

# Synthesis of Fischer Carbene Complexes of Iridium by C–H Bond Activation of Methyl and Cyclic Ethers: Evidence for Reversible $\alpha$ -Hydrogen Migration

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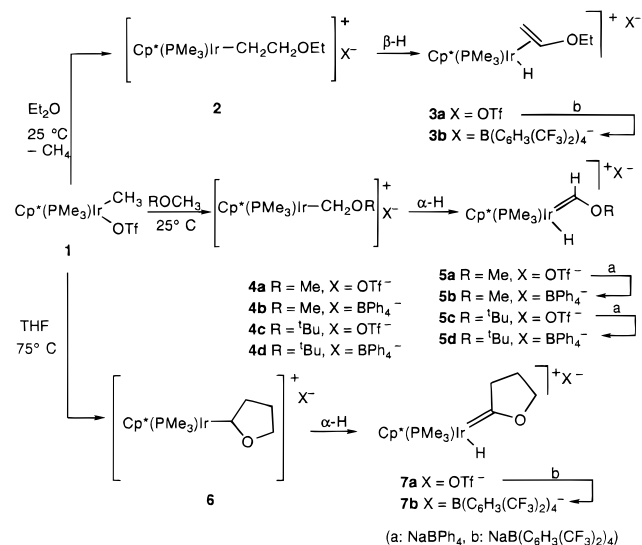
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Since the discovery of the first stable example in 1964,<sup>1</sup> the study and use of transition-metal carbene complexes has flourished. However, the most intense investigation has been focused on carbene complexes of metals in groups 5–7, while less is known about the reactivity of carbene complexes of groups 8–10, though these late-metal carbene complexes have been implicated as reactive intermediates in several catalytic processes.<sup>2</sup> This apparent lack of study is perhaps due to the small number of rational synthetic methods available to generate these complexes. We report here a mild and versatile route to Fischer carbene complexes of iridium via the activation of C–H bonds of methyl and cyclic ethers, along with our preliminary studies of this rare<sup>3–6</sup> family of carbene complexes.

We demonstrated earlier<sup>7</sup> that the Ir(III) complex Cp\*(PMe<sub>3</sub>)Ir(Me)(OTf) (**1**) (Cp\* =  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>, OTf = OSO<sub>2</sub>CF<sub>3</sub>) is capable of activating a variety of alkane and arene C–H bonds. These studies also revealed that the thermodynamic product of C–H bond activation often involves subsequent rearrangement of the initially formed complex, presumably due to the lability of the triflate ligand and the generation of a coordinatively unsaturated cationic intermediate. We have now found that (1) triflate **1** reacts with diethyl ether at 75 °C, presumably *via* methyl-activated intermediate **2**, to give methane and hydrido (methyl vinyl ether) complex **3** in 87% yield and (2) in contrast, **1** reacts with methyl ethers (ROME, R = Me, <sup>t</sup>Bu) at 25 °C to give cationic hydridocarbene complexes Cp\*(PMe<sub>3</sub>)Ir(H)(=C(H)(OR))<sup>+</sup>OTf<sup>–</sup> (R = Me (**5a**), <sup>t</sup>Bu (**5c**)). Due to poor crystallinity of the triflate salts, the anion was exchanged with sodium tetraphenylborate, and the carbene complex salts **5b,d** were isolated in ~86% yield after recrystallization (Scheme 1). These complexes exhibit characteristic low-field resonances in both their <sup>1</sup>H ( $\delta$  ~13 ppm) and <sup>13</sup>C NMR ( $\delta$  ~250 ppm) spectra corresponding to the  $\alpha$ -hydrogen and  $\alpha$ -carbon atoms of the carbene ligand, as well as a high-field resonance at ~–16 ppm in the <sup>1</sup>H NMR spectrum characteristic of terminal iridium(III) hydrides. The hydride resonances appear as doublets (<sup>2</sup>J<sub>P–H</sub> ≈ 14 Hz) due to coupling to the <sup>31</sup>P nuclei of the trimethylphosphine ligands, but the  $\alpha$ -hydrogen resonances appear as broad singlets with no distinct three-bond <sup>31</sup>P coupling.

