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C-H Borylation Catalysis of Heteroaromatics by a Rhenium Boryl Polyhydridea

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ABSTRACT: Transition metal complexes bearing metal-boron bonds are of particular relevance to catalytic C-H borylation reactions, with iridium polyboryl and polyhydrido-boryl complexes the current benchmark catalysts for these transformations. Herein, we demonstrate that polyhydride boryl phosphine rhenium complexes are accessible and catalyze the C-H borylation of heteroaromatic substrates. Reaction of $[\text{K}(\text{DME})(18\text{-c-}6)][\text{ReH}_4(\text{Bpin})(\eta^2\text{-HBpin})(\kappa^2\text{-H}_2\text{Bpin})]$ **1** with 1,3-bis(diphenylphosphino)propane (dppp) produced $[\text{K}(18\text{-c-}6)][\text{ReH}_4(\eta^2\text{-HBpin})(\text{dppp})]$ **2** through substitution of two equivalents of HBpin, and protonation of **2** formed the neutral complex $[\text{ReH}_6(\text{Bpin})(\text{dppp})]$ **3**. Combined X-ray crystallographic and DFT studies show that **2** is best described as a σ -borane complex, whereas **3** is a boryl complex. Significantly, the boryl complex **3** acted as a catalyst for the $\text{C}(\text{sp}^2)\text{-H}$ borylation of a variety of heteroarenes (14 examples including furan, thiophene, pyrrole and indole derivatives) and displayed similar reactivity to the iridium analogues.

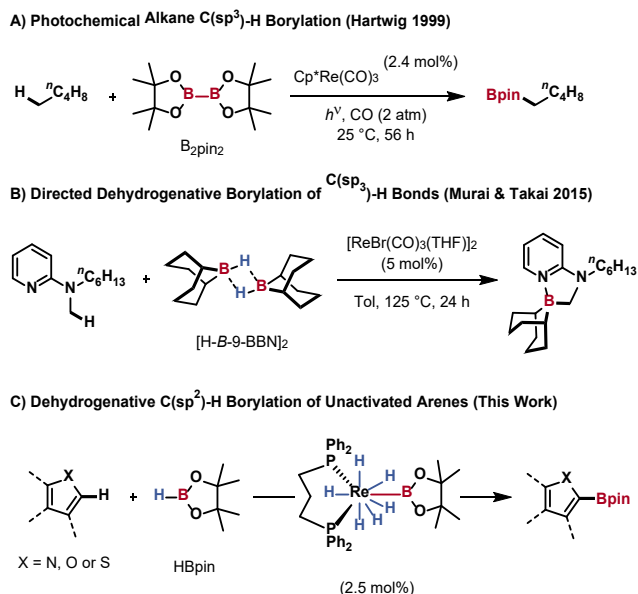
KEYWORDS: heteroarene; hydride; borane; phosphine; homogeneous catalysis; crystallography; AIRSS

INTRODUCTION

The synthesis of transition metal complexes containing metal-boron bonds is of particular interest due to the relevance of these complexes as intermediates in catalytic C-X (X = H or halogen) borylation to prepare synthetically valuable organoboronate esters.¹⁻⁴ The borylation of unactivated $\text{C}(\text{sp}^2)\text{-H}$ bonds can be catalyzed by a number of transition metal boryl complexes of Ir,⁵⁻¹⁰ Rh,^{6, 11-13} Co,¹⁴⁻¹⁶ Fe,¹⁷⁻²⁰ Ni²¹⁻²³ and Pt.²⁴ The most widely used catalysts are Ir complexes typically of the form $[\text{Ir}(\text{Bpin})_3(\text{L})_2]$, where L is a neutral monodentate or bidentate ligand, and invoke an Ir(III)/Ir(V) redox couple. The most commonly used catalyst systems use bulky bipyridine or phenanthroline ligands, first developed by Hartwig and co-workers.^{25, 26} Smith and co-workers demonstrated the use of the bidentate phosphine complex, $[\text{Ir}(\text{Bpin})_3(\text{dppe})]$, as a catalyst for the selective C-H borylation of arenes in the presence of haloarenes; the catalyst was formed *in situ* from the reaction of $[(\eta^5\text{-indene})\text{Ir}(\text{COD})]$ with dppe and HBpin.⁷ The related 5-coordinate complexes $[\text{Ir}(\text{Bpin})_3(\text{L})]$ (where L = dtbpe or dippe) have also been shown to mediate C-H borylation of arenes, albeit stoichiometrically.²⁷ Further studies of the stoichiometric reactivity of $[\text{Ir}(\text{Bpin})_3(\text{dippe})]$ reveal a series of borylene, hydrido and hydrido boryl complexes that can be formed under catalytic C-H borylation conditions.²⁸

