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# Synthesis and reaction chemistry of boryliridium hydride complexes formed by oxidative addition of catecholborane to iridium(I): Lessons for metal-catalyzed hydroboration

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ABSTRACT

The mechanism of catalytic hydroboration was studied through the use of an iridium model complex. Oxidative addition of the B–H bond in (1,2-phenylenedioxy)borane (catecholborane) to $(Me_3P)_3Ir(COE)(Cl)$ (COE = cyclooctene) produces *mer*-$(Me_3P)_3Ir(Cl)(H)(BO_2C_6H_4)$ (**1**). Compound **1** reacted with alkynes to form vinyliridium complexes and will catalyze the hydroboration of alkynes with (1,2-phenylenedioxy)borane. The mechanism of catalytic hydroboration of acetylenes with catecholborane involves: oxidative addition of the B–H bond to the iridium center, followed by chloride dissociation and acetylene coordination, migratory-insertion into the Ir–H bond to form the metallo-vinyl complex, and finally reductive elimination to produce trans-alkylvinylboronate esters.

A stable metallo-vinyl complex was produced in the reaction of **1** with dimethylacetylene dicarboxylate and displayed two isomers in solution, one of which showed fluxional behavior. Single crystal X-ray diffraction elucidated a single solid-state structure, but the structures of the isomers in solution and the fluxional properties were studied with NMR spectroscopy and DFT calculations.



## 1. Introduction

Hydroboration is arguably one of the most versatile reactions in organic synthesis [1–5]. This versatility was extended even further by the use of transition metal catalysts to change the selectivity of the hydroboration reaction, in some cases allowing for asymmetric catalysis with non-chiral boranes [6–8]. Some time ago, we published a communication on the synthesis of an iridium complex formed by the oxidation addition of catecholborane to iridium(I), $Ir(H)(Cl)(BO_2C_6H_4)(PMe_3)_3$, **1**, equation (2) [9]. Since the publication of our paper, the chemistry of iridium boryl compounds, especially related to catalysis, has been investigated quite extensively. Mechanistic studies by Evans et al. have been valuable in the understanding of the mechanism of rhodium catalyzed hydroboration and its synthetic applications [10–13]. Marder et al. have made significant contributions to this field, both in the syntheses of iridium–boron compounds and in their reactivity [14–18]. Studies on the chemistry of rhodium–boron compounds have also been described [19–22].

Catalytic hydroboration with rhodium or iridium has found utility in an number of interesting systems (in addition to those referenced above) such as in the formation of B-protected B-styrylboronic acids [23], the hydroboration of vinylarenes [24,25], allylic hydroboration [26], the asymmetric hydroboration of 1,2-diarylalkenes and alkynes [27] and unactivated alkenes [28].

The results reported here more fully describe the completed work based on the original communication and describe results that are still quite relevant since the communication appeared. Specifically, it provides details on the chemistry of **1** that sheds light on many of the steps involved in transition metal catalyzed hydroboration of alkynes.

## 2. Results and discussion

### 2.1. Synthesis

We have demonstrated that the iridium(I) complex, $[Ir(COD)(PMe_3)_3]Cl$, (COD = 1,5-cyclooctadiene) is a versatile starting material for oxidative addition reactions and can affect the oxidative cleavage of H–H [29], C–H [30], O–H [31,32] and N–H [33] bonds (equation (1)). However, the chelating olefin, COD, proved to be problematic for the oxidative addition reaction of B–H bonds and so we turned to the use of $Ir(COE)_2(PMe_3)_3Cl$ (COE = cyclooctene) which is significantly more reactive. Another, more reactive system, was reported by Marder et al., $[Ir(PMe_3)_4]Cl$ [34].

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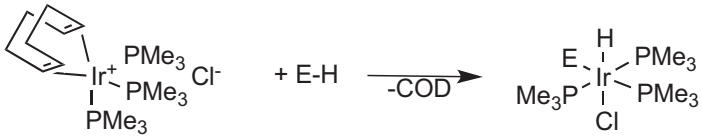
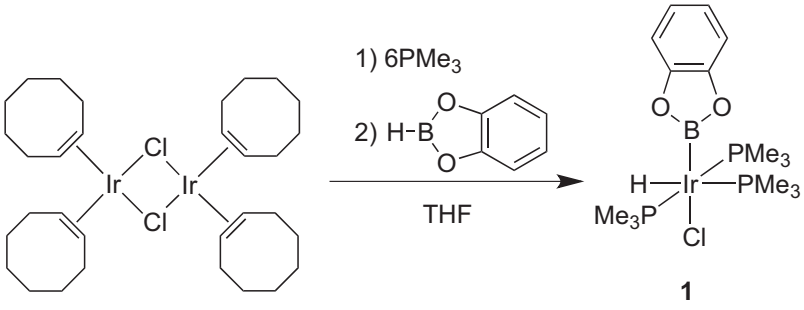



(1)

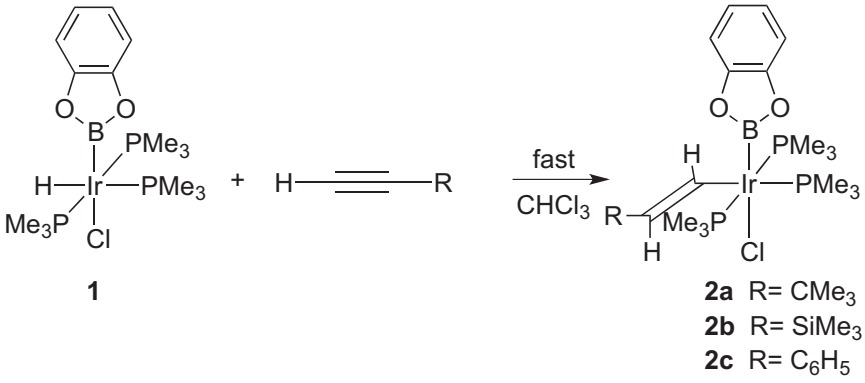
The cyclooctene complex was not isolated, but generated and used directly for the reaction with catecholborane as shown in equation (2) [9]. What is particularly interesting about **1** when compared with other $HIr(PMe_3)_3XY$ compounds synthesized in our labs, is that the hydride is cis to chloride while the boron is trans. Catecholborane is the only compound in our investigations that adds in this sense. This geometry is most easily determined by $^1H$ NMR spectroscopy in the hydride region of the spectrum. A single resonance at $\delta$ −9.69 ppm is a doublet of triplets with a large $J_{Ptrans-H}$ coupling constant of 136 Hz and a smaller $J_{Pcis-H}$ coupling constant of 21 Hz. The $^{11}B$ chemical shift of $\delta$ 32.8 ppm relative to $BF_3$ etherate is similar to that observed for other metal boryl species [35].

bond. Alkynes were chosen for the study because the metallovinyl compounds formed should be relatively stable, providing the opportunity to observe intermediates in the hydroboration scheme. However, in most cases there is a slow reductive elimination of the corresponding vinyl borane product. This reductive elimination has prevented an isolation and full characterization (to include C,H analysis) in all but one special case that will be discussed below. Nevertheless, the vinyl iridium compounds have sufficient lifetimes in solution that a detailed spectroscopic analysis could be obtained. Thus, for iridium, alkynes insert as indicated in equation (3).




**1**

(2)




**1**

**2a** R= $CMe_3$
**2b** R= $SiMe_3$
**2c** R= $C_6H_5$

(3)

The structure of **1** was confirmed by single crystal X-ray analysis and reported previously [9] (CCDC: 603276). The trans arrangement of B with respect to Cl is quite clear. The Ir—Cl bond length of 2.546(2) Å is significantly longer than that found for other compounds we have isolated with hydrogen trans to chloride and other elements cis to chlorine such as C (in the case of phenyl) with Ir—Cl = 2.506(2) Å (CCDC: 626064); N (in the case of indole) with Ir—Cl = 2.488(2) Å (CCDC: 599775); O (in the case of benzoate) with Ir—Cl = 2.499(3) Å (CCDC: 625751); and even H (from $H_2$ addition) with Ir-Cl = 2.500(2) Å (CCDC: 286783). Clearly, the trans influence of B is somewhat greater than H, a finding consistent with DFT calculations comparing boryl ligands with other strong trans influence groups [18].

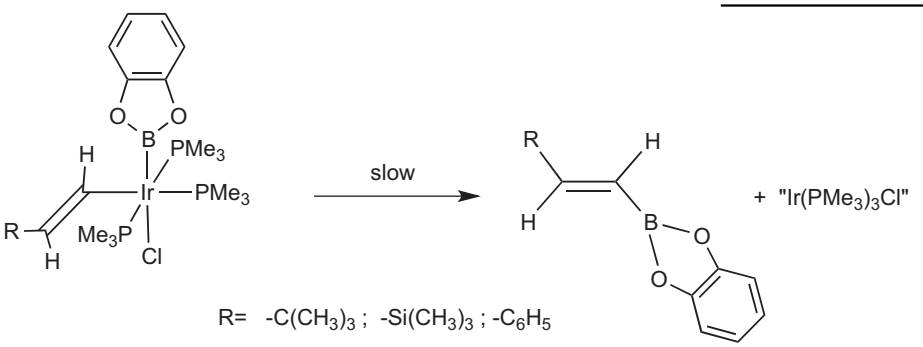
### 2.2. Reactions with alkynes

The iridium compound **1** reacts readily with alkynes to form products derived from the insertion of the alkyne into the Ir—H

Previous work in our laboratories with the product of phenyl C—H addition [30] showed that the hydridochlorophenyliridium complex was itself unreactive toward alkynes, but could be induced to react via chemical removal of $Cl^-$ by $Tl^+$. It was surprising to find that **1** reacted with alkynes directly, *without the need for chloride removal*.

