

Regioselective Ortho-Functionalization of Phenols Promoted by the “Cp*Ir” Unit in [Cp*Ir(oxo- η^5 -cyclohexadienyl)][BF₄] Complexes

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A series of alkylated phenols (phenol, 3,5-dimethylphenol and 3,4-dimethylphenol) were complexed by the [Cp*Ir(solvent)₃][BF₄]₂ (**1**) unit prepared in situ; subsequent treatment with NEt₃ produced the (oxo- η^5 -cyclohexadienyl)iridium complexes [Cp*Ir(η^5 -C₆H₃R₂O)][BF₄] [R = H (**2**); R = Me (**3**, **4**)]. The X-ray molecular structure of **3** was determined. These (oxo- η^5 -cyclohexadienyl)iridium derivatives react with NaOMe in methanol to give the novel iridium cyclohexadienone complexes [Cp*Ir(η^4 -C₆H₃R₂O(OMe))}] [R = H (**5**); R = Me (**6**, **7**)] in 75–90% yield with nucleophilic attack occurring exclusively at the ortho-position relative to the C=O function. Addition of HBF₄·Me₂O to these iridium cyclohexadienone complexes **5–7** affords the starting material (oxo- η^5 -cyclohexadienyl)iridium derivatives **2–4** with MeOH. Further exposure to HBF₄·Me₂O produces the corresponding phenolic compounds [Cp*Ir(η^6 -C₆H₃R₂OH)][BF₄]₂ (**8–10**); these chemical reactions are accompanied with hapticity changes $\eta^4 \rightarrow \eta^5 \rightarrow \eta^6$ of the coordinated π -hydrocarbon. The novel iridium cyclohexadienone complexes **5–7** can be oxidized easily by iodine to produce the free cyclohexadienones which rearomatize to give the free ortho-substituted phenols **11–13** in yields from 80% to quantitative.

Introduction

The activation of arenes toward nucleophilic attack has been known for several decades.¹ Such activation can be achieved by π -complexation of the aromatic substrate to transition metal centers (ML_n = Cr(CO)₃, Mn(CO)₃⁺, FeCp⁺, RuCp⁺, CoCp²⁺, etc.).² This area has attracted considerable interest in recent years due to its potential application in organic synthesis; further, more novel routes for the preparation of organic molecules were established which are often inaccessible by classical organic procedures.³ Nevertheless functionalization of phenols which are a particular class of arenes has not been reported so far. We report here the first example of regioselective ortho-functionalization of phenols and substituted phenols promoted by the Cp*Ir unit. Our approach can be described by nucleophilic addition of NaOMe to (oxo- η^5 -cyclohexadienyl)-

iridium complexes which occurs exclusively at the ortho position and affords the corresponding neutral (cyclohexadienone)iridium complexes. The latter can be easily demetalated to give the ortho-functionalized phenols.

Results and Discussion

Introduction of the [Cp*Ir(solvent)₃][BF₄]₂ (**1**) unit prepared in situ to the aromatic ring of the alkylated phenols (phenol, 3,5-dimethyl phenol, and 3,4-dimethylphenol) was accomplished in acetone/dichloromethane (Scheme 1).^{4a} Subsequent treatment with NEt₃ afforded the cationic (oxo- η^5 -cyclohexadienyl)iridium complexes [Cp*Ir(η^5 -C₆H₃R₂O)][BF₄] [R = H (**2**); R = Me (**3**, **4**)] in yields of 80–86%. Complex **2** was already reported in the literature^{4a} whereas the novel complexes **3** and **4** were identified by ¹H- and ¹³C-NMR spectroscopy (Tables 1 and 2) and elemental analysis. Generally in these complexes the cyclic π -hydrocarbon is coordinated to the metal center by only five carbons while the C=O unit is bent upward. Several X-ray molecular structures of Fe, Ru, and Rh complexes were reported by us and others.^{4,5} In this paper we also include the molecular

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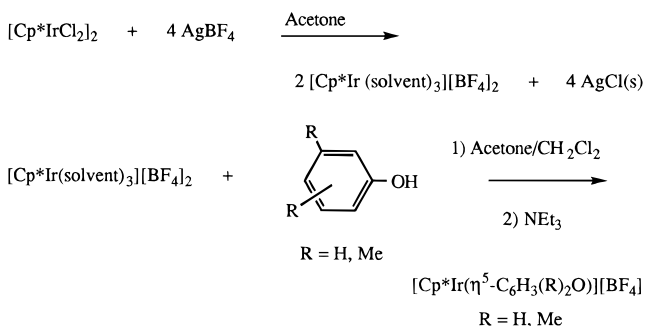
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Scheme 1. Syntheses of the (Oxo- η^5 -cyclohexadienyl)iridium Complexes 2–4



structure of $[\text{Cp}^*\text{Ir}(\eta^5\text{-C}_6\text{H}_3\text{Me}_2\text{O})][\text{BF}_4]$ (**3**), which confirms the previous observations.

