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Successive Activation of C–H and C–O Bonds of Vinyl Ethers by a Diphosphine and Hydrido-Bridged Diiridium Complex

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Abstract: The reaction of $[(Cp^*Ir)_2(\mu-dmpm)(\mu-H)][OTf]$ (**2**) [$Cp^* = \eta^5-C_5Me_5$, $dmpm = \text{bis}(\text{dimethylphosphino})\text{methane}$] with 2,3-dihydrofuran gives $[(Cp^*IrH)_2(\mu-dmpm)(\mu-(2,3\text{-dihydrofuranyl}))][OTf]$ (**3**) in an isolated yield of 70% via the C–H bond activation at the 5-position of 2,3-dihydrofuran. Complex **3** is slowly converted into $[(Cp^*Ir)_2(\mu-dmpm)(\mu-C=C(H)CH_2CH_2OH)][OTf]$ (**4**) quantitatively via the proton-mediated C–O bond activation. The reaction of **2** with ethyl vinyl ether gives $[(Cp^*Ir)_2(\mu-dmpm)(\mu-CH=CH_2)][OTf]$ (**5**) in the isolated yield of 64% via the successive activation of C–H and C–O bonds.

Keywords: iridium complex; multinuclear complex; C–H activation; C–O cleavage; vinyl ether

1. Introduction

Vinyl ethers are versatile substrates used to synthesize various oxygen-containing organic compounds, such as functionalized alkenes or ketones [1–5]. Many transition metal-catalyzed synthetic reactions using vinyl ethers as starting materials, such as the Heck-type reaction [6–9], hydrofunctionalization [10–13], cycloaddition [14–16], Claisen rearrangement [17–19], alcoholysis [20,21], and polymerization [22–24] have been known. Further reactions involving the C–H [25–28] or C–O [29,30] bond activation of vinyl ethers as a key step have been reported. These synthetic methods are powerful because there is no need for the pre-functionalization of substrates and specificity in their skeletal rearrangement. To obtain insight into the reaction mechanism and reactivity to develop better catalytic reactions, it must be important to reveal the fundamental aspects of the activation of vinyl ethers by transition metal complexes. However, although there are many studies on C–H [31–35] and C–O [36–41] bond activation reactions by transition metal complexes, fundamental studies on the C–H and C–O bond activation of vinyl ethers by transition metal complexes are relatively unexplored [42–53].

Meanwhile, much attention has been paid to the activation of organic molecules by multinuclear complexes in expectation of the synergetic effect of the multi-metal centers. Therefore, various multimetallic systems that are capable of the bond activation of organic substrates were disclosed [54–58]. We have reported the facile activation of the sp^2 C–H bonds of aromatic compounds and an olefin by a diphosphine and hydrido-bridged diiridium complex, $[(Cp^*Ir)_2(\mu-dmpm)(\mu-H)_2]^{2+}$ (**1**) [$Cp^* = \eta^5-C_5Me_5$, $dmpm = \text{bis}(\text{dimethylphosphino})\text{methane}$], in which the cationic $32e^- Ir^{II}-Ir^{II}$ complex, $[(Cp^*Ir)_2(\mu-dmpm)(\mu-H)]^+$ (**2**), would be a true active species [59–61]. In the course of our study on the chemistry of **2**, we have found that the reaction of **2** with vinyl ethers resulted in the activation of the vinylic C–H bond followed by the activation of the sp^2 C–O bond. In this paper, we report the successive activation of C–H and C–O bonds of 2,3-dihydrofuran and ethyl vinyl ether by **2**, which affords μ -vinylidene and μ -vinyl complexes.

