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Two Reversible σ-Bond Metathesis Pathways for Boron−Palladium Bond Formation: Selective Synthesis of Isomeric Five-Coordinate Borylpalladium Complexes

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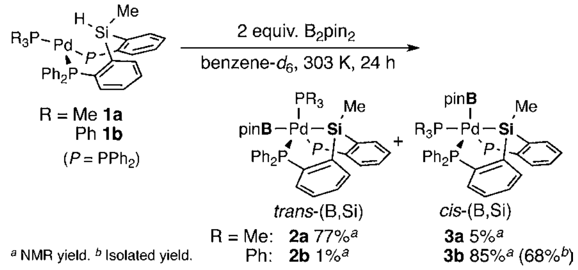
Supporting Information

ABSTRACT: Two reversible σ-bond metathesis pathways for B−B bond activation to give borylpalladium complexes are demonstrated in the reaction of η^2-(Si−H)Pd(0) complexes with B_2pin_2. These two pathways are connected by fluxional behavior of the Si−H bond and can be efficiently controlled by the appropriate choice of phosphine ligand, enabling the selective synthesis of two types of five-coordinate borylpalladium complexes.

Late transition metal-promoted activation of the B−B bond of diboron to give borylmetal complexes is an important elementary step in numerous catalytic borylation reactions.[1,2] The reaction generally proceeds via (1) oxidative addition of the B−B bond to the electron-rich metal center or (2) transfer of a boryl group to M−X (X = O, N, halogen), and a few examples of σ-bond metathesis with M−R bonds (R = C, B, etc.) have been reported.[3] Especially in the Pd-catalyzed reactions, the formation of borylpalladiums is mostly limited to the former two pathways, despite the wide use of Pd in a variety of borylation reactions using diboron.[4,5] The discovery of a new type of B−B bond activation by Pd complexes would be highly useful for the development of new catalytic borylation reactions. Herein we report two reversible σ-bond metathesis pathways for B−Pd bond formation in the reaction of η^2-(Si−H)Pd(0) complexes with bis(pinacolato)diboron (B_2pin_2) that are connected by fluxional behavior of the Si−H bond. The two pathways can be efficiently controlled by the appropriate choice of phosphine ligand, enabling for the first time the selective synthesis of two types of five-coordinate borylpalladium complexes.

We previously reported a new PSiP-pincer−Pd-catalyzed dehydrogenative borylation of alkenes in which the key intermediate, a PSiP−borylpalladium complex, is proposed to be generated by the reaction of B_2pin_2 with the palladium hydride generated from the corresponding palladium triflate complex and $AlEt_3$.[6] This finding prompted us to investigate the reaction of B_2pin_2 with η^2-(Si−H)Pd(0) complexes, which could act as palladium hydrides via oxidative addition of the Si−H bond.[7] Treatment of PMe_3-coordinated η^2-(Si−H)Pd(0) complex **1a** with 2 equiv of B_2pin_2 in benzene-d_6 at 303 K for 24 h afforded the five-coordinate borylpalladium complex *trans*-(B,Si)-**2a**, in which the B and Si atoms are in apical positions (Scheme 1).[8] Surprisingly, the same reaction of **1b** bearing PPh_3 instead of PMe_3 selectively gave in good yield another type of five-coordinate borylpalladium complex, *cis*-(B,Si)-**3b**, having the B and Si atoms at equatorial and apical positions (Scheme 1).

Scheme 1. Selective Synthesis of *trans*-2 and *cis*-3



[a] NMR yield. [b] Isolated yield.

