

# Unusual Me–O Bond Cleavage in a Metalated Crown-Ether: X-ray Molecular Structure of (5-Methoxy-4,6-dimethyl-1,3-xylylene-2-one)-15 Crown-4 Complex of Pentamethylcyclopentadienyl Iridium

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Received July 14, 1998

The reaction of  $[(C_5Me_5)Ir(Solvent)_3][BF_4]_2$  (**1**) with (2,5-dimethoxy-4,6-dimethyl-1,3-xylylene)-15 crown-4 (**2**) affords the metalated crown-ether complex  $[(\eta^5-C_5Me_5)Ir(\eta^6-C_{18}H_{28}O_6)][BF_4]_2$  (**3**) in 88% yield. Complex **3** undergoes a facile Me–O bond cleavage to give the related semiquinone form of the metalated crown-ether  $[(\eta^5-C_5Me_5)Ir(\eta^5-C_{17}H_{25}O_6)][BF_4]$  (**4**). A single-crystal X-ray structure determination of complex **4** is reported. Complex **4** crystallizes in the monoclinic space group  $P2_1/m$  with  $a = 8.187(5)$  Å,  $b = 17.193(4)$  Å, and  $c = 10.900(3)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 109.68(1)^\circ$ ,  $\gamma = 90^\circ$ , and  $Z = 2$ . The structure provides us with valuable information about the nature of the  $\eta^5$ -semiquinone form of the metalated crown-ether and reveals that, surprisingly, the Me–O unit close to the crown chain is the one that undergoes hydrolysis. A rationale consistent with the experimental results is advanced.

## Introduction

Pentamethylcyclopentadienyl iridium ( $C_5Me_5Ir$ ) is a very stabilizing entity, and its coordination chemistry toward arenes has been the focus of intense investigation, thus providing thermodynamically stable complexes of the type  $[(C_5Me_5)Ir(\eta^6-arene)][BF_4]_2$ .<sup>1</sup> Recent studies in our laboratory have shown the capacity of this metal to stabilize sensitive semiquinone ligands.<sup>2</sup> The hydroquinone iridium complex  $[(C_5Me_5)Ir(\eta^6-hydroquinone)][BF_4]_2$  can be easily deprotonated by a base to give the related semiquinone and *p*-benzoquinone complexes  $[(C_5Me_5)Ir(\eta^5-semiquinone)][BF_4]$  and  $[(C_5Me_5)Ir(\eta^4-p-benzoquinone)]$ , respectively.<sup>2</sup> The latter can be protonated to give the starting material without showing any sign of decomposition (Scheme 1). The fascinating stabilizing properties of the  $C_5Me_5Ir$  moiety have stimulated us to study its coordination chemistry toward more complex molecules in which the hydroquinone or, more specifically, its dimethyl ether is incorporated in a crown-ether system (Scheme 2). Although the chemistry of crown-ethers and their use for cation binding are well documented in the literature,<sup>3</sup> less is known about related metalated crown-ether and the influence of “metal-modifica-

tions” on the binding properties of such metalated crown-ethers. However, we note that Steed and Atwood have elegantly reported that the cavity of a cationic calixarene tetrairidium complex is capable of selective anion binding.<sup>4</sup> In addition to the reasons just mentioned, such complexes represent an attractive target in the area of organometallic architecture and hence their coordination and functionalization by an iridium center is an exciting prospect.

In this work we report on the synthesis and reactivity of the dicationic iridium crown-ether complex  $[(\eta^5-C_5Me_5)Ir(\eta^6-C_{18}H_{28}O_6)][BF_4]_2$  (**3**) obtained in a straightforward manner from crown-ether **2**. Surprisingly and interestingly, complex **3** undergoes facile Me–O bond cleavage to give the related semiquinone form of the metalated crown-ether  $[(\eta^5-C_5Me_5)Ir(\eta^5-C_{17}H_{25}O_6)][BF_4]$  (**4**), identified spectroscopically and by X-ray analysis. The solution behavior and reactivity of **4** is presented and discussed and a rationale to explain the facile cleavage of the Me–O bond is offered.