Recently, we reported the rhenium polyhydride borane anion $[\text{ReH}_4(\text{Bpin})(\eta^2\text{-HBpin})(\kappa^2\text{-H}_2\text{Bpin})]^-$ **1**, synthesized by the exhaustive deoxygenation of perrhenate, $[\text{ReO}_4]^-$, with HBpin, and showed that it is a catalyst for the hydroboration of *N*-het-

eroaromatic substrates.²⁹ Reaction of **1** with H-B-9-BBN resulted in reductive borane substitution to form a related dihydroborate complex. These simple methods provided straightforward access to reactive rhenium complexes containing boron-centred ligands that can be further functionalized. Interestingly, **1** also underwent stoichiometric $\text{C}(\text{sp}^2)\text{-H}$ borylation of toluene with high *meta*-selectivity; unfortunately, attempts to adapt these conditions for catalytic C-H borylation by addition of stoichiometric boron reagents or sacrificial H_2 acceptors were unsuccessful. It was therefore envisaged that strongly σ -donating, neutral ligands such as phosphines would help to stabilize the high oxidation state hydrido-boryl complexes involved in C-H bond activation and subsequent C-B bond formation. Rhenium-catalyzed C-H borylation has, to the best of our knowledge, only been reported using low oxidation-state complexes. For example, Hartwig and co-workers reported the C-H borylation of alkanes and arenes using $\text{Cp}^*\text{Re}(\text{CO})_3$ and B_2pin_2 under photochemical conditions and an atmosphere of CO (Scheme 1, A).³⁰ Murai and Takai reported the $\text{C}(\text{sp}^3)\text{-H}$ borylation of tertiary amines at the α -position, facilitated by a pyridyl directing group under thermal conditions using $[\text{ReBr}(\text{CO})_3(\text{THF})]_2$ as the catalyst and H-B-9-BBN as the boron source (Scheme 1, B).³¹ However, no examples of $\text{C}(\text{sp}^2)\text{-H}$ borylation of arenes were reported using this catalyst system.



Scheme 1. Examples of rhenium-catalyzed borylation of C-H bonds.

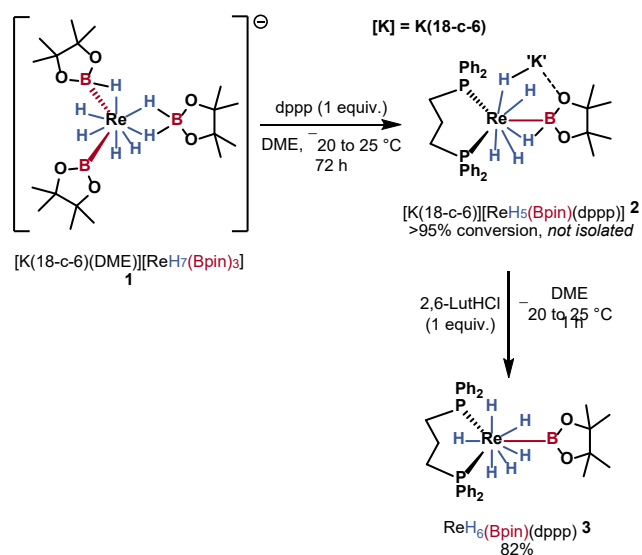
Herein, we report that the reaction of $[K(DME)(18-c-6)][ReH_4(Bpin)(\eta^2-HBpin)(\kappa^2-H_2Bpin)]$ **1** with dppp leads to HBpin ligand substitution to give the Re(V) phosphine complex $[K(18-c-6)][ReH_4(\eta^2-HBpin)(dppp)]$ **2**. Complex **2** reacts with 2,6-lutidinium chloride to give the neutral Re(VII) boryl complex $[ReH_6(Bpin)(dppp)]$ **3**, which acts as a catalyst for the C-H borylation of heteroarenes (Scheme 1, C). To the best of our knowledge, this work represents the first example of a high oxidation-state Re complex acting as a catalyst for this reaction and draws comparisons to existing reactivity shown by established iridium examples.