Three terminal alkynes were studied as indicated in equation (3) yielding vinyl complexes, **2a**—**c**. In all cases, the splitting patterns show that both of the vinyl protons were coupled to all three phosphines, as well as to each other, and that the vinyl group was in the plane of the meridional phosphines. Long range coupling between the three phosphines and the vinyl proton farthest from the metal is noted. This four-bond coupling has been observed before, as in an ethyl iridium complex described by Eisenberg [36], but is usually only seen with the phosphine trans to the vinyl group.

After a period of hours in solution, the boryl and vinyl groups of complexes, **2a**–**c**, undergo reductive elimination to give a single trans hydroboration product, with the E isomer formed in all cases (equation (4)). The iridium product has not been fully identified, but appears to be $(Me_3P)_3IrCl_3$, the product of "$(Me_3P)_3IrCl$" reacting with the solvent, chloroform-*d* [37]. The $^1H$ NMR spectrum revealed only one reductive elimination product for the monosubstituted alkynes studied. Uncatalyzed hydroboration of t-butylacetylene also results in a single trans product due to the bulk of the t-butyl group, as does the reaction of **1** with the same alkyne. However, uncatalyzed hydroboration with phenylacetylene produces 91% of the trans product and 9% of the geminal product [4]. This is in contrast to the 100% trans product formed through the reaction of **1** with phenylacetylene. The selectivity of the reaction with **1** demonstrates that a different mechanism is operating, in which the metal complex is responsible for enhancing the selectivity. The regioselectivity observed is also similar to the results obtained by other groups with metal catalyzed hydroboration of terminal olefins.

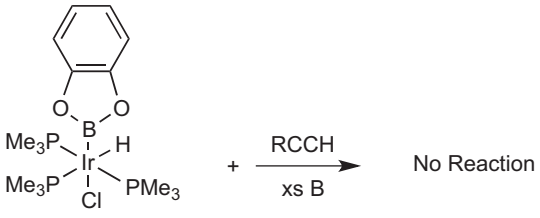



(4)

As mentioned before, the alkyl and boryl groups of **2a**–**c** undergo a slow reductive elimination and identical final trimethylphosphine resonances for the Ir complex were observed with all the alkynes used. These results gave reason to believe that this system might be catalytic in the presence of additional B–H and alkyne reagents. The iridium complex **1** was combined with 6 equiv of trimethylsilylacetylene and 5 equiv of catecholborane and the reaction monitored by $^1H$ NMR spectroscopy. A control experiment was also performed with 6 equiv of both the alkyne and borane in solution. After two days, approximately 5 equiv of trans vinylborole was detected in the solution containing **1**, while only 1 equiv was present in the control reaction. These experiments indicated that the reaction was slowly catalytic, providing support that this system was suitable for the study of catalytic hydroboration.

Up to this point, compounds have been described which represent several possible key steps in the model catalytic hydroboration reaction: a) B–H oxidative addition, b) alkyne migratory insertion, and c) reductive elimination (Fig. 1). For monosubstituted alkynes, the vinyl and boryl groups reductively eliminate to produce the vinyl boronate ester and the presumed tris-trimethylphosphine iridium chloride. Another equivalent of alkyne and catecholborane could then be added to repeat the cycle. It is believed that this makes a firm case that the cycle is a plausible one to describe catalytic hydroboration and may be applicable to systems discussed in the literature. With this evidence to provide support for an overall catalytic cycle, we turn our attention to the fine details concerning some of the individual steps.

An octahedral complex almost certainly undergoes a ligand dissociation in order to open a site for catalytic activity, in this case providing a vacant coordination site where the alkyne can π-bond. The hydride would then migrate to the alkyne through a four center interaction creating the metallo-vinyl complex. Competition of other Lewis bases with alkynes for that open site was probed. The iridium complex **1** was placed in the presence of trimethylsilylacetylene and various Lewis bases as in equation (5). The bases trimethylphosphine, carbon monoxide, and pyridine were found to inhibit the reaction totally, as evidenced by the lack of change in the NMR spectra for the starting materials. So, these Lewis bases apparently compete more strongly for the vacated site than did the alkyne. Interestingly, there is no visible change in the $^1H$ NMR spectrum of **1** on the addition of these bases so, while they compete for the alkyne, under these conditions they do not form any type of long-lived intermediate or stable complex.




(5)

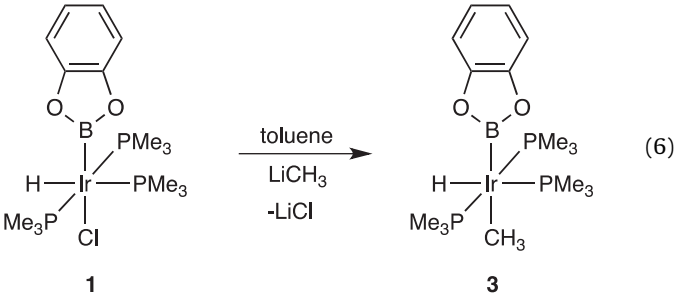
Obviously, for a dissociative mechanism, one of the ligands around iridium would have to leave to form an equilibrium between the six coordinate complex **1** and a five coordinate complex. One would not expect catecholboryl or hydride to be the leaving group, so the ligand most likely to dissociate is either trimethylphosphine or chloride, due to their stability as free ligands. A series of experiments was carried out to determine if either of these ligands dissociated in solution.

### 2.3. Probing for phosphine dissociation

To observe possible phosphine dissociation, two NMR experiments were performed with **1** in the presence of free phosphine. The first was variable temperature $^1H$ NMR spectroscopy. In the experiment with **1** and free phosphine, no broadening of peaks

occurred, even at temperatures as high as 90 °C and so it is concluded that no exchange occurs on the NMR time scale. In addition, a polarization transfer experiment was performed by irradiating the free $PMe_3$ resonance in the $^1H$ NMR spectrum. No attenuation was observed for the bound $PMe_3$ resonances, which indicates that, if exchange occurs, the first order rate constant must be less than $k_1 = 0.003\ s^{-1}$.

Another argument for a lack of phosphine dissociation in **1** is made based upon observations of *mer*-$(Me_3P)_3Ir(CH_3)(H)(-BO_2C_6H_4)$, **3**. This compound was made in situ by adding methyllithium to a solution of **1** in benzene-$d_6$, as shown in equation (6). Lithium chloride precipitated leaving **3** in solution. The complex was characterized solely by $^1H$ NMR spectroscopy, but this characterization is unambiguous, including its stereochemistry. The resonances at $\delta$ 1.35 ppm (t, $J_{H-P} = 3.4$ Hz, 18H) and $\delta$ 1.32 ppm (dd, $J_{H-P}$ = 8.5, 0.7 Hz, 9H) indicate that the phosphines are in a meridional arrangement with 4-bond coupling to a hydride ligand trans to one phosphine. An upfield resonance at $\delta$ −11.66 ppm (dt, $J_{H-P,trans} = 133.0$, $J_{H-P,cis} = 22.7$ Hz, 1H) indicates that the hydride ligand is in the plane of the meridional phosphines, coupled to two equivalent cis $PMe_3$ and one trans $PMe_3$, as in **1**. A resonance at $\delta$ −0.07 ppm (dq, $J_{H-P} = 7.0$, $J_{H-H} = 1.0$ Hz, 3H) indicates that the methyl group is oriented cis to all three phosphines. The closely spaced quartet of doublets indicates that the methyl group is coupled to three equivalent phosphorus nuclei. This is consistent with coupling to three cis phosphines, because the difference in environment between the mutually trans phosphines and the other phosphine gives an indistinguishable difference in coupling. The small coupling constant is due to 3-bond coupling of the methyl protons to the hydride ligand.

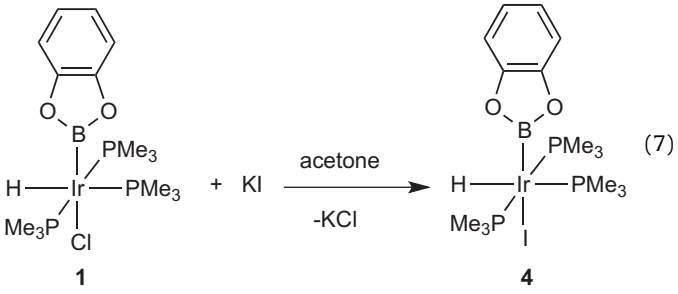



**1** **3** (6)

The structure of **3** is interesting because the hydride and the methyl ligands are oriented cis to one another. The thermal stability of **3** is contrary to the general trend of very rapid cis-alkyl-hydride reductive elimination [38]. This rapid reductive elimination has been observed with other cis-hydrido alkyliridium complexes [39–41]. Work by Milstein and others [42] suggests that reductive elimination can only occur if an octahedral complex is able to reach a five coordinate geometry through ligand dissociation. Compound **3** is stable in benzene at room temperature suggesting that the trimethylphosphines do not dissociate in this complex. When trimethylsilylacetylene was added to a solution of **3**, no reaction was observed by $^1H$ NMR spectroscopy over 18 h. While replacement of chloride with methyl may change the electronic character of the iridium in some unpredictable way, the lack of reactivity can most directly be explained by concluding that phosphine does not dissociate from this complex. This is consistent with other iridium phosphine complexes in the literature where phosphine dissociation is not observed [42]. After ruling out hydride and boryl, the only remaining ligand to consider is the chloride (A referee suggested that coordinative unsaturation may occur via reductive elimination of the catecholborane. This would be a non-productive path.).

