

# Ligand Cooperation in the Formal Hydrogenation of N<sub>2</sub>O Using a PC<sub>sp</sub><sup>2</sup>P Iridium Pincer Complex

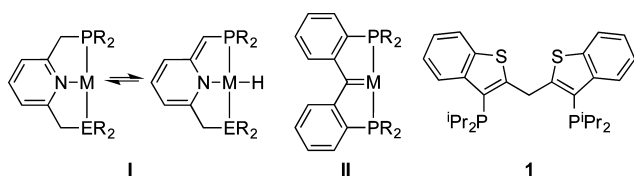
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**S** Supporting Information

**ABSTRACT:** A new PC<sub>carbene</sub>P pincer ligand with 2,3-benzo[*b*]thiophene linkers connecting the flanking dialkyl phosphine donors to the central carbene can be attached to Ir(I). The chloro derivative reacts with N<sub>2</sub>O with loss of N<sub>2</sub> to form an iridaepoxide species by addition of an oxygen atom to the Ir=C linkage. This compound reacts with H<sub>2</sub> to afford the oxidative addition product, in which the hydride ligands are *trans* to the Ir–O bond. Heating this dihydride results in slow release of H<sub>2</sub>O; kinetic and spectroscopic studies show that conversion of the dihydride to its isomer, in which the hydrides are *cis* to the Ir–O bond, is required for H<sub>2</sub>O elimination to take place. Together, these reactions constitute the stoichiometric conversion of N<sub>2</sub>O and H<sub>2</sub> to N<sub>2</sub> and H<sub>2</sub>O; further mechanistic studies suggest ways to make the system catalytic.

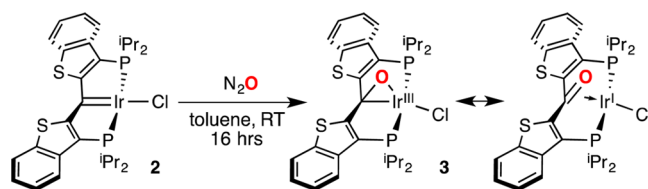
Pincer ligands<sup>1</sup> capable of shuttling hydrogen atoms through ligand cooperativity have been utilized effectively for mediating catalytic processes and activating small molecules.<sup>2</sup> For example, the dearomatization/aromatization equilibrium in pincer ligands such as **I** is a powerful tool for managing hydrogen atoms in a variety of reactions<sup>3</sup> including the splitting of water.<sup>4</sup> Recently, we introduced a PC<sub>sp</sub><sup>2</sup>P pincer variant, **II**,<sup>5</sup> which can potentially engage in cooperative behavior through reactivity across the M=C bond of the pincer framework.<sup>6,7</sup> In fact, dihydrogen can add reversibly to the Ir=C bond of iridium complexes of this ligand system incorporating dialkylphosphine arms.<sup>5</sup>



The ligand design in **II** allows for variation in the nature of the aromatic linker connecting the carbene donor with the phosphine arms. We therefore introduce a ligand system featuring a 2,3-benzo[*b*]thiophene linker, **1**, which is straightforwardly prepared from 2,3-dibromobenzo[*b*]thiophene and 3-bromobenzo[*b*]thiophene-2-carbaldehyde in three steps (see Supporting Information for details). Ligand attachment to iridium through double C–H activation protocols developed previously<sup>5,8,9</sup> occurs when **1** and [Ir( $\eta^2$ -C<sub>8</sub>H<sub>14</sub>)<sub>2</sub>Cl]<sub>2</sub> are refluxed together in *o*-xylene for 48 h. The

product iridium PC<sub>carbene</sub>P complex **2** (Scheme 1) was isolated in 87% yield as a dark brown powder and is characterized by a

