p-, *o*-η^4-Benzoquinone and the Related η^6-Hydroquinone, η^6-Catechol Complexes of Pentamethylcyclopentadienyliridium: Synthesis, Structures, and Reactivity

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Treatment of hydroquinone with [Cp*Ir(solvent)$_3$][BF$_4$]$_2$ (**1**) in acidic medium afforded the stable π-bonded complex [Cp*Ir(η^6-hydroquinone)][BF$_4$]$_2$ (**2**) in 93% yield. Complex **2** can be easily deprotonated by a base to give the related [Cp*Ir(η^5-semiquinone)][BF$_4$] (**3**) and [Cp*Ir(η^4-*p*-benzoquinone)] (**4**) compounds, identified by spectroscopic methods. Further, the X-ray molecular structure of *p*-benzoquinone iridium complex **4** is reported; such compounds are rare in the literature. Complex **4** reacts with an excess of HBF$_4$·Et$_2$O to give the starting material **2** quantitatively. Interestingly, the chemical transformations from **2** to **4** and vice versa occur with facile reversible changes of the oxidation state from Ir(III) to Ir (I). On the other hand, the oxo−dienyl iridium complex [Cp*Ir(η^5-2,6-dimethoxy-C$_6$H$_3$O)]-[BF$_4$] (**5**), identified by spectroscopic methods and X-ray analysis, reacts with NaOMe in methanol to give unexpectedly but reproducibly the substituted *o*-benzoquinone iridium compound [Cp*Ir{η^4-(3-methoxy)-*o*-benzoquinone}] (**6**). The solution behavior and the reactivity of **6**, as well as a rationale explaining its formation, is advanced.

Introduction

Sternberg, Markby, and Wender reported in 1958 the first duroquinone complex [Fe(CO)$_3$(η^4-duroquinone)] (duroquinone = 2,3,5,6-tetramethyl-1,4-benzoquinone).[1] Since then, the coordination chemistry of η^4-duroquinone and substituted η^4-benzoquinone have received intense investigation.[2−7] For instance, Liebeskind and co-workers reported a high-yield synthetic procedure for the preparation of substituted η^4-benzoquinone and η^4-naphthaquinone metal complexes.[8−10] Unlike η^4-duroquinone complexes, the π-complexation of the sensitive benzoquinone ligand has attracted less attention; this is due in part to the absence of a simple synthetic procedure for such π-complexes.

It has been reported that the deprotonation of the parent hydroduroquinone metal complexes leads directly to the corresponding η^4-duroquinone compounds.[5] Unfortunately the η^6-hydroquinone metal complexes are not well-known in the literature. For instance, (η^6-hydroquinone)Cr(CO)$_3$ is reported to be a heat- and air-sensitive compound and is identified spectroscopically but cannot be isolated as a pure solid.[11] However, recently, Sweigart and co-workers reported the synthesis of [η^6-hydroquinone Mn(CO)$_3$][PF$_6$], via arene displacement reaction from [(η^6-acenaphthene)Mn(CO)$_3$]$^+$ and hydroquinone.[12]

The above reasons stimulated us to study the π-complexation of hydroquinone by the [Cp*Ir(solvent)$_3$][BF$_4$]$_2$ (**1**) moiety. The latter is an electron-rich fragment and is well-known to stabilize sensitive ligands, providing stable [Cp*Ir(η^6-arene)][BF$_4$]$_2$ complexes.[5,13]

In this paper, we report a high-yield synthesis of [Cp*Ir(η^6-hydroquinone)][BF$_4$]$_2$ (**2**) from direct treatment of the solvated iridium complex [Cp*Ir(solvent)$_3$]-[BF$_4$]$_2$ (**1**) with hydroquinone. Complex **2** can be depro-

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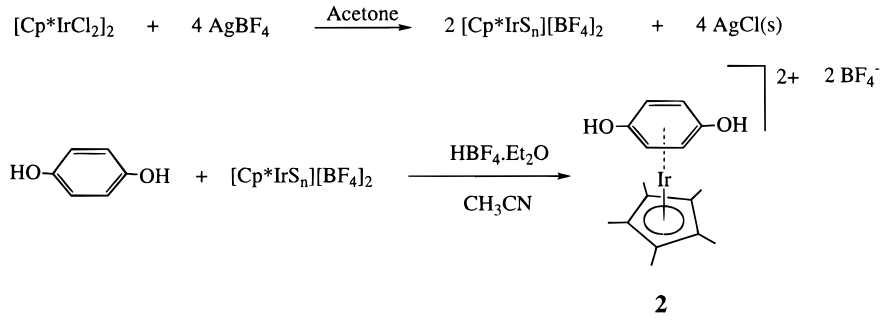
Scheme 1