### 2.4. Probing for chloride dissociation

Since no evidence was found to support trimethylphosphine dissociation, positive evidence in support of chloride dissociation was sought. The first experiment involved an attempt at exchanging other halides for chloride. An argument can be made that the third row iridium would make a stronger bond to the softer halide, iodide. Therefore, **1** was allowed to react with iodide, as in equation (7). A new and complete set of resonances with the same splitting patterns as for **1** appeared for the iodide complex, **4**. This provided conclusive evidence for substitution of chloride but, in addition, an X-ray crystal structure was obtained confirming the substitution (Fig. 2). Crystals were grown through the slow reaction of potassium iodide with **1** in acetone-$d_6$ and precipitation of **4** from acetone due to its limited solubility. The crystals belonged to the orthorhombic space group *Abm*2 with $a$ = 14.792(4) Å, $b$ = 13.369(4) Å, $c$ = 12.125(3) Å, $V = 2397.8(11)$ Å$^3$, $d_{calcd} = 1.845$ g cm$^{-3}$, for $Z = 4$. In this structure, **5** contains a mirror plane including Ir, I, P2 and the entire catecholboryl group. As with **1**, the Ir—P(1,1A) bond lengths of 2.314(3) Å were significantly shorter than the Ir—P2 bond length of 2.342(5) Å, most likely due to the influence of the hydride trans to P2. All three of these bond lengths are longer than the corresponding bond lengths in **1**. This agrees with the idea that **4** is more electron rich than **1** because iodide is less electronegative than chloride. The Ir—B bond length of 2.079(16) Å is almost 0.06 Å shorter than the corresponding bond length in **1**. This can possibly be explained by back donation of electron density through the more electron rich iridium d orbitals to the empty p orbital of boron, creating partial double bond character. The small bond angle P(1)—Ir—P(1A) of 164.8(2)° was also similar to the corresponding angle in **1**, due to the small steric demands of the hydride ligand.




**1** **4** (7)

These experiments established that chloride does dissociate in the solvents studied. Further, the reactivity of **1** depends upon what occupies the chloride position. Evidence for this is provided by the study of a series of experiments that substitute other groups for chloride. Chloride was removed from **1** *in situ* using thallium(I) hexafluorophosphate in the presence of a Lewis base as shown in Scheme 1. Thallium chloride precipitated and the base occupied the vacant position leaving the $PF_6^-$ salt in solution. The Lewis bases trimethylphosphine, carbon monoxide, pyridine, and acetone, were used. No attempt was made to isolate the product, but the $^1H$ NMR spectrum clearly showed the new ligand entering the position vacated by the chloride – there was no rearrangement of the stereochemistry. When the trimethylphosphine and carbon monoxide systems were combined with trimethylsilylacetylene at room temperature, there was no reaction after 50 min. When the acetone and pyridine systems were combined with trimethylsilylacetylene the corresponding vinyl complex formed. The rate of reaction was qualitatively found to depend on the Lewis base in the sixth coordination site, with acetone resulting in the fastest rate, followed by chloride and then pyridine. This evidence suggests that the reaction

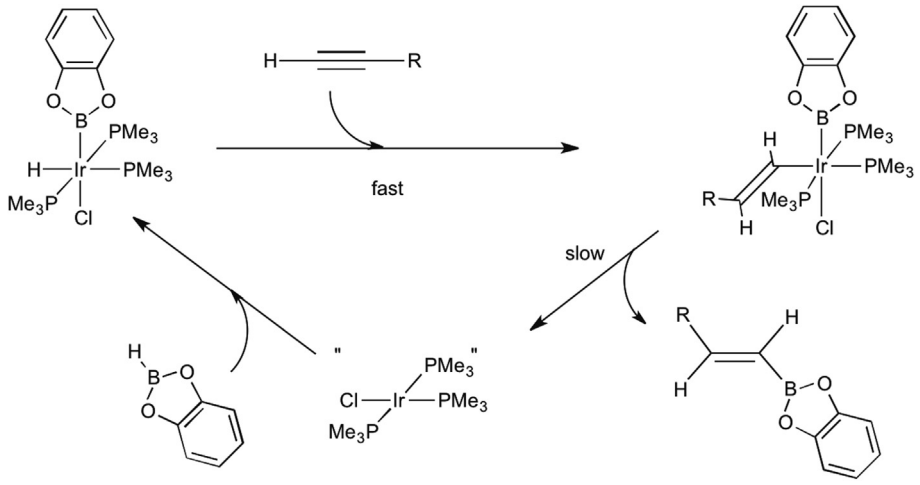



**Fig. 1.** General catalytic cycle for hydroboration of alkynes.

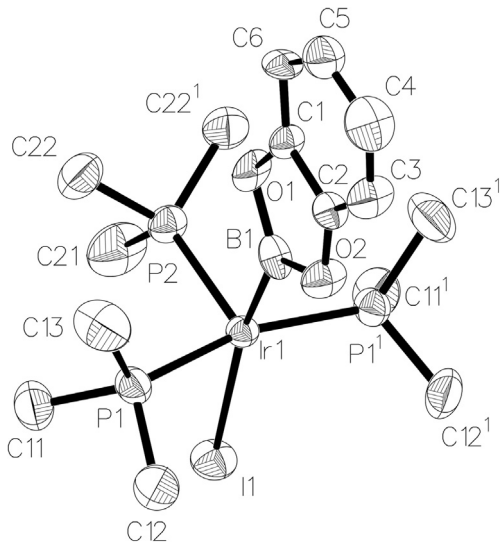
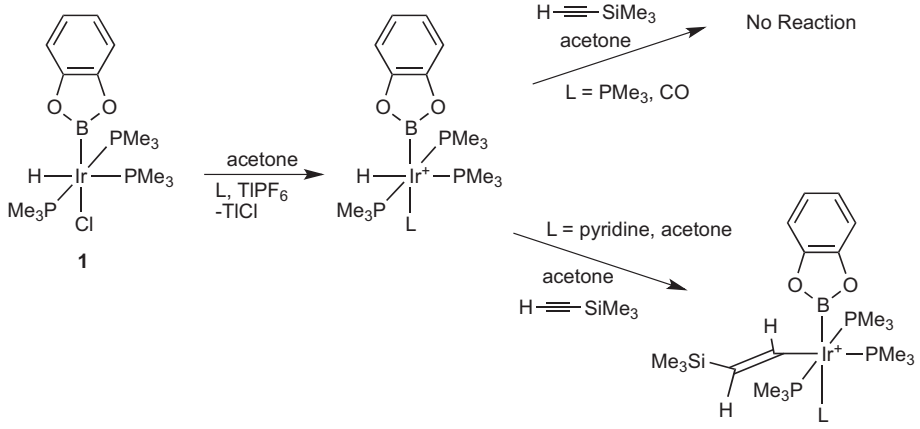



**Fig. 2.** Thermal ellipsoid plot of **4**. Hydrogen atoms omitted for clarity. Atoms designated with ([1]) are generated by the operation ($x$, 3/2 − $y$, $z$). Selected bond distances: Ir1–I1, 2.8328(12); Ir1–P1, 2.314(2); Ir1–P2, 2.342(3); Ir1–B1, 2.023(3) Å. Selected bond angles: P1–Ir1–P1′, 163.93(13); P1–Ir1–I1, 88.93(13); P1–Ir1–P2, 98.03(7); P2–Ir1–I1, 97.84(8); B1–Ir1–I1, 169.20(5)°.

of **1** with alkynes is particularly sensitive to the basicity and/or steric demands of the group in the chloride position.

Another series of experiments relating to the dissociation of the chloride was performed by carrying out the reaction of **1** with trimethylsilylacetylene in various solvents. Using acetone, chloroform, benzene and cyclohexane, it was seen that the reaction rate roughly follows the polarity of the solvent. As shown in Table 1, the formation of the vinyl complex **2b** was fastest in chloroform followed by acetone and then benzene. The reaction did not proceed at all in cyclohexane after seven days at room temperature. This is ostensibly the most direct evidence for chloride having to dissociate to form a cation–anion pair before the alkyne can insert into a vacant coordination site and continue with a migratory-insertion reaction. Of the non-coordinating solvents, the rate of reactivity increases with the polarity of the solvent. Acetone, on the other hand, is the most polar of the group, but it is a weakly coordinating ligand and could have inhibited the reaction. Because acetone is a difficult solvent to dry, it is also possible that the presence of a small amount of water was responsible for the slower rate.

A final piece of evidence supporting chloride dissociation was found in the variable temperature $^1$H NMR experiments performed with **1** in toluene-$d_8$. In Fig. 3 it can be seen that the hydride resonance shifts in frequency with changing temperature. None of the other resonances for **1** showed any significant change, indicating that the hydride ligand was the only hydrogen measurably




**Scheme 1.** Effect of ligand in the position cis to H on insertion reactivity of **1**.

**Table 1**
$t_{1/2}$ for reactions between **1** and trimethylsilylacetylene in various solvents.

| Solvent | $t_{1/2}$ for reaction of **1** with trimethylsilylacetylene | Dielectric constant for solvent |
|---|---|---|
| Chloroform | 429 s | 4.7 |
| Acetone | 1370 s | 20.7 |
| Benzene | $1.3 \times 10^5$ s | 2.28 |
| Cyclohexane | No reaction | 2.02 |

affected. As this resonance shifted, the splitting pattern due to phosphorus coupling did not change, a further confirmation that phosphine ligand dissociation was not occurring and responsible for the change in frequency. Because chloride is the only remaining ligand close enough to significantly affect the hydride ligand, the change in frequency is attributed to chloride dissociation.