2. Results and Discussion

2.1. C–H Activation of 2,3-Dihydrofuran

As we previously reported, the treatment of **1** with methyl triflate at $-30\text{ }^{\circ}\text{C}$ followed by warming to room temperature afforded the $32e^-$ complex **2** as a purple powder, which is highly active for C–H activation [60]. The addition of 2,3-dihydrofuran to the preformed **2** followed by stirring at $0\text{ }^{\circ}\text{C}$ for 18 h gave complex **3** in an isolated yield of 70% via selective C–H activation at the 5-position and iridation at the 4-position (Equation (1)). We have already reported the regioselective C–H activation of furan at the 2-position by the reaction with preformed **2**, giving stable product without C–O bond activation [59]. In the ^1H NMR spectrum of **3**, two doublets due to hydrides were observed at $\delta -16.27$ ($J_{\text{PH}} = 32\text{ Hz}$) and -18.23 ($J_{\text{PH}} = 42\text{ Hz}$), which indicated that these hydrides coordinated to each iridium center with terminal fashion. In the $^{13}\text{C}\{^1\text{H}\}$ NMR, a signal due to C^5 was observed at a lower field ($\delta 220.4$), which indicated its carbene character. On the other hand, a signal due to C^4 was observed at a relatively high field ($\delta 47.4$). By considering these signal patterns, the structure of **3** can be described as oxacarbene (I) rather than μ -vinyl (II) [62], which would be simply formed via the C–H activation at the right iridium center followed by the coordination of $\text{C}=\text{C}$ moiety to the left iridium center (Figure 1). The structure of **3** was confirmed by X-ray diffraction study (details are indicated in the Supplementary Materials). The molecular geometry of **3** is shown in Figure 2. The length of the $\text{Ir}(1)\text{--C}(26)$ bond [$1.978(11)\text{ \AA}$] is slightly longer than that of typical iridium-carbon double bond [63,64] but it is considerably shorter than that of the iridium-alkenyl carbon single bond [65,66]. The distance between $\text{Ir}(2)$ and $\text{C}(26)$ [$2.875(12)\text{ \AA}$] indicates that there is no bonding interaction. Therefore, the solid state structure of **3** can be described as the oxacarbene (I).

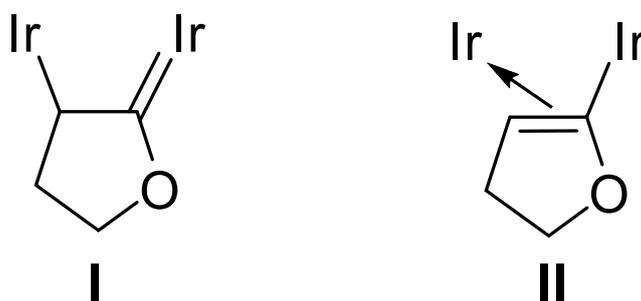
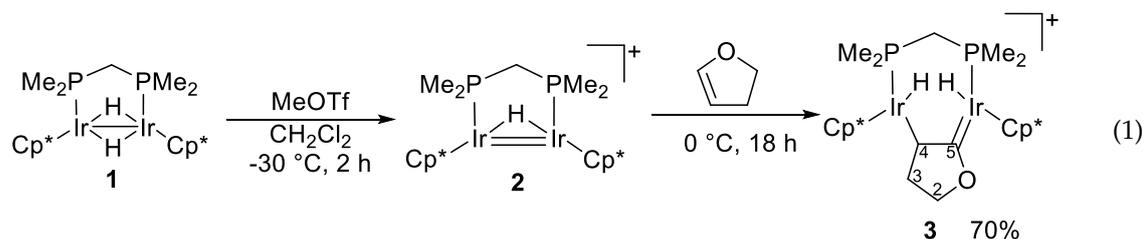


Figure 1. Binding modes in the complex **3**.

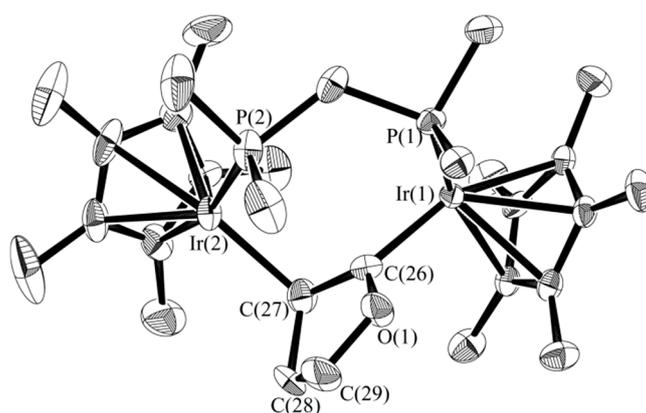


Figure 2. ORTEP drawing of the cationic part of **3**. Hydrogen atoms are omitted for clarity.