**Scheme 1**



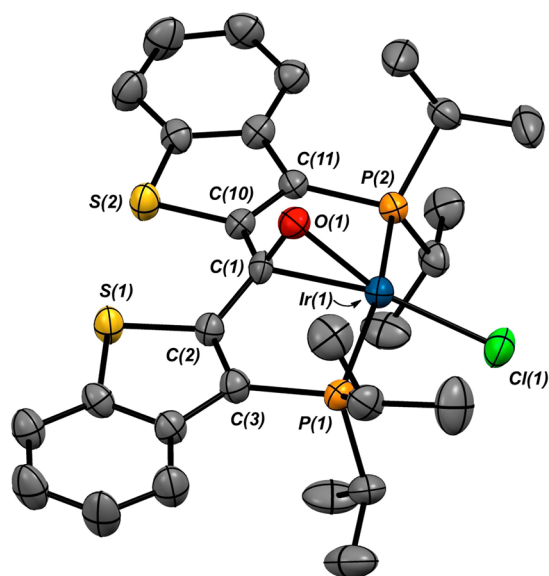
triplet (<sup>2</sup>J<sub>CP</sub> = 2.7 Hz) in the <sup>13</sup>C NMR spectrum at 166.3 ppm for the anchoring carbene carbon. This is upfield of the value for the phenylene linked ligand, which appears at 199.7 ppm.<sup>5</sup>

While this compound is water tolerant, exposure of solutions of complex **2** to ambient atmosphere resulted in decomposition to a number of species, as judged by <sup>31</sup>P NMR spectroscopy. One of these was identified as the iridaepoxide complex **3**, formed by the addition of an oxygen atom to the Ir=C bond in **2**. Presumably the oxygen atom source is atmospheric O<sub>2</sub>, since exposure of **2** to pure oxygen leads to similar mixtures. Complex **3** can be prepared cleanly and quantitatively via treatment of the carbene chloride **2** with an excess of N<sub>2</sub>O at room temperature in toluene. This reaction takes about 16 h (Scheme 1), but heating to 100 °C increases the rate of the reaction such that it is finished in <2 h. An iridaepoxide has been proposed as an intermediate in the reaction of N<sub>2</sub>O with an iridabenzene,<sup>10</sup> but well-defined examples of these compounds are rare for iridium. Most metallaepoxides are derived from low valent metals and ketones, but formation by addition of N<sub>2</sub>O to a metal carbene has some precedent.<sup>11</sup>

Iridaepoxide **3** is a bright red compound that crystallizes readily, even from mixtures; indeed, that is how it was first identified. Figure 1 shows its molecular structure along with selected metrical parameters. Formulation of **3** as an iridaepoxide is one extreme of a continuum between this Ir(III) structure and an iridium  $\eta^2$ -carbonyl representation similar to that found for an Ir stabilized phenoxonium cation by Milstein et al.,<sup>12</sup> in which the Ir center is formally in the +1 oxidation state (Scheme 1). The <sup>13</sup>C chemical shift for the iridaepoxide carbon is moderately upfield at 65.0 ppm, but is not particularly diagnostic. The C(1)–O(1) distance of 1.350(7) Å is between that normal for C–O double ( $\approx$  1.21 Å) and single ( $\approx$  1.45 Å) bonds, and the Ir(1)–C(1) and O(1)

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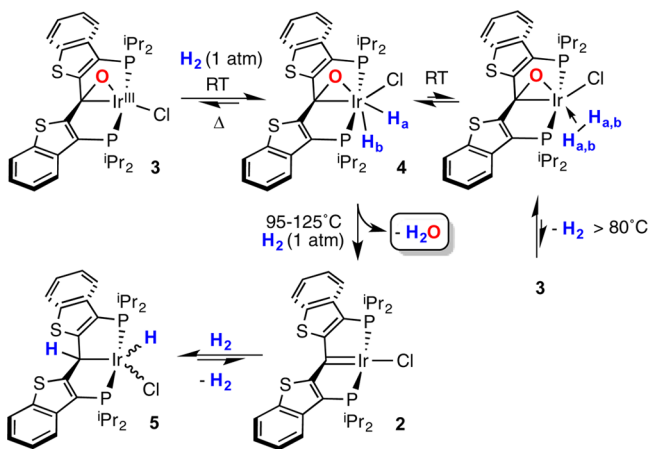


**Figure 1.** Molecular structure of **3**. Hydrogen atoms have been omitted for clarity. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å): Ir(1)–P(1), 2.314(2); Ir(1)–P(2), 2.309(2); Ir(1)–C(1), 2.080(6); Ir(1)–O(1), 2.034(4); C(1)–O(1), 1.350(7); C(1)–C(2), 1.484(8); C(2)–C(3), 1.367(9). Selected bond angles (deg): C(1)–Ir(1)–O(1), 38.3(2); C(1)–O(1)–Ir(1), 72.7(3); Ir(1)–C(1)–O(1), 69.0(3) P(1)–Ir(1)–P(2), 162.42(6).