(1) X-ray Molecular Structure of $[\text{Cp}^*\text{Ir}(\eta^5\text{-C}_6\text{H}_3\text{Me}_2\text{O})][\text{BF}_4]$ (3**).** Crystals of **3** suitable for an X-ray analysis were grown from acetone/ether solution. The compound crystallizes in the orthorhombic unit cell, space group $P2_12_12_1$. Figure 1 shows the Cameron view of $[\text{Cp}^*\text{Ir}(\eta^5\text{-C}_6\text{H}_3\text{Me}_2\text{O})]^+$; crystallographic data collection parameters and selected bond lengths and angles are listed in Tables 3–5. The structure shows that the Cp^*Ir unit is coordinated to only five carbons of the oxocyclohexadienyl unit with $d(\text{Ir}-\text{C}(2-6))_{\text{av}} = 2.21 \text{ \AA}$ while the bond length $d(\text{Ir}-\text{C}(1)) = 2.52 \text{ \AA}$; loss of aromaticity in the bonded oxo- η^5 -cyclohexadienyl unit is manifested by the irregularity of the arene C–C bond lengths. Another important feature of this structure is described by the short bond distance $\text{C}(1)-\text{O}(1) = 1.23 \text{ \AA}$. This bond distance is shorter than that of the analogous rhodium complex $[\text{Cp}^*\text{Rh}(\eta^5\text{-PhO})]^+$ with $d(\text{C}-\text{O}) = 1.25 \text{ \AA}$ ^{4a} and longer than that of the rhodium-hormone complex $[\text{Cp}^*\text{Rh}(\eta^5\text{-C}_{18}\text{H}_{23}\text{O}_2)]^+$ with $d(\text{C}-\text{O}) = 1.20 \text{ \AA}$.^{5a} The dihedral angle θ across $\text{C}(2)-\text{C}(6)$ is 19° ; this angle is greater than that reported for the phenoxide complexes $[\text{Cp}^*\text{M}(\eta^5\text{-PhO})]^{n+}$ of Rh, ($n=1$), Ru ($n=0$), and Fe ($n=0$) with $\theta = 14, 4,$ and 2° , respectively.^{4a,5b,c}

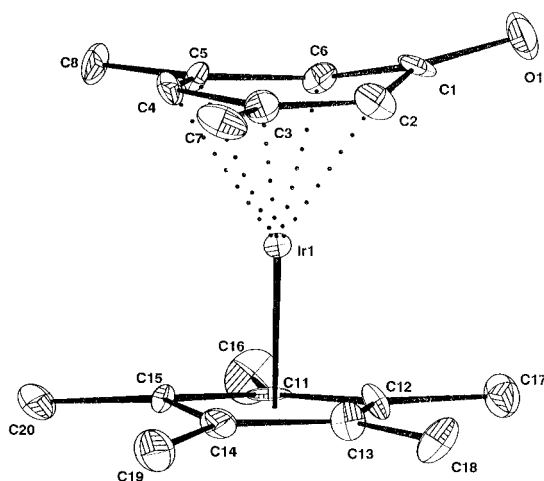
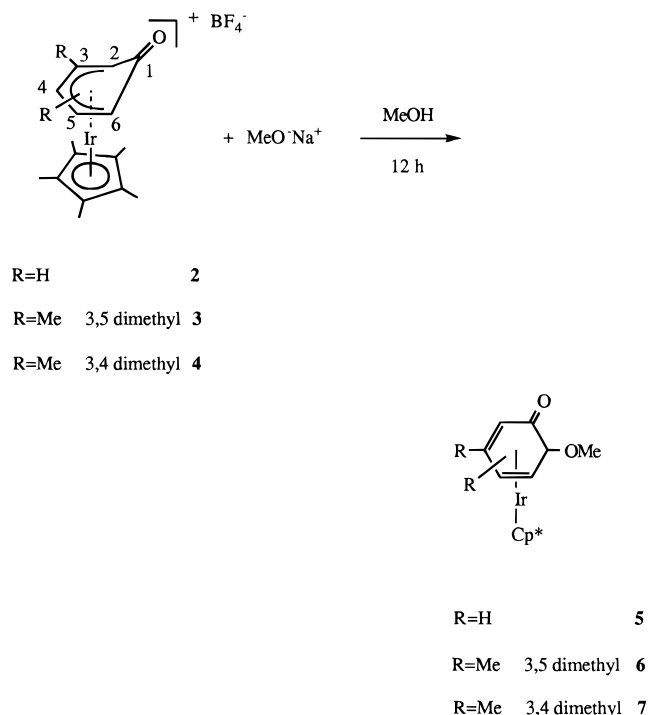


Figure 1. View of the cation in $[\text{Cp}^*\text{Ir}(\eta^5\text{-C}_6\text{H}_3\text{Me}_2\text{O})][\text{BF}_4]$ (**3**), showing the atom-numbering system.

(2) Reactivity of $[\text{Cp}^*\text{Ir}(\text{oxo-}\eta^5\text{-cyclohexadienyl})][\text{BF}_4]$ (2–4**) with NaOMe.** Treatment of $[\text{Cp}^*\text{Ir}(\eta^5\text{-C}_6\text{H}_5\text{O})][\text{BF}_4]$ (**2**) with 5 equiv of NaOMe in methanol for 12 h gave a light yellow solution. The solvent was removed under vacuum and the residue was extracted