RESULTS AND DISCUSSION

An equivalent of bis(diphenylphosphino)propane (dppp) was added to a solution of **1** in DME at -20 °C which, on warming slowly to room temperature and stirring for 72 h, produces a single phosphine-ligated complex **2** with liberation of two equivalents of HBpin. Complex **2** was then reacted with 1 equivalent of 2,6-lutidinium chloride which results in protonation without H₂ evolution to form the neutral complex $[ReH_6(Bpin)(dppp)]$ **3** (Scheme 2). The ¹H NMR spectrum of **3** displays a triplet at -5.57 ppm for 6 hydrides and the ³¹P NMR spectrum exhibits a broad signal at 6.24 ppm. As with **2**, these resonances are unchanged at -80 °C. A broad signal at 47.3 ppm is seen in the ¹¹B NMR spectrum of **3** and corresponds to a Re-Bpin environment.

Single crystal X-ray diffraction analysis of **3** shows the P and B atoms arranged in a distorted trigonal planar geometry (Figure 2). The hydrides were located in the difference Fourier map and display an average Re-H bond length of 1.50(3) Å which is comparable to other terminal hydride bond lengths. The Re-B bond length is 2.188(3) Å and B1-H1 distance is 1.69(3) Å, both of which are within the range of other high oxidation-state, elongated σ -borane or hydrido boryl complexes.^{32, 33} The usual caveats of locating hydrides with confidence from the X-ray structure apply here. As such, possible hydride positions were identified using *ab initio* random structure searching (AIRSS, see supporting information for details) with the initial positions

of the heavier atoms derived from the crystal structure and geometric constraints on prospective initial hydride positions to ensure H₂ is not formed.^{34, 35} This approach generates a series of structures with various combinations of hydride, boryl, σ -borane, and hydroborate ligands that are then ranked in order of increasing energy (ESI). From a data set of 24 optimized structures obtained, a series of 21 closely related, low-energy structures (within 5 kJ mol⁻¹) reveal a geometry that matches the solid-state structure (Figure 1). Given the long B1-H1 distances in both the solid-state and calculated structures and that the crystals of **3** are colorless, it is evident that **3** is best described as a boryl hexahydride complex (i.e., Re^{VII}).



Scheme 2. Reaction of 1 with dppp to produce the neutral phosphine complex 3 via the anionic complex 2.

The time course of the reaction between **1** and dppp was monitored by NMR spectroscopy in d₈-THF and revealed full conversion of **1** to a monodentate complex (major) and a bidentate complex (minor) after 2 h. The monodentate complex corresponds to a doublet at -8.05 ppm in the ¹H NMR spectrum and a broad signal at 52.9 ppm in the ¹¹B NMR spectrum. This monodentate complex then slowly converts to the bidentate complex which is characterized by a triplet at -8.16 ppm in the ¹H NMR spectrum and a broad signal at 53.8 ppm in the ¹¹B NMR spectrum. Correlations between the hydride signals and two signals at 24.5 and 11.6 ppm in the ³¹P NMR spectrum are observed in the ¹H-³¹P HMBC NMR spectrum. This suggests that the second equivalent of HBpin is significantly less labile than the first. A screen of phosphine ligands showed that the range of ligands that can successfully and selectively coordinate to **1** is narrow (ESI Figure 2.4).

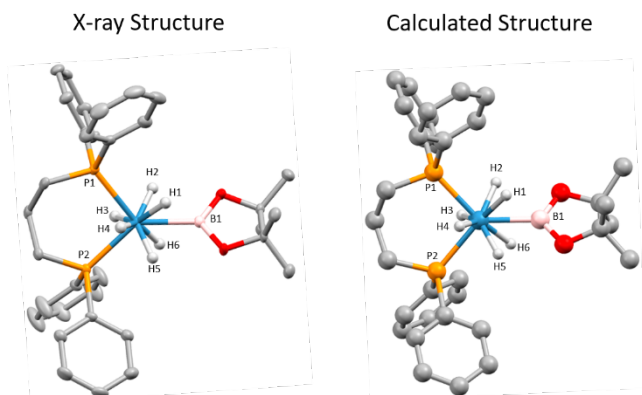


Figure 1. The X-ray crystal structure (left) and calculated structure (right) of **3** (toluene solvate and all hydrogen atoms except for the Re hydrides are omitted; displacement ellipsoids are drawn at 50% probability). X-ray crystal structure selected distances (Å) and angles (°): Re1-B1 2.188(3); Re1-H 1.50(3) avg., B1-H1 1.69(3), Re1-P1 2.4053(9); Re1-P2 2.4106(9); P2-Re1-P1 96.22(3); P1-Re1-B1 127.9(1); P2-Re1-B1 135.9(1).