## Results and Discussion

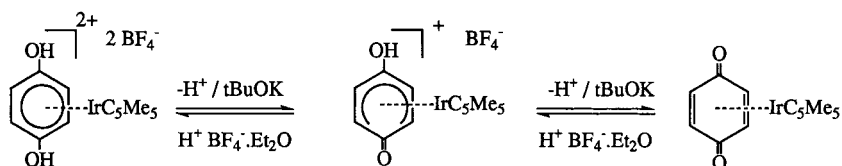
Treatment of  $[(C_5Me_5)Ir(Solvent)_3][BF_4]_2$  (**1**) prepared in situ with (2,5-dimethoxy-4,6-dimethyl-1,3-xylylene)-15 crown-4 (**2**)<sup>5</sup>

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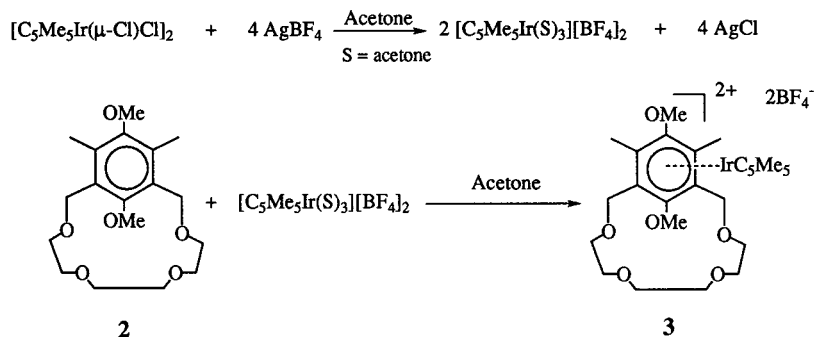
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## Scheme 1



## Scheme 2



in acetone for several hours and reaction workup provided the new dicationic metallic crown-ether **3** in 88% yield (Scheme 2). The spectroscopic data for **3** are in accord with the proposed formula. For instance, the proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectrum of **3** recorded in  $\text{CD}_3\text{CN}$  shows dramatic changes in the chemical shifts of the two methoxy groups, from 3.63 and 3.64 ppm for the free crown-ether **2** to 3.82 and 4.35 ppm, respectively, for complex **3**. Furthermore, the crown-ether signals are slightly deshielded (0.1–0.3 ppm shift downfield). The  $^1\text{H}$  NMR spectrum also shows a singlet at 2.03 ppm that is attributed to the methyl protons of  $\eta\text{-C}_5\text{Me}_5\text{Ir}$ , whereas the benzylic protons  $-\text{CH}_2-$  resonate as an AB-system at 4.40 ppm.

When the reaction just described was allowed to continue for 24 h, a new complex **4** in addition to **3** was formed. The  $^1\text{H}$  NMR spectrum of this new compound recorded in  $\text{CD}_3\text{CN}$  showed the presence of only one methoxy group at 3.84 ppm, the benzylic protons resonated as a pair of doublets at 3.95 and 4.25 ppm, respectively, and a singlet corresponding to the methyl protons of coordinated  $\text{C}_5\text{Me}_5\text{Ir}$  resonated upfield at 1.89 ppm. Furthermore the signals attributed to the methylene protons of the crown-ether cage ( $-\text{CH}_2\text{CH}_2\text{O}-$ )<sub>3</sub> showed fine splitting and appeared in the area 3.30–3.90, suggesting a dramatic change in their environment relative to that of complex **3**. The  $^{13}\text{C}$  NMR data of **4** were very informative showing, in addition to the signals of the crown-ether, the presence of a singlet at 169.50 ppm attributed to a  $\text{C}=\text{O}$  function of an oxo  $\eta^5$ -dienyl iridium complex, in analogy to the  $^{13}\text{C}$  shifts seen in NMR spectra of other phenoxo-iridium complexes.<sup>6</sup> The infrared spectrum of complex **4** recorded in KBr showed a strong absorption at  $1608 \text{ cm}^{-1}$  attributed to the  $\text{C}=\text{O}$  function. These data suggest that complex **3** undergoes  $\text{Me}-\text{O}$  bond cleavage to give the related semiquinone derivative of the metalated crown-ether (**4**). Interestingly we noticed that the related 2,6-dimethyl-1,4-hydroquinone–dimethyl ether complex  $[(\text{C}_5\text{Me}_5)\text{Ir}(\eta^6\text{-MeO}-\text{C}_6\text{H}_2\text{Me}_2-\text{OMe})][\text{BF}_4]_2$  (**5**) is stable in solution and unlike complex **3** it does not hydrolyze to give the corresponding semiquinone derivative. We have also found that addition of

$\text{NEt}_3$  to a  $\text{CD}_3\text{CN}$  solution of **3** affords instantaneous and quantitative conversion to **4**.