From the evidence presented up to this point, it would not be amiss to conclude that chloride dissociation is necessary to allow for the observed reactivity. Looking back at the series of iridium complexes formed by oxidative addition of C–H, N–H, O–H and H–H bonds, the Ir–Cl bond distances observed across all of these systems now can be seen to correlate nicely with reactivity. As reported earlier, the Ir–Cl bond length of 2.546(2) Å is significantly longer than that found for other compounds we have isolated with hydrogen trans to chloride and other elements cis to chlorine such as C (in the case of phenyl) with Ir–Cl = 2.506(2) Å; N (in the case of pyrrole) with Ir–Cl = 2.488(2) Å; O (in the case of benzoate) with Ir–Cl = 2.499(3) Å; and even H (from $H_2$ addition) with Ir–Cl = 2.500(2) Å. So the greater trans influence [18] of boron also manifests in a greater trans effect as well.

### 2.5. Dimethylacetylenedicarboxylate product

An oddity in this system is worthy of some discussion. It was found that dimethylacetylene dicarboxylate (DMAD) would react with **1** yielding a vinyl compound, **5**, from insertion of the DMAD into the Ir–H bond (equation (8)). However, this dicarboxylate vinyl complex proved to be unique in several respects. It was stable in air in the solid state, and was also stable toward reductive elimination. Even after refluxing in toluene under nitrogen for 3 h, reductive elimination of the boryl and vinyl groups did not occur. The electron withdrawing properties of the carboxylate groups strengthen the metal–ligand bond, which accounts for the stability of **5** in these respects. The complex is also unique in that two isomers were identified in solution, one of which is itself fluxional between two isomers. Complete characterization of **5** follows, including discussion of its isomeric properties.

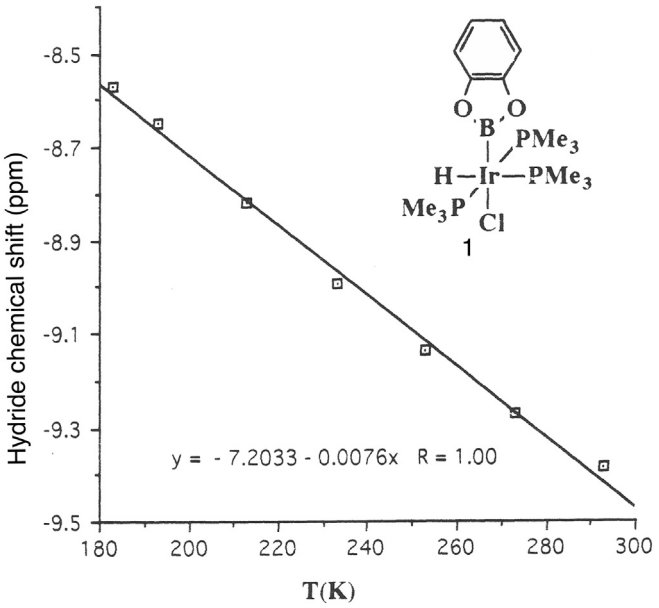
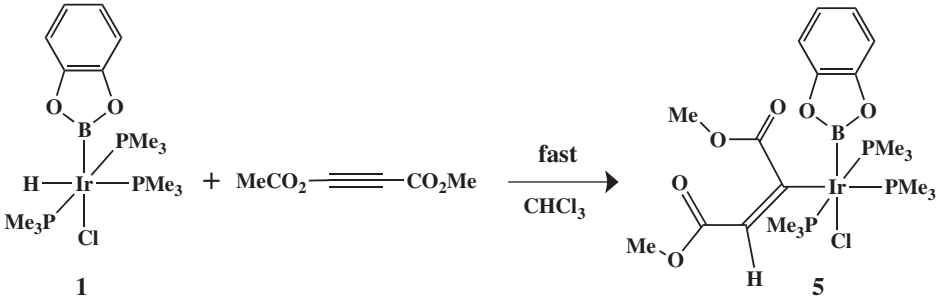



**Fig. 3.** Hydride resonance shift as a function of temperature for *mer*-$(Me_3P)_3Ir(Cl)(H)(BO_2C_6H_4)$ (**1**) $^1$H NMR (270 MHz, toluene-$d_8$).

orthorhombic space group $P2_12_12_1$ with $a$ = 10.538(4) Å, $b$ = 16.073(5) Å, $c$ = 17.364(6) Å, $V$ = 2941.2(17) Å$^3$ and $d_{calcd}$ = 1.621 g cm$^{-3}$ for $Z$ = 4. The arrangement of ligands around the metal center is identical to the arrangement in **2a**–**c**, with the vinyl substituent in the plane of the meridional phosphines and the boryl and chloride groups mutually trans. The Ir–B bond distance of 2.012(11) Å is about the same as in **1**. The Ir–P2 bond length of 2.356(3) Å is similar the Ir–P1,3 bond lengths of 2.366(3) and 2.367(3) Å, respectively. This is in contrast to **1**,where the Ir–P2 bond length was longer than the other two and indicates that the electron withdrawing effect of the vinyl group makes it a weaker trans influence ligand than H. The bond angle of 171.8(1)° for P1–Ir–P3 is still bent away from P2, indicating that the vinyl group is less sterically demanding than the phosphine trans to it, but the bond angle is significantly closer to the ideal octahedral geometry than in **1**.

The structure of **5** is similar to the structures deduced for **2a**–**c** and therefore helps to confirm the structural assignments made for **them** since similar assignments are made for signals in the solution NMR spectra of **5**. However, as stated previously, **5** is unlike **2a**–**c** in that two complete sets of signals were observed in solution for the




(8)

The stability of this complex permitted the determination of an X-ray crystal structure and the thermal ellipsoid plot of **5** is shown in Fig. 4. Crystals were grown by slow diffusion of pentane into a methylene chloride solution of **5**. The crystals belong to the

proton, phosphorus, and carbon spectra, indicating the presence of two isomers in solution.

In Fig. 5, the various regions of the $^1$H NMR spectrum for **5** are shown with assignments for the protons as well as an indication of

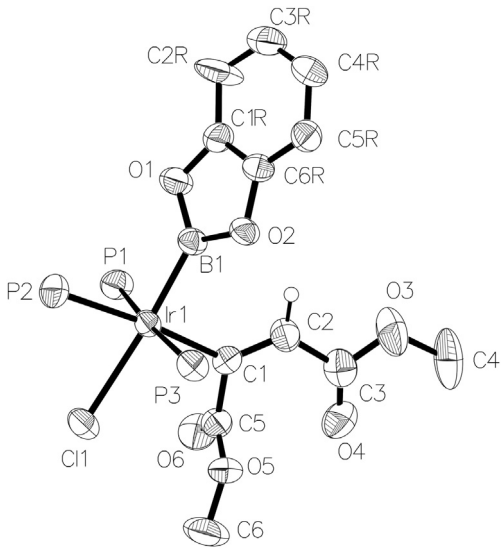



**Fig. 4.** Thermal ellipsoid drawing of **5**. Phosphorus methyl groups and hydrogen atoms (with the exception of the vinyl H) have been removed for clarity. Selected bond distances: Ir1–Cl1, 2.548(2); Ir1–P1, 2.366(2); Ir1–P2, 2.356(3); Ir1–P3, 2.367(2); Ir1–C1, 2.095(8); and Ir1–B1, 2.011(10) Å. Selected bond angles: P1–Ir1–Cl1, 90.79(8); P1–Ir1–P3, 171.83(9); P2–Ir1–Cl1, 81.81(9); P2–Ir1–P1, 94.34(10); P2–Ir1–P3, 93.78(10); P3–Ir1–Cl1, 91.18(8); C1–Ir1–Cl1, 93.1(3); C1–Ir1–P1, 86.0(2); C1–Ir1–P2, 174.9(3); C1–Ir1–P3, 86.0(2); B1–Ir1–Cl1, 175.5(3); B1–Ir1–P1, 89.2(3); B1–Ir1–P2, 93.7(3); B1–Ir1–P3, 89.4(3); B1–Ir1–C1, 91.4(4)°.

which belong to the major and minor isomers. Notably, what would normally be a virtual triplet for the mutually trans $PMe_3$ protons of the major isomer is a very broad signal with little fine structure at around $\delta$ 1.55 ppm compared with the clear virtual triplet for those resonances belonging to the minor isomer at $\delta$ 1.45 ppm. In the carbon spectrum, analogous resonances were found for the methoxy carbons as in the $^1$H NMR spectrum. The $^{13}$C NMR spectrum was also consistent with two isomers in solution, but with one oddity with respect to the vinyl carbon resonances. The vinyl resonances were observed at $\delta$ 128.51 ppm (t, $J_{C-P}$ = 3.8 Hz, IrC=**C**(H)) and $\delta$ 176.64 ppm (d, $J_{C-P}$ = 6.1 Hz, Ir**C**=C(H)) for the major isomer and at $\delta$ 126.51 ppm (t, $J_{C-P}$ = 4.5 Hz, IrC=**C**(H)), and $\delta$ 164.99 ppm (dt, $J_{C-P}$ = 9.2, 2.3 Hz, Ir**C**=C(H)) for the minor isomer. The vinyl carbon in each isomer bound to a proton provided the surprising pattern of a triplet. This pattern suggests that these carbons are coupled only to the phosphorus atoms cis to the vinyl ligand and not to the phosphorus atom trans to the vinyl ligand. This is an unusual occurrence because coupling is generally stronger for atoms trans to one another than for those cis to one another. In view of these observations, a DEPT NMR experiment was performed to differentiate between carbons bearing one, two or three protons [43]. This experiment confirmed that these triplets belong to the carbons that bear a single proton. The resonance assigned to the iridium bound carbon of the minor isomer provided the more typical doublet of triplets pattern in keeping with the vinyl ligand being in the plane of the meridional phosphines. The resonance assigned to the iridium bound carbon of the major isomer appears as a doublet. This indicates that the carbon is coupled only to the phosphorus atom trans to itself. The lack of coupling to the phosphorus atoms cis to the vinyl ligand may be caused by the observed fluxionality (to be discussed below) of these atoms, but it is difficult to be certain at this point.