by Et_2O to give an off-white material in 90% yield. This compound was identified by spectroscopic methods (2D homonuclear correlation spectroscopy (COSY), $^{13}\text{C}-^1\text{H}$ chemical shift correlation spectroscopy) and elemental analysis as a neutral π -cyclohexadienone derivative of iridium $[\text{Cp}^*\text{Ir}\{\eta^4\text{-C}_6\text{H}_5\text{O}(\text{OMe})\}]$ (**5**) (Scheme 2). It is most likely, (in the absence of an X-ray structure of **5**) that nucleophilic attack occurs exclusively at the ortho-position with exo-stereochemistry relative to the organometallic unit “ Cp^*Ir ”. Evidently the nucleophilic addition to the π -complexed oxo- η^5 -cyclohexadienyl is accompanied by a change of the oxidation state of the iridium center from Ir(III) to Ir(I). The $^1\text{H-NMR}$ of **5** (Table 6) recorded in C_6D_6 exhibits five multiplets in the area 3.2–4.8 ppm attributed to the arene protons, while the MeO^- unit appears as a singlet at 3.57 ppm. The $^{13}\text{C-NMR}$ of **5** (Table 7) indicates the presence of 9 peaks and in particular a singlet at 184.16 ppm assigned to the $\text{C}=\text{O}$ function. The infrared spectrum of **5** shows the $\nu(\text{C}=\text{O})$ absorption at 1623 cm^{-1} which is very close to that reported at 1620 cm^{-1} for the $\nu(\text{C}=\text{O})$ of the (cyclohexadienone)ruthenium species $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\eta^4\text{-C}_6\text{H}_6\text{O})]$.⁶ Further we note the absence of the large band at 1050 cm^{-1} attributed to the free anion BF_4^- ; evidently this large band is present in the starting material $[\text{Cp}^*\text{Ir}(\eta^5\text{-C}_6\text{H}_5\text{O})][\text{BF}_4]$ (**2**).^{4a}

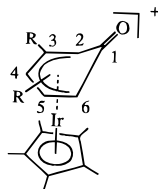
Scheme 2. Syntheses of the Neutral (η^4 -Hexadienone)iridium Complexes 5–7



Vollhardt and co-workers have reported the double addition of NaOMe to the dicationic mixed sandwich complex $[\text{C}_5\text{H}_5\text{Co}(\eta^6\text{-C}_6\text{H}_6)]^{2+}$. The nucleophilic additions occur with exo-stereochemistry to give the corresponding diene species $[\text{C}_5\text{H}_5\text{Co}(\eta^4\text{-dimethoxycyclohexadiene})]$. The product was characterized by $^1\text{H-NMR}$; but due to its instability this complex was not isolated.⁷

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Table 1. ^1H NMR Data for Complexes **3** and **4** in Acetone- d_6 at 250 MHz

R	η^5 -phenoxo	Cp*	others
Compound 3			
Me	6.63 (1H, br s, H ₄)	2.21 (s, 15H, Me-Cp)	2.40 (6H, s, Me-phenoxo)
3,5-dimethyl	5.61 (2H, d, H ₂ and H ₆)		
Compound 4			
Me	6.45 (1H, d, H ₅)	2.21 (s, 15H, Me-Cp)	2.33 (6H, br s, Me-phenoxo)
3,4-dimethyl	5.63–5.58 (2H, m, H ₂ , H ₆)		

Table 2. ^{13}C NMR Data for Complexes **3** and **4** in Acetone- d_6 at 62.90 MHz^a

R	η^5 -phenoxo	Cp*	others
Compound 3			
Me	163.50 (C ₁)	111.04 (C=C)	18.51 (s, Me-phenoxo)
3,5-dimethyl	99.25 (C ₃ and C ₅), 86.27 (C ₄), 80.77 (C ₂ and C ₆)	9.22 (Me-Cp)	
Compound 4			
Me	164.27 (C=O)	109.94 C=C	15.18 (Me-phenoxo)
3,4-dimethyl	99.34, 97.83 (C ₃ or C ₄), 96.31 (C ₅), 81.77, 80.42 (C ₂ or C ₆)	9.14 (Me-Cp)	17.00 (Me-phenoxo)

^a See numbering scheme in Table 1.**Table 3.** Crystal Data for C₁₈H₂₄OBF₄Ir

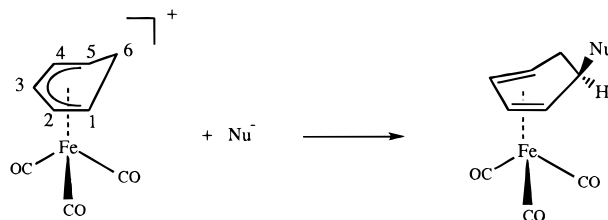
fw	535.4
a (Å)	10.061(4)
b (Å)	13.506(7)
c (Å)	13.554(5)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å ³)	1842
Z	4
cryst system	orthorhombic
space group	P2 ₁ 2 ₁ 2 ₁
linear abs coeff μ (cm ⁻¹)	72.6
density ρ (g·cm ⁻³)	1.93
diffractometer	Philips PW1100
radiation	Mo K α (λ = 0.710 69 Å)
scan type	$\omega/2\theta$
scan range (deg)	1.20 + 0.345 tan θ
θ limits (deg)	2–30
temp of measmt	room temp
octants colld	0 to 14; 0 to 18; 0 to 19
no. of data colld	3045
no. of unique data colld	3020
no. of unique data used for refinement	1684, (F _o) ² > 3 σ (F _o) ²
R = $\sum F_o - F_c /\sum F_o $	0.0373
R _w = $[\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$	0.0402, w = 1.0
sec ext coeff (10 ⁻⁶)	125
abs corr	DIFABS (min = 0.90, max = 1.15)
no. of variables	228
$\Delta\rho_{\text{min}}$ (e Å ⁻³)	-1.38
$\Delta\rho_{\text{max}}$ (e Å ⁻³)	1.48

Addition of nucleophiles to [(CO)₃Fe(η^5 -cyclohexadienyl)]⁺ complexes has been investigated⁸ with nucleophilic additions occurring at C(1) to give the corresponding diene complexes (Scheme 3). In these products the two double bonds are conjugated. We also note that Powell⁹ reported on the addition of NaOMe to cationic

Table 4. Interatomic Distances (Å) for [Ir(Cp*)(C₈H₉O)] [BF₄]