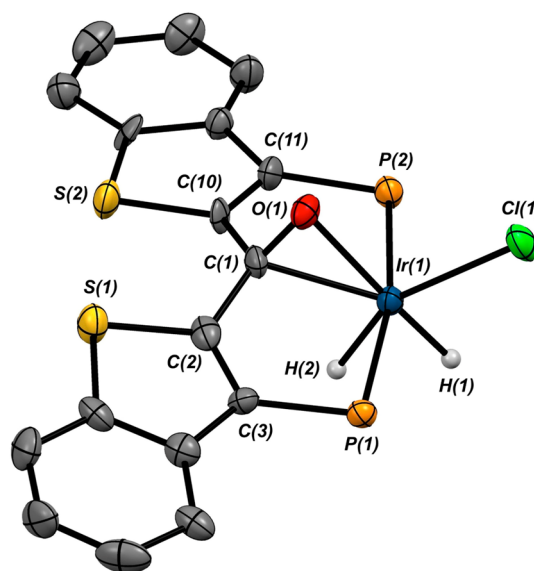
distances are consistent with single bonds.<sup>13</sup> The compound is therefore perhaps best viewed as a hybrid of the two extreme formulations.

Iridaepoxide **3** is thermally stable up to at least 100 °C but undergoes decomposition to ill-defined mixtures under irradiation at 254 nm. It reacts cleanly with dihydrogen<sup>14,15</sup> (Scheme 2) over the course of 2 h to give a dihydride complex

**Scheme 2**



characterized by two triplets at  $-7.58$  and  $-15.22$  ppm; both exhibit  $^2J_{\text{HP}}$  coupling constants of 10.7 Hz. A determination of the structure via X-ray crystallography reveals the product in which the hydrides occupy coordination sites *trans* to the C–O unit of the iridaepoxide (for selected metrical parameters, see Figure 2). The C(1)–O(1) distance is shorter than that in **3**, and the Ir(1)–C(1) and Ir(1)–O(1) bonds are slightly longer, which suggest that this species is closer to an  $\eta^2$ -carbonyl



**Figure 2.** Molecular structure of **4**. *iso*-propyl carbons and all hydrogens except H(1) and H(2) omitted for clarity. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å): Ir(1)–P(1), 2.309(3); Ir(1)–P(2), 2.323(3); Ir(1)–C(1), 2.126(10); Ir(1)–O(1), 2.155(7); Ir(1)–H(1), 1.50(14); Ir(1)–H(2), 1.66(10); C(1)–O(1), 1.303(12); C(1)–C(2), 1.514(15); C(2)–C(3), 1.334(15). Selected bond angles (deg): C(1)–Ir(1)–O(1), 35.4(3); C(1)–O(1)–Ir(1), 71.1(5); Ir(1)–C(1)–O(1), 73.5(5); P(1)–Ir(1)–P(2), 168.18(10); H(1)–Ir(1)–H(2), 67(6).

complex, that is, formally Ir(III) as opposed to Ir(V). Consistent with this, the  $^{13}\text{C}$  NMR chemical shift for C(1) in **4** is downfield shifted by  $\sim 35$  ppm to 99.5 ppm compared to that observed for **3**.

