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# Reversible addition of ethylene to a pincer-based boryl-iridium unit with the formation of a bridging ethylidene†

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This report examines reactions of a series of Ir complexes supported by the diarylboryl/bis(phosphine) PBP pincer ligand with ethylene: (PBP)IrH<sub>4</sub> (1), (PBP)IrH<sub>2</sub>(CO) (2), and (PBP)Ir(CO)<sub>2</sub> (3). The outcomes of these reactions differ from those typical for Ir complexes supported by other pincer ligands and do not give rise to simple ethylene adducts or products of insertion of Ir into the C–H bond of ethylene. Instead, the elements of ethylene are incorporated into the molecules to result in B–C bonds. In the case of 2 and 3, ethylene addition results in the formation of B/Ir bridging ethylidene complexes 5 and 6. For 6, the addition of ethylene (and the analogous addition of 1-hexene) is shown to be partially reversible. Addition of ethylene to 2 and 3 is remarkable because they are saturated at Ir and yet the net outcome is such that ethylene binds without replacing any ligands already present. A mechanistic inquiry suggests that dissociation of CO from 3 or 6 is necessary in order for the addition or loss of ethylene to proceed.

## Introduction

The nature of the elementary reactions of binding ethylene and other alkenes to transition metal centers is of importance to many common and impactful catalytic processes that utilize alkenes as feedstocks.<sup>1–5</sup> The initial interaction between a suitably unsaturated transition metal complex and an alkene (Scheme 1) typically results in a  $\pi$ -complex (A),<sup>6</sup> which may then undergo C–H oxidative addition to yield a vinyl hydride isomer (B),<sup>7,8</sup> or isomerization *via* an initial insertion product C to a metal alkylidene complex (D),<sup>9–11</sup> or even a hydrido/alkylidene isomer (E).<sup>12,13</sup> The latter two isomerizations typically require the presence of hydride ligands in the metal fragment and proceed by a combination of an insertion of the olefin into M–H and the subsequent single or double  $\alpha$ -H elimination. Moreover, since isomerization of a free hydrocarbon olefin into a free alkylidene is unfavourable by >70 kcal mol<sup>–1</sup>,<sup>14</sup> only the metal centers with an enormous preference for binding an alkylidene *vs.* olefin are thermodynamically capable of it.<sup>9–11</sup> This thermodynamic capacity is more or less restricted to highly electron-rich early-to mid-periodic table metals in low oxidation states and with propensity to form multiple metal–ligand bonds.

In the present work, we report unexpected findings that emerged in the course of our exploration of the reactivity of Ir complexes of a diarylboryl-containing PBP pincer ligand.<sup>15–18</sup> In particular, we discovered that ethylene can reversibly add to the boryl-iridium unit as a bridging ethylidene. Complexes of monodentate boryl ligands are well established and important intermediates in such organometallic catalytic processes as hydroboration<sup>19</sup> and C–H borylation.<sup>20</sup> Some variants of aromatic C–H borylation rely on the presence of sacrificial olefin reagents.<sup>20,21</sup> To the best of our knowledge, formation of alkylidenes bridging a boron and a transition metal in C–H borylation of arenes or olefins,<sup>20</sup> or in olefin hydroboration,<sup>19</sup> has not been documented or considered.



**Scheme 1** (Top) typical outcomes of a reaction between an olefin (ethylene for simplicity) and a transition metal complex. (Bottom) the new reactivity reported in this work.

