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Alex J. Kosanovich, Loren P. Press, Oleg V. Ozerov

PII: S0022-328X(16)30557-5

DOI: 10.1016/j.jorganchem.2016.12.006

Reference: JOM 19729

To appear in: Journal of Organometallic Chemistry

Received Date: 27 September 2016

Revised Date: 25 November 2016

Accepted Date: 2 December 2016

Please cite this article as: A.J. Kosanovich, L.P. Press, O.V. Ozerov, Boryl transfer reactivity of a POCOP-supported Ir-diboryl: Reduction of CO<sub>2</sub> to CO and borylation of other small molecules, *Journal of Organometallic Chemistry* (2017), doi: 10.1016/j.jorganchem.2016.12.006.

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# Boryl Transfer Reactivity of a POCOP-Supported Ir-diboryl: Reduction of $CO_2$ to COand Borylation of Other Small Molecules

Alex J. Kosanovich<sup>†</sup>, Loren P. Press<sup>†</sup>, Oleg V. Ozerov\*

Department of Chemistry, Texas A&M University, 3255 TAMU, College Station, TX 77842, USA.

ozerov@chem.tamu.edu

ABSTRACT. Reactions of a trivalent diboryl Ir complex  $Ir-(Bpin)_2$  supported with a POCOP-type pincer ligand with a series of small molecules have been explored (pin = pinacolate).  $Ir-(Bpin)_2$  deoxygenated CO<sub>2</sub> to make Ir-CO and  $O(Bpin)_2$ . Attempts to deoxygenate other carbonyl compounds were not successful. The reaction with CO led to loss of  $B_2pin_2$  by reductive elimination and its replacement on Ir with CO.  $Ir-(Bpin)_2$  did not react with p-trifluoromethylbenzaldehyde, acetone, ethyl acetate or benzonitrile. The reaction with ethyl formate resulted in formal deethoxylation of this substrate, with formation of Ir-CO and HBpin and EtOBpin. Finally, treatment of  $Ir-(Bpin)_2$  with ethylene resulted in diboration of ethylene to produce pinB-CH<sub>2</sub>CH<sub>2</sub>-Bpin and  $Ir-(C_2H_4)$ .

This manuscript is dedicated to Prof. Gerard van Koten on occasion of his 75<sup>h</sup> birthday.

Graphical abstract:



#### **1. Introduction**

Transition metal boryl complexes are subjects of intense study<sup>[1]</sup> primarily because of their importance in multiple C-B bond forming reactions such as hydroboration<sup>[2]</sup> and C-H borylation.<sup>[3]</sup> The commonly used boryl ligands, Bpin and Bcat (pin = pinacolate, cat = catecholate), are strong  $\sigma$ -donors and weak  $\pi$ -acceptors, and when attached to late transition metals they can exhibit nucleophilic behavior.<sup>[4]</sup>

We have recently reported a diboryl iridium complex supported by the <sup>Me</sup>POCOP ligand (**Ir-(Bpin)**<sub>2</sub>, Scheme 1). It was synthesized to examine its relevance as a potential intermediate in the catalytic C-H borylation catalyzed by Ir complexes of POCOP-type pincer ligands.<sup>[5]</sup> Surprisingly, unlike a number of other di- and triboryl complexes of trivalent Ir,<sup>[6-9]</sup> **Ir-(Bpin)**<sub>2</sub> did not react with arenes even at elevated temperature. We instead became interested in the reactivity of this complex with unsaturated substrates, especially those containing oxygens because of the high thermodynamic favorability of forming boron-oxygen bonds. A diboryl metal complex may in principle be viewed as a deoxygenating reagent where the metal center may stabilize the deoxygenated product by complexation. Deoxygenation using diboron<sup>[10]</sup> reagents, with<sup>[11,12]</sup> and without<sup>[13,14]</sup> a metal catalyst, has been reported. Herein we report the results of our investigation.

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Scheme 1. Reactions of Ir-(Bpin)<sub>2</sub> with various substrates.