Ir(1)–C(2)	2.24(2)	Ir(1)–C(3)	2.22(2)
Ir(1)–C(4)	2.17(2)	Ir(1)–C(5)	2.20(2)
Ir(1)–C(6)	2.22(2)	Ir(1)–C(11)	2.16(1)
Ir(1)–C(12)	2.16(2)	Ir(1)–C(13)	2.17(2)
Ir(1)–C(14)	2.21(2)	Ir(1)–C(15)	2.19(2)
O(1)–C(1)	1.23(2)	C(1)–C(2)	1.45(2)
C(1)–C(6)	1.46(2)	C(2)–C(3)	1.34(3)
C(3)–C(4)	1.44(4)	C(3)–C(7)	1.50(3)
C(4)–C(5)	1.42(3)	C(5)–C(6)	1.41(2)
C(5)–C(8)	1.54(3)	C(11)–C(12)	1.37(3)
C(11)–C(15)	1.44(3)	C(11)–C(16)	1.56(3)
C(12)–C(13)	1.40(2)	C(12)–C(17)	1.51(3)
C(13)–C(14)	1.45(3)	C(13)–C(18)	1.50(3)
C(14)–C(15)	1.51(3)	C(14)–C(19)	1.47(3)
C(15)–C(20)	1.43(4)		
B(1)–F(1)	1.26(4)	B(1)–F(2)	1.16(5)
B(1)–F(3)	1.36(4)	B(1)–F(4)	1.36(4)

iridium complexes of the type [CpIr(η^5 -pentadienyl)]⁺ (Scheme 4), where the η^5 -pentadienyl ligand is an open system (Davies–Green–Mingos rules).¹⁰ The author observed in this particular system that the nucleophilic attack occurs at C(3) rather than the terminal carbon; in this case the isolated iridium diene complex possesses two nonconjugated double bonds.

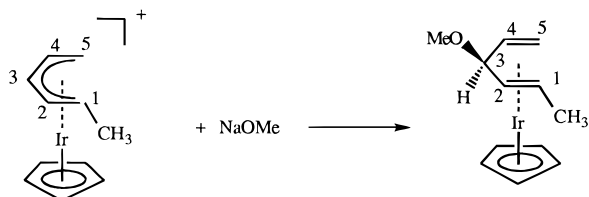
Scheme 3

MO calculations were carried out on (η^5 -cyclohexadienyl)metal systems in order to predict whether it is an orbital or charge control factor that influence the

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Scheme 4



observed regiochemistry. Kane-Maguire et al. reported an INDO MO calculations¹¹ on the cation $[\text{Fe}(\text{CO})_3(\eta^5\text{-C}_6\text{H}_7)]^+$. The analysis shows a correlation between the bond (or free valence) index values at each cyclohexadienyl carbon and the site of nucleophilic addition. The authors have also found that the positive charge variation (Figure 2) would predict that the site preferences is $\text{C}(2) > \text{C}(3) > \text{C}(1)$ whereas nucleophiles add exclusively at $\text{C}(1)$.

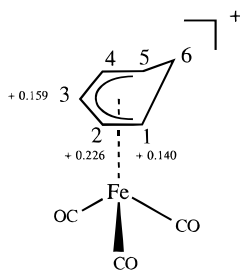


Figure 2.

Although the reactivity of the (η^5 -cyclohexadienyl)-metal complexes are well-known as illustrated by the previous examples, that of the oxo- η^5 -cyclohexadienyl system remained unknown. However Chung et al. have recently reported the synthesis of the phenoxide species $[(\text{CO})_3\text{Mn}(\eta^5\text{-C}_6\text{H}_5\text{O})]$ and its reactivity with nucleophiles to give anionic intermediates which can be quenched by subsequent treatment with electrophiles.¹² It is clear that our oxocyclohexadienyl species $[\text{Cp}^*\text{Ir}(\eta^5\text{-C}_6\text{H}_5\text{O})][\text{BF}_4]$ (**2**) behaves differently; in this respect it reacts with NaOMe to give the neutral stable (cyclohexadienone)iridium complex $[\text{Cp}^*\text{Ir}\{\eta^4\text{-C}_6\text{H}_5\text{O}(\text{OMe})\}]$ (**5**) involving hapticity changes of the coordinated hydrocarbon as $\eta^5 \rightarrow \eta^4$. To examine the regioselectivity of the above reaction we extended our investigation to alkylated iridium η^5 -phenoxide complexes **3** and **4**. Thus, the symmetrically substituted 3,5-dimethylphenoxide $[\text{Cp}^*\text{Ir}(\eta^5\text{-C}_6\text{H}_3\text{Me}_2\text{O})][\text{BF}_4]$ (**3**) was treated with NaOMe in MeOH for 12 h. Reaction workup afforded an off-white semisolid material in 75% yield and identified by ¹H- and ¹³C-NMR spectroscopy as $[\text{Cp}^*\text{Ir}\{\eta^4\text{-C}_6\text{H}_3\text{Me}_2\text{O}(\text{OMe})\}]$ (**6**) (Tables 6 and 7), where nucleophilic addition occurs exclusively at the ortho-position relative to the ketonic function. As for the unsymmetrically substituted 3,4-dimethyl phenoxide $[\text{Cp}^*\text{Ir}(\eta^5\text{-C}_6\text{H}_3\text{Me}_2\text{O})][\text{BF}_4]$ (**4**), the reaction with NaOMe is very interesting since there are two distinct ortho-positions available. Hence we would expect to obtain two cyclohexadienone derivatives. Surprisingly we have isolated only one complex $[\text{Cp}^*\text{Ir}\{\eta^4\text{-C}_6\text{H}_3\text{Me}_2\text{O}(\text{OMe})\}]$ (**7**) in 88% yield. In this complex the MeO⁻ attacks regioselectively the less sterically hindered ortho-position $\text{C}(6)$

