of these species are shown in SI16.



Scheme 1.
A cobalt pincer complex **1** and its catalyzed borylation reactions.

Table 1.

Results for the release of H₂ at the level of ω B97XD/Def2TZVP(SMD)// ω B97XD/BS4. Values in kcal/mol are G_{C6H6} , H_{C6H6} (G_{gas}), and are relative to 2^R, respectively.

R	TS ₉₋₁₀ ^R	11 ^R + H ₂	TS ₂₋₁₂ ^R	12 ^R + H ₂
Ir	18.2[19.5](17.2)	10.7[21.3](4.8)	31.5[32.4](32.0)	6.1[17.1](5.0)
Ph	32.5[34.4](31.8)	17.4[28.8](16.3)	36.8[36.8](39.0)	14.3[24.3](18.1)
Ir_Ph	19.1[20.5](18.0)	-0.6[11.6](-7.8)	28.9[29.3](28.7)	6.3[17.6](7.5)
Ir_Ph_tBu	35.0[34.5](35.7)	9.1[20.1](8.3)	34.2[34.2](36.2)	12.1[22.7](17.2)
Ir_Ph_tBu	41.5[45.9](42.6)	9.0[20.0](8.2)	33.5[34.1](35.5)	10.9[22.1](15.5)

Calculated barriers (in kcal/mol) for transition states TS₁₁₋₁₃ and TS₁₈₋₁₉ relative to separate 11 and C₆H₆ by using different functionals and basis sets.

Table 2.

	TS ₁₁₋₁₃	TS ₁₈₋₁₉
ω B97XD/Def2TZVP(SMD)// ω B97XD/BS1	24.2	25.2
M06/Def2TZVP(SMD)//M06/BS1	30.1	30.7
B3LYP/Def2TZVP(SMD)//B3LYP/BS1	43.0	44.5
B3LYP(GD3BJ)/Def2TZVP(SMD)//B3LYP(GD3BJ)/BS1	25.8	27.2
M06L/Def2TZVP(SMD)//M06L/BS1	26.5	26.4
ω B97XD/Def2TZVP(SMD)// ω B97XD/BSS ²	23.5	25.0
ω B97XD/Def2TZVP(SMD)// ω B97XD/BS4 ¹	24.2	26.0
ω B97XD/Def2TZVP(SMD)// ω B97XD/BSS ²	24.7	25.9
M06/Def2TZVP(SMD)//M06/BSS ²	30.4	32.3
B971/Def2TZVP(SMD)//B971/BSS ²	36.6	38.8
TPSS/Def2TZVP(SMD)//TPSS/BSS ²	34.8	36.1
TPSS/Def2TZVP(SMD)//TPSS/BS1	34.8	35.8

¹Co uses LANL2DZ and the others use 6-31G* in BS4;

²Co uses 6-31+G* and the others use 6-31G* in BS5.