 $Ir-(Bpin)_2$  was isolated as a yellow solid via thermolysis of Ir-(TBE) in the presence of equimolar  $B_2pin_2$ . The relevance of Ir(I) olefin complexes in reactions of oxidative addition of non-polar bonds to pincer-supported Ir has been broadly explored by Goldman, Brookhart, Krogh-Jespersen, and coworkers.<sup>[15]</sup> Previously,  $Ir-(Bpin)_2$  was

found to be stable to heating in benzene solution.<sup>[5]</sup> Thus, we selected benzene- $d_6$  as solvent for the reactions with new substrates.

First, reactions of  $Ir-(Bpin)_2$  with CO<sub>2</sub> were examined (Scheme 1). Exposure of a C<sub>6</sub>D<sub>6</sub> solution of  $Ir-(Bpin)_2$  to 1 atm of CO<sub>2</sub> resulted in no reaction at ambient temperature (NMR evidence). However, heating  $Ir-(Bpin)_2$  at 80 °C in C<sub>6</sub>D<sub>6</sub> under 1 atm of CO<sub>2</sub> for 24 h resulted in quantitative formation of Ir-CO with concomitant production of (Bpin)<sub>2</sub>O in equimolar ratio observed by <sup>1</sup>H ( $\delta$  1.03 ppm) and <sup>11</sup>B NMR ( $\delta$  21.5 ppm) NMR spectroscopy. This reaction is driven thermodynamically by the formation of strong B-O bonds, as well as strong complexation of CO by the electron-rich Ir(I) center. Reduction of CO<sub>2</sub> to CO using homogeneous transition metal systems is a topic of considerable contemporary interest.<sup>[16-21]</sup> However, it must be noted that stoichiometric utilization of Bpin derivatives for CO<sub>2</sub> reduction is utterly impractical and the strong bonding of CO to the Ir(I) center precludes reasonable catalytic possibilities.

We next tested whether  $Ir-(Bpin)_2$  is capable of reducing carbon monoxide itself. Deoxygenation of CO might lead to a putative terminal carbide complex (<sup>Me</sup>POCOP)IrC. Terminal carbide complexes are unknown for group 9 metals, but have been characterized for neighboring Ru and Os.<sup>[22,23]</sup> Alas, iridium carbides remain unknown for the time being, as CO reacted with  $Ir-(Bpin)_2$  simply by inducing reductive elimination of  $B_2pin_2$ .<sup>24</sup> This reaction is fast at ambient temperature as indicated by a fast color change of the solution upon exposure of  $Ir-(Bpin)_2$  to CO atmosphere. Under CO atmosphere, the Ir product is  $Ir-(CO)_2$  but one of the CO ligands is lost upon removal of volatiles under vacuum resulting in the monocarbonyl Ir-CO. The weak binding of the second carbonyl is consistent with related literature examples where the  $2^{nd}$  CO in (pincer)Ir(CO)<sub>2</sub> complexes is typically readily lost upon workup and/or exposure to vacuum.<sup>[25,26]</sup>

Ir-(CO)<sub>2</sub> can be conveniently observed upon treatment of Ir-(TBE) with 1 atm of CO, and removal of volatiles allows isolation of complex Ir-CO. Ir-CO has not been previously reported, but it is closely analogous to other square planar Ir(I) monocarbonyl complexes supported by PCP and POCOP pincers.<sup>[27,28]</sup> Ir-CO features a singlet resonance by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy ( $\delta$  190.6 ppm) and a CO stretching frequency by IR spectroscopy at 1936 cm<sup>-1</sup>.

The investigation was then extended to organic substrates with C=O double bonds. It was envisaged that a successful deoxygenation might provide an unusual route to Ir(I) carbene complexes.<sup>[29]</sup> Surprisingly, no reaction was observed upon thermolysis (80 °C, 24 h) of **Ir-(Bpin)**<sub>2</sub> in the presence of acetone, 4-F<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>CHO, or ethyl acetate.<sup>30</sup> On the other hand, thermolysis in the presence of ethyl formate, resulted in complete consumption of **Ir-(Bpin)**<sub>2</sub>, but the dominant Ir product of this reaction was **Ir-CO**, not a putative carbene. <sup>1</sup>H NMR spectroscopic analysis revealed formation of EtOBpin (52%) and free HBpin (27%) as the two identifiable boron products, which were confirmed by <sup>11</sup>B NMR spectroscopy with singlet resonances at  $\delta$  22.2 and 28.1 ppm, respectively. **Ir-(Bpin)**<sub>2</sub> reacted similarly with dimethylformamide (DMF), with Ir-CO as the main Ir-based product. However, this reaction was less clean than with ethyl formate.