When dimethoxyethane (DME) is used as the reaction solvent, $[\text{K}(18\text{-c-}6)][\text{ReH}_4(\eta^2\text{-HBpin})(\text{dppp})]$ **2** is isolated by crystallization from the reaction mixture as large yellow blocks. However, **2** is unstable once isolated from the reaction mixture and decomposes rapidly upon drying under vacuum or at ambient temperature/pressure to give multiple phosphine-coordinated rhenium hydride complexes. This could be due to dissociation of HBpin or H_2 to form an unstable 16-electron complex which reacts unselectively with itself or with the solvent. The X-ray crystal structure of **2** (Figure 2) reveals a rhenium pentahydride anion in which the P and B atoms are arranged in a distorted T-shape geometry with an elongated Re-B bond (Re1-B1 = 2.149(4) Å) which could reflect contributions from σ -borane structures due to the close B1-H1 distance (1.48(4) Å). The hydrides were located in the difference Fourier map and refined freely. The structure also exhibits a close Re-H-K contact (H5-K1 = 2.74(5) Å), which is similar to the those seen in other potassium salts of rhenium polyhydride anions.³⁶ Once again, possible hydride positions were identified using AIRSS where, of the data set of 26 optimized structures thus generated, the same lowest energy geometry is obtained 18 times, in which the only significant difference to the X-ray structure is a closer K1-H4 contact (2.956 Å compared to 3.19(5) Å). The calculated structure contains an elongated B1-H1 distance compared with the solid-state structure (1.522 Å), although this bond distance remains in the range reported for σ -borane complexes and is within one esd range of the X-ray structure (Figure 1).^{32, 37} The hydride positions are consistent with those from the X-ray structure, indicating a high level of confidence for their assignment.

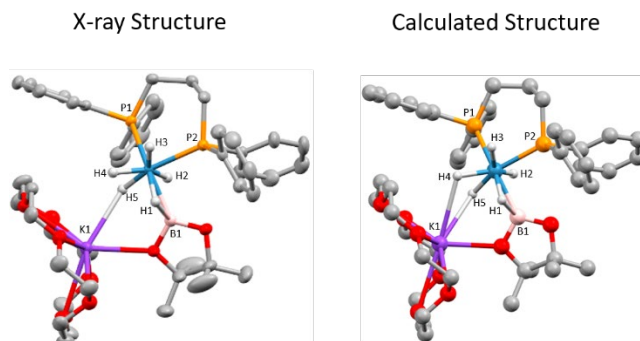
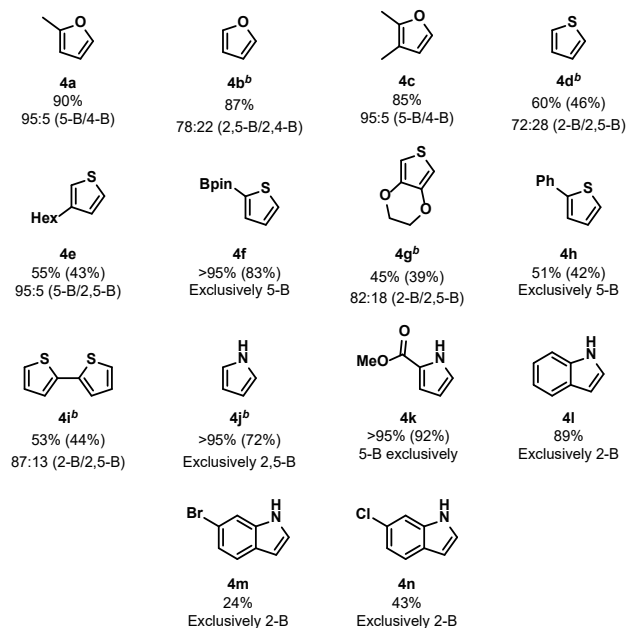
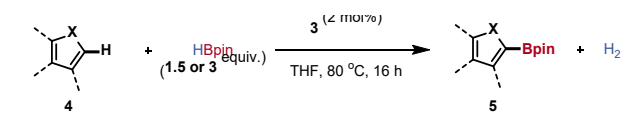


Figure 2. The X-ray crystal structure (left) and calculated structure (right) of **2** (all hydrogen atoms except for the Re hydrides are omitted; displacement ellipsoids are drawn at 50% probability). X-ray crystal structure selected distances (Å) and angles (°): Re1-B1 2.149(4); Re1-H 1.54(4) avg.; B1-H1 1.48(4); H5-K1 2.74(5); H4-K1 3.19(5); Re1-P1 2.3571(9); Re1-P2 2.3465(9); P2-Re1-P1 93.28(3); P2-Re1-B1 141.5(1); B1-Re1-P1 91.36(9).