2.2. C–O Bond Activation of **3**

In a dichloromethane solution, complex **3** was slowly converted to a μ -vinylidene complex **4**, which was formed by the activation of the C–O bond (Equation (2)). After the reaction at room temperature for 150 h, the quantitative formation of **4** was observed. In the ^1H NMR spectrum of **4**, a signal due to the bridging hydride was observed at $\delta -17.97$ as a triplet ($J_{\text{PH}} = 11$ Hz), and a signal due to the vinylic proton was observed at $\delta 5.21$. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, the signals due to the α - and β -carbon of the vinylidene moiety were observed at $\delta 192.5$ and 121.8 , respectively. These signal patterns are very similar to those of the vinylidene-bridged diiridium complexes, which have been previously reported by Cowie et al. [67,68]. The structure of **4** was unequivocally confirmed by X-ray diffraction study (Figure 3, details are indicated in the Supplementary Materials).

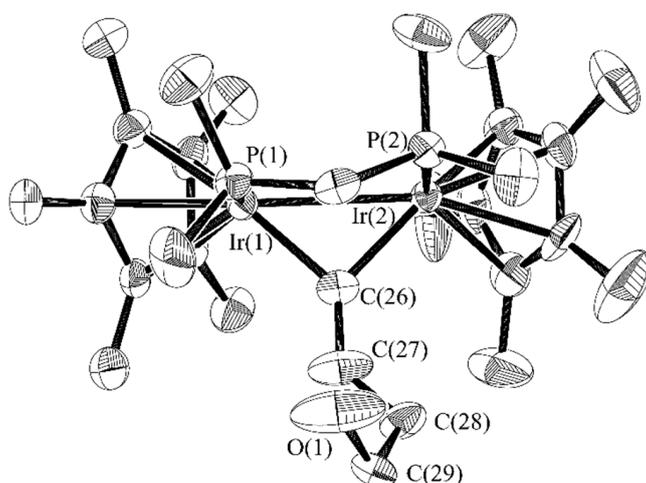
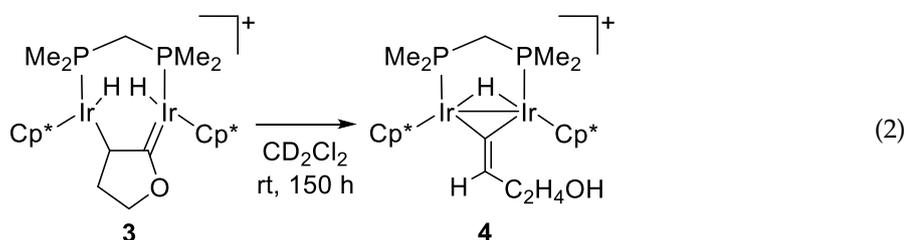
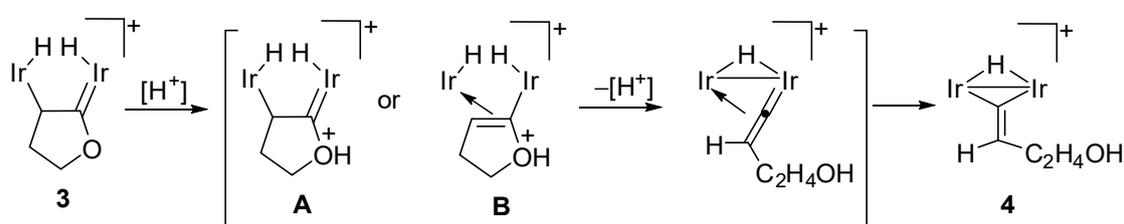


Figure 3. ORTEP drawing of the cationic part of **4**. Hydrogen atoms are omitted for clarity.