Table 5. Bond Angles (deg) for $[\text{Ir}(\text{Cp}^*)(\text{C}_8\text{H}_9\text{O})][\text{BF}_4]$

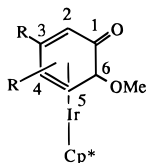
C(2)–Ir(1)–C(3)	34.9(7)	C(2)–Ir(1)–C(4)	64.0(9)
C(3)–Ir(1)–C(4)	38.3(11)	C(2)–Ir(1)–C(5)	77.5(6)
C(3)–Ir(1)–C(5)	69.4(12)	C(4)–Ir(1)–C(5)	37.9(8)
C(2)–Ir(1)–C(6)	64.6(6)	C(3)–Ir(1)–C(6)	79.4(9)
C(4)–Ir(1)–C(6)	66.4(8)	C(5)–Ir(1)–C(6)	37.2(6)
C(2)–Ir(1)–C(11)	153.2(8)	C(3)–Ir(1)–C(11)	171.0(6)
C(4)–Ir(1)–C(11)	138.8(11)	C(5)–Ir(1)–C(11)	112.5(8)
C(6)–Ir(1)–C(11)	107.6(6)	C(2)–Ir(1)–C(12)	119.5(8)
C(3)–Ir(1)–C(12)	146.1(13)	C(4)–Ir(1)–C(12)	175.6(10)
C(5)–Ir(1)–C(12)	138.7(7)	C(6)–Ir(1)–C(12)	112.2(6)
C(11)–Ir(1)–C(12)	37.0(8)	C(2)–Ir(1)–C(13)	108.1(7)
C(3)–Ir(1)–C(13)	115.8(12)	C(4)–Ir(1)–C(13)	145.4(8)
C(5)–Ir(1)–C(13)	174.3(7)	C(6)–Ir(1)–C(13)	143.8(6)
C(11)–Ir(1)–C(13)	61.9(8)	C(2)–Ir(1)–C(14)	126.1(7)
C(3)–Ir(1)–C(14)	109.3(9)	C(4)–Ir(1)–C(14)	116.4(8)
C(5)–Ir(1)–C(14)	138.9(7)	C(6)–Ir(1)–C(14)	169.3(8)
C(11)–Ir(1)–C(14)	63.2(7)	C(2)–Ir(1)–C(15)	164.1(7)
C(3)–Ir(1)–C(15)	132.4(7)	C(4)–Ir(1)–C(15)	111.5(11)
C(5)–Ir(1)–C(15)	108.8(10)	C(6)–Ir(1)–C(15)	129.1(9)
C(11)–Ir(1)–C(15)	38.7(7)	C(12)–Ir(1)–C(13)	37.7(6)
C(12)–Ir(1)–C(14)	64.2(7)	C(13)–Ir(1)–C(14)	38.5(7)
C(12)–Ir(1)–C(15)	65.8(9)	C(13)–Ir(1)–C(15)	66.1(11)
C(14)–Ir(1)–C(15)	40.3(9)	O(1)–C(1)–C(2)	125.4(21)
O(1)–C(1)–C(6)	124.5(20)	C(2)–C(1)–C(6)	110.0(15)
Ir(1)–C(2)–C(1)	83.4(10)	Ir(1)–C(2)–C(3)	71.7(11)
C(1)–C(2)–C(3)	128.5(22)	Ir(1)–C(3)–C(2)	73.4(10)
Ir(1)–C(3)–C(4)	69.2(12)	C(2)–C(3)–C(4)	114.7(24)
Ir(1)–C(3)–C(7)	129.2(16)	C(2)–C(3)–C(7)	127.2(32)
C(4)–C(3)–C(7)	118.0(20)	Ir(1)–C(4)–C(3)	72.5(12)
Ir(1)–C(4)–C(5)	72.1(10)	C(3)–C(4)–C(5)	123.1(22)
Ir(1)–C(5)–C(4)	70.0(12)	Ir(1)–C(5)–C(6)	72.0(9)
C(4)–C(5)–C(6)	116.3(19)	Ir(1)–C(5)–C(8)	127.8(14)
C(4)–C(5)–C(8)	121.7(21)	C(6)–C(5)–C(8)	122.0(19)
Ir(1)–C(6)–C(1)	839(10)	Ir(1)–C(6)–C(5)	70.8(10)
C(1)–C(6)–C(5)	123.2(17)	Ir(1)–C(11)–C(12)	71.4(9)
Ir(1)–C(11)–C(15)	71.6(9)	C(12)–C(11)–C(15)	114.1(18)
Ir(1)–C(11)–C(16)	124.0(14)	C(12)–C(11)–C(16)	126.9(18)
C(15)–C(11)–C(16)	119.0(24)	Ir(1)–C(12)–C(11)	71.6(10)
Ir(1)–C(12)–C(13)	71.7(11)	C(11)–C(12)–C(13)	107.3(16)
Ir(1)–C(12)–C(17)	123.9(13)	C(11)–C(12)–C(17)	126.8(17)
C(13)–C(12)–C(17)	125.9(20)	Ir(1)–C(13)–C(12)	70.7(11)
Ir(1)–C(13)–C(14)	72.2(11)	C(12)–C(13)–C(14)	109.6(18)
Ir(1)–C(13)–C(18)	124.8(15)	C(12)–C(13)–C(18)	125.9(20)
C(14)–C(13)–C(18)	124.5(19)	Ir(1)–C(14)–C(13)	69.3(10)
Ir(1)–C(14)–C(15)	69.0(9)	C(13)–C(14)–C(15)	107.0(16)
Ir(1)–C(14)–C(19)	128.9(15)	C(13)–C(14)–C(19)	125.8(21)
C(15)–C(14)–C(19)	127.1(20)	Ir(1)–C(15)–C(11)	69.7(9)
Ir(1)–C(15)–C(14)	70.7(10)	C(11)–C(15)–C(14)	101.7(23)
Ir(1)–C(15)–C(20)	130.1(20)	C(11)–C(15)–C(20)	131.9(25)
C(14)–C(15)–C(20)	125.5(20)		
F(1)–B(1)–F(2)	113.8(51)	F(1)–B(1)–F(3)	104.8(25)
F(2)–B(1)–F(3)	106.4(34)	F(1)–B(1)–F(4)	109.2(29)
F(2)–B(1)–F(4)	106.7(31)	F(3)–B(1)–F(4)	116.2(34)