To ascertain the structure of this new species without ambiguity, an X-ray study was performed on a suitable crystal of **4**. Complex  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\eta^5\text{-C}_{17}\text{H}_{25}\text{O}_6)][\text{BF}_4]$  (**4**) crystallizes in the  $P2_1/m$  unit cell. Figure 1 shows the CAMERON views of the cationic portion of the molecule **4** with the atom numbering system. Crystallographic data collection parameters, selected bond lengths and angles are listed in Tables 1 and 2.

The structure confirms the spectroscopic data and shows that the  $\text{C}_5\text{Me}_5\text{Ir}$  moiety is coordinated to only five carbons of the six-membered ring. Loss of aromaticity is manifested by the irregularity of the  $\text{C}-\text{C}$  bond distances of the oxodienyl unit (see Table 2); furthermore, the  $\text{C}11-\text{O}2$  bond distance is  $1.22(1) \text{ \AA}$ , which is a characteristic of a  $\text{C}=\text{O}$  double bond of a ketonic function. We also note that the carbonyl function is bent away from the organometallic unit  $\text{C}_5\text{Me}_5\text{Ir}$  by an angle  $\theta = 21^\circ$ , where  $\theta$  is defined by the dihedral angle along  $\text{C}(12)-\text{C}(12')$ . The structure provides us with valuable information and shows that the methoxy unit close to the crown-ether chain is hydrolyzed (see Figure 1 side view representation). It is noteworthy that the organometallic moiety  $\text{C}_5\text{Me}_5\text{Ir}$  binds to the arene unit but away from the crown-ether cage; therefore, we would expect that the binding properties the crown-ether cage is not affected sterically, at least in the solid state.

At this point, a brief comment on  $\text{Me}-\text{O}$  bond cleavage is appropriate. Cleavage of alkyl aryl ethers has been reported to occur, following treatment with Grignard reagents under drastic conditions.<sup>7</sup> Another method for the cleavage of the  $\text{Me}-\text{O}$  bond of (2-methoxy-1,3-xylylene)-15 crown-4 involves the attack by lithium iodide at  $115^\circ\text{C}$  for several hours; subsequent hydrolysis provides the related (2-hydroxy-1,3-xylylene)-15 crown-4.<sup>8</sup>

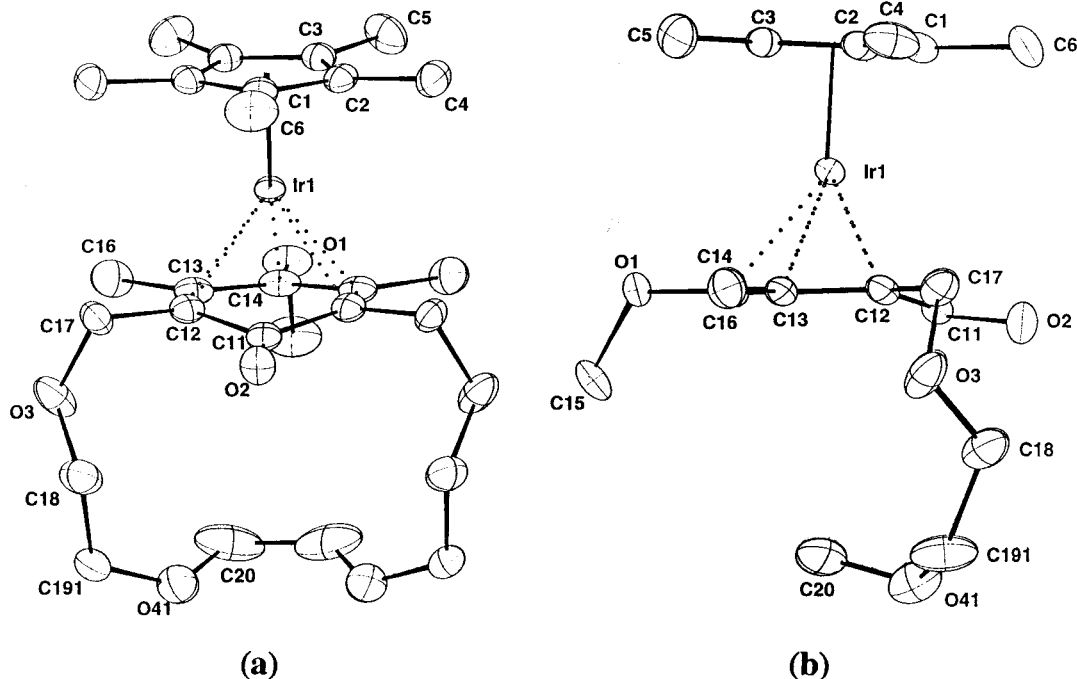
Thus, whereas the  $\text{Me}-\text{O}$  bonds in (2,5-dimethoxy-4,6-dimethyl-1,3-xylylene)-15 crown-4 (**2**) are more reactive than those in normal methoxy arenes, they are stable and resistant to hydrolysis unless treated with a Grignard reagent. In this

(5) This compound was prepared by an improved synthetic procedure of the literature method; see: Delgado, M.; Wolf, E. R., Jr.; Hartman, J. R.; McCafferty, G.; Yagbassan, R.; Rawle, S. C.; Watkin, D. J.; Cooper S. R. *J. Am. Chem. Soc.* **1992**, *114*, 8983.