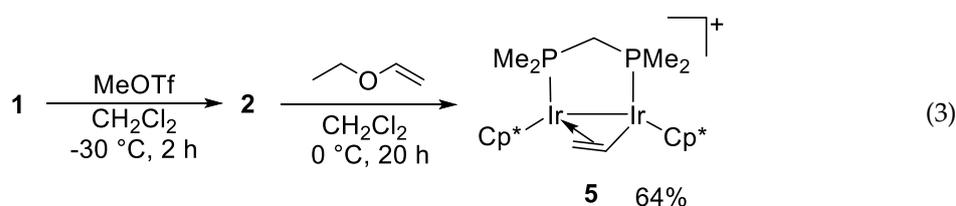
The proton-mediated ring opening reaction of a [5-(2,3-dihydrofuranyl)]ruthenium complex has been reported by Gunnoe [48]. Thus, we next examined the effect of Brønsted acid and base towards the conversion of **3** into **4**. When the solution of **3** in dichloromethane containing acetic acid (0.9 equiv.) was stirred at room temperature, complete conversion into **4** was observed after 75 h, while the reaction in the absence of the acid required 150 h (vide supra). The employment of stronger acid resulted in the formation of unidentified byproduct, probably by the unexpected decomposition of the intermediate. On the other hand, the addition of a base (2,2,6,6-tetramethylpiperidine) suppressed the conversion into **4** (similar reaction of **3** in the presence of 2,2,6,6-tetramethylpiperidine (1.8 equiv.) resulted in the formation of **4** in ca. 10% yield after 100 h). The employment of other base gave rise to the formation of other byproduct, probably formed by the ligation to the iridium centers. These results obviously suggest that the C–O bond cleavage is proton-mediated. A plausible pathway for the transformation of **3** into **4** is as follows (Scheme 1): First, protonation at the oxygen atom in **3** affords **A** or **B**. Then, the C–O bond cleavage and elimination of one of the iridium hydrides as a proton occurs to give product **4**. It should be noted that this pathway corresponds to the reverse reaction of intramolecular hydroalkoxylation of 3-butyne-1-ols to produce 2,3-dihydrofurans [69].



Scheme 1. Plausible pathway for the transformation of **3** into **4**.

2.3. Successive Activation of C–H and C–O Bonds of Ethyl Vinyl Ether

We next studied the reactivity of **2** with acyclic vinyl ether. The reaction of the preformed **2** with ethyl vinyl ether at 0 °C for 20 h gave a μ -vinyl complex **5** in an isolated yield of 64% with a concomitant formation of ethanol (Equation (3)) (similar reactions of **2** with *n*-butyl vinyl ether and isopropyl vinyl ether gave the same μ -vinyl complex **5** accompanied by the release of 1-butanol and 2-propanol, respectively). In the ^1H NMR spectrum of **5**, the two signals due to Cp* ligands were non-equivalently observed at δ 1.93 and 1.78 and three signals due to μ -vinyl protons were observed at δ 7.62, 3.82, and 2.02. No signals for hydrides were observed. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, the signals due to the μ -vinyl carbons were observed at δ 113.2 (C^α) and 45.6 (C^β). All the NMR data of **5** were consistent with the proposed structure, and the signal patterns were similar to the related dicationic μ -vinyl complex $[(\text{Cp}^*\text{Ir})_2(\mu\text{-dmpm})(\mu\text{-CH=CH}_2)(\mu\text{-H})][\text{OTf}]_2$, which was previously reported by us [70]. In addition, the structure of **5** was confirmed by X-ray diffraction study (Figure 4, details are indicated in the Supplementary Materials).