Formation of EtOBpin and HBpin in the reaction with ethyl formate could be formally viewed as capture of ethanol by the two Bpin units. In a separate reaction, thermolysis of  $Ir-(Bpin)_2$  with isopropanol at 80 °C for 24 h in C<sub>6</sub>D<sub>6</sub> resulted in formation of Ir-((H/D)Bpin) (independently confirmed) as the major organometallic product in 67% spectroscopic yield (<sup>31</sup>P{<sup>1</sup>H} NMR,  $\delta$  191.9 ppm). <sup>1</sup>H NMR spectroscopy revealed quantitative formation of mono-deuterated <sup>i</sup>PrOBpin ((CH<sub>3</sub>)<sub>2</sub>C(D)OBpin) in which the methine had become fully deuterated. The isopropyl methyl resonance shows a 1:1:1 triplet at  $\delta$  0.95 ppm (<sup>3</sup>J<sub>H-D</sub> = 0.9 Hz), with a concomitant increase in residual protio-benzene solvent intensity. Facile exchange of H for D in the [(H/D)Bpin] moiety of **Ir-((H/D)Bpin)** in C<sub>6</sub>D<sub>6</sub> was previously documented,<sup>[5]</sup> but the mechanism responsible for the selective deuteration of the methine position in the isopropoxy group is not clear. An analogous reaction of **Ir-(Bpin)<sub>2</sub>** with water resulted in the formation of a complex mixture of multiple products.

In order to test other carbon-element multiple bonds besides C=O, we carried out reactions of  $Ir-(Bpin)_2$  with benzonitrile (C=N) and ethylene (C=C). No reaction was observed upon heating of a solution of  $Ir-(Bpin)_2$  in the presence of benzonitrile at 80 °C for 24 h. Exposure of  $Ir-(Bpin)_2$  in C<sub>6</sub>D<sub>6</sub> to 2 atm of ethylene at room temperature also resulted in no observable change. However, heating the resultant solution at 110 °C for 30 h led to the formation of the ethylene adduct  $Ir-(C_2H_4)$  as the major organometallic product in >94% NMR spectroscopic yield. <sup>1</sup>H NMR spectroscopy revealed the concomitant formation of BpinCH<sub>2</sub>CH<sub>2</sub>Bpin, the product of ethylene diboration,<sup>[31]</sup> in 93% yield. The identity of BpinCH<sub>2</sub>CH<sub>2</sub>Bpin was confirmed *in situ* by <sup>11</sup>B ( $\delta$  34.2) and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy as well.

#### **3. Discussion and Summary.**

Our investigations revealed a rather diverse range of outcomes of reactions of the diboryl complex,  $Ir-(Bpin)_2$ , with substrates containing multiple carbon-oxygen, carbonnitrogen, and carbon-carbon bonds. While the reaction with CO<sub>2</sub> resulted in the formal oxygen atom abstraction by the two boryls of  $Ir-(Bpin)_2$ , no such oxygen atom abstraction was observed in reactions with CO, an aldehyde, a ketone, or an ester. The reaction with CO<sub>2</sub> likely proceeds via initial insertion of a C=O bond in CO<sub>2</sub> into an Irboryl bond. This insertion can be envisioned to proceed in 1,2- or 2,1-fashion (Scheme 2). Analogous possibilities were analyzed<sup>[12]</sup> for insertion of CO<sub>2</sub> into Sadighi's<sup>[11]</sup> Cu-Bpin bond. Insertion with the formation of O-B bond would produce Int1, from which CO deinsertion to give Int2 and O-B reductive elimination would furnish the products. Insertion with the formation of a O-Ir bond would produce Int3, which may be expected to eliminate BCO<sub>2</sub>B<sup>[32]</sup> by O-B reductive elimination, and reinsertion of Ir into the B-C bond of BCO<sub>2</sub>B would lead again to Int1.