Generation of HBpin was also observed by ^1H NMR spectroscopy in both reactions. The structures of these complexes were characterized by X-ray analyses (Figure 1). The geometry around the metal center seems to be trigonal-bipyramidal in both complexes. This is the first example of the synthesis and isolation of five-coordinate borylpalladium complexes.[9] Facile formation of the five-coordinate structure would be attributed to the pyramidalized central Si(sp^3) atom of the pincer ligand, which made the four-coordinate square-planar structure more strained. The stereochemistry of these complexes was confirmed to be retained in solution, as determined by NMR analyses [see the Supporting Information (SI)]. The configura-

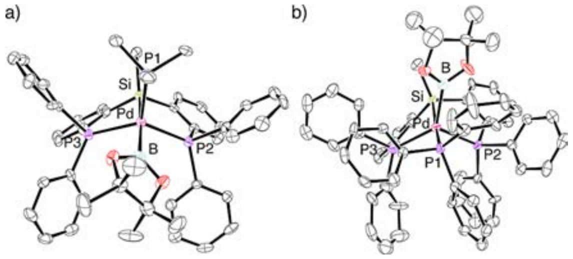


Figure 1. ORTEP diagrams of the five-coordinate borylpalladium complexes (a) *trans*-(B,Si)-**2a** and (b) *cis*-(B,Si)-**3b**. Thermal ellipsoids are shown at the 50% probability level; H atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for *trans*-(B,Si)-**2a**: Pd−B, 2.120(8); Pd−Si, 2.396(2); Pd−P1, 2.350(2); Pd−P2, 2.312(2); Pd−P3, 2.304(2); P1−Pd−P2, 113.81(6); P2−Pd−P3, 131.67(6); P3−Pd−P1, 113.66(6). For *cis*-(B,Si)-**3b**: Pd−B, 2.095(9); Pd−Si, 2.338(2); Pd−P1, 2.371(2); Pd−P2, 2.448(2); Pd−P3, 2.394(2); P1−Pd−P2, 102.87(6); P2−Pd−P3, 113.11(7); P3−Pd−P1, 101.93(7).

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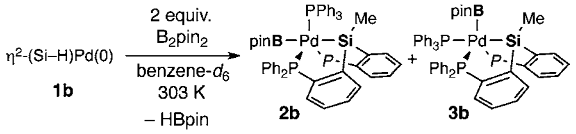
tional stability of **2a** and **3b** is noteworthy since such five-coordinate Pd(II) complexes are often proposed as transient intermediates in cis–trans isomerization reactions of 16-electron Pd(II) complexes via an associative mechanism.[10] Thus, this is a quite rare example of the selective formation and isolation of either a trans or a cis complex simply by changing one of the ligands in a five-coordinate Pd complex.[11,12]

Several experimental results shed light on the mechanism and the origin of the stereoselectivity as follows. Monitoring of the time dependence of the reaction of PPh_3-coordinated complex **1b** with B_2pin_2 at 303 K revealed that *trans*-(B,Si)-**2b** was actually generated in the beginning along with HBpin, and **2b** gradually disappeared as *cis*-(B,Si)- was formed with time (Table 1). At first, we considered the possibility that the initially formed *trans*-(B,Si)-**2b** underwent thermal isomerization to *cis*-(B,Si)-**3b**. However, isolated *trans*-(B,Si)-**2b** itself was confirmed to be mostly stable in benzene-d_6 at 303 K even after 24 h (14% of **2b** was converted to **3b**), indicating that such thermal isomerization was negligible under the reaction conditions.

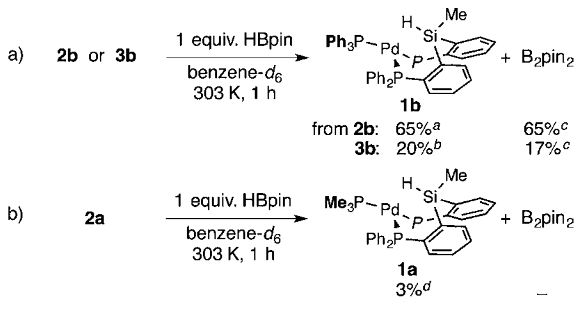
Table 1. Time Course Analysis of the Reaction of 1b with B_2pin_2



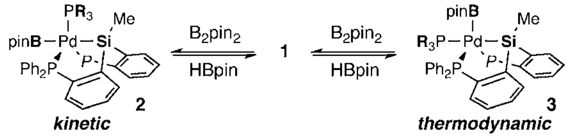
entry	time	1b	*trans*-(B,Si)-2b	*cis*-(B,Si)-3b
1	30 min	77%	18%	5%
2	1 h	71%	15%	14%
3	2 h	59%	9%	32%
4	5 h	28%	3%	70%

