

# Cationic and Neutral Iridium(III) Hydride Complexes Supported by a Rigid, Bidentate Boryl/Phosphine Ligand

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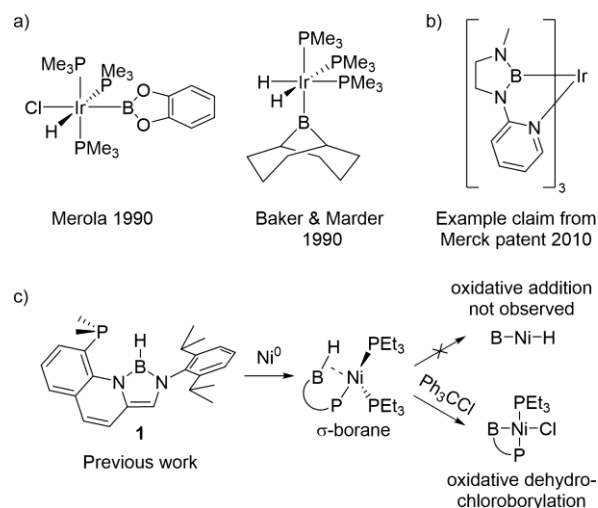
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**ABSTRACT:** We here report the oxidative addition of the hydroborane ligand to two low valent Ir(I) precursors to furnish Ir(III) hydride complexes bearing a bidentate boryl/phosphine ligand. One cationic iridium complex easily displaces a THF and 1,5-COD supporting ligand by hydrogenation in benzene, to form a stable Ir(III)  $\eta^6$ -benzene complex. The strong arene coordination thus gives insight to possible poisoning by arenes in catalytic reactions.

New organometallic chemistry is often tied to the development of new ligand platforms which more and more take advantage of exotic donor functions such as the extremely  $\sigma$ -donating boryls.<sup>1</sup> In the development of the organometallic chemistry and application of boryl donors, iridium as a metal so far played a pivotal role: for example, the first crystallographic characterization of boryl complexes was reported for Ir(III) complexes produced by oxidative addition of hydroboranes to low valent Ir(I) precursors (Figure 1a),<sup>2-3</sup> their application in catalysis near exclusively focuses on their iridium complexes,<sup>4-14</sup> while in a commercial context their iridium complexes appear already in 2010 in a patent claim by Merck on OLED emitters (Figure 1b).<sup>15</sup>

We recently reported the synthesis of a new rigid bidentate hydroborane/phosphine ligand **1** (Figure 1c),<sup>16</sup> which was developed in the context of group 10 catalyzed olefin polymerization reactions.<sup>17-18</sup> The ligand did not undergo an oxidative addition of the hydroborane function with Ni(0) but rather formed Ni(0)  $\sigma$ -borane complexes. It was eventually converted to a Ni(II) boryl species via an oxidative dehydrochloroborylation reaction by addition of the hydride abstractor trityl chloride. Here we report the synthesis and reactivity of Ir complexes bearing ligand **1** (Scheme 1): By oxidative addition of the hydroborane function in **1** to low valent Ir(I) precursors, two Ir(III) hydride complexes **2** and **3** were obtained. Strong benzene coordination in a cationic Ir(III)  $\eta^6$ -benzene complex **4** is also discussed.

When ligand **1** was heated with a stoichiometric amount of IrH(CO)(PPh<sub>3</sub>)<sub>2</sub> at 60 °C, the oxidative addition of the hydroborane to the Ir(I) center was observed under loss of two triphenylphosphine supporting ligands and concomitant coordination of the dimethylphosphine in **1** to give the Ir(III) boryl dihydride complex **2** in 78% yield (Scheme 1, top). X-ray analysis of a single crystal of the octahedral complex **2** implies two hydrides at two open, equatorial coordination sites in *cis*- and *trans*-position of the dimethylphosphine motif (Figure 2a), but their exact position could not be determined from their residual electron density peaks. Overall due to the high degree of disorder in the structure and limited quality of the dataset a