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**Figure 1.** X-ray molecular structure of cationic portion of complex (**4**). (a) CAMERON view showing the atom-numbering system. Note the presence of a crystallographic mirror plane passing through Ir(1), O(1), and O(2) and dividing the molecule into two equal halves. (b) Side view showing the coordination mode of the  $C_5Me_5Ir$  to only five carbons of the arene, whereas C11—O2 is bent away from the metal and over the crown-ether chain cavity.

**Table 1.** Crystal Data and Structure Refinement for **4**

empirical formula	$[C_{27}H_{40}O_6Ir][BF_4]$
fw	739.6
crystal system	$P2_1/m$
$a$ , Å	8.187(5)
$b$ , Å	17.193(4)
$c$ , Å	10.900(3)
$\alpha$ , deg	90
$\beta$ , deg	109.68(4)
$\gamma$ , deg	90
$V$ , Å <sup>3</sup>	1445(1)
$Z$	2
$\rho$ (calcd), g/cm <sup>3</sup>	1.70
$\mu$ (Mo K $\alpha$ ), cm <sup>-1</sup>	46.6
crystal size, mm	0.18 $\times$ 0.4 $\times$ 1.0
$T$ , °C	20
$\lambda$ (Mo K $\alpha$ ), Å	0.710 69
$R^a$	0.0323
$Rw^b$	0.0433

$$^a R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}. \quad ^b Rw = \frac{[\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}}{\sum w F_o^2}$$

**Table 2.** Selected Bond Distances (Å) and Angles (deg) for **4**

Bond Lengths			
Ir(1)—C(1)	2.167(9)	Ir(1)—C(2)	2.173(6)
Ir(1)—C(3)	2.191(6)	Ir(1)—C(12)	2.235(6)
Ir(1)—C(13)	2.236(6)	Ir(1)—C(14)	2.213(8)
C(11)—O(2)	1.22(1)	C(11)—C(12)	1.473(8)
C(12)—C(13)	1.435(8)	C(13)—C(14)	1.406(8)
C(13)—C(16)	1.516(9)	C(12)—C(17)	1.538(9)
C(17)—O(3)	1.440(8)	O(41)—C(191)	1.38(2)
Bond Angles			
C(12)—C(11)—C(12')	111.9 (7)	C(11)—C(12)—C(13)	122.2(6)
C(12)—C(13)—C(14)	117.5(6)	C(13)—C(14)—C(13')	123.5(8)
C(12)—C(17)—O(3)	107.9(6)	C(17)—O(3)—C(18)	115.2(6)
C(12)—C(11)—O(2)	123.3(4)	C(16)—C(13)—C(12)	121.2(6)

respect, Bickelhaupt has recently reported that (2-methoxy-1,3-xylylene)-15 crown-4 undergoes Me—O bond cleavage when treated with  $Ph_2Mg$  in ether.<sup>9</sup> A detailed mechanism for this Me—O bond cleavage was proposed, involving the crown-ether chain participation. Analysis of the reaction mixture by gas

chromatography (GC) and GC/mass spectroscopy (MS) showed the formation of toluene, which reinforces the premise that Me—O bond cleavage is occurring and not loss of a methoxy group.