It was first believed that the two isomers were present in the reaction mixture and that the crystal structure had been obtained of only one component that provided suitable crystals. The X-ray diffraction experiment showed no disorder in the crystal structure as might occur with similar isomers co-crystallizing. Several crystals were screened from the reaction mixture and all showed the same unit cell and so were of the same compound. While it would be extremely tedious to screen every crystal, a sufficient number of crystals were screened to be fairly certain that the solid contains only one compound. This evidence led to the conclusion that the isomers are formed in solution. Indeed, dissolving a single crystal of **5** in solution led to the same NMR spectra as dissolving the bulk solid. In addition the major to minor ratio appears to have a solvent dependence, being 5:1 in chloroform and 3:1 in benzene and acetone.

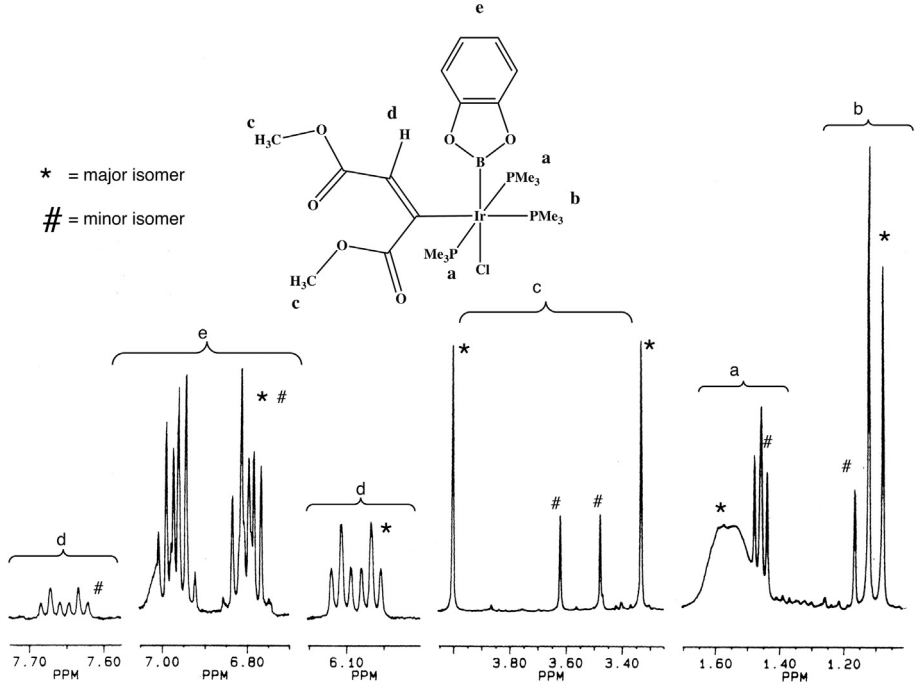



**Fig. 5.** $^1$H NMR spectrum of **5** showing assignments for each set of resonances.

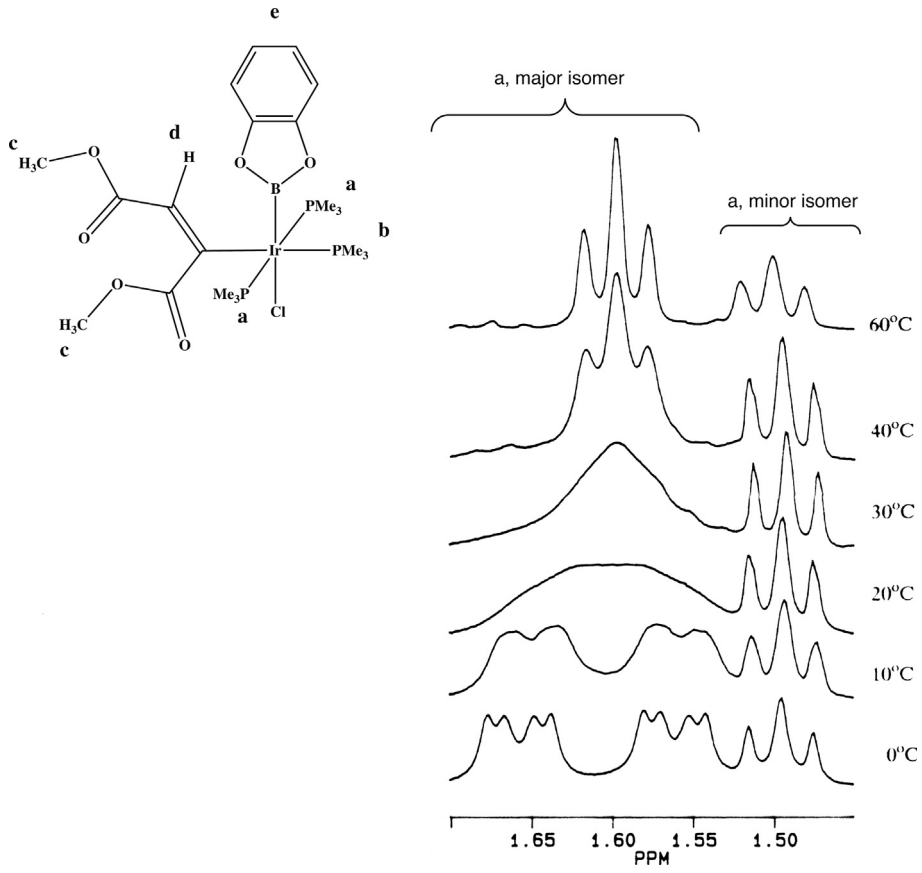



**Fig. 6.** $^1$H variable temperature NMR spectrum of the mutually trans $PMe_3$ ligands in **5**.

The reaction of DMAD with various metal complexes, especially metal hydrides often yields interesting structural motifs [31,44]. Two theories may be put forth to account for the presence of both isomers in solution. One is that the two isomers can be cis and trans isomers of the vinyl ligand. An example of such an occurrence is found in W. Jones' work [45], where these two types of structures are found for an analogous rhodium dicarboxylate vinyl complex (CCDC: 592347) (CCCD: 592348). Jones showed that interconverting cis/trans isomers accounted for the behavior of his system. However, neither a variable temperature $^1$H NMR study of **5** nor a saturation transfer experiment indicated any interconversion between the two isomers. In the case of **5** the first order rate constant $k_1$ for any process to interconvert can be no greater than 0.002 $s^{-1}$.

The second, and more likely explanation is that there are significant rotation barriers around some of the bonds resulting in multiple isomers. A large barrier to rotation about the iridium–carbon bond of the vinyl ligand in **5** caused by steric hindrance of the trimethylphosphine ligands cis to the vinyl group could be responsible for two isomers. It is possible to have isomers with the vinyl proton pointed "up" in the direction of the boryl ligand, or "down" in the direction of the chloride ligand. If the rotation barrier was significantly high about this bond, two isomers that do not interconvert on the NMR time scale could be formed.

Although variable temperature $^1$H NMR spectra did not reveal exchange between the two isomers of **5** it did reveal the unique fluxional behavior of one of the isomers (Fig. 6). For **5**, a very broad single peak was observed for the mutually trans trimethylphosphine ligands at room temperature. As the temperature was increased, the broad signal changed into the typical pattern of a well-defined triplet. As the temperature was lowered, the broad signal separated into a pair of doublet of doublets. These observations indicate that the major isomer of **5** has an activation barrier of 15 kcal/mol between yet two more isomers in solution. The room temperature spectrum is intermediate between the two clear coupling patterns, indicating that the rate of interchange between the two new isomers matches the time scale of the experiment, which results in an averaging of signals. The two doublet of doublets patterns at low temperature show that the mutually trans trimethylphosphine ligands are losing their equivalency that usually gives rise to the virtual triplet pattern. At high temperature, rotation is rapid enough to average the $PMe_3$ environment while at low temperature, they are inequivalent. Fig. 7 is an illustration of possible rotations that could give rise to the behavior observed. The rotation marked "1" on the figure, a rotation about the C2–C3 bond is likely to have minimal effect on the environment of the mutually trans $PMe_3$ groups and DFT calculations indicate a very low barrier to rotation about that bond (about 7 kcal/mol). Rotation about Ir1–C1 ("3" in Fig. 6) was calculated to be approximately 31 kcal/mol, a barrier that is high enough to be responsible for finding two isomers in solution: one with the C1–C2 bond pointing "down" toward the chloride and the other with the C1–C2 bond pointing "up" toward the boryl group. The relative energy difference between those two rotamers is about 1.3 kcal/mol, a difference that is in keeping with isomer ratio in the 2:1 to 3:1 ratio. Finally, it can be seen from examining the figure that rotation about the C1–C5 bond can have a large effect on the environments of the flanking $PMe_3$ groups and will definitely make one $PMe_3$ distinct from the other. The rotation about this bond was calculated to be about 20 kcal/mol. This is in keeping with a rough measure of the rotation barrier from the $^1$H NMR spectrum of 15 kcal/mol. In a previous system

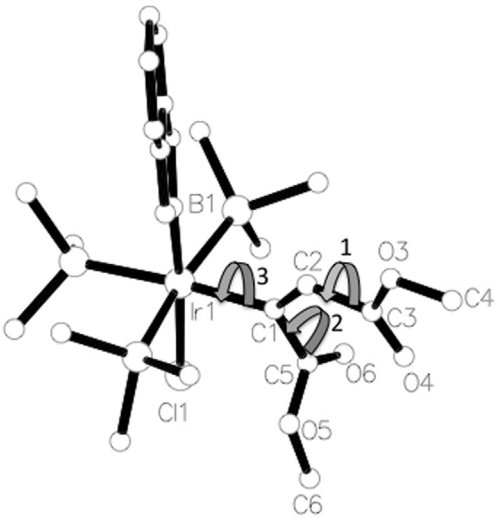



**Fig. 7.** Ball and stick drawing of **5** showing the 3 rotations measured with Gaussian09.

with a phenyl group on iridium flanked by mutually trans $PMe_3$ ligands, a chloride and a hydride, we also observed a very high rotation about the iridium–carbon bond making all 5 phenyl protons and all 6 carbon atoms unique with no evidence of rotation at temperatures as high as 90 °C.

