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Adaptability of the SiNN Pincer Ligand in Iridium and Rhodium Complexes Relevant to Borylation Catalysis

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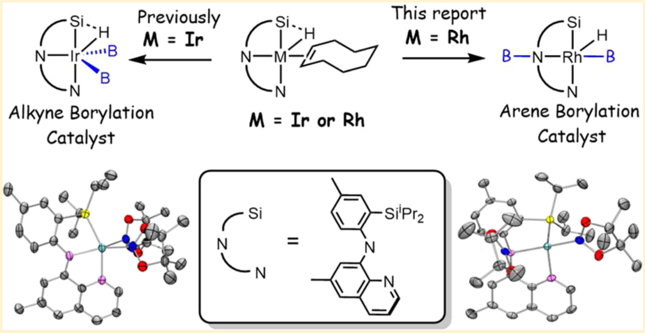
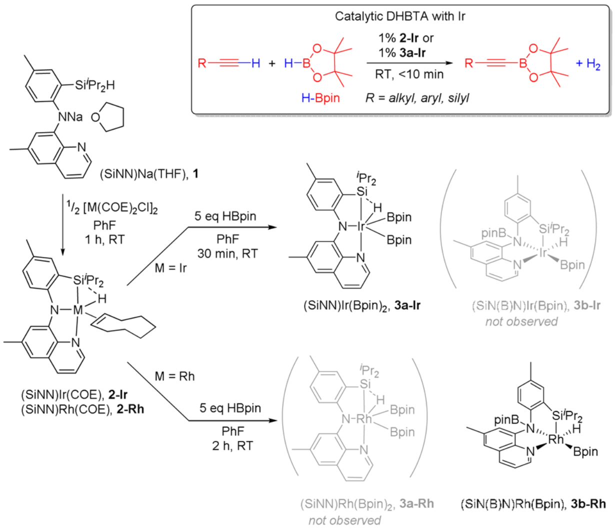
Supporting Information

ABSTRACT: A comparison of Rh and Ir complexes of the SiNN ligand (combining Si−H, amido, and quinoline donors) reveals its great degree of adaptability. The amido donor can function as a boryl group acceptor, and the Si−H/metal interaction is highly variable. In contrast to Ir analogues, complexes of Rh do not catalyze dehydrogenative borylation of terminal alkynes but do act as modest benzene borylation catalysts.



Transition-metal-catalyzed borylation of C−H bonds has become an important synthetic tool over the last two decades.[1−3] The products of C−H borylation, organoboronate esters, are versatile building blocks in organic synthesis, enabling facile formation of new carbon−carbon and carbon−heteroatom bonds. In particular, much attention has been dedicated to Ir-catalyzed borylation of aromatic C−H bonds where considerable success has been achieved.[4−6] Our group recently reported a complementary Ir catalyst capable of dehydrogenative C−H borylation of terminal alkynes (DHBTA; Scheme 1).[7] This Ir system was based on a novel SiNN pincer ligand that combines nitrogenous amido and quinoline-type donors with the Si−H functionality. Complex **2-Ir** can be rapidly converted to **3a-Ir** in the presence of HBpin, and either **2-Ir** or **3a-Ir** can be used as a precatalyst (Scheme 1). The present work explores Rh analogues of these Ir SiNN complexes. Although the new Rh compounds turned out to be inactive as DHBTA catalysts, they brought to light an unusual dual noninnocence[6] behavior of the SiNN ligand. The (SiNN)Rh system also turned out to be a modest benzene borylation catalyst.

Scheme 1. Synthesis of SiNN Complexes of Ir and Rh and DHBTA Catalysis by Ir Complexes