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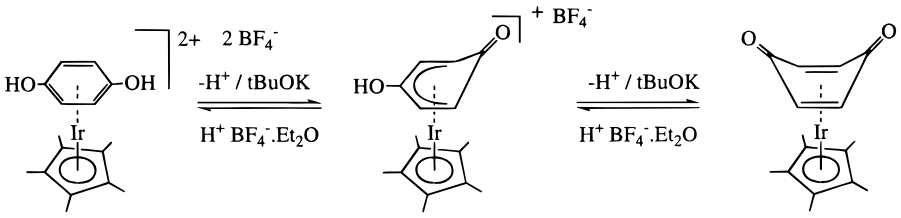
Scheme 2



2 **3** **4**

tonated by the appropriate base to give the related η^5-semiquinone (**3**) and the η^4-*p*-benzoquinone (**4**) iridium complexes (*p* = para). Treatment of **4** by $HBF_4 \cdot Et_2O$ quantitatively gave back the parent complex [Cp*Ir(η^6-hydroquinone)][BF_4]$_2$ (**2**). These deprotonation/protonation reactions were found to be reversible for the iridium series. Further, the X-ray structure of [Cp*Ir(η^4-*p*-benzoquinone)] (**4**) was determined and shows that the quinone ligand adopts a boat conformation.

On the other hand, we have found that treatment of the phenoxide complex [Cp*Ir(η^5-2,6-dimethoxy-C_6H_3O)][BF_4] (**5**) with NaOMe in methanol afforded unexpectedly but reproducibly the substituted η^4-*o*-benzoquinone iridium complex [Cp*Ir{η^4-(3-methoxy)-*o*-benzoquinone}] (**6**) in 62% yield (*o* = ortho). It is noteworthy that there are few complexes of η^4-*o*-benzoquinone reported in the literature, where the ligand is π-bonded to the metal center via a carbon−carbon π-network.[14−16] In this paper, we also report the chemistry and solution behavior of this novel stable η^4-*o*-benzoquinone iridium complex **6**. Part of this work has been published as a preliminary communication.[17]

Results and Discussion

Synthesis, Solution Behavior, and Reactivity of [Cp*Ir(η^6-hydroquinone)][BF_4]$_2$ (2) and [Cp*Ir(η^4-*p*-benzoquinone)] (4). Attachment of the [Cp*Ir(solvent)$_3$][BF_4]$_2$ (**1**) unit, prepared in situ, to the aromatic ring of the hydroquinone was accomplished in acetone/THF (Scheme 1). Subsequent treatment with $HBF_4 \cdot Et_2O$ in CH_3CN afforded the dicationic η^6-hydroquinone iridium complex [Cp*Ir(η^6-hydroquinone)][BF_4]$_2$ (**2**) as a white microcrystalline solid in 93% yield. Complex **2** was identified by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis.

The white compound **2** was found to be moisture sensitive and should be kept under argon. Further, the complex [Cp*Ir(η^6-hydroquinone)][BF_4]$_2$ (**2**) showed the tendency to lose its phenolic proton; therefore, the NMR spectra of **2** were performed in an acidic medium (see Experimental Section). This phenomenon is not surprising since the [Cp*Ir]$^{2+}$ fragment dramatically increases the acidity of the η^6-hydroquinone relative to that of the free molecule, as previously observed for the related phenol complex [Cp*Ir(η^6-phenol)][BF_4]$_2$.[18] Further, the analogous dicationic cobalt complex [Cp*Co(η^6-hydroduroquinone)][BF_4]$_2$ was also found to deprotonate easily in solution, even during recrystallization.[5] This behavior stimulated us to study the properties and stability of complex **2** in acidic and basic media.