At room temperature, EXSY spectroscopy indicates that the inequivalent hydrides in **4** undergo exchange (Figure S1) on the NMR time scale. Exposure of **4** to  $\text{D}_2$  does not, however, result in deuterium incorporation into **4** under ambient conditions, but heating these solutions to  $>80$  °C does result in H/D exchange, along with observation of small amounts of regenerated **3**, which indicates that  $\text{H}_2$  oxidative addition is reversible under these conditions. However, the dominant reaction pathway exhibited by **4** upon heating involves loss of one equivalent of *water*, not  $\text{H}_2$ , as evidenced by the appearance of a broad signal at 0.5 ppm<sup>16</sup> and the emergence of familiar resonances for the  $\text{PC}_{\text{carbene}}\text{P}$  chloride **2** in the  $^1\text{H}$  NMR spectrum over the course of several hours at  $>95$  °C. Monitoring the thermolysis of dihydride **4** by  $^{31}\text{P}$  NMR spectroscopy similarly indicates that, at early reaction times,  $\text{H}_2$  loss competes with  $\text{H}_2\text{O}$  elimination. As expected,<sup>5</sup> the  $\text{H}_2$  produced reacts with the carbene chloride **2** resulting from  $\text{H}_2\text{O}$  elimination to give the Ir(III)  $\text{PC}_{\text{sp}^3}\text{P}$  hydrido chloride **5** (Scheme 2); thus, compounds **2**–**5** are all apparent in the  $^{31}\text{P}$  NMR spectrum after heating for 1 h (Figure S2). Compound **5** is a known intermediate in the formation of **2**, and its formation is reversible; thus, continued heating of the mixture eventually results in near quantitative conversion of **4** into **2** and water (Figure S3). The production of water was confirmed by carrying out the reaction with  $d_2$ -**4** and detecting  $\text{D}_2\text{O}$  by  $^2\text{H}$  NMR spectroscopy. Note that although **5** is also known to reversibly bind  $\text{H}_2$  (see Supporting Information), this species is not important in this system due to the high temperatures involved.

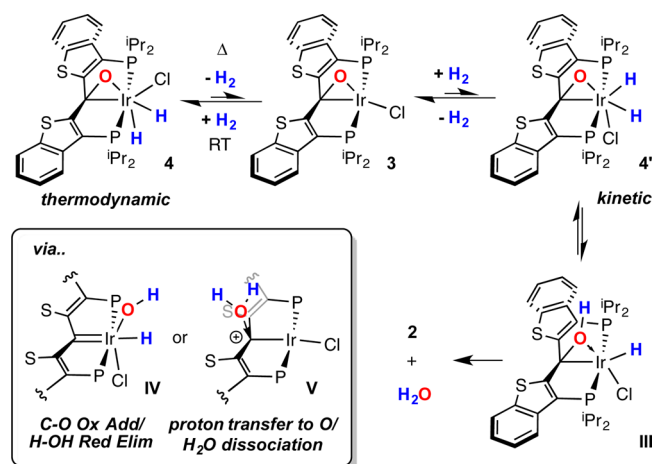
The sequence of reactions from 2 to 3 (Scheme 1), 3 to 4, and 4 back to 2 (Scheme 2) is significant because it represents a formal hydrogenation of  $\text{N}_2\text{O}$  to  $\text{N}_2$  and  $\text{H}_2\text{O}$ . The metal-catalyzed decomposition of  $\text{N}_2\text{O}$  is of current interest due to the role of this molecule in both global warming and ozone depletion and the fact that its level in the atmosphere is rising.<sup>17</sup> Homogeneous catalysts that mediate its degradation<sup>18,19</sup> or hydrogenation to water<sup>20,21</sup> are scarce, and development of such systems is of considerable interest. Therefore, we examined the mechanisms of elimination of  $\text{H}_2\text{O}$  from 4 and  $\text{H}_2$  addition to 3 using a combination of kinetic and spectroscopic studies.

To simplify the analysis of the data, the kinetics of water loss was evaluated in the presence of 1 atm of  $\text{H}_2$  to suppress the concentration of 3. The conversion of 4 to the hydrido chloride 5 (via 2) using  $^1\text{H}$  NMR spectroscopy at four temperatures between 95 and 125 °C was monitored in this way. Under these conditions, no iridaepoxide 3 (the product of  $\text{H}_2$  elimination) was observed by  $^1\text{H}$  or  $^{31}\text{P}$  NMR spectroscopy (Figure S4). The elimination of water from 4 was found to be cleanly first order in [4], (Figure S5) and an Eyring analysis gave the following activation parameters:  $\Delta H^\ddagger = 34(2)$  kcal mol<sup>-1</sup>;  $\Delta S^\ddagger = 13(4)$  cal mol<sup>-1</sup> K<sup>-1</sup> (Figure S6). Analysis of the rate of  $\text{D}_2\text{O}$  elimination from  $d_2$ -4 at 105 °C gave a moderate  $k_{\text{H}}/k_{\text{D}}$  of 1.7(1) (Figure S7).