By analogy with the synthesis of **2-Ir**, **1** smoothly reacted with 1/2 equiv of $[(COE)_2RhCl]_2$ in fluorobenzene at ambient temperature to produce a blue solution of **2-Rh** (Scheme 1). Workup of the reaction mixture by filtration and recrystallization allowed isolation of **2-Rh** in 66% yield as an analytically pure blue solid. ^1H and $^{13}C\{^1H\}$ NMR spectra of **2-Rh** displayed the expected features that were similar to those of **2-Ir**, with the resonances corresponding to the organic framework of SiNN and of COE readily identifiable. An upfield ^1H NMR resonance was observed at −16.9 ppm corresponding to the Si−H hydrogen bound to Rh (cf. δ −21.1 ppm in **2-Ir**). This resonance displayed coupling to ^{103}Rh (J_{Rh-H} = 31 Hz) and possessed satellites from coupling to ^{29}Si (J_{Si-H} = 51 Hz). A single-crystal X-ray diffraction study (Figure 1) established that **2-Rh** is isomorphous with **2-Ir**, crystallizing in the same space group ($P2_1/n$) with unit cell volumes within 0.5% of each other. On the molecular level, **2-Rh** and **2-Ir** are nearly superimposable,[9] with only small differences in the metrics associated with the coordination sphere of the metals.

Treatment of **2-Rh** with 5 equiv of HBpin resulted in the predominant formation of a new product (**3b-Rh**) that could be isolated as a yellow solid in 59% yield. It contained ^1H NMR

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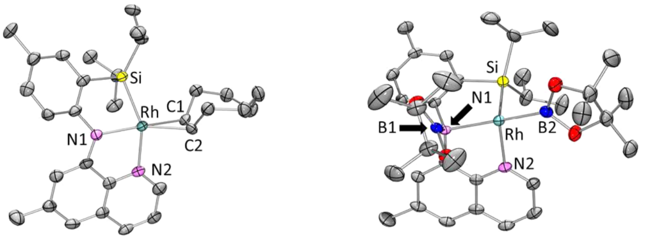


Figure 1. ORTEP drawings of **2-Rh** (left, 80% probability ellipsoids) and **3b-Rh** (right, 50% probability ellipsoids) showing selected atom labeling. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) for **2-Rh**: Rh−Si, 2.3787(13); C1−C2, 1.388(8); Si−Rh−N2, 140.87(11). Selected bond distances (Å) and angles (deg) for **3b-Rh**: Rh−Si, 2.2223(9); Rh−B2, 2.007(3); N1−B1, 1.459(4); Si−Rh−N2, 106.51(7); N1−Rh−B2, 175.33(11).

resonances expected for all of the constituent groups in "(SiNN)Rh(Bpin)$_2$"; however, several features distinguishing it from **3a-Ir** were immediately apparent. The yellow color of **3b-Rh** was suspect, as **3a-Ir** is purple whereas both **2-Ir** and **2-Rh** are blue. Instead of a single resonance for the Bpin methyl groups (as is the case for **3a-Ir**), **3b-Rh** exhibited several.[10] In the ^{11}B NMR spectrum, **3b-Rh** exhibited two resonances at 41.3 and 23.8 ppm (**3a-Ir** shows a single resonance at 28.9 ppm). Finally, the $J_{\text{Si-H}}$ value for **3b-Rh** was not discernible (assumed <1 Hz). This was inconsistent with **3a-Rh**, the exact structural analogue of **3a-Ir** ($J_{\text{Si-H}}$ = 32 Hz), because the change from Ir to Rh dramatically increased the $J_{\text{Si-H}}$ value in **2-Rh** (51 Hz) vs **2-Ir** (8 Hz). These observations led us to envision a different, isomeric structure for **3b-Rh**, which was confirmed by a single-crystal X-ray diffraction study (Figure 1). The connectivity in **3b-Rh** differs from that in **3a-Rh** by migration of one of the boryl groups onto the central N of the SiNN ligand. The hydride in **3b-Rh** was not located by XRD methods, but its presence is apparent from the doublet ($J_{\text{Rh-H}}$ = 30 Hz) at −15.0 ppm in the ^{1}H NMR spectrum. We previously observed B−N$_{\text{amido}}$ bond formation in addition reactions of HBcat and B$_2$cat$_2$ (cat = catecholate) with the cationic amido/bis(phosphine) [(PNP)Pd]$^+$ complex.[11]

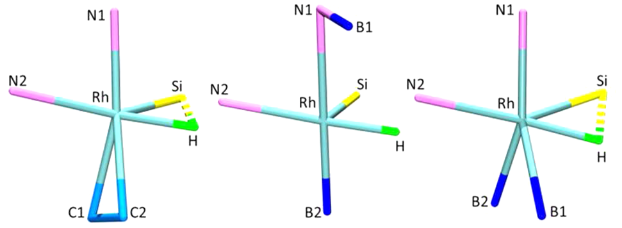


Figure 2. Drawings of the DFT calculated structures of **2-Rh** (left), **3b-Rh** (middle), and **3a-Rh** (right). N2 is the quinoline N.