In view of the slow isomerization of *trans*-(B,Si)-**2b** under thermal conditions, the possibility that B_2pin_2 or HBpin might be involved in this isomerization process was investigated. Although treatment of **2b** with B_2pin_2 caused no reaction, it was a surprise to find that **2b** actually reacted with 1 equiv of HBpin *within 1 h* at 303 K to give **1b** in 65% yield along with the formation of B_2pin_2 (65% as determined by GC) (Scheme 2a). Thus, the B–Pd bond formation is reversible. The same reaction of *cis*-(B,Si)-**3b** with HBpin also afforded **1b** and B_2pin_2, but in lower yield (ca. 20%). Both reactions finally came to equilibrium after 24 h to give a ca. 70:30 **1b**:**3b** mixture. These results indicate that the formation of *trans*-(B,Si)-**2b** is kinetically favored but also reversible and that the reaction affords the thermodynamically more stable product, *cis*-(B,Si)-**3b**, as the major product in 24 h. Furthermore, it was found that PMe_3-coordinated *trans*-(B,Si)-**2a** scarcely reacted with 1 equiv of HBpin, giving **1a** in only 3% yield after 1 h (Scheme 2b). This result indicates that in the case of PMe_3-coordinated complexes, the reverse reaction of the kinetic product, *trans*-(B,Si)-**2a**, is very slow at room temperature because of the stronger coordination of PMe_3 than PPh_3.[13,14] Thus, the two reaction pathways to give the trans- or cis-(B,Si) product are controllable by the appropriate choice of the monophosphine ligand (Figure 2). The relative energy differences of **1**–**3** were estimated from the equilibrium constants for **1b** and **3b** and for **1a** and **2a** (HBpin/B_2pin_2-mediated reaction) and for the phosphine-exchange reactions of **1a**–**3a** with PPh_3 at 298 K (Table 2; see the SI for details). These studies clarify that (1) *cis*-(B,Si)-**3** is more stable than *trans*-(B,Si)-**2** by 2–3 kcal/mol for both phosphine ligands; (2) the PMe_3-coordinated borylpalladium complex is more stable than PPh_3-coordinated one by ca. 6 kcal/mol for each isomer; and (3) PPh_3-coordinated *trans*-(B,Si)-**2b** is less stable than the starting complex **1b**, whereas PMe_3-coordinated *trans*-(B,Si)-**2a** is more stable than **1a**.

Scheme 2. Reversibility of B–Pd bond formation



[a] ***2b***:*5%,* ***3b***:*30%.* [b] ***2b***:*2%,* ***3b***:*78%.* [c] *GC yield.* [d] ***2a***:*96%.*



PR_3 = PPh_3 : • The equilibrium gave the **thermodynamic** product **3b**.
PMe_3 : • The **kinetic** product **2a** was mainly obtained due to slow reverse reaction.

Figure 2. Two reversible B–Pd bond formation reactions.