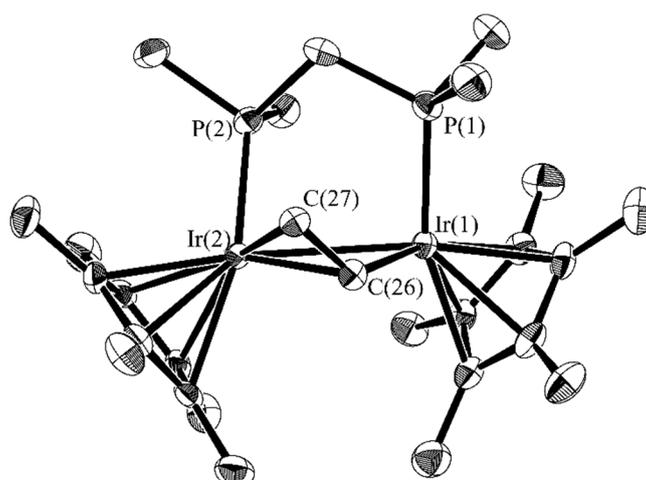


Figure 4. ORTEP drawing of the cationic part of **5**. Hydrogen atoms are omitted for clarity.

To obtain information concerning the mechanism of the formation of **5**, the reaction of **2** with ethyl vinyl ether was monitored by the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR analyses from $-40\text{ }^\circ\text{C}$ to room temperature. At the early stage of the reaction (45 min at $-40\text{ }^\circ\text{C}$, 75% conversion of **2**), the formation of an intermediate **C** (Figure 5, ca. 30% yield) was observed, which was afforded by the C–H activation of terminal vinyl moiety in ethyl vinyl ether. In addition to **C**, the formation of other two species, those might be intermediates in the transformation of **C** to **5**, was observed during the NMR monitoring. However, we could not determine their structures so far. The observed ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR signals for **C** are as follows: In the ^1H NMR spectrum, two signals due to hydrides were observed at $\delta -16.76$ (terminal) and at $\delta -26.05$ (bridge), which is a typical signal pattern for the C–H activation product formed from **2** [60]. The signals due to two vinylic protons were observed at $\delta 6.72$ and 5.74 . These signals were mutually coupled ($J_{\text{HH}} = 6\text{ Hz}$), indicating cis configuration of the alkenyl moiety. The signals for ethoxy group were found at $\delta 3.68$ and 1.23 . In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, two signals were observed at $\delta -34.8$ and -42.9 as doublets coupling to each other ($J_{\text{PP}} = 52\text{ Hz}$). Upon warming the sample to room temperature, the intermediate **C** disappeared, and **5** was formed quantitatively accompanied by the release of ethanol. Although the detailed mechanism for the C–O activation (**C** to **5**) is currently not clear, we believe that this is also a proton-mediated process, similar to the formation of **3**.

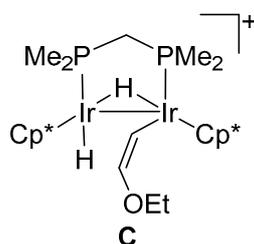


Figure 5. Structure of intermediate **C**.

3. Materials and Methods

3.1. General

All manipulations were performed under a dry argon atmosphere with standard Schlenk techniques. ^1H NMR spectra were measured with JEOL EX-270 and JEOL A-500 spectrometers (JEOL Ltd., Tokyo, Japan). Elemental analyses were carried out at the Microanalysis Center of Kyoto University. The complex **1** was prepared according to the literature [60]. Solvents were dried by

using standard procedures and distilled prior to use. Other reagents were used as obtained from commercial sources.