Density functional theory (at the M06/SDD/6-311G** level)[12] was used to calculate the structures of **2-Rh**, **3a-Rh**, and **3b-Rh**. Figure 2 shows the immediate coordination environment in the three calculated Rh structures. The non-H atom positions reproduce those in the available XRD determinations well. The calculated structures of **2-Ir** and **3a-Ir** were reported by us previously,[7] using the same DFT methods. The three distinct X-type ligands (boryl, silyl, hydride) in **3b-Rh** are each of a very strong trans influence and adopt a facial arrangement. The approximately square pyramidal coordination sphere about Rh is completed by two neutral nitrogenous donors (quinoline and borylated diarylamine); the silyl ligand is trans to the empty site.[13] DFT-calculated free energies of the **3a-M**/**3b-M** isomers are consistent with the experimental facts: for Ir, **3a-Ir** is preferred by 1.8 kcal/mol, while for Rh, **3b-Rh** is favored by 5.2 kcal/mol. The free energy barrier[14] for the direct migration of the boryl from M in **3a-M** to N was calculated to be 16.9 kcal/mol for M = Ir and 12.0 kcal/mol for M = Rh (i.e., 17.2 kcal/mol barrier from the ground state **3b-Rh** to **3a-Rh**); both are consistent with reversible migration on the time scale of experimental handling at ambient temperature.

Figure 3 depicts the geometries of the M/Si/H triangles in compounds **2** and **3**. The variation of the geometric parameters within these structures can be viewed as reflective of the continuum between Si−H σ complexes and silyl/hydride oxidative addition.[15] **2-Rh** and **3a-Rh** clearly belong to the former, while **3b-Ir** and **3b-Rh** belong to the latter. As discussed previously,[7] **2-Ir** is probably best viewed as a silyl/hydride complex while **3a-Ir** is a borderline structure. The geometrical changes in **2** and **3** are not limited only to the Si−H distances. As the Si−H distances increase, the Si−M−H angles necessarily open up while the M−Si and M−H distances decrease. This is consistent with the strengthening of M−Si and M−H interactions upon diminishment of the Si−H interactions. The complexity of interactions of Si−H bonds with transition metals has been thoroughly studied and analyzed,[15] but Si−H as an adaptable spectator donor site in a chelating ligand has not been widely used.[16] The migration of boryl from M (**3a-M**) to N (**3b-M**) can be viewed as B−N reductive coupling which happens in concert with Si−H oxidative cleavage. Thus, the two adaptable features of the SiNN ligand serve to smooth out the electronic changes at the metal. The structure **3a** maximizes the number and the strength of metal−ligand bonds, which is more favorable for the 5d metal iridium.[17]

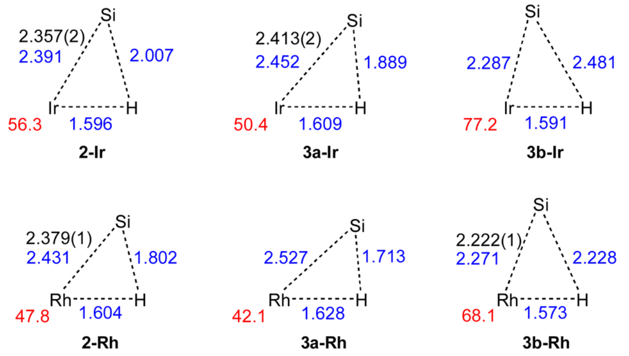


Figure 3. Metric parameters in the M/Si/H triangles (M = Rh, Ir) in compounds **2** and **3**. DFT calculated distances (Å) are given in blue, Si−M−H angles (deg) in red, and XRD-determined M−Si distances in black.