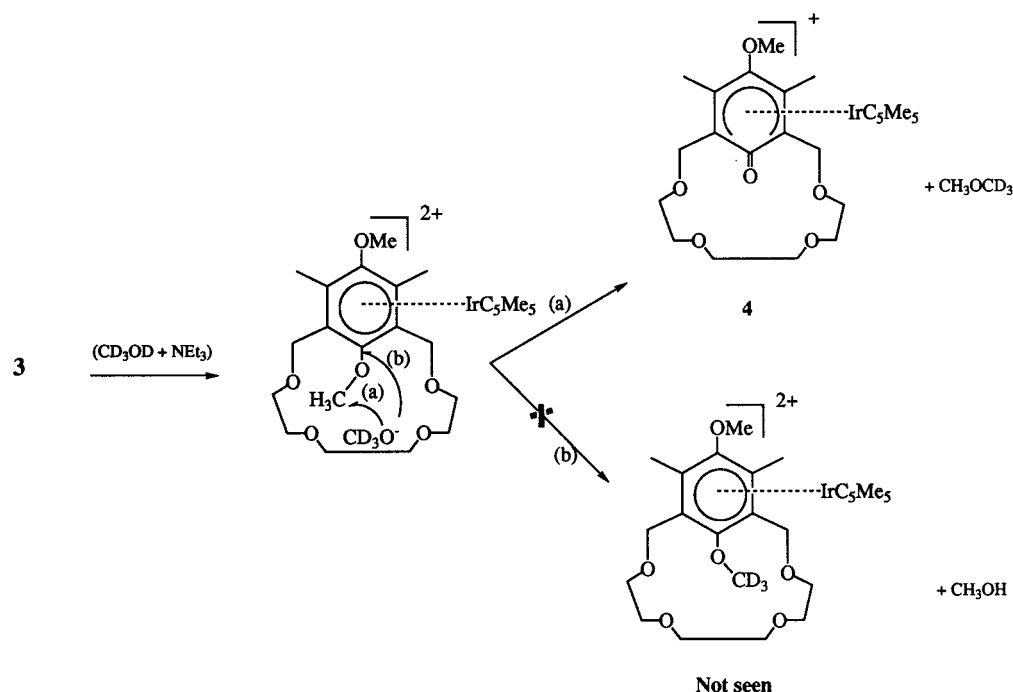
To elucidate the mechanism of formation of  $[(\eta^5-C_5Me_5)Ir(\eta^5-C_{17}H_{25}O_6)][BF_4]$  (**4**), an NMR sample of complex **3** was prepared in  $CD_3OD$  containing  $NEt_3$ , and the reaction was monitored by  $^1H$  NMR. Analysis of the solution mixture showed quantitative formation of **4** and a new singlet at 3.40 ppm, presumably attributed to  $CH_3OCD_3$ . Addition of a small amount of  $CH_3OH$  gave yet another new singlet at 3.34 ppm (chemical shift of  $CH_3OH$  in  $CD_3OD$ ).<sup>10</sup> Thus, in a manner similar to that reported by the Bickelhaupt group, we feel that in complex **3** the Me—O bond of the inner MeO group is cleaved. The oxygen centers of the crown-ether may form hydrogen bonds to the nucleophilic precursor ( $H_2O$  or methanol) before deprotonation by  $NEt_3$ ; subsequent attack at the methyl group of the inner Me—O unit {Scheme 3 path (a)}, labilized by the cationic effect of the  $C_5Me_5Ir^{2+}$  unit, would afford complex **4**. Overall, this pull—push sequence provokes the facile cleavage of the Me—O bond.

Protonation of complex  $[(\eta^5-C_5Me_5)Ir(\eta^5-C_{17}H_{25}O_6)][BF_4]$  (**4**) by  $HBF_4 \cdot Et_2O$  produced the related dicationic phenol—crown-ether complex  $[(\eta^5-C_5Me_5)Ir(\eta^6-C_{17}H_{25}O_6)][BF_4]_2$  (**6**), which was isolated as a white microcrystalline material (Scheme 4). The  $^1H$  NMR of **6** recorded in  $CD_3CN$  showed remarkable changes relative to the starting material; for examples, the benzylic protons changed in morphology and appeared as an AB-system centered at 4.50 ppm, the crown-ether signals are slightly deshielded (0.1–0.3 ppm shift downfield) compared with the starting material **4**, and the singlet attributed to the methyl protons of  $\eta^5-C_5Me_5Ir$  is now centered at 2.01 ppm

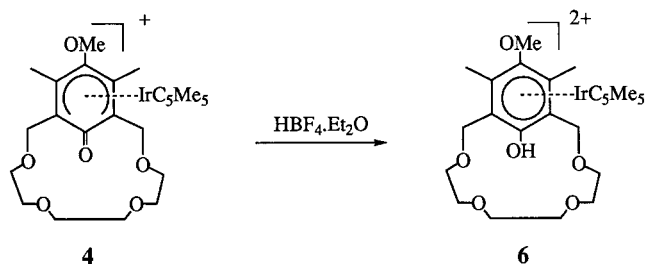
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Scheme 3



Scheme 4



compared with 1.89 ppm for complex **4**. Finally, the infrared spectrum of **6** shows the absence of the strong absorption at  $1608\text{ cm}^{-1}$ , suggesting that protonation has occurred at the C=O function.