relative to the methyl groups. The ¹H-NMR (Table 6) of **7** recorded in C₆D₆ shows the presence of 3 signals in the area 3.0–3.9 ppm attributed to the arene protons, while the coordinated MeO⁻ unit appears at 3.58 ppm. The ¹³C-NMR (Table 7) is in accord with the proposed structure of **7**; in particular we note the presence of a singlet at 186.72 ppm attributed to the carbonyl function (C=O) of the coordinated arene. In summary the nucleophilic attacks by NaOMe on these cationic iridium complexes $[\text{Cp}^*\text{Ir}(\text{oxo-}\eta^5\text{-dienyl})][\text{BF}_4]$ occur at the ortho position $\text{C}(2)$ and/or $\text{C}(6)$ for **2** and **3** but exclusively at $\text{C}(6)$ for complex **4**. Attempts to grow crystals of these novel iridium cyclohexadienone species **5–7** have shown so far to be unsuccessful.

At this stage a brief comment on the nature of the novel (η^4 -dienone)iridium complexes is appropriate. Evidently the π -cyclic ligands in these complexes are the dienone forms of ortho-substituted phenols which do not exist as free ligands (Scheme 5). However, their

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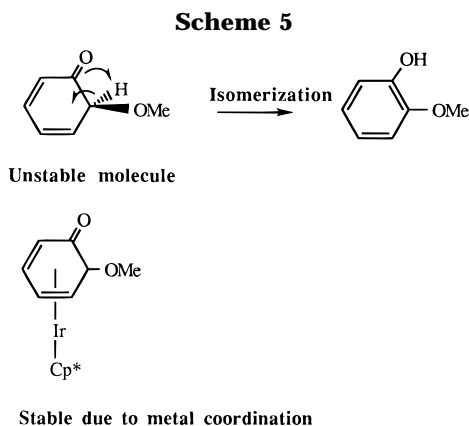
Table 6. ^1H NMR Data for Complexes 5–7 in C_6D_6 at 250 MHz

R	η^4 -dienone	Cp*	others
Compound 5			
H	4.76 (1H, td, H ₃), 4.49 (1H, tt, H ₄), 3.80 (1H, dd, H ₆), 3.74 (1H, dd, H ₂), 3.20 (1H, td, H ₅)	1.63 (15H, s, Me–Cp)	3.57 (3H, s, OMe)
Compound 6			
Me	4.17 (1H, br s, H ₄)	1.54 (15H, s, Me–Cp)	3.63 (3H, s, OMe)
3,5-dimethyl	3.69 (1H, m, H ₆), 3.62 (1H, m, H ₂)		1.64 (3H, s, Me–dienone), 1.43 (3H, s, Me–dienone)
Compound 7			
Me	3.81 (1H, dd, H ₆)	1.55 (15H, s, Me–Cp)	3.58 (3H, s, OMe)
3,4-dimethyl	3.64 (1H, d, H ₂), 3.03 (1H, d, H ₅)		1.64 (3H, s, Me–dienone), 1.61 (3H, s, Me–dienone)

Table 7. ^{13}C NMR Data for Complexes 5–7 Recorded in C_6D_6 at 62.90 MHz^a

R	η^4 -dienone	Cp*	others
Compound 5			
H	184.16 (C ₁), 76.23 (C ₆), 70.97 (C ₃), 67.50 (C ₄), 57.74 (C ₂), 39.34 (C ₅)	89.61 (C=C), 9.98 (Me–Cp)	57.68 (OMe)
Compound 6			
Me	184.18 (C ₁), 82.96 (C ₃), 81.18 (C ₄), 72.09 (C ₆)	89.16 (s, C=C)	58.97 (OMe)
3,5-dimethyl	59.90 (C ₂), 47.30 (C ₅)	9.27 (Me–Cp)	21.75 (Me–dienone), 18.67 (Me–dienone)
Compound 7			
Me	186.72 (C ₁)	88.49 (C=C)	57.44 (OMe)
3,4-dimethyl	82.16, 78.86 (C ₃ or C ₄), 77.06 (C ₆), 60.23 (C ₂), 42.46 (C ₅)	9.24 (Me–Cp)	16.34 (Me–dienone), 16.08 (Me–dienone)

^a See numbering scheme in Table 6.



metal complexes 5–7 are stable under argon due to coordination of the η^4 - π -cyclic hydrocarbon to the Cp^*Ir unit. This example beautifully illustrates the stabilizing effects of the “ Cp^*Ir ” moiety (Scheme 5). Further, the nucleophilic addition occurs presumably with exo-stericochemistry and involving changes in hapticity of the coordinated π -cyclic hydrocarbon as $\eta^5 \rightarrow \eta^4$. We have found that this hapticity change is reversible when the dienone iridium complexes 5–7 were treated with $\text{HBF}_4 \cdot \text{Me}_2\text{O}$.