Table 2. Energies of 1–3 (in kcal/mol) Relative to 1a at 298 K

2a	−1.9	**1a**	0.0	**3a**	−4.1
2b	+4.4	**1b**	+2.5	**3b**	+1.5

Density functional theory (DFT) calculations indicated that there exist two distinct reaction pathways from **1** and B_2pin_2 to give *trans*-(B,Si)-**2** and *cis*-(B,Si)-**3** through reversible oxidative addition/reductive elimination of the Si–H bond with Pd (i.e., fluxional behavior of Si–H bond) (Figure 3).[15–17] The five-coordinate trans-(B,Si) borylpalladium complex **E** is formed through the reaction of η^2-(Si–H)Pd(0) complex **A** and B_2 [a model of B_2pin_2 in which B = B(ethylene glycolato)] via transition state $\mathbf{TS^{BC}}$, leading to square-planar borylpalladium complex **D**. Coordination of PMe_3 to **D** affords **E**.[18] On the other hand, **A** can function as a palladium hydride, **F**, through reversible oxidative addition/reductive elimination of the Si–H bond with Pd via $\mathbf{TS^{AF}}$, as previously proposed.[7] The pathway to cis-(B,Si) complex **I** involves the reaction of **F** and B_2 via TS^{GH}. Dissociation of HB (a model of HBpin) from complex **H** followed by coordination of PMe_3 results in the formation of cis complex **I** as a more stable product than the trans complex **E** by 4.8 kcal/mol. Generation of the coordinatively unsaturated η^2-(Si–H)Pd(0) complex **A** in the initial step is strongly supported by the experimental result that addition of 1 equiv of phosphine significantly retarded the reaction of **1** with B_2pin_2 (see the SI).[19] Both Pd–B bond-forming steps ($\mathbf{TS^{BC}}$ and $\mathbf{TS^{GH}}$) are easily feasible energetically, while the conversion of **A** to **F** ($\mathbf{TS^{AF}}$) requires the highest activation energy through the reaction ($\mathbf{TS^{BC}}$ = +16.5, $\mathbf{TS^{GH}}$ = +15.8, $\mathbf{TS^{AF}}$ = +24.1 kcal/mol). Therefore, the formation of **E** via $\mathbf{TS^{BC}}$ is the kinetically favored

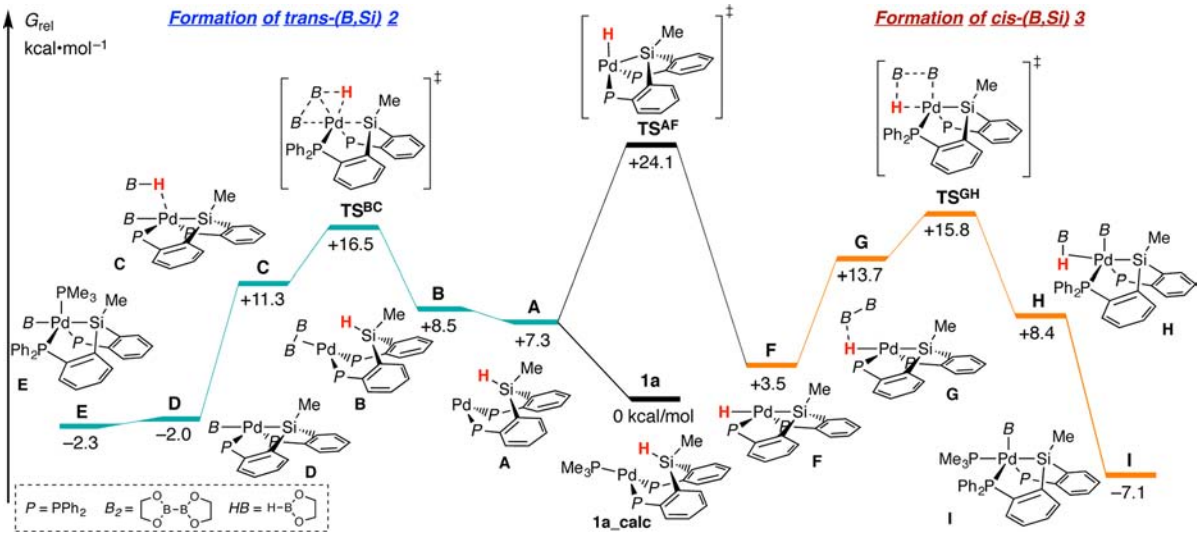


Figure 3. Free energy profiles calculated using DFT at the PW91PW91/[6-31G(d,p)/LANL2DZ] level in THF(PCM). B_2 is a model of B_2pin_2 in which the pinacolato moiety is replaced by ethylene glycolato.

pathway, and the formation of **I** via **TS^{AF}** followed by **TS^{GH}** is the thermodynamically favorable process.[20] It is clear that the kinetic pathway becomes easily reversible in the case of the PPh_3 system according to the energy relationships clarified in Table 2.