In conclusion, we reported a high yield synthesis of an iridium-crown-ether complex  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\eta^6\text{-C}_{18}\text{H}_{28}\text{O}_6)]\text{[BF}_4\text{]}_2$  (**3**). This metalated crown-ether undergoes facile Me—O bond cleavage caused by the iridium center to give the related semiquinone complex  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\eta^5\text{-C}_{17}\text{H}_{25}\text{O}_6)]\text{[BF}_4\text{]}$  (**4**). Intriguingly, the Me—O unit close to the crown chain is the one that undergoes hydrolysis, therefore, this Me—O unit is more reactive than the one situated outside and away from the crown-ether chain.

Currently we are investigating the binding properties of the cationic and dicationic iridium crown-ether complexes, and the results will be the subject of future reports.

### Experimental Section

**General Procedures.** All manipulations were carried out under argon atmosphere using Schlenk techniques. Solvents were purified and dried prior to use by conventional distillation techniques. MeOH was distilled over traces of Na and used immediately. All reagents obtained from commercial sources were used without further purification. The synthesis of crown-ether **2** was performed using a modified literature procedure.<sup>5</sup> The NMR spectra were recorded on Bruker AM 250 and 200 MHz instruments. Chemical shifts are reported in parts per million referenced to residual solvent proton resonance for  $^1\text{H}$ ,  $^{13}\text{C}$ . Infrared spectra were obtained on a Bruker IR 45 spectrometer from samples

prepared on KBr disks. Elemental analysis were performed by the Microanalytical Laboratory of the University of Paris VI.

**Synthesis of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\eta^6\text{-C}_{18}\text{H}_{28}\text{O}_6)]\text{[BF}_4\text{]}_2$  (**3**).** A solution of  $\text{AgBF}_4$  (390 mg, 2 mmol) in acetone (20 mL) was added to  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\mu\text{-Cl})\text{Cl}]_2$  (398 mg, 0.5 mmol) in acetone (30 mL), to rapidly give a white precipitate of AgCl. The reaction mixture was stirred for 15 min, and then the resulting orange solution of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{acetone})_3]\text{[BF}_4\text{]}_2$  was filtered into a dry Schlenk tube kept under argon. To this orange solution was then added (2,5-dimethoxy-4,6-dimethyl-1,3-xylylene)-15 crown-4 (**2**) (510 mg, 1.5 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 mL), and the mixture was stirred for 4 h. During this time, the solution becomes lighter. Then the light orange solution was reduced under vacuum, and subsequent addition of  $\text{Et}_2\text{O}$  (40 mL) afforded an oil-like material. This compound was washed several times with  $\text{Et}_2\text{O}$  and dried under vacuum to give a yellow microcrystalline complex. Yield 88% (740 mg). Spectroscopic data for complex **3**. IR(KBr disk)/ $\text{cm}^{-1}$   $\tilde{\nu}(\text{BF}_4^-)$ : 1083;  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ , 250 MHz)  $\delta$ : 2.03 (s, 15H,  $\eta^5\text{-C}_5\text{Me}_5$ ), 2.42 (s, 6H,  $-\text{CH}_3$ ), 3.4–3.8 (m, 12H,  $(-\text{CH}_2-\text{CH}_2-\text{O})$ ), 3.84 (s, 3H,  $-\text{OMe}$ ), 4.36 (s, 3H,  $-\text{OMe}$ ), 4.40(AB-system, 4H,  $-\text{CH}_2$ -benzylic).  $^{13}\text{C}$  NMR (62.89 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$ : 9.38 ( $-\text{CH}_3$ ,  $-\text{C}_5\text{Me}_5$ ), 11.48 ( $-\text{CH}_3$ ), 62.14 ( $-\text{OMe}$ ), 62.78 ( $-\text{OMe}$ ), 64.40 ( $-\text{CH}_2$ , benzylic-carbon), 69.86, 70.97, 71.57 ( $-\text{CH}_2-\text{CH}_2-\text{O}$ ), 95.80 (C— $\text{CH}_3$  aromatic), 104.60 (C=C,  $-\text{C}_5\text{Me}_5$ ), 106.17 (C— $\text{CH}_2-\text{O}$ ), 128.02, 159.35 (C— $\text{OMe}$ , aromatic).