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## Results and discussion

### Reaction of ethylene with (PBP)Ir complexes

For the reactions with ethylene, we chose the recently disclosed complexes **1**, **2**, and **3**.<sup>17b</sup> Solutions of **1**, **2**, and **3** in toluene or benzene were blanketed with an atmosphere of ethylene and allowed to react overnight (Scheme 2). Reactions with **1** and **2** proceeded at ambient temperature, while reaction with **3** required thermolysis at 50 °C for 36 h. Upon removal of the volatiles and recrystallization, the new complexes **4**, **5**, and **6** were obtained in pure form. NMR spectroscopic analysis of **4** indicated that it possesses an intact PBP ligand with apparent  $C_s$  symmetry, an  $sp^3$ -hybridized boron center ( $^{11}\text{B}$  NMR:  $\delta$  20.3 ppm), a single hydride, an Ir-bound ethylene, and a vinyl group. These data point to the structure depicted in Scheme 2, which was confirmed by an X-ray diffraction study (*vide infra*). **4** is the product of addition of two equivalents of ethylene to the (PBP)Ir fragment. This is atypical for reactions of (pincer)IrH<sub>2</sub> or (pincer)IrH<sub>4</sub> with an olefin, which normally yield either a (pincer)Ir( $\eta^2$ -olefin) complex or a (pincer)Ir(H)(alkenyl) isomer in cases of high steric congestion,<sup>7</sup> both being products of the reaction of the pincer complex with only one molecule of alkene.

Complexes **5** and **6** both contained all the expected  $^1\text{H}$  NMR resonances for the PBP ligand and their  $^{11}\text{B}$  NMR chemical shifts (17.8 and 20.4 ppm, respectively) also indicated  $sp^3$  hybridization at boron. However, there were no resonances in either **5** or **6** that could be ascribed to a  $\pi$ -bound ethylene or a vinyl group. Instead, **5** and **6** each possessed a pair of  $^1\text{H}$  NMR resonances in a 1 : 3 integral ratio consistent with a CHCH<sub>3</sub> fragment (**5**:  $\delta$  3.37 (m, 1H) and 1.75 (d,  $J_{\text{H-H}} = 7.0$  Hz, 3H) ppm; **6**:  $\delta$  2.72 (m, 1H) and 1.39 (dd,  $J_{\text{H-H}} = 7.0$ ,  $J_{\text{P-H}} = 0.7$  Hz, 3H) ppm). **5** displayed resonances for two inequivalent hydrides (−11.10 and −12.88 ppm), whereas **6** displayed none. These data were consistent with the presence of an ethylidene (CHCH<sub>3</sub>) unit bridging B and Ir. Furthermore, the observed  $C_1$  symmetry in the NMR spectra of **5** and **6** was consistent with the presence of a carbon center with four different substituents (the methine carbon of the bridging alkylidene). IR spectroscopic

observations suggested the presence of a single CO ligand in **5** ( $\nu_{\text{CO}} = 1977$   $\text{cm}^{-1}$ ) and two CO ligands in **6** ( $\nu_{\text{CO}} = 1987$  and  $1942$   $\text{cm}^{-1}$ ).

Interestingly, addition of ethylene to **3** is partially reversible. Thermolysis of a solution of **6** at 90 °C led to the appearance of signals for **3** and free ethylene. Traces of free ethylene were also observed upon thermolysis of **5** at 80 °C for 10 min.

### Structural characterization

Solid-state structures of **4**, **5**, and **6** were determined by single-crystal X-ray diffractometry (Fig. 1). The structure of **5** contained two independent molecules in the asymmetric unit. Both molecules displayed disorder, which was successfully modelled through varying the positions of the atoms in the Ir-CHMe unit, as well as CO for one of the molecules. The disorder likely involves other atoms in the molecules, but it was not possible to improve the model *via* consideration of the other atom positions. Because of this, while the connectivity of the non-hydrogen atoms was unambiguously established, the metrics associated with the immediate coordination sphere of Ir could not be reliably interpreted.

In the structure of **4**, the coordination sphere of Ir contains a hydride, two phosphines, two olefin donors, and a relatively distant interaction with a boron center (2.396(3) Å). If the latter were ignored, the molecule could be viewed as a monovalent,



Scheme 2 Reactions of **1**, **2** and **3** with ethylene.