The reaction with ethylene is also most simply interpreted via coordination of ethylene, followed by insertion into the Ir-B bond to give **Int4**, and then C-B reductive elimination to give product pinBCH<sub>2</sub>CH<sub>2</sub>Bpin. On the other hand, the outcome of the reaction with ethyl formate does not appear to arise from insertion of the C=O bond into an Ir-B bond of **Ir-(Bpin)**<sub>2</sub>. Moreover, the lack of reaction with benzonitrile, acetone, and p-trifluoromethylbenzaldehyde suggests that the C=O and C=N insertion in the Ir-B bond does not easily take place. If it did, the favorability of formation of B-O and B-N bonds would be expected to drive the reactions forward.



Scheme 2. Plausible pathways for reactions of Ir-(Bpin)<sub>2</sub> with CO<sub>2</sub> and ethylene.

The reaction with CO proceeds differently, and presumably simply by coordination of CO to  $Ir-(Bpin)_2$ , followed by reductive elimination of  $B_2pin_2$ . The fact that  $B_2pin_2$  was not observed in the reaction of  $Ir-(Bpin)_2$  with CO<sub>2</sub> or ethyl formate suggests that free CO is not produced as an intermediate in these transformations.

In summary, we have been able to demonstrate that a diboryl complex of trivalent iridium is capable of undergoing reactions with unsaturates. The outcomes of these reactions are diverse and the underlying reasons for differences in reactivity are not fully understood at this time.

#### 4. Experimental Section

#### 4.1 General considerations.

Unless specified otherwise, all manipulations were performed under an argon atmosphere using standard Schlenk or glovebox techniques. Pentane, diethyl ether, and benzene were dried over sodium-benzophenone ketyl, distilled or vacuum transferred and stored over molecular sieves in an Ar-filled glovebox. All liquid reagents were degassed and stored over molecular sieves in an Ar-filled glovebox prior to use. Ir-(H)(Cl), Ir-(Bpin)<sub>2</sub>, and Ir-(TBE) were prepared according to literature procedure.<sup>[5]</sup> All other chemicals were used as received from commercial vendors. All NMR spectra were recorded on either a Varian Inova 400 spectrometer (<sup>1</sup>H NMR, 399.755 MHz; <sup>13</sup>C{<sup>1</sup>H} NMR, 100.518 MHz; <sup>11</sup>B NMR 128 MHz, <sup>31</sup>P{<sup>1</sup>H} NMR 181.822 MHz), or a Varian Inova NMR 500 (<sup>1</sup>H NMR, 499.425 MHz/ 499.683 MHz; <sup>13</sup>C{<sup>1</sup>H} NMR, 75.424 MHz/ 125.580 MHz; <sup>31</sup>P{<sup>1</sup>H} NMR, 202.171 MHz; <sup>19</sup>F NMR, 469.854 MHz) spectrometer. All spectra were recorded at ambient temperature unless otherwise noted. Chemical shifts are reported in  $\delta/\text{ppm}$ . For <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra, the residual solvent peak was used as an internal reference. <sup>11</sup>B NMR spectra were referenced externally using neat BF<sub>3</sub>OEt<sub>2</sub> at  $\delta = 0$  ppm, <sup>31</sup>P{<sup>1</sup>H} NMR spectra were referenced externally using 85% H<sub>3</sub>PO<sub>4</sub> at  $\delta = 0$ ppm, and <sup>19</sup>F NMR spectra were referenced externally using 1.0 M CF<sub>3</sub>CO<sub>2</sub>H in CDCl<sub>3</sub> at  $\delta = -78.5$  ppm.