The ready synthesis of this well-defined Re(VII) boryl complex prompted its exploration as a catalyst for the $\text{C}(\text{sp}^2)\text{-H}$ borylation of arenes (Scheme 3). Optimized conditions were established for the C-H borylation of 2-methylfuran **4a** using 2 mol% of **3** and 1.5 equiv. of HBpin in THF at 80 °C for 16 h (See ESI for full details); this gives the borylated furan **5a** with high selectivity for the C5-Bpin regioisomer over the C4-Bpin regioisomer (>95% conversion, 95:5). No product is seen using B_2pin_2 as the boron source for this reaction. Increasing the catalyst loading results in an enhanced rate of reaction and lowering the loading of HBpin from 1.5 equiv. to 1.0 equiv. decreases conversion. In contrast, catalytic borylation reactivity is not observed using complexes **1** or **2** showing that the neutral, phosphine-coordinated complex **3** displays significant differences in reactivity.

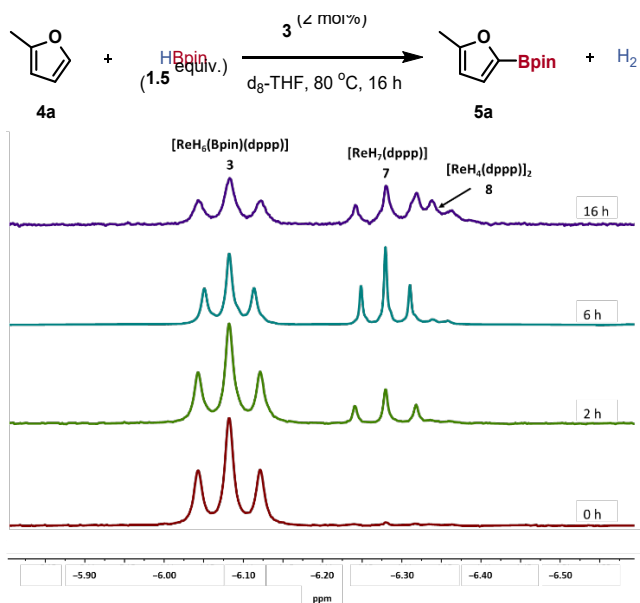
Mono- and disubstituted furans **4a** – **4c** are tolerated under these reaction conditions with good selectivity for the C5-Bpin regioisomer. Furan **4b** reacts with 3 equivalents of HBpin to give the doubly borylated products exclusively. Thiophene substrates are also converted to borylated products although the yields are lower than seen for furans. Thiophene **4d** gives a mixture of 2-boryl and 2,5-diboryl thiophenes. Monosubstituted thiophenes **4e** – **4i** are converted with high selectivity for the 5-boryl products. 3,4-Ethylenedioxythiophene (EDOT) **4g** and 2,2'-bithiophene **4i** give a mixture of monosubstituted (major) and disubstituted (minor) boronic ester products. Pyrroles and indoles **4j** – **4n** are tolerated and give high yields and regioselectivities. Notably, substrates containing carbon halide bonds (C-Cl/Br) **4m** and **4n** favor C-H borylation over Miyaura borylation of the C-X bond. *N*-Methyl and *N*-Boc protected pyrroles and indoles only show trace conversion. Similarly, di-*ortho*-substituted heteroaromatics show significantly reduced conversion to the boronic ester products. No $\text{C}(\text{sp}^3)\text{-H}$, N-H, or dppp borylation is seen in these reactions.



^aReaction conditions: heteroarene **4** (0.50 mmol), HBpin (0.75 mmol), catalyst **3** (0.0125 mmol), THF (2.5 mL), 80°C for 16 h. NMR yields determined by ¹H NMR spectroscopy by integration against mesitylene (10 μ L, 0.0719 mmol), isolated yields in parentheses.^b 3 equivalents of HBpin (1.50 mmol).