Fig. 1 ORTEP drawings showing selected atom labeling for **4**, **5** and **6**. Hydrogen atoms (except Ir-H) are omitted for clarity. **4**: Ir1–B1, 2.396(3) Å; Ir1–C1, 2.200(3) Å; Ir1–C2, 2.223(3) Å; Ir1–C3, 2.213(3) Å; Ir1–C4, 2.248(3) Å; C1–C2, 1.402(4) Å; C3–C4, 1.405(4) Å; C3–B1, 1.556(4) Å; C5–B1–C6, 120.4(2)°; C6–B1–C3, 117.5(2)°; C3–B1–C5, 115.6(2)°. **5**: the structure contains two independent molecules and each is disordered, including the Ir position. One of the independent molecules is drawn. See ESI† for additional information. **6**: Ir1–B1, 2.475(4) Å; Ir1–C3, 2.262(4) Å; C3–C4, 1.523(6) Å; C3–B1, 1.530(6) Å; C1–O1, 1.160(5) Å; C2–O2, 1.136(6) Å; C1–Ir1–C3, 175.7(2)°; P1–Ir1–P2, 140.36(4)°; C5–B1–C6, 122.0(3)°; C6–B1–C3, 118.2(3)°; C3–B1–C5, 114.6(3)°.





Scheme 4 Reaction of **3** with 1-hexene.

spectroscopic features closely matched those of **6**, except for the presence of a pentyl group in place of a methyl in the bridging alkylidene (See Table S1†). Interestingly, the reaction of **3** with *trans*-2-hexene also gave **6c** as the major product after 5 d at 100 °C (see ESI†). We then examined the progress of reactions of **3** with 1-hexene under the atmosphere of Ar vs. CO but otherwise identical conditions (C<sub>6</sub>D<sub>6</sub> solution 50 °C, 90 h) and concentrations. NMR analysis revealed 73% consumption of **3** (all converted to **6'**) under Ar. Under CO, only a trace of **3** was consumed to form a water adduct we previously described,<sup>34</sup> with no evidence for the formation of **6'**. Higher concentrations of 1-hexene correlated with faster conversion of **3** to **6'**. Thus, the reaction displays positive dependence on [1-hexene] and apparent inverse dependence on [CO], indicating that reversible dissociative displacement of CO with 1-hexene constitutes the rate-determining sequence.

The mechanism proposed in Scheme 3 suggested, by the principle of microscopic reversibility, that loss of ethylene from **6** should also be retarded by the presence of free CO. Indeed, thermolysis (100 °C, 2 h) of two identically constituted C<sub>6</sub>D<sub>6</sub> solutions of **6** resulted in diminished conversion to **3** (20% vs. 40% after 2 h, see details in the ESI†) in the reaction carried out under 1 atm of CO as opposed to 1 atm of Ar. This difference is not dramatic, and may indicate that rate of the back-reaction of **11** with CO is competitive with the loss of ethylene from **11**, or even that multiple mechanisms for ethylene loss may be operative. With that qualifier, the CO inhibition experiments are consistent with the proposed mechanism (Scheme 3) for the reactions of **3**. It is also reasonable to think that the reaction of **2** with ethylene proceeds by a similar mechanism, initiated by the dissociation of CO or H<sub>2</sub> from **2**. The product of the reaction of **3** with ethylene can be viewed as analogous to the intermediate **10** in Scheme 3 (with η<sup>2</sup>-ethylene in place of CO).

## Conclusion

In summary, we have described a series of unusual outcomes in the reactions of ethylene with simple pincer complexes of Ir. These reactions demonstrate that the boryl of the PBP ligand is not merely an electronically special ligand or even a potential Lewis acid to Lewis basic sites. The presence of the boryl donor in the pincer can also significantly alter the preferred reactions products when contrasted with pincer complexes with different central heteroatoms.

## Conflicts of interest

There are no conflicts to declare.

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