# 4.2 Synthesis and characterization of $Ir-(CO)_2$ in situ

A J. Young NMR tube was charged with **Ir-(TBE)** (23 mg, 0.036 mmol) and  $C_6D_6$ . The solution was frozen then the headspace was evacuated and charged with 1 atm CO. The solution changed color from dark red to yellow. The reaction was analyzed by NMR spectroscopy and found to be >95% pure  $Ir-(CO)_2$ . Free TBE was observed in the <sup>1</sup>H NMR spectrum. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  6.58 (s, 2H- Ar-*H*), 2.17 (s, 3H, Ar-CH<sub>3</sub>), 2.16-2.08 (m, 4H, PCH(CH<sub>3</sub>)<sub>2</sub>), 1.10-1.02 (m, 24H, PCH(CH<sub>3</sub>)<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  171.3.

#### 4.3 Synthesis of Ir-CO

Ir-(H)(Cl) (65 mg, 0.11 mmol) was added to a 50 mL Teflon screw cap round bottom flask and dissolved in benzene. Tert-butyl ethylene (100 µL, 0.78 mmol) was added via syringe followed by sodium tert-butoxide (11.8 mg, 0.12 mmol). The reaction was stirred for 4 h and then, after an initial degassing via freeze-pump-thaw, the headspace of the flask was charged with 1 atm of carbon monoxide. This resulted in an immediate color change from a dark red to orange-yellow solution and  $Ir-(CO)_2$  could be observed as the major product by  ${}^{31}P{}^{1}H$  NMR ( $\delta$  171.8). The reaction was stirred an additional 2 h, then transferred into a glovebox and filtered through a thin pad of silica over Celite. Removal of solvent under reduced pressure provided the product as a yellow-orange solid. Yield: 56 mg (88%), <sup>1</sup>H NMR (500 MHz,  $C_6D_6$ ):  $\delta$  6.69 (s, 2H, Ar-H), 2.14 (m, 4H,  $CH(CH_3)_2$ ), 2.12 (s, 3H), 1.12 (m, 24H,  $CH(CH_3)_2$ ). <sup>13</sup>C{<sup>1</sup>H} (126 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ 198.6 (t,  $J_{P-C} = 4.5$  Hz, Ir-CO), 169.4 (t,  $J_{P-C} = 8.5$  Hz, Ar), 145.8 (t,  $J_{P-C} = 9.1$  Hz, Ar), 140.3 (s, Ar), 105.4 (t,  $J_{P-C} = 6.1$  Hz, Ar), 31.7 (t,  $J_{P-C} = 16.3$  Hz,  $PCH(CH_3)_2$ ), 21.9 (s, Ar-CH<sub>3</sub>), 18.5 (t,  $J_{P-C} = 3.4$  Hz, PCH(CH<sub>3</sub>)<sub>2</sub>), 17.6 (s, PCH(CH<sub>3</sub>)<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} (202 MHz,  $C_6D_6$ ):  $\delta$  190.6. IR v(CO) = 1936 cm<sup>-1</sup>. Anal. Calcd. for **3**: C, 41.73 ; H, 5.78 . Found: C, 41.75; H, 5.86.

#### 4.4 Synthesis of Ir-((H/D)Bpin)

Ir-((H/D)Bpin) was prepared using a modified literature procedure.<sup>[5]</sup> The preparation of this compound was carried out with natural abundance reagents and solvents. However, NMR analysis was performed using C<sub>6</sub>D<sub>6</sub> and H/D exchange of Ir-((H/D)Bpin) with benzene is noticeable even at ambient temperature. To a screw capped culture tube equipped with a stir bar was added Ir-(H)(Cl) (105.4 mg, 0.180 mmol), B<sub>2</sub>pin<sub>2</sub> (46.0 mg, 0.181 mmol) and 2 mL Et<sub>2</sub>O. NaO<sup>t</sup>Bu (17.3 mg, 0.180 mmol) was added and the resultant suspension was placed in a 50 °C oil bath for 24h. The resultant orange-red solution was brought into the glovebox, filtered through Celite and solvent was removed under reduced pressure providing an orange residue. The residue was extracted with pentane, filtered through Celite and placed in a freezer at -30 °C for 12 h resulting in precipitation of red-orange solids. Pentane was decanted and the solids were dried in vacuo providing a sticky red solid of which Ir-((H/D)Bpin) was the major product in 72% purity by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR. Two other unidentified products were present in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum at 168.8 (11%) and 166.1 (17%) ppm. <sup>t</sup>BuOBpin was also present in the <sup>1</sup>H NMR spectrum. Yield: 70 mg (40.2%). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ 6.75 (s, 2H), 2.14 (s, 3H, p-Me), 1.37 (s, 12H, Bpin), 1.23 (m, 24H), -10.15 (br s, 1H, Ir-H). Resonances for the POCOP iPr methines could not be reliably identified presumably due to overlap, broadness of signals, or possible H/D exchange in solution.<sup>11</sup>B NMR (128 MHz, C<sub>6</sub>D<sub>6):</sub> δ 27.5. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>): δ 169.7, 142.1, 104.6 (t, J = 5.8 Hz), 81.8, 29.9, 18.73. <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  191.9. 4.5 Synthesis and characterization of  $Ir-(C_2H_4)$  in situ.