**Synthesis of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\eta^5\text{-C}_{17}\text{H}_{25}\text{O}_6)]\text{[BF}_4\text{]}$  (**4**).** This complex was prepared via two different procedures. Method I: A solution of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\eta^6\text{-C}_{18}\text{H}_{28}\text{O}_6)]\text{[BF}_4\text{]}_2$  (**3**) in  $\text{CH}_2\text{Cl}_2$  (20 mL) was allowed to stir for 2–3 days. The reaction was monitored by  $^1\text{H}$  NMR, which indicates the evolution of complex **3** toward **4**; however, the latter could not be isolated as pure complex. Method B: A solution of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\eta^6\text{-C}_{18}\text{H}_{28}\text{O}_6)]\text{[BF}_4\text{]}_2$  (**3**) (150 mg, 0.178 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 mL) was treated by  $\text{NEt}_3$ , and the reaction was stirred for 30 min. The solvent was reduced under vacuum, and subsequent addition of  $\text{Et}_2\text{O}$  (40 mL) afforded complex **4** quantitatively as a light yellow precipitate. This compound was washed several times with ether and dried under vacuum. We find that method II is easier and reproducible. Spectroscopic data for **4**: IR(KBr disk)/ $\text{cm}^{-1}$   $\tilde{\nu}(\text{BF}_4^-)$ : 1083r, (b)  $\tilde{\nu}(\text{C}=\text{O})$  1608 (s);  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ , 250 MHz)  $\delta$ : 1.89 (s, 15H,  $\eta^5\text{-C}_5\text{Me}_5$ ), 2.29 (s, 6H,  $-\text{CH}_3$ ), 3.34 (m, 6H,  $(-\text{CH}_2-\text{CH}_2-\text{O})$ ), 3.50 (m, 2H,  $(-\text{CH}_2-\text{CH}_2-\text{O})$ ), 3.87 (m, 4H,  $(-\text{CH}_2-\text{CH}_2-\text{O})$ ), 3.84 (s, 3H,  $-\text{OMe}$ ), 3.95 (d,  $J_{\text{H-H}} = 12.50\text{ Hz}$ , 2H,  $-\text{CH}_2$ -benzylic), 4.51 (d,  $J_{\text{H-H}} = 12.50\text{ Hz}$ , 2H,  $-\text{CH}_2$ -benzylic);  $^{13}\text{C}$  NMR (62.89 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$ :



8.95 (–CH<sub>3</sub>,  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>), 11.83 (–CH<sub>3</sub>), 61.04 (–OMe), 64.31 (–CH<sub>2</sub>, benzylic-carbon), 70.90, 71.77, 72.85 (–CH<sub>2</sub>–CH<sub>2</sub>–O), 88.95 (C–CH<sub>3</sub> semiquinone), 98.82 (C=C,  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>), 106.17 (C–CH<sub>2</sub>–O), 121.87 (C–OMe, semiquinone), 168.23 (C=O, semiquinone)

**Synthesis of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\eta^6\text{-C}_{10}\text{H}_{14}\text{O}_2)][\text{BF}_4]_2$  (5).** A solution of AgBF<sub>4</sub> (195 mg, 1.0 mmol) in acetone (10 mL) was added to  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\mu\text{-Cl})\text{Cl}]_2$  (199 mg, 0.5 mmol) in acetone (20 mL), to rapidly give a white precipitate of AgCl. The reaction mixture was stirred for 15 min, and then the resulting orange solution of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{acetone})_3][\text{BF}_4]_2$  was filtered into a dry Schlenk tube kept under argon. To this orange solution was then added (2,6-dimethyl-1,4-hydroquinone dimethyl ether (166 mg, 1.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and the mixture was stirred for 2 h, during which time the solution becomes lighter and a white precipitate was formed. The solvent was reduced under vacuum and subsequent addition of Et<sub>2</sub>O (40 mL) afforded more white precipitate. This compound was separated and washed several times with Et<sub>2</sub>O and dried under vacuum to yield 90% (300 mg). Spectroscopic data for **5**. IR (KBr disk)/cm<sup>–1</sup>  $\tilde{\nu}(\text{BF}_4^-)$ : 1080; <sup>1</sup>H NMR (CD<sub>3</sub>CN, 250 MHz)  $\delta$ : 2.10 (s, 15H,  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>), 2.46 (s, 6H, –Me), 3.99 (s, 3H, –OMe), 4.00 (s, 3H, –OMe), 7.03 (s, 2H aromatic protons); <sup>13</sup>C{<sup>1</sup>H}-NMR (62.87 MHz, CD<sub>3</sub>CN)  $\delta$ : 9.05 (–CH<sub>3</sub>,  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>), 14.22 (–CH<sub>3</sub>), 60.33 (–OMe), 62.23 (–OMe), 84.77 (–CH, aromatic carbon), 104.15 (C=C,  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>), 108.56 (C–CH<sub>3</sub> aromatic), 131.0 (C–OMe, aromatic), 142.15 (C–OMe, aromatic). Anal. Calcd for C<sub>20</sub>H<sub>29</sub>O<sub>2</sub>IrB<sub>2</sub>F<sub>8</sub>: C, 35.98; H, 4.34. Found C, 35.82, H, 4.35.