3.2. C–H Bond Activation of 2,3-dihydrofuran to Give 3

A two-necked 30 mL flask was charged with **1** (238 mg, 0.299 mmol) and dichloromethane (6 mL) at $-30\text{ }^{\circ}\text{C}$. Methyl triflate (49.1 mg, 0.299 mmol) was added to the solution and the reaction mixture was stirred for 2 h. After the removal of the solvent in vacuo at $-30\text{ }^{\circ}\text{C}$, the flask was warmed to room temperature. The brown solid was turned into purple. To the purple solid, 2,3-dihydrofuran (6 mL) was added at $-30\text{ }^{\circ}\text{C}$ and stirred for 18 h at $0\text{ }^{\circ}\text{C}$. After the removal of the solvent in vacuo, the washing of the residue with toluene and hexane gave the light yellow powder of **3** (213 mg, 70%). ^1H NMR (500 MHz, CD_2Cl_2): δ 4.23 (1H, d, $J = 5\text{ Hz}$, C=CH–), 4.04–3.88 (2H, m, O–CH₂–CH₂), 2.49 (1H, m, CH–CHH–CH₂), 1.91 (15H, d, $J = 3\text{ Hz}$, Cp*), 1.87 (15H, s, Cp*), 1.76 (3H, d, $J = 10\text{ Hz}$, PMe), 1.66 (d, $J = 9\text{ Hz}$, PMe and overlapped CH–CHH–CH₂), 1.65 (3H, d, $J = 10\text{ Hz}$, PMe), 1.53 (3H, d, $J = 10\text{ Hz}$, PMe), -16.27 (1H, d, $J = 32\text{ Hz}$, Ir–H), -18.23 (1H, d, $J = 42\text{ Hz}$, Ir–H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.65 MHz, CD_2Cl_2): δ 220.4 (m, Ir–C), 121.4 (q, $J = 322\text{ Hz}$, CF₃), 95.7 (d, $J = 2\text{ Hz}$, C₅Me₅), 95.0 (d, $J = 2\text{ Hz}$, C₅Me₅), 75.5 (s, O–CH₂–CH₂), 47.4 (s, C=CH), 39.1 (s, CH–CHH–CH₂), 26.6 (dd, $J = 43\text{ Hz}$, 35 Hz, P–CH₂–P), 22.8 (dd, $J = 39\text{ Hz}$, 5 Hz, PMe), 22.1 (d, $J = 32\text{ Hz}$, PMe), 21.8 (dd, $J = 35\text{ Hz}$, 5 Hz, PMe), 17.2 (d, $J = 33\text{ Hz}$, PMe), 10.7 (s, C₅Me₅), 10.2 (s, C₅Me₅). $^{31}\text{P}\{^1\text{H}\}$ NMR (109.25 MHz, CD_2Cl_2): δ -33.2 (d, $J = 8\text{ Hz}$), -41.7 (d, $J = 8\text{ Hz}$). Anal calcd for C₃₀H₅₁F₃Ir₂O₄P₂S: C, 35.63; H, 5.08. Found: C, 35.35; H, 5.01.

3.3. Conversion of 3 into Vinylidene Complex 4

In a NMR tube, **3** (21.8 mg, 0.0216 mmol) and CD_2Cl_2 (0.6 mL) were placed. The progress of the reaction was monitored by ^1H NMR analysis. Quantitative conversion of **3** into the μ -vinylidene complex **4** was observed after 150 h. Samples for the elemental analysis were obtained by the slow diffusion of hexane into a dichloromethane solution of **4**. ^1H NMR (500 MHz, CD_2Cl_2): δ 5.21 (1H, m, C=CH), 3.69–3.57 (2H, m, CH₂–CH₂–OH), 2.67 (m, 1H, =CH–CHH–CH₂), 2.39 (m, 1H, =CH–CHH–CH₂), 2.02 (15H, s, Cp*), 1.91 (15H, s, Cp*), 1.63–1.56 (9H, m, 3 PMe), 1.48 (3H, d, $J = 8\text{ Hz}$, PMe), -17.97 (1H, t, $J = 11\text{ Hz}$, Ir–H–Ir). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.65 MHz, CD_2Cl_2): δ 192.5 (t, $J = 9\text{ Hz}$, Ir–C–Ir), 121.8 (s, C=CH), 121.3 (q, $J = 322\text{ Hz}$, CF₃), 96.5 (d, $J = 2\text{ Hz}$, C₅Me₅), 95.9 (d, $J = 2\text{ Hz}$, C₅Me₅), 63.9 (s, CH₂–CH₂–OH), 39.0 (s, CH–CH₂–CH₂), 23.1 (t, $J = 37\text{ Hz}$, P–CH₂–P), 20.1–19.6 (m, two PMe carbons), 15.6 (dd, $J = 32\text{ Hz}$, 15 Hz, PMe), 13.0 (dd, $J = 35\text{ Hz}$, 13 Hz, PMe), 11.1 (s, C₅Me₅), 10.4 (s, C₅Me₅). $^{31}\text{P}\{^1\text{H}\}$ NMR (109.25 MHz, CD_2Cl_2): δ -14.84 , -14.86 . Anal calcd for C₃₀H₅₁F₃Ir₂O₄P₂S: C, 35.63; H, 5.08. Found: C, 35.58; H, 4.97.