 $Ir-(Bpin)_2$  (33 mg, 0.041 mmol) was added to a J. Young NMR tube and dissolved in  $C_6D_6$ . After an initial degassing via freeze-pump-thaw, the headspace of the NMR tube

was charged with ethylene (2 atm) resulting in no reaction after 20 min at room temperature. After 3 h at 110 °C the reaction changed from yellow to light red and **Ir**-(**C**<sub>2</sub>**H**<sub>4</sub>) was observed by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy (32%). After 30 h at 110 °C BpinCH<sub>2</sub>CH<sub>2</sub>Bpin was observed in a 93% yield and **Ir**-(**C**<sub>2</sub>**H**<sub>4</sub>) was identified as the main organometallic product. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  6.79 (s, 2H), 2.64 (t, *J* = 2.5 Hz, 4H), 2.30 (sept, *J* = 5.7 Hz, 4H), 2.17 (s, 3H), 1.13 (dvt, *J* = 13.8, 6.9 Hz, 12H), 1.03 (dvt, *J* = 16.3, 7.4 Hz, 12H). <sup>13</sup>C{<sup>1</sup>H} NMR(126 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  165.9 (m), 134.7, 105.5 (d, *J* = 5.9 Hz), 33.3, 31.0 (t, *J*<sub>P-C</sub> = 16.2 Hz), 17.9, 17.2. <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ 182.6.

#### 4.6 Reaction of Ir-(Bpin)<sub>2</sub> with CO.

**Ir-(Bpin)**<sub>2</sub> (21 mg, 0.027 mmol) was added to a J. Young NMR tube and dissolved in  $C_6D_6$ . After an initial degassing via freeze–pump–thaw, the headspace of the NMR tube was charged with 1 atm of carbon monoxide resulting in an instant color change from bright yellow to colorless-yellow. Analysis via <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy revealed quantitative conversion to **Ir-(CO)**<sub>2</sub>. <sup>1</sup>H NMR revealed a sharp singlet at 1.01 ppm (24 H) indicating free B<sub>2</sub>pin<sub>2</sub>. A sharp singlet at  $\delta$  31 ppm via <sup>11</sup>B NMR confirmed free B<sub>2</sub>pin<sub>2</sub>. Removal of solvent *in vacuo* followed by dissolving the resulting yellow solids in C<sub>6</sub>D<sub>6</sub> found pure **Ir-CO** and free B<sub>2</sub>pin<sub>2</sub>.

# 4.7 Reaction of Ir-(Bpin)<sub>2</sub> with CO<sub>2</sub>.

 $Ir(Bpin)_2$  (22 mg, 0.027 mmol) was added to a J. Young NMR tube and dissolved in  $C_6D_6$ . After an initial degassing via freeze–pump–thaw, the headspace of the NMR tube was charged with  $CO_2$  (1 atm) resulting in no reaction after 20 minutes at room temperature. Heating at 80 °C for 24 h resulted in quantitative formation of **Ir-CO** and

O(Bpin)<sub>2</sub> as seen by <sup>1</sup>H, <sup>11</sup>B and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopic analysis. Removal of volatiles followed by dissolution of the resulting residue in CDCl<sub>3</sub> and comparing to literature values confirmed the identity of O(Bpin)<sub>2</sub>.<sup>33</sup> O(Bpin)<sub>2</sub> <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.03 (s, 24H, pin CH<sub>3</sub>). <sup>11</sup>B NMR (128 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  21.5 (br s). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  82.9, 24.7.