The last question remaining is the solvent dependence on the ratio of the two isomers. Again, we look to the chloride dissociation from **5** to account for this behavior. Even though the two isomers do not interconvert on the NMR timescale, it is still clear that they can achieve an equilibrium and it is likely that dissociation of chloride to a stereochemically non-rigid 5-coordinate intermediate provides a low enough energy pathway for the "major" isomer to convert to some extent to the "minor" isomer.

## 3. Conclusion

The iridium system described herein has provided a great deal of information on intermediates involved in catalytic hydroboration. Thus, by direct observation, the steps of B–H oxidative addition, alkyne insertion, and reductive elimination of product were studied in depth. Further, this proved to be a system in which, although $PMe_3$ loss was not accessible, chloride loss allowed for the creation of coordinative unsaturation and, hence, further reactivity. This system is quite sensitive to solvent as one might expect with chloride loss being the route to the creation of an open site for substrate. One particular product, derived from the reaction between **1** and DMAD (complex **5**) was particularly stable and allowed for in-depth NMR studies as well as a single crystal X-ray study. The solution behavior of **5** provided a fascinating study of both an isomer mixture that was dependent on the nature of solvent as well as fluxional behavior displayed by one of the isomers.

## 4. Experimental

### 4.1. General comments

All reactions were carried out on a Schlenk line under an atmosphere of nitrogen, using oven-dried glassware. The solvents: toluene, tetrahydrofuran, and pentane were purchased from Fisher Scientific and distilled from potassium/benzophenone under nitrogen; methylene chloride was distilled from $P_2O_5$ under nitrogen; acetone-$d_6$, benzene-$d_6$, and chloroform-$d$ were purchased from Aldrich Chemical Co. and Chemical Dynamics Corp. and were all dried over molecular sieves. Iridium trichloride was, in part, graciously on loan from Johnson Matthey and the balance purchased from Johnson Matthey and used as received. All other chemicals were of reagent grade and were used as received: purchased from Aldrich Chemical Co., Strem Chemicals, Farchan Laboratories or Fisher Scientific.

$^1$H NMR spectra were obtained using either a Bruker WP-270 or WP-200 NMR spectrometer. $^{31}$P, $^{13}$C, $^{11}$B NMR spectra were obtained using the Bruker WP-200 NMR spectrometer. The $^{13}$C NMR spectrum and DEPT spectra were obtained using a Varian Unity 400 spectrometer. Chemical shifts are reported in $\delta$ units, ppm down field from TMS using the appropriate deuterated solvent peak as a reference. $^1$H NMR: acetone-$d_6$, $\delta$ 2.04 ppm; benzene-$d_6$, $\delta$ 7.15 ppm; chloroform-$d$, $\delta$ 7.24 ppm; toluene-$d_8$, $\delta$ 2.09 ppm. $^{13}$C NMR: acetone-$d_6$, $\delta$ 29.8 ppm; benzene-$d_6$, $\delta$ 128.0 ppm; chloroform-$d$, $\delta$ 77.0 ppm. $^{31}$P NMR: $H_3PO_4$ external reference, $\delta$ 0.0 ppm. $^{11}$B NMR: $BF_3\cdot$THF external reference, $\delta$ 0.0 ppm. All dry box manipulations were carried out in a MB-150-M glove box purchased from M. Braun, Germany.

Elemental analyses were performed by Atlantic Microlab, Norcross, Georgia.

### 4.2. Synthesis

#### 4.2.1. Synthesis of mer-$(Me_3P)_3Ir(Cl)(H)(BO_2C_6H_4)$, **1**

A 100 mL side arm flask, equipped with a septum, was charged with dry $[Ir(COE)_2Cl_2]$ (2.00 g, 2.23 mmol) and degassed with nitrogen on a Schlenk line. Tetrahydrofuran (70 mL) was added and the solution was stirred vigorously with a magnetic stirring bar. To this mixture, trimethylphosphine (1.39 mL, 13.39 mmol) was added dropwise via syringe. As the trimethylphosphine was added a white precipitate formed, but then immediately redissolved, turning the solution a clear, dark red. The solvent, excess trimethylphosphine, and 1 equiv of cyclooctene were removed under vacuum. Tetrahydrofuran (50 mL) was added and the solution was stirred. A catecholborane solution (4.46 mL, 1.0 M in THF) was added dropwise via syringe, again with vigorous stirring. The final solution was still dark red. The tetrahydrofuran volume was reduced under vacuum to <5 mL, cooled to −78 °C and the precipitated product collected on a medium frit filter tube. The crude product was washed with 3 × 3 mL of −78 °C tetrahydrofuran giving a white, flaky solid. The solvent of the filtrate was removed under vacuum and the residue washed as before. The combined yield was 0.99 g (1.72 mmol, 39% based on $[Ir(COE)_2Cl_2]$) of *mer*-$(Me_3P)_3Ir(Cl)(H)(BO_2C_6H_4)$. Analysis (%). calculated (found) for $C_{15}H_{32}BClIrO_2P_3$: C, 31.29 (31.21); H, 5.60 (5.59). $^1$H NMR (chloroform-$d$): $\delta$ −9.69 (dt, $J_{H-Ptrans}$ = 136.3, $J_{H-Pcis}$ = 21.1 Hz, 1H, Ir**H**), 1.58 (d, $J_{H-P}$ = 5.1, 9H, P**Me**$_3$), 1.64 (t, $J_{H-P}$ = 3.5, 18H, P**Me**$_3$), 6.95 ppm (AA′BB′, 4H, $BO_2C_6$**H**$_4$); (benzene-$d_6$): $\delta$ −9.28 (dt, $J_{H-Ptrans}$ = 138.9, $J_{H-Pcis}$ = 21.2 Hz, 1H, Ir**H**), 1.36 (d, $J_{H-P}$ = 8.1, 9H, P**Me**$_3$), 1.44 (t, $J_{H-P}$ = 3.6, 18H, P**Me**$_3$), 6.95 ppm (AA′BB′, 4H, $BO_2C_6$**H**$_4$). $^{31}$P NMR (benzene-$d_6$, $H_3PO_4$ external standard): $\delta$ −46.35 (t, $J_{P-P}$ = 21 Hz, **P**Me$_3$), −39.61 ppm (d, $J_{P-P}$ = 21 Hz, **P**Me$_3$). $^{13}$C NMR (benzene-$d_6$): $\delta$ 18.49 (d, $J$ = 27, P**Me**$_3$), 20.42 (t, $J$ = 19, P**Me**$_3$), 110.81 (s, $BO_2$**C**$_6$H$_4$), 121.20 (s, $BO_2$**C**$_6$H$_4$), 150.97 ppm (s, $BO_2$**C**$_6$H$_4$). Single crystal X-ray diffraction data can be found in Appendix.

#### 4.2.2. Synthesis of mer-$(Me_3P)_3Ir(Cl)(C(H)=C(H)(CMe_3))(BO_2C_6H_4)$, ***2a***

An oven dried NMR tube was taken into a glove box under nitrogen and charged with *mer*-$(Me_3P)_3Ir(Cl)(H)(BO_2C_6H_4)$ (20 mg, 0.035 mmol) and taken out equipped with a septum. 3,3-Dimethyl-1-butyne (4.3 μL, 0.035 mmol) was added to the NMR tube via syringe followed by chloroform-$d$. Monitoring the reaction by $^1$H NMR spectroscopy showed that the alkyne inserted into the Ir–H

bond giving an iridium vinyl complex. The vinyl and catecholboryl groups then reductively eliminated to produce *trans*-2-phenylethenyl-1,3,2-benzodioxaborole. *mer*-$(Me_3P)_3Ir(Cl)(C(H)=C(H)C(Me_3))-(BO_2C_6H_4)$: $^1$H NMR (chloroform-*d*): $\delta$ 0.94 (s, 9H, C**Me**$_3$), 1.50 (t, $J_{H-P}$ = 3.7, 18H, P**Me**$_3$), 1.57 (d, $J_{H-P}$ = 8.2, 9H, P**Me**$_3$), 5.84 (ddt, $J_{H-H}$ = 17.0, $J_{H-Ptrans}$ = 7.0, $J_{H-Pcis}$ < 3 Hz, 1H, vinyl **H**CCMe$_3$), 6.66 (ddt, $J_{H-H}$ = 17.0, $J_{H-Ptrans}$ = 3.5, $J_{H-Pcis}$ = 3.5 Hz, 1H, vinyl IrC**H**), 6.96 ppm (AA′BB′, 4H, $BO_2C_6$**H**$_4$). *trans*-$Me_3CC(H)=C(H)BO_2C_6H_4$: $^1$H NMR (chloroform-*d*): $\delta$ 1.08 (s, 9H, C**Me**$_3$), 5.68 (d, $J_{H-H}$ = 18.4 Hz, 1H, vinyl $Me_3CC$**H**), 7.03 (d, $J_{H-H}$ = 18.3 Hz, 1H, vinyl **H**CB), 7.11 ppm (AA′BB′, 4H, $BO_2C_6$**H**$_4$).