In contrast to its iridium analogue, **2-Rh** showed no DHBTA activity: treatment of **2-Rh** with HBpin in C_6D_6, followed by 4-MeC$_6$H$_4$CCH, did not give rise to any alkynylboronate after 3 days at room temperature. Instead, incomplete and unselective hydroboration of 4-MeC$_6$H$_4$CCH to various alkenylboronates took place.

When pure **3b-Rh** was dissolved in C_6D_6, it underwent degradation over time, with C$_6$D$_5$Bpin signals detectable in the mixture. Pure **3b-Rh** also slowly decomposed in a cyclohexane-d_{12} solution, with release of free HBpin. Thermolysis of **2-Rh** or

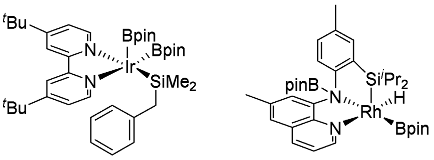
3b-Rh in C_6D_6 in the presence of excess HBpin resulted in catalytic production of C_6D_5Bpin, with ca. 30 turnovers after 48 h at 80 °C (Table 1). Using B_2pin_2 in place of HBpin resulted in a smaller number of turnovers of C_6D_6 under the same conditions. Although there are examples of Rh C−H borylation catalysts in the literature,[18] their efficiency is far outstripped by the best examples of Ir catalysis.[4−6] The catalytic reactivity of the (SiNN)Rh system is in contrast with the lack of arene borylation with (SiNN)Ir.

Table 1. Catalytic Borylation of Neat C_6D_6 (80 °C, 48 h) using 2-Rh and 3b-Rh

Rh catalyst[a]	boron source	C_6D_5Bpin yield (%)[b]
2-Rh	HBpin	27
3b-Rh	HBpin	33
2-Rh	B_2pin_2	7
3b-Rh	B_2pin_2	5

[a] Rh:Bpin ratio of 1:100. [b] Yield based on equivalents of Bpin, determined by ^{1}H NMR vs C_6Me_6 internal integration standard.

Interestingly, recent work on the "traditional" iridium aromatic C−H borylation catalysts supported by bipyridine-type ligands highlighted the usefulness of an Si−H moiety as a directing group in the substrate.[19] The intermediate **A** proposed[19a] by Hartwig et al. (Figure 4) bears a structural resemblance to **3b-Rh** in that the coordination sphere of the metal in A also contains three facially disposed strong trans influence X-type ligands (silyl, boryl, boryl) and two neutral nitrogenous donors. The use of supporting bidentate and tridentate ligands containing spectating silyl ligands in Ir-catalyzed aromatic borylation has also been reported recently.[20,21]



A **3b-Rh**

Figure 4. Intermediate proposed by Hartwig et al. (A)[19a] and **3b-Rh**.

In summary, the study of the new Rh complexes of the SiNN ligand uncovered its unusual adaptability. In addition to its capacity to adjust the degree of interaction of the Si−H moiety with the metal center, the SiNN ligand also possesses an amido site that can serve to accept a boryl ligand from the metal. The migration of the boryl proceeds in concert with the Si−H bonding change. While the integrity of the Si−H moiety would likely be challenged in reactions involving polar reagents, the unusual adaptability of SiNN may be advantageous in catalysis with nonpolar substrates. This adaptability may be related to the activity of its iridium complexes in the borylation of terminal alkynes and the modest activity of its Rh complexes in benzene borylation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of experimental procedures, spectroscopic characterization, and X-ray structural studies (including CIF files). This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic information in the form of CIF files is also available for free from the Cambridge Crystallographic Data Centre: CCDC 1027428 (**2-Rh**); CCDC 1027429 (**3b-Rh**).

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Notes

The authors declare no competing financial interest.

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(9) See the Supporting Information (Figure S1) for a side-by-side view.

(10) The observation of a single resonance in the spectrum of **3a-Ir** is likely a consequence of accidental degeneracy and possible fluxionality—in the static structure of **3a-Ir**, the two boryls are inequivalent. Moreover, each Bpin group in **3a-Ir** or **3b-Rh** should give rise to two or four Me resonances, depending on whether the rotation about the M−B or N−B bond is rapid on the NMR time scale.

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(14) Transition state geometries (**3TS-Rh** and **3TS-Ir**) are available in the Supporting Information.

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