When a CD_3CN solution of [Cp*Ir(η^6-hydroquinone)][BF_4]$_2$ (**2**) was exposed to an excess of tBuOK, a yellow color formed rapidly. The ^{1}H NMR of the sample shows the total disappearance of **2** and formation of the related η^5-semiquinone and η^4-quinone iridium complexes (**3** and **4**) (Scheme 2). When the reaction was allowed to continue, complete deprotonation occurred, exclusively yielding the η^4-quinone complex [Cp*Ir(η^4-*p*-benzoquinone)] (**4**). The latter can be prepared quantitatively and isolated as a light yellow microcrystalline solid. Further, the molecular structure of **4** was identified by X-ray analysis (vide infra). When complex **4** was protonated by $HBF_4 \cdot Et_2O$ in CH_3CN, the parent complex **2** was recovered in quantitative yield. The protonation/deprotonation reactions were found to be reversible without showing any minor decomposition of the iridium complexes.

At this stage, a brief comment on these π-complexes of iridium is adequate. The remarkable stability of these complexes **2**−**4** is no doubt related to the nature of the "Cp*Ir" moiety, which helps to stabilize the different coordination modes, η^4, η^5, and η^6, of the sensitive quinone family of ligands. We also note that

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Table 1. Crystal Data for 4 and 5

formula	$C_{16}H_{19}O_2Ir \cdot 2H_2O$	$C_{18}H_{24}O_3Ir \cdot BF_4$
fw	471.6	567.4
a (Å)	14.032(2)	7.158(6)
b (Å)	15.578(4)	24.056(5)
c (Å)	14.474(3)	22.525(6)
α (deg)	90	90
β (deg)	90	92.24(4)
γ (deg)	90	90
V (Å^3)	3163.7(2)	3876(3)
Z	8	8
cryst syst	orthorhombic	monoclinic
space group	*Pbca*	$P2_1/n$
linear abs coeff μ (cm^{-1})	84.2	69.1
density ρ (g cm^{-3})	1.98	1.95
diffractometer	CAD4 Enraf-Nonius	MACH3 Enraf-Nonius
radiation	Mo Kα (λ = 0.710 69 Å)	Mo Kα (λ = 0.710 69 Å)
scan type	$\omega/2\theta$	$\omega/2\theta$
scan range (deg)	0.8 + 0.345 tan θ	0.8 + 0.345 tan θ
θ limits (deg)	2−21	1−25
temp of measment	room temp	room temp
octants collcd	0−18; 0−20; 0−19	0−8; 0−28; −26 to 26
no. of data collcd	4276	7614
no. of unique data collcd	3819	6824
no. of unique data used for refinement	2659	3684
$R = \sum\|\|F_o\| - \|\|F_c\|\|/\sum\|F_o\|$	0.0326	0.0668
$R_w{}^a = [\sum w(\|F_o\| - \|F_c\|)^2/\sum wF_o{}^2]^{1/2}$	0.0347	0.0762
abs corr	ψ scan	
ext param	109	<Tr>
goodness of fit s	1.03	<Tr>
no. of variables	192	477
$\Delta\rho_{min}$ (e Å^{-3})	−1.46	−2.43
$\Delta\rho_{max}$ (e Å^{-3})	0.93	2.16

[a] $w = w'[1 - ((||F_o| - |F_c||)/6s(F_o))^2]^2$ with $w' = 1/S_rA_rT_r(X)$ with 3 coefficients −9.39, −4.72, 7.13 for compound **4**, 5.84, −0.74, 4.25 for compound **5**—for a Chebychev Serie, for which X is F_o/F_o(max).

the reversible deprotonation/protonation reactions occur via changes of the oxidation state from Ir(III) to Ir(I) and inversely.

X-ray Molecular Structure of [Cp*Ir(η^4-*p*-benzoquinone)] (4). Suitable crystals of **4** were obtained by recrystallization from a CH_3CN/Et_2O solution. Although several X-ray structures of η^4-duroquinone complexes were reported in the literature,[4,10,19] those of simple η^4-*p*-benzoquinone are rare.[20] Complex **4** crystallizes with two molecules of water in the orthorhombic space group *Pbca*. Figure 1 shows a Cameron view of **4** with the atom-numbering system, and crystallographic data collection parameters are listed in Table 1.