This process can be extended to the formation of a cyclic carbene complex by C–H activation of THF. Thermolysis of **1** in THF at 75 °C for 6 h results in the formation of cyclic carbene complex **7** (82% yield following anion metathesis with

Scheme 1



NaB(C<sub>6</sub>H<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>)<sub>4</sub>) with the release of CH<sub>4</sub>. This reaction is of additional importance in that it represents the first example of secondary sp<sup>3</sup> C–H bond activation by **1**. The <sup>13</sup>C NMR spectrum of **7b** contains a low-field resonance at  $\delta$  256 ppm, which is consistent with the  $\alpha$ -carbon chemical shifts observed for **5b,d**. Additionally, the <sup>1</sup>H NMR spectrum of **7b** contains a hydride resonance at  $\delta$  –16.4 ppm. A single-crystal X-ray diffraction study of **7b** (see ORTEP diagram in supporting information, Figure S-1) reveals an Ir–C<sub>α</sub> bond distance of 1.930(8) Å and planar geometry about C<sub>α</sub>. A peak in the difference Fourier map was ascribed to the hydride ligand, but its position was not refined.

The formation of **5b,d** and **7b** presumably proceeds by initial C–H bond activation to form the intermediate cationic iridium alkyl complexes **4a,c** and **6**, which subsequently rearrange to the observed hydridocarbene complexes by a rapid  $\alpha$ -hydrogen migration<sup>8–15</sup> (Scheme 1). Theoretical studies suggest that  $\alpha$ -hydrogen migrations can be kinetically favorable if a coordinatively unsaturated species can be accessed.<sup>16,17</sup> Thus, the lability of the triflate ligand presumably facilitates this process. Further evidence for the rapidity, as well as reversibility, of this rearrangement was obtained by NMR analysis. Broadening of the hydride and  $\alpha$ -hydrogen resonances was observed in variable-temperature NMR studies of methoxycarbene complex **5b**, but thermal decomposition has prevented the measurement of an accurate coalescence temperature. We therefore turned to spin saturation transfer experiments to examine this process. Upon irradiation of either the hydride or the  $\alpha$ -hydrogen resonance, significant spin saturation transfer (SST) was ob-

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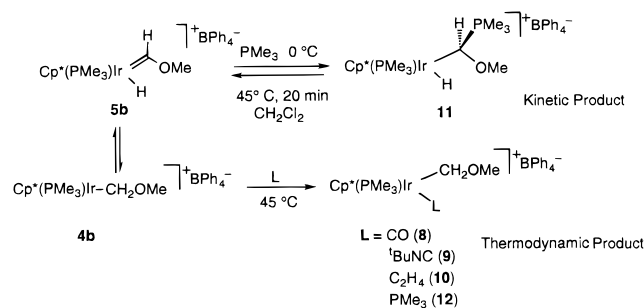
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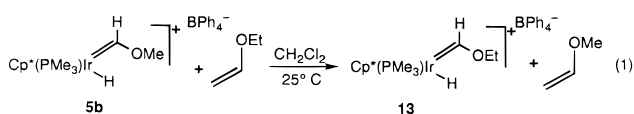
## Scheme 2



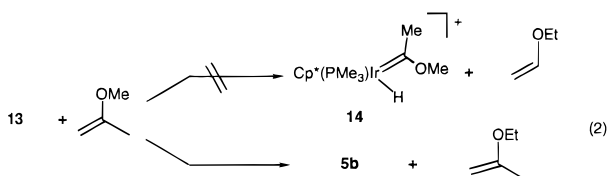
served down to  $-29.2^\circ\text{C}$  between the two sites, indicating that these protons are exchanging rapidly (several other reversible  $\alpha$ -H migrations are now known<sup>8,10,18,19</sup>). The small coupling constant between the hydride and the  $\alpha$ -carbon ( $^3J_{\text{C-H}} \approx 3$  Hz) suggests that there is no unusual one-bond interaction between these nuclei responsible for the facility of the exchange.

Additional evidence for reversible  $\alpha$ -hydrogen migration is found by trapping the intermediate alkoxy methyl species **4** using a variety of Lewis bases. The addition of CO, <sup>t</sup>BuNC, and C<sub>2</sub>H<sub>4</sub> to a CH<sub>2</sub>Cl<sub>2</sub> solution of hydridocarbene complex **5b** at  $25^\circ\text{C}$  resulted in rapid formation of the trapped complexes **8–10** (Scheme 2). Further, thermolysis of **5b** in THF at  $105^\circ\text{C}$  for 3 h results in the formation of **7** and dimethyl ether. This is consistent with reversible generation of unsaturated intermediate **4**, which is capable of activating C–H bonds in a manner analogous to that of **1**. However, the addition of trimethylphosphine at  $0^\circ\text{C}$  to a CH<sub>2</sub>Cl<sub>2</sub> solution of **5b** resulted in the formation of the trimethylphosphine adduct **11** (Scheme 2). Thermolysis of kinetic product **11** resulted in rearrangement to the thermodynamic product of the reaction, **12**, which is analogous to the other Lewis base adducts (**8–10**). We assume that this occurs by reversion of **11** to **5b** (Scheme 2) at the higher reaction temperature.