#### 4.2.3. Synthesis of mer-$(Me_3P)_3Ir(Cl)(C(H)=C(H)Si(Me_3))(BO_2C_6H_4)$, **2b**

An oven dried NMR tube was taken into a glove box under nitrogen and charged with *mer*-$(Me_3P)_3Ir(Cl)(H)(BO_2C_6H_4)$ (20 mg, 0.035 mmol) and taken out equipped with a septum. Trimethylsilylacetylene (4.9 μL, 0.035 mmol) was added to the NMR tube via syringe followed by chloroform-*d*. Monitoring the reaction by $^1$H NMR spectroscopy showed that the alkyne inserted into the Ir–H bond giving an iridium vinyl complex. The vinyl and catechol groups then reductively eliminated to produce *trans*-2-trimethylsilyl-ethenyl-1,3,2-benzodioxaborole. *mer*-$(Me_3P)_3Ir(Cl)(C(H)=C(H)Si(Me_3))(BO_2C_6H_4)$: $^1$H NMR (chloroform-*d*): $\delta$ −0.04 (s, 9H, Si**Me**$_3$), 1.49 (t, $J_{H-P}$ = 3.7 Hz, 18H, P**Me**$_3$), 1.57 (d, $J_{H-P}$ = 8.1 Hz, 9H, P**Me**$_3$), 6.72 (ddt, $J_{H-H}$ = 20.2, $J_{H-Ptrans}$ = 11.2, $J_{H-Pcis}$ < 3 Hz, 1H, vinyl **H**CSiMe$_3$), 6.99 (AA′BB′, 4H, $BO_2C_6$**H**$_4$), 8.23 ppm (ddt, $J_{H-H}$ = 20.2, $J_{H-Ptrans}$ = 5.9, $J_{H-Pcis}$ = 3.8 Hz, 1H, vinyl IrC**H**). *trans*-$Me_3SiC(H)=C(H)BO_2C_6H_4$: $^1$H NMR (chloroform-*d*): $\delta$ 0.12 (s, 9H, Si**Me**$_3$), 6.53 ppm (d, $J_{H-H}$ = 22 Hz, 1H, vinyl Si**CH**), 7.13 (AA′BB′, 4H, $BO_2C_6$**H**$_4$), 7.53 ppm (d, $J_{H-H}$ = 22 Hz, 1H, vinyl **H**CB).

#### 4.2.4. Synthesis of mer-$(Me_3P)_3Ir(Cl)(C(H)=C(H)(C_6H_5))(BO_2C_6H_4)$, **2c**

An oven dried NMR tube was taken into a glove box under nitrogen and charged with *mer*-$(Me_3P)_3Ir(Cl)(H)(BO_2C_6H_4)$ (20 mg, 0.035 mmol) and taken out equipped with a septum. Phenylacetylene (3.8 μL, 0.035 mmol) was added to the NMR tube via syringe followed by chloroform-*d*. Monitoring the reaction by $^1$H NMR spectroscopy showed that the alkyne inserted into the Ir–H bond giving an iridium vinyl complex. The vinyl and boryl groups then reductively eliminated to produce *trans*-2-(t-butylethenyl)-1,3,2-benzodioxaborole. *mer*-$(Me_3P)_3Ir(Cl)(C(H)=C(H)(C_6H_5))(BO_2C_6H_4)$: $^1$H NMR (chloroform-*d*): $\delta$ 1.51 (t, $J_{H-P}$ = 3.7 Hz, 18H, P**Me**$_3$), 1.63 (d, $J_{H-P}$ = 8.2 Hz, 9H, P**Me**$_3$), 7.03 (AA′BB′, 5H, $BO_2C_6$**H**$_4$ and vinyl **H**CPh), 8.17 (ddt, $J_{H-H}$ = 17.4, $J_{H-Ptrans}$ = 3.0, $J_{H-Pcis}$ = 3.5 Hz, 1H, vinyl IrC**H**), 7.19 (s, **Ph**), 7.22 (s, **Ph**), 7.24 (s, **Ph**), 7.30 (s, **Ph**), 7.33 (s, **Ph**), 7.36 ppm (s, **Ph**), 5H total for Ph. *trans*-$C_6H_5C(H)=C(H)BO_2C_6H_4$: $^1$H NMR (chloroform-*d*): $\delta$ 6.47 (d, $J_{H-H}$ = 18 Hz, 1H, PhC**H**), 7.16 (AA′BB′, 4H, $BO_2C_6$**H**$_4$), 7.38 (m, 3H, **Ph**), 7.58 (dd, $J_{H-H}$ = 7.9, 2.0 Hz, 2H, **Ph**), 7.75 ppm (d, $J_{H-H}$ = 18 Hz, 1H, vinyl **H**CB).

#### 4.2.5. Synthesis of mer-$(Me_3P)_3Ir(Cl)(C(=C(H)COOMe)(COOMe))(BO_2C_6H_4)$, **5**

An oven dried 100 mL side arm flask, equipped with a septum, was taken into a glove box under nitrogen and charged with *mer*-$(Me_3P)_3Ir(Cl)(H)(BO_2C_6H_4)$ (0.250 g, 0.434 mmol) and taken out. The flask was attached to a Schlenk line and methylene chloride (5 mL) was added followed by dimethylacetylenedicarboxylate (53 μL, 0.434 mmol) via syringe. The solution was stirred magnetically for 2 h and the solvent removed under vacuum, giving a pale yellow powder. The solid was washed with 2 × 1 mL of cold tetrahydrofuran and filtered with a medium frit filter tube under nitrogen. Excess solvent was removed under vacuum leaving a white powder. In solution, $^1$H NMR spectroscopy revealed two isomers. The ratio of these isomers is solvent dependent: acetone-$d_6$ (3:1), chloroform-*d* (5:1), benzene-$d_6$ (3:1). Analysis (%). calculated (found) for $C_{21}H_{38}BClIrO_6P_3$: C, 35.13 (35.18); H, 5.34 (5.31). **Major isomer**: $^1$H NMR (benzene-$d_6$): $\delta$ 1.11 (d, $J_{H-P}$ = 8.7 Hz, 9H, P**Me**$_3$), 1.56 (br s, 18H, P**Me**$_3$), 3.33 (s, 3H, COO**Me**), 3.99 (s, 3H, COO**Me**), 6.08 (dt, $J_{H-Ptrans}$ = 8.0, $J_{H-Pcis}$ = 2.6 Hz, 1H, vinyl **H**), 6.88 ppm (AA′BB′, 4H, $BO_2C_6$**H**$_4$). $^{31}$P NMR (benzene-$d_6$, $H_3PO_4$ external standard): $\delta$ −49.00 (t, $J_{P-P}$ = 22 Hz, 1P, **P**Me$_3$), −42.28 (d, $J_{P-P}$ = 22 Hz, 1P, **P**Me$_3$), −42.45 ppm (d, $J_{P-P}$ = 22 Hz, 1P, **P**Me$_3$). $^{13}$C NMR (benzene-$d_6$): $\delta$ 17.36 (distorted dt, $J_{C-P}$ = 1.9, 18.7 Hz, P**Me**$_3$), 18.13 (dd, $J_{C-P}$ = 34.3, 1.9 Hz, P**Me**$_3$), 49.08 (s, COO**Me**), 50.35 (s, COO**Me**), 111.61 (s, $BO_2$**C**$_6H_4$), 122.23 (s, $BO_2$**C**$_6H_4$), 128.51 (t, $J_{C-P}$ = 3.8 Hz, IrC=**C**(H)), 150.43 (s, $BO_2$**C**$_6H_4$), 164.99 ppm (dt, $J_{C-P}$ = 9.2, 2.3 Hz, Ir**C**=C(H)), not observed (**C**OOMe). **Minor isomer**: $^1$H NMR (benzene-$d_6$): $\delta$ 1.15 (d, $J_{H-P}$ = 8.6 Hz, 9H, P**Me**$_3$), 1.46 (t, $J_{H-P}$ = 4.0 Hz, 18H, P**Me**$_3$), 3.47 (s, 3H, COO**Me**), 3.61 (s, 3H, COO**Me**), 6.90 (AA′BB′, 4H, $BO_2C_6$**H**$_4$), 7.64 ppm (dt, $J_{H-Ptrans}$ = 7.4, $J_{H-Pcis}$ = 2.6 Hz, 1H, vinyl **H**). $^{31}$P NMR (benzene-$d_6$, $H_3PO_4$ external standard): $\delta$ −48.86 (t, $J_{P-P}$ = 20 Hz, **P**Me$_3$), −43.09 ppm (d, $J_{P-P}$ = 20 Hz, **P**Me$_3$). $^{13}$C NMR (benzene-$d_6$): $\delta$ 16.92 (dt, $J_{C-P}$ = 1.9, 19.1 Hz, P**Me**$_3$), 19.37 (dd, $J_{C-P}$ = 33.6, 1.9 Hz, P**Me**$_3$), 50.80 (s, COO**Me**), 50.46 (s, COO**Me**), 111.32 (s, $BO_2$**C**$_6H_4$), 121.85 (s, $BO_2$**C**$_6H_4$), 126.51 (t, $J_{C-P}$ = 4.5 Hz, IrC=**C**(H)), 150.69 (s, $BO_2$**C**$_6H_4$), 176.64 (d, $J_{C-P}$ = 6.1 Hz, Ir**C**=C(H)), not observed (s, **C**OOMe). Single crystal X-ray diffraction data can be found in Appendix.