Scheme 3. Substrate scope for the catalytic dehydrogenative C-H borylation of heteroarenes.^a

The time course of a catalytic borylation using **4a** was monitored by ¹H NMR spectroscopy in d₈-THF (Figure 3). Over 16 h, the hydride signal at –6.08 ppm corresponding to complex **3** diminishes and two new signals at –6.27 (t) and –6.34 (p) ppm are observed. Both signals correspond to catalyst deactivation and are identified as arising from the heptahydride complex [ReH₇(dppp)] **7** and the dinuclear octahydride complex [ReH₄(dppp)]₂ **8**, respectively (Figure 3). Heptahydride **7** has been previously reported and was synthesized independently to confirm this assignment.³⁸ The complex was originally reported to be inert to H₂ loss when heated under reflux in THF in the presence of PPh₃, pyridine and hydrosilanes. Interestingly, we find that **7** acts as a catalyst for C-H borylation, albeit at a significantly reduced rate compared with **3**, achieving only 48% NMR yield after 16 h (Scheme 4, A). In contrast, *in situ* ¹H/¹¹B/³¹P NMR spectroscopy shows that dinuclear complex **8** is inactive in C-H borylation catalysis and inert to hydride substitution by HBpin, reinforcing its role in a deactivation pathway.

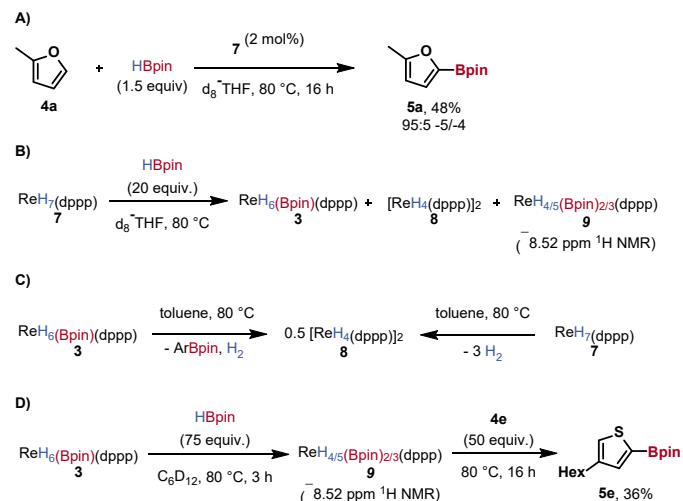


^aReaction conditions: heteroarene **4** (0.20 mmol), HBpin (0.3 mmol), catalyst **3** (0.004 mmol), d₈-THF (0.5 mL), 80°C for 16 h.

Figure 3. Analysis by ¹H NMR spectroscopy of the Re hydride species during the catalytic C-H borylation of 2-methylfuran **4a**.^a

Complex **7** is presumably formed during standard catalytic conditions from boryl complex **3** by coordination of H₂, liberated by C-H borylation of the substrate, to a transiently formed ReH₅(dppp). When heptahydride **7** was heated in the presence of an excess of HBpin a small amount of boryl complex **3** is seen in the ¹H NMR spectrum, along with dinuclear **8** and an unknown complex **9** which has a hydride resonance at –8.52 ppm (Scheme 4, B). To assess the effect of H₂ evolution and its role within catalysis, the borylation of 3-hexylthiophene **4e** was conducted under standard conditions in a Teflon-tapped NMR tube and compared to a reaction under static vacuum to enable the H₂ formed during the reaction to escape into the head-space of the NMR tube. The progress of both reactions and Re hydride speciation was monitored by *in situ* ¹H NMR spectroscopy (ESI). By comparing the yield of borylated product **5e** in each reaction over time, it is clear that both reactions follow the same profile until ~240 mins, upon which they diverge with the rate of reaction for the standard reaction slower than that of the reaction under partial static vacuum. At 1000 mins the final yield of **5e** is 37% for the standard reaction and 44% for the vacuum reaction, indicating the deleterious effect of H₂ on catalysis. Quantification of the Re hydride species present by integration of the relevant hydride signals in the ¹H NMR spectra show a much higher proportion of heptahydride **7** in the standard reaction; this is as expected, given the higher concentration of H₂ in this reaction compared with the reaction under static vacuum. Given the decreased catalytic activity of heptahydride **7** compared with boryl **3**, the increased concentration of **7** supports the observed decrease in the rate of reaction. The standard reaction also appears to have a higher relative concentration of dimer **8** compared with the reaction under static vacuum, which again supports the lower rate of reaction by loss of active Re hydride species through this deactivation pathway. Significantly, the changes in speciation correlate with the observed evolution of

H₂ (4.55 ppm in the ¹H NMR spectra) during the course of the reaction, with a consistently lower concentration of H₂ seen in solution in the reaction under static vacuum compared with the standard reaction.



Scheme 4. Mechanistic investigation of catalytic C-H borylation.