The core structures of the transition states involved in B−Pd bond formation are depicted in Figure 4. **TS^{BC}** is best described as a structure in which the Si−H bond is mostly cleaved and the B1−H bond of the borane is forming on Pd (Figure 4a,b). This structure can be regarded as the TS for a σ-bond metathesis reaction between the B1−B2 bond and the H−Pd bond of the transient trigonal-pyramidal palladium hydride generated by oxidative addition of the Si−H bond to Pd(0) (similar to **TS^{AF}**). In **TS^{GH}**, the B2−H, H−Pd, and B1−Pd bond lengths are 1.40, 1.74, and 2.26 Å, respectively, indicating that formation of the B2−H and B1−Pd bonds and cleavage of the B1−B2 and H−Pd bonds proceed simultaneously in a σ-bond metathesis reaction (Figure 4c,d). No Pd(IV) intermediates were found before and after **TS^{BC}** and **TS^{GH}** by intrinsic reaction coordinate calculations. This is the first demonstration of a σ-bond metathesis mechanism involvinig a B−B bond and Pd−H bond,[21] and it should provide new mechanistic aspects of the activation of B−B bonds. It should be noted that the PSi(sp^3)P pincer ligand would facilitate the formation of a six-coordinate-like structure around Pd in these transition states, with the P1−Pd−P2 angles largely bent away from 180° (115.5° in **TS^{BC}**; 124.2° in **TS^{GH}**).[22] This reaction is quite unique in that (1) two reversible σ-bond metathesis pathways for B−Pd bond formation via B−B bond activation are demonstrated; (2) the two pathways are connected via fluxional behavior of the Si−H bond; and (3) the appropriate choice of monophosphine ligand enables efficient control of the two pathways, leading to the stereoselective synthesis of two types of borylpalladium complexes.

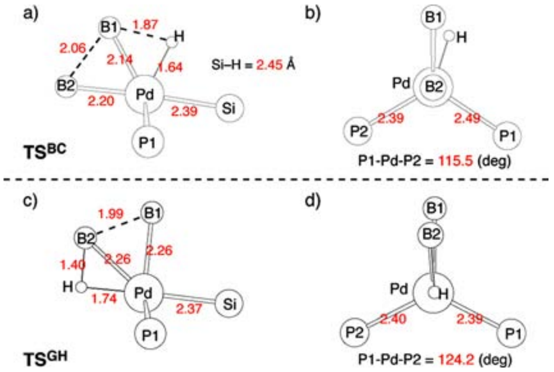


Figure 4. Core structures of (a, b) **TS^{BC}** and (c, d) **TS^{GH}**: (a, c) side views; (b, d) front views.

In conclusion, we have demonstrated two reversible σ-bond metathesis pathways for B−Pd bond formation in the reaction of η^2-(Si−H)Pd(0) complexes with B_2pin_2 that are connected by fluxional behavior of Si−H bond. The two pathways can be efficiently controlled by the appropriate choice of the phosphine ligand, enabling the selective synthesis of two types of five-coordinate borylpalladium complexes. We envision that such σ-bond metathesis reactivity of PSiP−Pd(II) complexes in B−B bond activation will open up new possibilities for the development of new borylation reactions. Further mechanistic studies and the development of new synthetic reactions utilizing these phenomena are ongoing in our group.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental computational details; spectral and analytical data for **1**−**3**; and crystallographic data for **1a**, **2a**, **2b**, **3a**, and **3b** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(5) Fernández and Gulyás reported a Pd-catalyzed diboration reaction of alkenes in which transmetalation of an alkylpalladium intermediate with diboron was proposed as a catalyst regeneration step, but no experimental or theoretical support for this has been demonstrated. See ref 2i.

(6) The square-planar PSiP−borylpalladium complex has been isolated and structurally characterized. See: Takaya, J.; Kirai, N.; Iwasawa, N. *J. Am. Chem. Soc.* **2011**, *133*, 12980.

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(8) Isolation of **2a** from excess B_2pin_2 in Scheme 1 was unsuccessful because of its high solubility. Pure **2a** was obtained by the reaction of square-planar borylpalladium with PMe_3 followed by recrystallization (see the SI for details).