#### 4.2.6. Synthesis of mer-$(Me_3P)_3Ir(I)(C(=C(H)COOMe)(COOMe))(BO_2C_6H_4)$, **6**

A 5 mm NMR tube was charged with *mer*-$(Me_3P)_3Ir(Cl)(C(=C(H)COOMe)-(COOMe))(BO_2C_6H_4)$ (**5**) (0.011 g, 0.0153 mmol) and KI (0.010 g, 0.0602 mmol) and then degassed on a Schlenk line (NMR tube was equipped with a septum). Acetone-$d_6$ (0.5 mL) was added and the solution left to stand at room temperature (Most of the KI did not go into solution.). After 4 h, a $^1$H NMR spectrum was recorded which revealed small amounts of two new complexes slowly appearing. After 3 days, $^1$H NMR spectroscopy revealed only the two new complexes – presumably two isomers of an iodine complex where $I^-$ took the place of $Cl^-$. As the reaction progressed, a fine white powder precipitated out of solution, presumably KCl. The major to minor isomer ratio is (1.3:1). The broad triplet observed for the trans PMe$_3$s of *mer*-$(Me_3P)_3Ir(Cl)(C(=C(H)COOMe)(COOMe))-(BO_2C_6H_4)$ (**3**) was not duplicated in the product. $^1$H NMR (acetone-$d_6$): **major isomer**: $\delta$ 1.78 (d, $J_{H-P}$ = 8.8 Hz, 9H, P**Me**$_3$), 1.82 (t, $J_{H-P}$ = 4.0 Hz, 18H, P**Me**$_3$), 3.46 (s, 3H, COO**Me**), 3.50 (s, 3H, COO**Me**), 7.05 (AA′BB′, 4H, $BO_2C_6$**H**$_4$), 7.29 ppm (dt, $J_{H-Ptrans}$ = 7.6, $J_{H-Pcis}$ = 2.6 Hz, 1H, vinyl **H**); **minor isomer**: $\delta$ 1.79 (d, $J_{H-P}$ = 8.8 Hz, 9H, P**Me**$_3$), 1.88 (t, $J_{H-P}$ = 4.0 Hz, 18H, P**Me**$_3$), 3.40 (s, 3H, COO**Me**), 3.66 (s, 3H, COO**Me**), 5.51 (dt, $J_{H-Ptrans}$ = 7.4, $J_{H-Pcis}$ = 2.6 Hz, 1H, vinyl **H**), 7.12 ppm (AA′BB′, 4H, $BO_2C_6$**H**$_4$).

#### 4.2.7. Synthesis of mer-$(PMe_3)_3Ir(CH_3)(H)(BO_2C_6H_4)$, **3**

A 5 mm NMR tube was taken into a dry box (nitrogen), charged with *mer*-$(Me_3P)_3Ir(Cl)(H)(BO_2C_6H_4)$ (0.020 g, 0.035 mmol), and brought out equipped with a septum. To this NMR tube was added 35 μL (0.035 mmol) of LiMe in diethylether via syringe. The diethyl ether was removed under vacuum and benzene-$d_6$ (0.5 mL) was then added. Lithium chloride precipitated from solution and was centrifuged to the bottom of the tube. The resulting product was characterized by $^1$H NMR spectroscopy, indicating the presence of clean *mer*-$(Me_3P)_3Ir(Me)(H)(BO_2C_6H_4)$ in the solution. $^1$H NMR (benzene-$d_6$): $\delta$ −11.66 (dt, $J_{H-Ptrans}$ = 133.0, $J_{H-Pcis}$ = 22.7 Hz, 1H, Ir**H**), −0.07 (dq, $J_{H-P}$ = 7.0, $J_{H-H}$ = 1.0 Hz, 3H, Ir**Me**), 1.32 (dd, $J_{H-P}$ = 8.5, $J_{H-H}$ = 0.7 Hz, 9H, P**Me**$_3$), 1.35 (t, $J_{H-P}$ = 3.4 Hz, 18H, P**Me**$_3$),

**Table 2**
Crystal data and refinement parameters for **4** and **5**.

| | **4** | **5** |
|---|---|---|
| Formula | $C_{15}H_{32}BIIrO_2P_3$ | $C_{21}H_{38}BClIrO_6P_3$ |
| Formula wt. | 667.27 | 717.88 |
| *T*, K | 290 | 298 |
| Space group | *Abe*2 | $P2_12_12_1$ |
| *a*, Å | 14.729(3) | 10.538(2) |
| *b*, Å | 13.369(3) | 16.073(3) |
| *c*, Å | 12.125(2) | 17.364(4) |
| $\alpha$, ° | 90 | 90 |
| $\beta$, ° | 90 | 90 |
| $\gamma$, ° | 90 | 90 |
| *V*, Å$^3$ | 2387.6(8) | 2941.2(10) |
| *Z* | 4 | 4 |
| $\rho_{calcd}$, g/cm$^3$ | 1.854 | 1.621 |
| $\mu$(Mo K$\alpha$), mm$^{-1}$ | 7.098 | 4.825 |
| Total data | 1508 | 3525 |
| Unique data | 1508 | 3525 |
| Parameters | 32 | 203 |
| $R_1$ (all data)[a] | 0.0327 | 0.0452 |
| $wR_2$ (all data)[b] | 0.0824 | 0.0794 |
| Flack | −0.005(12) | −0.017(12) |
| GOF | 1.050 | 1.022 |
| Of max, min, e/Å$^3$ | 1.22, −2.14 | 1.16, −0.86 |

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR_2 = \left[\sum w(F_o^2 - F_c^2)^2 / \sum w\left(F_o^2\right)^2\right]^{1/2}$.

7.05 ppm (AA′BB′, 4H, $BO_2C_6\mathbf{H}_4$). $^{31}$P NMR (benzene-$d_6$, $H_3PO_4$ external standard): $\delta$ −58.0 (t, $J_{P-P}$ = 22 Hz, P**Me**$_3$), −47.3 ppm ($\delta$, $J_{P-P}$ = 22 Hz, P**Me**$_3$).

#### 4.2.8. Synthesis of mer-$(Me_3P)_3Ir(I)(H)(BO_2C_6H_4)$

A 5 mm NMR tube was taken into a dry box (nitrogen) and charged with *mer*-$(Me_3P)_3Ir(Cl)(H)(BO_2C_6H_4)$ (0.01 g, 0.017 mmol) and an excess of KI. The KI had been dried under vacuum (~1 mmHg) at 250 °C for 16 h. The tube was then removed from the dry box equipped with a septum. Acetone-$d_6$ was added via syringe. Most of the KI did not go into solution. After 15 min, $^1$H NMR spectroscopy showed a new complex forming with the same splitting patterns as the starting Ir complex, only at different chemical shifts. At this time (15 min) the ratio was 45:55 new complex:starting complex. After 1 h, the Ir–I to Ir–Cl ratio was 66:33. Crystals of the Ir–I complex grew in the tube in a few days, therefore enabling an X-ray crystal structure to be obtained which confirmed the exchange of $Cl^-$ for $I^-$ on iridium. *mer*-$(Me_3P)_3Ir(I)(H)(BO_2C_6H_4)$ $^1$H NMR (acetone-$d_6$): $\delta$ −10.80 (dt, $J_{H-P}$ = 134.3, 20.4 Hz, 1H, IrH), 1.73 (t, $J_{H-P}$ = 3.6 Hz, 18H, $PMe_3$), 1.76 (dd, $J_{H-P}$ = 8.2, 0.9 Hz, 9H, $PMe_3$), 6.99 (AA′BB′, 4H, $BO_2C_6H_4$).

### 4.3. Reactivity studies

Details on reactivity studies utilizing NMR spectroscopy can be found in Supplementary material.

### 4.4. Computational studies

All calculations were performed using gaussian 09 [46] on the Virginia Tech Chemistry Department Cluster, “Cerebro”, using the WebMO interface. Full geometry optimizations and single-point energy calculations of all structures were performed via density functional theory (DFT) with the Becke-3-parameter exchange functional [47] and the Lee–Yang–Parr correlation functional [48,49]. Because iridium is not covered in the cc-pVDZ basis set used, computations involving Ir employed Stuttgart/Dresden quasi-relativistic pseudopotentials [50]. Data can be found in Supplementary material.

### 4.5. Single crystal X-ray diffraction

Single crystal diffraction experiments were performed on a Nicolet R3m/V diffractometer with the SHELXTL-PLUS software as supplied by Nicolet Corporation. More recently, the data was re-refined using Shelxl-2013 [51] and manipulations and publication figures were performed within the Olex2 program. Crystal data and refinement parameters for compounds **4** and **5** are found in Table 2.

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## Appendix A. Supplementary material

CCDC 957402 (for complex **4**) and CCDC 957403 (for complex **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary material associated with this article can be found, in the online version at http://dx.doi.org/10.1016/j.jorganchem.2013.10.049.

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