The cationic hydridocarbene complexes **5** undergo unprecedented reactions with alkyl vinyl ethers. Addition of 2 equiv of ethyl vinyl ether to a CD<sub>2</sub>Cl<sub>2</sub> solution of **5b** resulted in the gradual formation of a product exhibiting a new  $\alpha$ -hydrogen resonance at  $\delta$  13.88 ppm, indicating the formation of a new secondary carbene complex. The isolated products of the

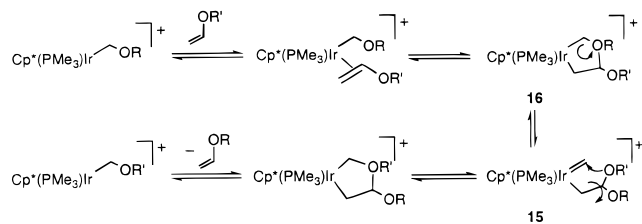


reaction were determined to be the ethoxy-substituted Fischer carbene complex **13** (83% yield) and methyl vinyl ether (77% yield by <sup>1</sup>H NMR). To determine whether this reaction involves cleavage of the carbon–carbon double bond (alkene metathesis), we examined the reaction of ethoxycarbene complex **13** with 2-methoxypropene. Olefin metathesis product **14** was not observed; instead, exclusive formation of **5b** (96%) and 2-ethoxypropene (93%) was observed. This result requires that the alkene C=C bond is preserved in the exchange process.



To further probe the mechanism of this reaction, we synthesized <sup>17</sup>O-enriched carbene complex **5a** by the reaction of **1** with CH<sub>3</sub><sup>17</sup>OCH<sub>3</sub> and treated this labeled material with ethyl vinyl ether. Analysis of the products **13** and methyl vinyl

## Scheme 3



ether by <sup>17</sup>O NMR revealed that the <sup>17</sup>O label was exclusively located in the methyl vinyl ether product. This result indicates that the exchange involves formal transfer of alkoxy groups between the alkoxy carbene complex and the vinyl ether. To rule out the possibility that the exchange reaction is catalyzed by free alcohol, the reaction of **5b** and ethyl vinyl ether was run in the presence of 1 equiv of CH<sub>3</sub>CD<sub>2</sub>OH. Analysis of the carbene product **13** by <sup>2</sup>H NMR revealed that <5% deuterium was incorporated into the carbene product during the exchange.

The above experiments rule out the conventional mechanisms that we can conceive of for the vinyl ether exchange. In light of the rapid reactivity of **5b** with  $\pi$  bases such as ethylene, we suggest that the exchange involves initial formation of an alkene adduct, which undergoes an intramolecular attack by the pendant alkoxy group, leading to cyclic intermediate **16**, as illustrated in Scheme 3. The intermediate can then undergo C–O bond cleavage to form cationic methylene complex **15** and return along an analogous pathway to accomplish the exchange. This mechanism is consistent with all observed experimental results and finds additional precedent in the intermolecular reactivity of iridium alkoxy methyl complexes with electrophilic carbon centers.<sup>20</sup>

In conclusion, we have found a C–H bond activation route that provides mild and general synthetic access to Fischer carbene complexes of iridium. The reversible  $\alpha$ -hydrogen migration that these complexes undergo provides an unusual opportunity for reactivity at both the metal center and the carbene ligand. We have also discovered an unprecedented reaction between the cationic carbene complexes and vinyl ethers that formally involves alkoxy group exchange. Future studies will focus on additional chemistry of the hydridocarbene complexes and experiments designed to confirm the proposed mechanism and test the catalytic utility of the vinyl ether exchange.

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**Supporting Information Available:** Spectroscopic and analytical data for **3–13** and X-ray diffraction data (ORTEP diagrams, crystal and data collection parameters, positional parameters, and intramolecular distances and angles) for **7b** (17 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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