(9) Synthesis and structural analysis of borylpalladium complexes are rather limited compared with boryl complexes of Pt or group 8 or 9 metals. See: (a) Onozawa, S.; Hatanaka, Y.; Sakakura, T.; Shimada, S.; Tanaka, M. *Organometallics* **1996**, *15*, 5450. (b) Onozawa, S.; Tanaka, M. *Organometallics* **2001**, *20*, 2956. (c) Onozawa, S.; Tanaka, M. *J. Synth. Org. Chem., Jpn.* **2002**, *60*, 826. (d) Braunschweig, H.; Gruss, K.; Radacki, K.; Uttinger, K. *Eur. J. Inorg. Chem.* **2008**, 1462. (e) Zhu, Y.; Chen, C.-H.; Fafard, C. M.; Foxman, B. M.; Ozerov, O. V. *Inorg. Chem.* **2011**, *50*, 7980.

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(12) The observation of two types of isomers of five-coordinate Pt complexes $[\mathrm{PtMe(X)}(\overset{\frown}{\mathrm{NN}})(\mathrm{alkene})]$ and the isolation and structural characterization of one of them by using appropriate X and alkene ligands have been reported. See: Albano, V. G.; Monari, M.; Orabona, I.; Ruffo, F.; Vitagliano, A. *Inorg. Chim. Acta* **1997**, *265*, 35.

(13) After 24 h: **1a**, 15%; **2a**, 75%; **3a**, 10%.

(14) The ^{31}P NMR spectrum showed that *trans*-(B,Si)-**2b** is in equilibrium with a square-planar borylpalladium complex, **5**, and free PPh_3 at room temperature. It is estimated that **2b** is slightly more stable than **5** by 0.2 kcal/mol. PMe_3-coordinated **2a** did not shows such dissociation behavior even under heating conditions. We assume that the electron-donating nature of the PMe_3 ligand is the main reason for the stability of **2**. See the SI.

(15) The DFT calculations were carried out with model complexes in which the Bpin moiety was replaced by B(ethylene glycolato) and PMe_3 was the monophosphine ligand. The energies include all of the reagents in all of the structures and are expressed relative to **1a_calc** + B_2pin_2.

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(17) Interconversion between η^2-(Si−H)Pd(0) and H−Pd−Si complexes via oxidative addition/reductive elimination of the Si−H bond has been reported. See: (a) Boyle, R. C.; Mague, J. T.; Fink, M. J. *J. Am. Chem. Soc.* **2003**, *125*, 3228. (b) Boyle, R. C.; Pool, D.; Jacobsen, H.; Fink, M. J. *J. Am. Chem. Soc.* **2006**, *128*, 9054. (c) Reference 7. Also see: (d) Suh, H.-W.; Schmeier, T. J.; Hazari, N.; Kemp, R. A.; Takase, M. K. *Organometallics* **2012**, *31*, 8225. (e) Mitton, S. J.; Turculet, L. *Chem.—Eur. J.* **2012**, *18*, 15258.

(18) As indicated in ref 14 and Table 2, the experimentally estimated difference in the energies of **2a** and square-planar borylpalladium **5** is 6.5 kcal/mol. Thus, this model calculation seems to overestimate the stability of **D** and/or underestimate the stabilities of phosphine-coordinated complexes **1a_calc**, **E**, and **I**. However, the relative energies of **1a_calc**, **E**, and **I** are in good agreement with the experimetally estimated values.

(19) Pt-mediated dehydrogenative coupling of borane was reported to proceed via σ-bond methathesis without dissociation of the phosphine ligand. See: Braunschweig, H.; Brenner, P.; Dewhurst, R. D.; Guethlein, F.; Jimenez-Halla, J. O.; Radacki, K.; Wolf, J.; Zöllner, L. *Chem.—Eur. J.* **2012**, *18*, 8605.

(20) These results also afford useful insight into the reaction mechanism for the formation of the square-planar borylpalladium complex in the catalytic dehydrogenative borylation (see ref 6). Detailed mechanistic studies under such conditions are ongoing, and the results will be reported in due course.

(21) Theoretical studies have proposed σ-bond metathesis reactions of Pd−C with B−X to give C−B and Pd−X bonds. See: (a) Cui, Q.; Musaev, D. G.; Morokuma, K. *Organometallics* **1998**, *17*, 1383. (b) Lam, K. C.; Marder, T. B.; Lin, Z. *Organometallics* **2010**, *29*, 1849.

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