4.8 Reaction of Ir-(Bpin)<sub>2</sub> with isopropanol.

**Ir**-(**Bpin**)<sub>2</sub> (13.3 mg, 0.017 mmol) was added to a J. Young NMR tube and dissolved in C<sub>6</sub>D<sub>6</sub>. Isopropanol (3 μL, 0.034 mmol) was added and the solution was heated in an oil bath at 80°C for 24 h. <sup>31</sup>P{<sup>1</sup>H} NMR analysis shows formation of **Ir**-((**H/D)Bpin**) (67%) as the major organometallic product, with unidentified products at δ 180.1 (10%) and δ 168.6 (23%) ppm. <sup>1</sup>H NMR spectroscopy reveals quantitative formation of <sup>i</sup>PrOBpin in which the methine has become fully deuterated showing a 1:1:1 triplet, with concomitant increase in residual solvent intensity, expected for H/D exchange. (CH<sub>3</sub>)<sub>2</sub>CDOBpin: <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ 1.06 (s, 12H), 0.95 (t, <sup>3</sup>J<sub>H-D</sub> = 0.9 Hz, 6H).

4.9 Reaction of Ir-(Bpin)<sub>2</sub> with ethyl formate.

**Ir**-(**Bpin**)<sub>2</sub> (14.7 mg, 0.018 mmol) was added to a J. Young NMR tube and dissolved in C<sub>6</sub>D<sub>6</sub>. Ethyl formate (2 μL, 0.025 mmol) was added and the solution was heated in an oil bath at 80°C for 24 h.<sup>31</sup>P{<sup>1</sup>H} NMR NMR analysis revealed that **Ir**-**CO** had formed in 92% spectroscopic yield along with another unidentified product at δ 173.4 ppm (7%). <sup>1</sup>H NMR revealed the organic products to be EtOBpin (52%), HBpin (27%), and other Bpin containing products (21%). <sup>11</sup>B NMR analysis also confirmed the presence of EtOBpin (δ 22.2) and free HBpin (δ 28.1).

#### 4.10 Reaction of Ir-(Bpin)<sub>2</sub> with ethyl acetate

*Ir-(Bpin)*<sub>2</sub> (17.2 mg, 0.021 mmol) was added to a J. Young NMR tube and dissolved in C<sub>6</sub>D<sub>6</sub>. Ethyl acetate (4  $\mu$ L, 0.041 mmol) was added and the solution was heated in an oil bath at 80 °C for 24 h. No reaction was observed by <sup>31</sup>P{<sup>1</sup>H} or <sup>1</sup>H NMR spectroscopy.

#### 4.11 Reaction of Ir-(Bpin)<sub>2</sub> with dimethylformamide

*Ir-(Bpin)*<sub>2</sub> (10.9 mg, 0.014 mmol) was added to a J. Young NMR tube and dissolved in C<sub>6</sub>D<sub>6</sub>. Dimethylformamide (3  $\mu$ L, 0.04 mmol) was added and the solution was heated in an oil bath at 80 °C and monitored spectroscopically. After 48 h, the reaction was determined to be complete by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. <sup>31</sup>P{<sup>1</sup>H} NMR analysis revealed that **Ir-CO** had formed in 51% spectroscopic yield with another unidentified product at  $\delta$  173.4 ppm (49%). <sup>1</sup>H NMR showed formation of B<sub>2</sub>pin<sub>2</sub>, Me<sub>2</sub>NBpin, and other Bpin containing products.