The geometry of dihydride 4, in which the hydride ligands are *trans* to the oxygen atom with which they must form bonds to produce water, suggests that some kind of isomerization must take place in order to favor O–H bond formation. When the formation of 4 from iridaepoxide 3 and  $\text{H}_2$  is monitored by  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectroscopy at room temperature, no intermediates are observed, but when 3 is treated with  $\text{H}_2$  at –78 °C, clear evidence for another species is obtained. In the  $^{31}\text{P}$  NMR spectrum (Figure S8), the resonance at 25.1 ppm for 3 is broadened considerably at –78 °C. Furthermore, in addition to a trace amount of dihydride 4 (24.5 ppm, formed during sample preparation), a slightly broadened singlet at 23.0 ppm is observed; the ratio of 3 to this new species is ~3:1. Upon warming, the signal at 23.0 broadens and migrates downfield slightly, while it decreases in intensity as the temperature is raised, until it is essentially gone at –18 °C; meanwhile, the resonance for 3 sharpens. The corresponding  $^1\text{H}$  NMR experiment shows that, like 4, the new species has two inequivalent hydride ligands that are manifested by two broad triplets at –5.71 and –12.21 ppm in the –78 °C spectrum (Figure S9). Warming of the sample results in broadening of the new hydride resonances and eventual disappearance of this species at about –38 °C.

We interpret these observations according to the chemistry in Scheme 3, where the transient species is assigned to be a kinetic isomer of 4, that is, 4', in which the hydrides are located *cis* to the iridaepoxide oxygen. While loss of  $\text{H}_2$  is facile from 4', it is from this kinetic isomer that O–H bond formation occurs, since reductive elimination of the O–H moiety is now geometrically primed. The product of O–H bond formation would be the putative  $\text{PC}_{\text{carbene}}\text{P}$  hydrido chloride species III, in which an OH substituent is present on the anchoring carbon atom of the pincer ligand. While O–H bond formation is quite likely reversible, elimination of  $\text{H}_2\text{O}$  from III is not, since the carbene chloride 2 does not react with water, and this step completes the reaction. Since we do not see any evidence of III in the reaction, in this scenario, the rate limiting step in the

Scheme 3

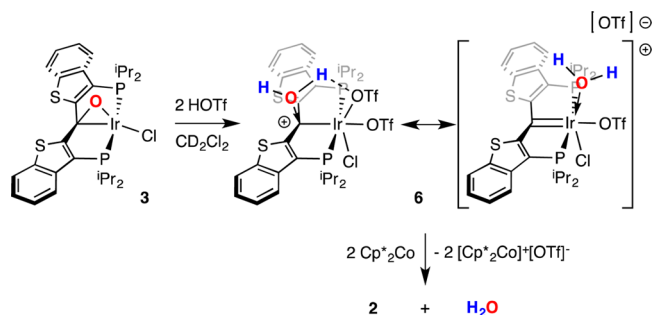


elimination of water from 4 involves the reductive elimination of  $\text{H}_2$  such that kinetic isomer 4' may be accessed for O–H bond formation. The kinetic data acquired as described above, particularly the positive  $\Delta S^\ddagger$  value and the observed  $k_{\text{H}}/k_{\text{D}}$ ,<sup>22</sup> are consistent with this proposal.

While the evidence for formation of a kinetic isomer and the proposal of O–H bond formation from this species to give III are (in our view) reasonable, the process by which water is eliminated from III remains somewhat opaque. Two possibilities are proffered in Scheme 3. In the first, formal oxidative addition of the C–O bond in III would lead to the  $\text{PC}_{\text{carbene}}\text{P}$  Ir(III) species IV, from which reductive elimination of water would be expected to be rapid. Alternatively, migration of the remaining iridium hydride (as a proton) to the O–H group on the  $\alpha$  carbon would lead to V, which can be formulated as a water-ligated carbocation; water dissociation would be expected to be rapid. In both cases, loss of water leads directly to the observed product, carbene chloride 2.

Indirect evidence from experiments involving protonation of iridaepoxide 3 suggests that a mechanism involving a species akin to V may be viable. Treatment of 3 with two equivalents of triflic acid in  $\text{CD}_2\text{Cl}_2$  leads to clean formation of a new product, 6, which we formulate as depicted in Scheme 4. When treated

Scheme 4



with one equivalent of acid, only the new compound 6 and unreacted 3 are observed; therefore, the species formed upon monoprotonation of 3 (presumably related to putative III, Scheme 3) is significantly more basic than 3 itself.