3.4. Reaction of Complex 1 with Ethyl Vinyl Ether to Give 5

After the treatment of complex **1** (202 mg, 0.255 mmol) with MeOTf (41.8 mg, 0.255 mmol) similar to the procedure described above (Section 3.2), ethyl vinyl ether (5 mL) and dichloromethane (2.5 mL) were added to the purple residue. The solution was stirred at $0\text{ }^{\circ}\text{C}$ for 20 h then volatiles were removed in vacuo. The residue was washed with toluene to give the orange powder of **5** (157 mg, 64%). ^1H NMR (500 MHz, CD_2Cl_2): δ 7.62 (1H, m, Ir–CH=), 3.82 (1H, m, –CH=CHH), 3.12 (1H, m, P–CHH–P), 2.23 (1H, m, P–CHH–P), 2.02 (m, –CH=CHH and overlapped PMe), 1.93 (15H, d, $J = 2\text{ Hz}$, Cp*), 1.78 (15H, d, $J = 3\text{ Hz}$, Cp*), 1.67 (3H, d, $J = 10\text{ Hz}$, PMe), 1.67 (3H, d, $J = 11\text{ Hz}$, PMe), 1.49 (3H, d, $J = 11\text{ Hz}$, PMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.65 MHz, CD_2Cl_2): δ 121.4 (q, $J = 320\text{ Hz}$, CF₃), 113.2 (dd, $J = 7\text{ Hz}$, 2 Hz, Ir–C), 94.7 (d, $J = 2\text{ Hz}$, C₅Me₅), 94.1 (d, $J = 3\text{ Hz}$, C₅Me₅), 45.7 (d, $J = 6\text{ Hz}$, CH=CH₂), 29.1 (d, $J = 46\text{ Hz}$, PMe), 19.9 (d, $J = 39\text{ Hz}$, PMe), 17.6 (dd, $J = 36\text{ Hz}$, 9 Hz, PMe), 16.6 (dd, $J = 32\text{ Hz}$, 11 Hz, PMe), 10.7 (s, C₅Me₅). $^{31}\text{P}\{^1\text{H}\}$ NMR (109.25 MHz, CD_2Cl_2): δ -34.8 (d, $J = 52\text{ Hz}$), -42.9 (d, $J = 52\text{ Hz}$). Anal calcd for C₂₈H₄₇F₃Ir₂O₃P₂S: C, 34.77; H, 4.90. Found: C, 34.47; H, 4.78.

4. Conclusions

We described the successive C–H and C–O bond activation of vinyl ethers by a diphosphine and hydrido-bridged diiridium complex. In the reaction of **2** with 2,3-dihydrofuran, a rapid C–H activation at the 5-position occurred to afford dinuclear oxacarbene complex **3**, which was slowly converted into μ -vinylidene complex **4** via the C–O activation mediated by a proton. On the other hand, the reaction of **2** with ethyl vinyl ether resulted in the rapid successive activation of the C–H and C–O bonds to give the μ -vinyl complex **5**. It should be noted that the activation of the sp^2 C–O bond in vinyl ethers is very rare, and the results shown here provide important information regarding the activation of vinyl ethers by transition metal complexes.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2304-6740/7/10/121/s1>, results of X-ray diffraction studies of the complexes **3–5**; the cif and checkcif output files for **3–5**.

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Conflicts of Interest: The authors declare no conflict of interest.

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