## 4.12 Reaction of Ir-(Bpin)<sub>2</sub> with ethylene.

**Ir-(Bpin)**<sub>2</sub> (33 mg, 0.041 mmol) was added to a J. Young NMR tube and dissolved in C<sub>6</sub>D<sub>6</sub>. After an initial degassing via freeze–pump–thaw, the headspace of the NMR tube was charged with ethylene (2 atm) resulting in no reaction after 20 min at room temperature. After 3 h at 110 °C the reaction changed from yellow to light red and **Ir**-(**C**<sub>2</sub>**H**<sub>4</sub>) was observed by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy (32%). After 30 h at 110 °C BpinCH<sub>2</sub>CH<sub>2</sub>Bpin was observed in a 93% yield and **Ir**-(**C**<sub>2</sub>**H**<sub>4</sub>) (94%) was the main organometallic product. Removal of volatiles followed by dissolution of the resulting residue in CDCl<sub>3</sub> and comparing to literature values confirmed the identity of BpinCH<sub>2</sub>CH<sub>2</sub>Bpin.<sup>[34]</sup> BpinCH<sub>2</sub>CH<sub>2</sub>Bpin: <sup>1</sup>H NMR (RT, C<sub>6</sub>D<sub>6</sub>): δ 1.21 (br s, 4H), 1.09 (s,

24H). <sup>11</sup>B NMR (RT, C<sub>6</sub>D<sub>6</sub>): 34.2. <sup>13</sup>C{<sup>1</sup>H} NMR (RT, C<sub>6</sub>D<sub>6</sub>):  $\delta$  82.8, 25.0, 5.2 (br s, (Bpin)*C*H<sub>2</sub>*C*H<sub>2</sub>(Bpin)).

4.13 Reaction of  $Ir-(Bpin)_2$  with  $H_2O$ .

*Ir-(Bpin)*<sub>2</sub> (13.5 mg, 0.017 mmol) was added to a J. Young NMR tube and dissolved in C<sub>6</sub>D<sub>6</sub>. H<sub>2</sub>O ( 0.5  $\mu$ L, 0.027 mmol) was added and the solution was heated in an oil bath at 80 °C for 6 h and monitored by NMR spectroscopy. After 6 h, <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy showed that the sample contained a mixture of unreacted *Ir-(Bpin)*<sub>2</sub> (82%), *Ir-((H/D)Bpin)* (11%) and an unidentified product at  $\delta$  135.7 ppm. Further heating of the solution at 80 °C for another 4 h produced an intractable mixture of unidentified products by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy (ca  $\delta$  150 ppm). <sup>1</sup>H NMR spectroscopy revealed a mixture of Bpin-containing decomposition products.

# 4.14 Reaction of Ir-(Bpin)<sub>2</sub> with benzonitrile

*Ir-(Bpin)*<sub>2</sub> (13.4 mg, 0.017 mmol) was added to a J. Young NMR tube and dissolved in  $C_6D_6$ . Two equivalents of benzonitrile (4 µL, 0.034 mmol) were added and the solution was heated in an oil bath at 80 °C for 24 h. No reaction was observed by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy.

## 4.15 Reaction of Ir-(Bpin)<sub>2</sub> with acetone

*Ir-(Bpin)*<sub>2</sub> (13.4 mg, 0.017 mmol) was added to a J. Young NMR tube and dissolved in  $C_6D_6$ . Two equivalents of acetone (3 µL, 0.034 mmol) were added and the solution was heated in an oil bath at 80 °C for 24 h. No reaction was observed by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy.

4.16 Reaction of Ir-(Bpin)<sub>2</sub> with p-(trifluoromethyl)benzaldehyde

*Ir-(Bpin)*<sub>2</sub> (15.0 mg, 0.019 mmol) was added to a J. Young NMR tube and dissolved in C<sub>6</sub>D<sub>6</sub>. p-(trifluoromethyl)benzaldehyde (3  $\mu$ L, 0.022 mmol) was added and the solution was heated in an oil bath at 80 °C for 24 h. No reaction was observed by <sup>31</sup>P{<sup>1</sup>H} or <sup>19</sup>F NMR spectroscopy.

**Acknowledgments**. We are grateful for the support of this work by the US National Science Foundation (grant CHE-1300299 to O.V.O. and an NSF LSAMP Fellowship to A.J.K. via grant HRD-1406755), and the Welch Foundation (grant A-1717 to O.V.O.).

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