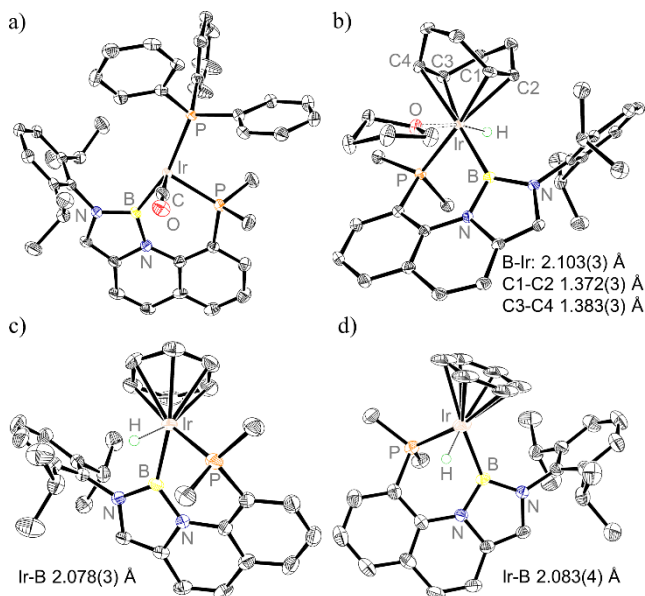
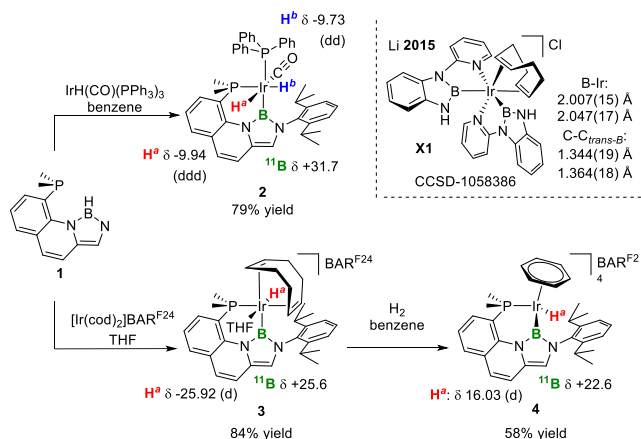
**Figure 1.** a) First crystallographic characterized boryl complexes synthesized by an oxidative addition to low valent Ir(I). b) Exemplary iridium OLED emitter from Merck patent. c) Our previous report on the synthesis of ligand **1** and its nickel chemistry.

quantitative discussion of the structure of **2** is not appropriate. Still, in the <sup>1</sup>H-NMR spectrum of **2** the hydrides can be unambiguously observed at -9.73 (dd, *trans*) and -9.94 ppm (ddd, *cis*). Although the complex contains five strongly *trans*-influencing ligands, we were unsuccessful in enforcing ligand dissociation and/or exchange – an observation typically made for octahedral Ir(III) complexes<sup>19</sup> – overall rendering the complex inert towards possible catalysis. E.g. no changes were observed by NMR analysis when **2** was heated with 100 eq hex-1-ene under Ar or 0.5 MPa H<sub>2</sub>, or when **2** and 100 eq hex-1-ene were irradiated with a high-pressure mercury lamp under 0.5 MPa H<sub>2</sub> or syngas at room temperature. An attempted CO or phosphine oxidation with trimethylamine N-oxide led to the decomposition of the iridium-boryl function, likely by formation of a N<sub>2</sub>B-O-Ir type motif as previously observed for a ruthenium complex of a PBP pincer ligand, but not removal of one of the supporting

ligands (See Table S1).<sup>20</sup> The driving force for the decomposition of the boryl motif is likely the formation of strong B-O bonds.<sup>21</sup>