The dinuclear complex **8** is the sole product formed on heating **3** or **7** at 80 °C in toluene and crystallizes directly from the reaction mixture (Scheme 4, C). The NMR spectra of isolated **8** match the signals corresponding to the hydride resonance at -6.34 (p), observed under standard catalytic conditions. It should be noted that the formation of **8** by heating **3** at 80 °C for 16 hours in toluene results in stoichiometric borylation of toluene to give a 74:26 regioisomeric mixture of the *meta* and *para* borylated products in 48% NMR yield against an internal standard. The borylation of carboarenes is limited to stoichiometric reactivity using **3**. The X-ray crystal structure of **8**, which has two chemically equivalent but crystallographically independent molecules in the asymmetric unit (Figure 4), confirms that it is a dimeric complex with four bridging hydrides between the Re atoms and two terminal hydrides on each Re atom; the hydride atoms were located in the difference Fourier map and refined freely. Similar dinuclear complexes have been synthesized bearing monodentate or tridentate phosphines;³⁹⁻⁴¹ however, to the best of our knowledge, complex **8** is the first example with a bidentate phosphine.

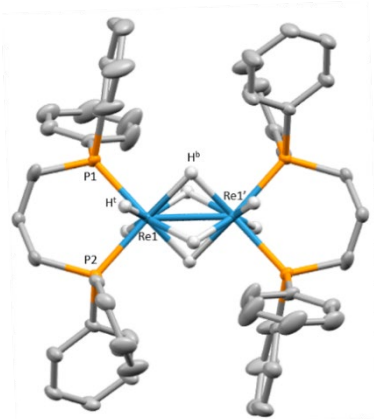
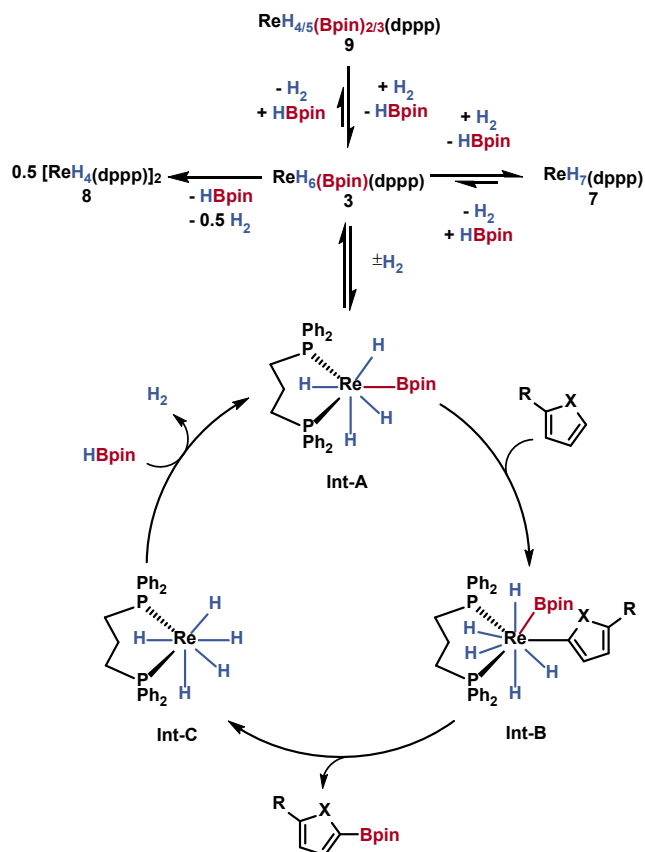


Figure 4. The X-ray crystal structure of **8 (one of the two molecules in the asymmetric unit is shown, all hydrogen atoms except for the Re hydrides are omitted; displacement ellipsoids are drawn at 50% probability). Selected distances (Å) and angles (°): Re1-H^a 1.47(4) avg.; Re1-H^b 1.89(4) avg.; Re1-Re1' 2.5383(5); Re1-P1 2.327(1); Re1-P2 2.3265(8); P1-Re1-P2 96.62(3); P1-Re1-Re1' 133.81(3); P2-Re1-Re1' 129.57(3); P1-Re1-Re1'-P1' 180.00(5).**