(3) Reactivity of $[\text{Cp}^*\text{Ir}\{\eta^4\text{-(cyclohexadienone-OMe)}\}]$ with $\text{HBF}_4 \cdot \text{Me}_2\text{O}$ and Solution Behavior. When a CD_3CN solution of the neutral iridium dienone complex $[\text{Cp}^*\text{Ir}\{\eta^4\text{-C}_6\text{H}_5\text{O(OMe)}\}]$ (5) was exposed to $\text{HBF}_4 \cdot \text{Me}_2\text{O}$ the corresponding (oxocyclohexadienyl)-iridium complex $[\text{Cp}^*\text{Ir}(\eta^5\text{-C}_6\text{H}_5\text{O})][\text{BF}_4]$ (2) was formed with liberation of MeOH (Scheme 6). Further treatment of 2 with $\text{HBF}_4 \cdot \text{Me}_2\text{O}$ afforded the corresponding phenolic species $[\text{Cp}^*\text{Ir}(\eta^6\text{-C}_6\text{H}_5\text{OH})][\text{BF}_4]_2$ (8). When the

latter was treated by a base, the oxocyclohexadienyl complex $[\text{Cp}^*\text{Ir}(\eta^5\text{-C}_6\text{H}_5\text{O})][\text{BF}_4]$ (2) was recovered. These acid–base reactions were also observed with the alkylated iridium dienone series 6 and 7.

It is worth mentioning that the above chemical transformations are accompanied with hapticity changes $\eta^4 \rightarrow \eta^5 \rightarrow \eta^6$ and in a reversible fashion. Hapticity changes in mixed sandwich compounds of iridium and rhodium $[\text{Cp}^*\text{M}(\eta^6\text{-C}_6\text{Me}_6)]^{2+}$ ($\text{M} = \text{Rh}, \text{Ir}$) were investigated by Geiger and co-workers. The authors reported on the electrochemical reduction of these dicationic species to yield the corresponding neutral $[\text{Cp}^*\text{M}(\eta^4\text{-C}_6\text{Me}_6)]$ ($\text{M} = \text{Rh}, \text{Ir}$) species.¹³ To our knowledge our Ir complexes represent the first oxo- η^5 -cyclohexadienyl system which exhibits such a behavior whereby all the species are stable and can be isolated without major difficulties. Perhaps this is related to the strong π -backbonding character of the Cp^*Ir unit which stabilizes the different hapticities, η^4 , η^5 , and η^6 , of the coordinated π -cyclic hydrocarbon.

(4) Oxidative Decomplexation and Regioselective Ortho-Functionalization of Phenols. Treatment of $[\text{Cp}^*\text{Ir}\{\eta^4\text{-C}_6\text{H}_5\text{O(OMe)}\}]$ (5) with iodine in C_6D_6 solution at room temperature and analysis of the solution mixture by ^1H -NMR shows the formation of 2-methoxyphenol (guaiacol) (11); this was also confirmed by comparison to the ^1H -NMR spectrum of an authentic sample of 2-methoxyphenol. The oxidation of the (cyclohexadienone)iridium derivative 5 by I_2 occurs rapidly to produce presumably the free substituted cyclohexadienone; subsequent rearrangement occurs to give the more stable substituted phenol molecule (Scheme 7). Similar results were obtained for the alkylated (cyclo-

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several times with Et₂O and dried under vacuum with an overall yield of 85% (170 mg). The ¹H and ¹³C data are included in Tables 1 and 2.

IR (KBr disk)/cm⁻¹: ν(C=O) 1631, ν(B–F) 1055. Anal. Calcd for C₁₈H₂₄BF₄IrO: C, 40.38; H, 4.52. Found: C, 40.38; H, 4.49.

Synthesis of [Cp*Ir(η⁵-C₆H₅Me₂O)][BF₄] (4). This complex was prepared in a similar fashion to that of **3** and isolated as a white microcrystalline solid in 86% yield. The ¹H and ¹³C data are included in Tables 1 and 2.

IR (KBr disk)/cm⁻¹: ν(C=O) 1630, ν(B–F) 1050. Anal. Calcd for C₁₈H₂₄BF₄IrO: C, 40.38; H, 4.52. Found: C, 40.32; H, 4.37.

Synthesis of [Cp*Ir{η⁴-C₆H₅O(OMe)}] (5). A methanolic solution of NaOMe (1 mmol) [freshly prepared from NaH (25 mg) in distilled methanol (4 mL)] was added to a solution of [Cp*Ir(η⁵-C₆H₅O)][BF₄] (**2**) (100 mg, 0.19 mmol) in 10 mL of MeOH. The reaction mixture was stirred for 12 h at room temperature, and then the solvent was removed completely and dried under vacuum. The residue was then extracted with 60 mL of Et₂O and filtered into a dry Schlenck tube under argon. The diethyl ether was removed under vacuum affording an off-white microcrystalline solid in 90% yield (81 mg). The ¹H and ¹³C data are included in Tables 6 and 7.

IR (KBr disk)/cm⁻¹: ν(C=O) 1623, ν(C=C) 1606. Anal. Calcd for C₁₇H₂₃IrO₂: C, 45.22; H, 5.13. Found: C, 44.72; H, 5.02.