In search for a complex with labile supporting ligands, we found that the oxidative addition of ligand **1** to  $[\text{Ir}(\text{cod})_2]\text{BAR}^{\text{F24}}$  ( $\text{BAR}^{\text{F24}} = \text{B}[3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3]_4$ ) in chilled THF provided the Ir(III) hydride complex **3** in 84% yield (Scheme 1, bottom left). During complex synthesis the solvent THF tends to polymerize. Attempts to synthesize potentially more stable diethyl ether or tetrahydropyran complexes were unsuccessful. Crystallographic analysis of **3** shows a distorted octahedral iridium center in which two equatorial positions *cis* to the phosphine donor are occupied by a hydrido and an *O*-bound THF ligand (Figure 2b). In accord with the crystallographic characterization, the hydrido ligand is seen in the  $^1\text{H}$ -NMR at -25.92 ppm with a *cis*-typical coupling to the phosphine of  $^2J_{\text{P-H}} = 17.0$  Hz. The olefins in the 1,5-COD ligand occupy the remaining two coordination sites *trans* to the boryl and phosphine donors. The B-Ir bond of 2.103(3) Å is significantly longer as for a structurally related cationic and octahedral boryl complex **X1** containing a 1,5-COD supporting ligand allocated *trans* to boryl functions (Scheme 1 top right; B-Ir 2.007(15) and 2.047(17) Å; two independent molecules in the unit cell).<sup>4</sup> In complex **3**, the C-C double bond at *trans* to the boryl is also longer than the conventionally reported values for 1,5-COD ligands, which further support the extreme *trans*-influence of B-donor ligand **1** (*trans*-P: C1-C2 1.372(3) Å; *trans*-B: C3-C4 1.383(3) Å; bond lengths of the *trans*-B located olefin functions in the 1,5-COD ligand of **X1**: 1.344(19) and 1.364(18) Å).

**Scheme 1.** Synthesis of iridium complexes **2/3/4** starting from borane/phosphine ligand **1**. Complex **X1** was previously reported by Li *et al.*<sup>4</sup>



**Figure 2.** Single crystal structure analyses of the iridium complexes a) **2**, b) **3**, c) **4**, major conformer, d) **4**, minor conformer. All  $\text{BAR}^{\text{F24}}$  counterions, solvent molecules, non-hydride hydrogens and deuterons are omitted for clarity.

hydride positions. The Ir-B bonds of 2.078(3) and 2.083(4) Å for the benzene complex **4** appear shortened by ca. 0.02 Å in comparison to its precursor 1,5-COD/THF complex **3**. In a  $\text{CD}_2\text{Cl}_2$  solution, the protons of the coordinated benzene molecule appear as a singlet at 6.23 ppm, highfield shifted by 1.12 ppm compared to free benzene. The bond lengths in the coordinated benzene C-C bonds show small alterations between 1.378(6) and 1.425(6) Å by XRD, and no angular tilt of the C-D bonds out of coplanarity with the arene ring was observed within the DFT optimizations of the individual disorder structure parts. While the upfield shift of NMR peak and the C-C bond alternation pattern in the benzene ring implies the dearomatization of the benzene ring, the benzene carbons mostly maintain planar structures. The result suggests that the strong coordination of arene functionalities drastically poisons these kinds of complexes in potential catalytic applications. Previous reports on structurally related rhodium and iridium hydrogenation catalysts also described poisoning by arenes.<sup>30</sup>

To conclude, we synthesized two new Ir(III) boryl complexes **2** and **3** by oxidative addition of the hydroborane in ligand **1** to two different low valent Ir(I) precursors. While the supporting ligands in the octahedral phosphine/carbonyl complex **2** appeared inert to our attempts for ligand displacement, we could show that a THF and 1,5-COD ligand in the cationic complex **3** can be displaced upon addition of hydrogen gas in benzene, to form a cationic pianostool-like  $\eta^6$ -benzene boryl hydride complex **4**. This strong  $\eta^6$ -type coordination by the arene may therefore reflect in catalyst poisoning by aromatic functions.

## ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website.

Description of methods; synthetic procedures, data on X-ray crystallographic and related DFT analyses,  $^1\text{H}/^{11}\text{B}/^{13}\text{C}/^{19}\text{F}/^{31}\text{P}/^2\text{D}$  NMR- as well as IR-spectra for compounds **2/3/4** (PDF)

We noticed that upon addition of hydrogen gas to a suspension of complex **3** in benzene, the compound dissolves and a single new species is formed under concomitant formation of free THF and cyclooctane through hydrogenation of the 1,5-COD ligand (See Figure S13). X-ray crystallographic analysis of a single crystal obtained from an NMR scale reaction in deuterobenzene revealed the formation of a piano stool arene complex **4** (Figure 2c/d). The iridium(hydrido)( $\eta^6$ -benzene) motifs show a disorder over two positions in which the hydrides and the tilted arenes occupy pseudo-mirrored positions in the irida-pianostool with respect to the boryl ligand plane. The hydride positions could be observed from their residual electron densities, but required restraints based on DFT (BP86-D4/def2-TZVP)<sup>22-29</sup> optimized

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