The reactivity of Re polyhydrides is largely determined by their ability to generate vacant coordination sites by liberation of H₂, either thermally or photochemically, and they have been shown to participate in C-H bond activation chemistry.⁴² It is likely that complex **3** participates in a similar manner to activate the C-H bonds of the heteroarenes. However, under catalytic conditions there is potential for the boryl complex **3** to sequentially lose equivalents of H₂ and add equivalents of HBpin to form higher-order boryl complexes which may be catalytically relevant. To investigate this, a solution of the boryl complex **3** and HBpin (20 equiv.) in d₁₂-cyclohexane was heated at 80 °C and monitored by NMR spectroscopy (Scheme 4, D). After 3 h, a broad singlet is seen at -8.50 ppm in the ¹H NMR spectrum corresponding to a phosphine-coordinated Re hydride complex **9** (Scheme 4, B and D), as well as several minor signals between -6.00 and -7.50 ppm; H₂ evolution is also observed (singlet at 4.55 ppm). The formation of **9** does not coincide with the observation of an obvious Re-B resonance in the ¹¹B NMR spectrum. A similar, but shorter-lived complex is seen if the reaction is undertaken in d₈-THF, but it is not present under standard catalysis conditions. It was not possible to isolate complex **9** as it is unstable under vacuum and its formulation is difficult to discern as integration of the ¹H NMR spectrum is inconclusive due to some decomposition. It is likely, however, that **9** is a higher order boryl complex, for example ReH₄(BPin)₃(dppp).²⁸ Complex **9** is found to be active in the catalytic borylation of 3-hexylthiophene **4e**: complex **9** was generated *in situ* by the reaction between **3** and HBpin for 3 hours in d₁₂-cyclohexane, after which addition of **4e** and further heating for 16 hours results in the borylated product **5e** in 36% yield. Complex **9** does not react with **4e** at room temperature but, after 20 minutes heating in the presence of thiophene **4e**, it is almost fully consumed with the only hydride species seen being **3**. From this point, the reaction follows a similar profile to standard catalytic reaction conditions using **3**. Complex **9** is only observed in significant quantities in the presence of a large excess of HBpin and in the absence of substrate, therefore it may only be formed transiently under standard catalytic conditions. These results suggest that **9** is likely a higher-order boryl complex such as ReH₄(BPin)₃(dppp) which may act similarly to the known iridium tris(boryl) complexes in hydroborylation catalysis.⁴³⁻⁴⁵



Scheme 5. Proposed catalytic cycle for the C-H borylation of heteroarenes.

Based on these results a catalytic cycle is proposed with complex **9** as an off-cycle intermediate present in very low concentrations and in equilibrium with **3** (Scheme 5, A): (1) Elimination of an equivalent of H_2 from pre-catalyst **3** forms a coordinatively unsaturated boryl complex **Int-A**; (2) oxidative addition of the arene substrate gives a Re aryl intermediate **Int-B**; (3) reductive elimination of the boronic ester product and formation of a coordinatively unsaturated pentahydride complex **Int-C**; (4) addition of an equivalent of HBpin and elimination of H_2 reforms **Int-A**. The reaction of pre-catalyst **3** with an excess of HBpin will lead to the formation of the higher-order boryl **9** and the reaction of **3** with H_2 will form heptahydride **7**. Catalyst deactivation can occur through the dimerization of **3** or **7** to form **8**. We cannot discount a mechanism involving **9** as an active species for C-H borylation where it is present as an on-cycle intermediate. The formation of **9** under high HBpin concentrations may also limit the formation of the off-cycle heptahydride **7**. Computational studies on the reaction intermediates and potential reaction pathways may provide more definitive insight into the reaction mechanism.

CONCLUSIONS

Two new Re boron-polyhydride complexes **2** and **3** have been synthesized and characterized from the previously reported **1**. The boryl complex **3** is an effective catalyst for the C-H borylation of heteroarenes proceeding with good yields and regioselectivities. An investigation of the mechanism of this reaction identifies potential reactive intermediates and deactivation

pathways. This work represents a new application of high-oxidation-state Re complexes in C-H functionalization catalysis and may have applications to related transformations, for example C-H silylation and germylation. Further work to optimize the ligand structure to inhibit the formation of heptahydride **7** and dimer **8** could develop a class of catalysts that can compete with established Ir examples. Exploration of ligand scaffolds other than phosphines may also enable the catalytic C-H borylation of more challenging $\text{C}(\text{sp}^2)\text{-H}$ bonds of carboarenes and pyridines, and $\text{C}(\text{sp}^3)\text{-H}$ bonds of alkanes and is subject to ongoing investigations in our laboratory.

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Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ASSOCIATED CONTENT

Supporting Information.

Syntheses and characterization, NMR spectra, crystallographic details, AIRSS/CASTEP details for **2**, **3** and **8**, synthetic and spectroscopic details.

Crystallographic data for **2** (CCDC 2060777) (CIF)

Crystallographic data for **3** (CCDC 2060776) (CIF)

Crystallographic data for **8** (CCDC 2060778) (CIF)

AIRSS/CASTEP data for **2** and **3** (RES)

This material is available free of charge via the Internet at <http://pubs.acs.org>.

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