**Synthesis of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\eta^6\text{-C}_{17}\text{H}_{26}\text{O}_6)][\text{BF}_4]_2$  (6).** To a solution of **4** (50 mg, 0.078 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added HBF<sub>4</sub>·Et<sub>2</sub>O (100  $\mu$ L), and the reaction mixture was stirred for 30 min and then filtered through Celite. The solvent was concentrated under vacuum to a volume of 1 mL. Addition of Et<sub>2</sub>O (20 mL) afforded an oil-like precipitate that was separated and washed several times by cold Et<sub>2</sub>O and dried under vacuum to yield a white microcrystalline material in 85% yield (48 mg). Spectroscopic data for **6**. IR (KBr disk/cm<sup>–1</sup>)  $\tilde{\nu}(\text{–OH})$ : 3250–3500 (br);  $\tilde{\nu}(\text{B–F})$  1084; <sup>1</sup>H NMR (CD<sub>3</sub>CN, 250 MHz)  $\delta$ : 2.01 (s, 15H,  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>), 2.38 (s, 6H, –CH<sub>3</sub>), 3.50–3.95 (m, 12H, (–CH<sub>2</sub>–CH<sub>2</sub>–O)), 3.84 (s, 3H, –OMe), 4.50 (AB-system, 4H, –CH<sub>2</sub>–benzylic); <sup>13</sup>C NMR (62.89 MHz, CD<sub>3</sub>CN)  $\delta$ : 9.20 (–CH<sub>3</sub>, –C<sub>5</sub>Me<sub>5</sub>), 11.6 (–CH<sub>3</sub>), 62.10 (–OMe), 64.10 (–CH<sub>2</sub>, benzylic-carbon), 69.50, 71.0, 71.40 (–CH<sub>2</sub>–CH<sub>2</sub>–O), 95.60 (C–CH<sub>3</sub> aromatic), 103.36 (C=C, –C<sub>5</sub>Me<sub>5</sub>), 106.71 (C–CH<sub>2</sub>–O), not observed (C–OMe, aromatic), not observed (C–OH, aromatic).

**X-ray crystallography of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\eta^6\text{-C}_{17}\text{H}_{26}\text{O}_6)][\text{BF}_4]_2$  (4).** Suitable crystals of **4** were obtained by recrystallization from acetone/Et<sub>2</sub>O solution. The selected crystal of **4** was glued on the top of a glass stick. Accurate cell dimensions and an orientation matrix were obtained by least-squares refinements of 25 accurately centered reflections on a Nonius CAD4 diffractometer equipped with graphite-monochromated MoK $\alpha$  radiation. No significant variations were observed in the intensities of two checked reflections during data collection. Absorption corrections were applied using  $\Psi$ -scan method with ( $T_{\text{min}} = 0.80$  and  $T_{\text{max}} = 1$ ). Complete crystallographic data and collection parameters for **4** are listed in Table 1. The data were corrected for Lorentz and polarization effects. Computations were performed by using the PC version of CRYSTALS.<sup>11</sup> Scattering factors and corrections for anomalous dispersion were taken from Cromer.<sup>12</sup> The structure was solved by Fo-Patterson and Fourier maps technique and refined by full-matrix least squares with anisotropic thermal parameters for all atoms. Two atoms, O(4) and C(19), are disordered and both are located on two different sites with half occupation each; namely, O(41), O(42) and C(191), C(192). The BF<sub>4</sub> anion is also disordered around an inversion center on which is located the B atom. The crystallographic mirror plane orthogonal to *b* axis at *y* = 0.25 is a plane of symmetry for the molecule where Ir(1), O(1), O(2), C(1), C(6), C(11), C(14), and C(15) atoms are lying in this plane (Figure 1). Hence, all nonlabeled atoms are related to the labeled ones by the resultant symmetry operation. Atoms O(42) and C(192) are not shown for clarity.

**Acknowledgment.** We thank Phosphoenix for a loan of IrCl<sub>3</sub>·xH<sub>2</sub>O. The CNRS is gratefully acknowledged for supporting this work.

**Supporting Information Available:** An X-ray crystallographic file in CIF format, for the structure determination of complex **4** is available free of charge on the Internet at <http://pubs.acs.org>.

IC980811S

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