Synthesis of [Cp*Ir{η⁴-C₆H₃Me₂O(OMe)}] (6). This compound was prepared in a similar way to that of **5** and obtained as an off-white semisolid material (gummy substance). Yield: 75%.

IR (KBr disk)/cm⁻¹: ν(C=O) 1619. Due to its oil-like character, an analysis could not be obtained. The NMR data (¹H, ¹³C) included in Tables 6 and 7 confirm the purity of this complex.

Synthesis of [Cp*Ir{η⁴-C₆H₃Me₂O(OMe)}] (7). Complex **7** was synthesized in a similar way to that described for **5** and **6**. This iridium dienone complex was obtained as an off-white microcrystalline solid with an 88% yield.

IR (KBr disk)/cm⁻¹: ν(C=O) 1603. Anal. Calcd for C₁₉H₂₇IrO₂: C, 47.58; H 5.67. Found: C, 46.80; H, 5.74.

Protonation of [Cp*Ir{η⁴-C₆H₃Me₂O(OMe)}] (6) by HBF₄·Me₂O. To a 5 mm ¹H-NMR tube of **6** (10 mg, 0.02 mmol) in 0.6 mL of (CD₃)₂CO was added 10 μL of HBF₄·Me₂O. Analysis of the solution mixture by NMR showed the disappearance of the starting material **6** and the formation of the oxo-dienyl complex [Cp*Ir(η⁵-C₆H₃Me₂O)][BF₄] (**3**) (ca. 33%) and the novel η⁶-phenol complex [Cp*Ir(η⁶-C₆H₃Me₂OH)][BF₄]₂ (**9**) (66%). We also note the presence of a singlet at 3.15 ppm attributed to free MeOH. In a similar way the (cyclohexadienone)iridium species [Cp*Ir{η⁴-C₆H₅O(OMe)}] (**5**) reacts with HBF₄·Me₂O to give the oxo-dienyl complex [Cp*Ir(η⁵-C₆H₅O)][BF₄] (**2**) and the corresponding phenolic derivative [Cp*Ir(η⁶-C₆H₅O)][BF₄]₂ (**8**). The NMR data for these known complexes correspond to those reported by us previously.^{4a}

¹H-NMR data for [Cp*Ir(η⁶-C₆H₃Me₂OH)][BF₄]₂ (**9**) ((CD₃)₂-CO, 250 MHz): δ 7.20 (H_{para}, s, 1H), 6.90 (H_{ortho}, s, 2H), 2.67 (Me-phenol, s, 6H), 2.31 (Me-Cp, s, 15H).

Oxidation of [Cp*Ir{η⁴-C₆H₅O(OMe)}] (5) by Iodine. To a 5 mm ¹H-NMR tube of **5** (10 mg, 0.02 mmol) in 0.5 mL of

C₆D₆ was added 25 mg of iodine (an excess), and the tube was shaken for 5–10 min. Analysis of the solution mixture by ¹H NMR showed quantitative formation of 2-methoxyphenol and the disappearance of **5**. The oxidative decomplexation process can be carried out in CDCl₃, however, the formation of 2-methoxyphenol is very slow (24 h for 50% conversion). We also note the presence of a singlet at 1.83 ppm which corresponds to the chemical shift of [Cp*IrI₂]₂ as reported in the literature.¹⁵ ¹H-NMR data for 2-methoxyphenol (**11**) (C₆D₆, 200 MHz): δ 7.07 (1H, dd), 6.74 (2H, m), 6.44 (1H, dd), 5.56 (1H, br s, –OH), 3.12 (3H, s, OMe).

Oxidation of [Cp*Ir{η⁴-C₆H₃Me₂O(OMe)}] (6) by Iodine. In a similar way the oxidation of **6** in C₆D₆ by I₂ affords the free substituted phenol **12** in 80% yield. ¹H NMR of **12** (C₆D₆, 200 MHz): δ 6.77 (1H, m), 6.38 (1H, m), 5.33 (1H, br s, –OH), 3.20 (3H, s, OMe), 2.09 (3H, s, Me-phenol), 2.05 (3H, s, Me-phenol).

Oxidation of [Cp*Ir{η⁴-C₆H₃Me₂O(OMe)}] (7) by Iodine. In a similar fashion the oxidation of the iridium dienone complex **7** in C₆D₆ by I₂ affords the free substituted phenol **13** in 85% yield. ¹H NMR for **13** (C₆D₆, 200 MHz): δ 6.91 (1H, s), 6.40 (1H, s), 5.30 (1H, br s, –OH), 3.20 (3H, s, OMe), 2.04 (3H, s, Me-phenol), 1.96 (3H, s, Me-phenol).

X-ray Crystallography. Suitable crystals of [Cp*Ir(η⁵-C₆H₃Me₂O)][BF₄] (**3**) were obtained by recrystallization from acetone/Et₂O solution. The selected crystal (prismatic, 0.50 × 0.56 × 0.60 mm) 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. No significant variations were observed in the intensities of two checked reflections during data collection. Complete crystallographic data and collection parameters are listed in Tables 3–5. The data were corrected for Lorentz and polarization effects. Computations were performed by using the PC version of CRYSTALS.¹⁶ Scattering factors and corrections for anomalous dispersion were taken from ref 17. The structure was solved by standard Patterson and Fourier techniques and refined by full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were introduced in calculated positions in the last refinements and were allocated an overall refinable isotropic thermal parameter.

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Supporting Information Available: Anisotropic displacement parameters (Table S1) and fractional parameters (Table S2) for **3** (2 pages). Ordering information is given on any current masthead page.

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