The diprotonated compound 6 is a dark red colored crystalline solid that has thus far evaded crystallographic analysis due to a tendency to slowly decompose in both

solution and the solid state. However, spectroscopic data obtained on freshly prepared samples are consistent with the proposed structures shown in Scheme 4. For example, a signal appears at 6.52 ppm in the  $^1\text{H}$  NMR spectrum, integrating to two protons, and may be assigned to the coordinated water. In the  $^{13}\text{C}$  NMR spectrum, a strongly downfield resonance at 215.8 ppm for the carbocation (or carbene) carbon is observed. Two signals at  $-78.2$  and  $-80.2$  ppm in the  $^{19}\text{F}$  NMR spectrum argue for two inequivalent triflate anions that may or may not be coordinated.<sup>23</sup> While compound **6** is relatively stable at room temperature, both in solution and the solid state, heating solutions result in decomposition to ill-defined species. Significantly, however, treatment with two equivalents of permethylcobaltocene ( $\text{Cp}^*_2\text{Co}$ ) leads to rapid, clean conversion to the carbene chloride **2**. Presumably, one equivalent of  $\text{H}_2\text{O}$  was also generated, but in this solvent, its expected resonance at  $\sim 1.5$  ppm<sup>16</sup> is obscured by ligand and  $\text{Cp}^*$  resonances. Treatment of this mixture with 4 equiv of  $\text{Me}_3\text{SiCl}$  produced  $\text{Me}_3\text{SiOSiMe}_3$  in amounts consistent with the loss of 1 equiv of  $\text{H}_2\text{O}$  (Figure S10). Reduction of **6** by two electrons would be expected to generate a species akin to **V** in situ, which results in the observed product mixture.

In principle, the observed chemistry constitutes a potential catalytic cycle for the hydrogenation of  $\text{N}_2\text{O}$  to  $\text{N}_2$  and  $\text{H}_2\text{O}$ . Control experiments indicate that dihydride **4** does not react with  $\text{N}_2\text{O}$ <sup>20</sup> at  $110^\circ\text{C}$ , the  $\text{PC}_{\text{sp}_3\text{P}}$  hydrido chloride **5** does react with  $\text{N}_2\text{O}$  at high temperature to give iridaepoxide **3**, and *all* of the compounds involved (**2**–**5**) are tolerant of  $\text{H}_2\text{O}$  at  $100^\circ\text{C}$ . Accordingly,  $\text{PC}_{\text{carbene}}\text{P}$  compound **2** in toluene was exposed to 1.5 atm  $\text{N}_2\text{O}/\text{H}_2$  ( $\approx 1:1$ ) and heated to  $110^\circ\text{C}$ ; unfortunately, only (rather catastrophic) decomposition of the iridium compound was observed; no evidence for catalytic turnover was observed. We hypothesize that this stems mainly from two factors, namely the slow reaction of carbene chloride (which must be generated by loss of  $\text{H}_2$  from **5**) with  $\text{N}_2\text{O}$ , and second, the need to access the kinetic isomer **4'** from the thermodynamic dihydride compound **4** to release  $\text{H}_2\text{O}$ , both of which are high barrier processes.

In summary, we have observed the stoichiometric reduction of  $\text{N}_2\text{O}$  using  $\text{H}_2$ , mediated at an iridium center supported by the new  $\text{PC}_{\text{carbene}}\text{P}$  ligand **1**. The reaction sequence features an unusual mechanism involving the addition of an oxygen atom to the anchoring  $\text{Ir}=\text{C}$  motif in complex **2**, a novel form of ligand cooperativity. Reaction of the iridaepoxide complex **3** with  $\text{H}_2$  leads to dihydride **4**, which eliminates  $\text{H}_2\text{O}$  upon heating and regenerates **2**. Catalytic turnover for the hydrogenation of nitrous oxide was not realized, so we are currently enacting ligand modifications to lower the barrier to oxygen atom addition to the  $\text{Ir}=\text{C}$  linkage.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Full experimental details for the syntheses and characterization of new complexes. Crystallographic data files for **3** and **4** (CCDC 1037789, 1037790). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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