The structure shows that the Cp*Ir fragment is indeed coordinated to only four carbons of the quinone ligand, whereby the distance from the metal to the centers of the π-bonded carbons is 1.69 Å for the quinone and 1.81 Å for η^5-C_5Me_5. Further, the quinone ligand acquires a boat-like conformation with dihedral angles across C2−C6 and C3−C5 of almost 16°. These angles are smaller than those reported for neutral and cationic rhodium complexes of η^4-duroquinone, which lie in the range of 20−28°.[19]

Synthesis, X-ray Structure, Solution Behavior and Reactivity of [Cp*Ir(η^4-3-methoxy-*o*-benzoquinone)] (6) and [Cp*Ir(η^6-3-methoxy-catechol)] (7). We recently reported a novel system for regioselective ortho-functionalization of phenols,[21] tetralols,

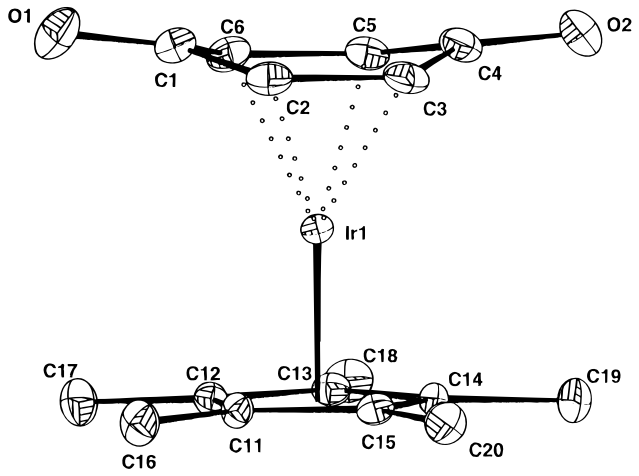

Figure 1. X-ray molecular structure of [Cp*Ir(η^4-*p*-benzoquinone)] (**4**) with atom-numbering system. Selected bond distances (Å) and angles (deg): Ir1−C2 = 2.188(6), Ir1−C3 = 2.182(6), Ir1−C5 = 2.192(6), Ir1−C6 = 2.218(6), O1−C1 = 1.252(8), O2−C4 = 1.260(8), C1−C2 = 1.45(1), C1−C6 = 1.449(9), C2−C3 = 1.434(9), C3−C4 = 1.45(1), C4−C5 = 1.43(1), C5−C6 = 1.456(9); C2−C1−C6 = 111.9(6), C3−C4−C5 = 112.0(6), C1−C2−C3 = 123.2(6), C2−C3−C4 = 122.3(6), C4−C5−C6 = 123.6(6), C5−C6−C1 = 121.4(6).

and steroids[22] promoted by the Cp*Ir fragment and using NaOMe as the attacking nucleophile (Scheme 3). The procedure consists of three steps: (a) placement of the Cp*Ir moiety at the aromatic ring, followed by treatment with NEt_3 affords the (oxocyclohexadienyl)-iridium complexes. (b) The latter react with NaOMe

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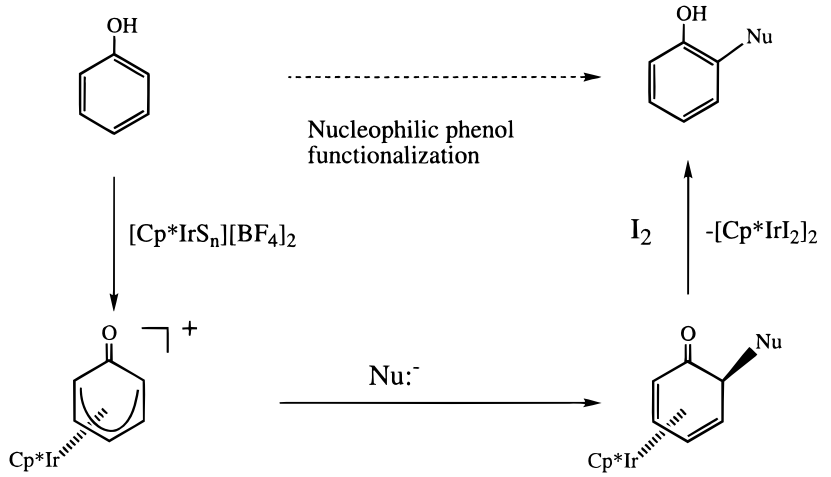
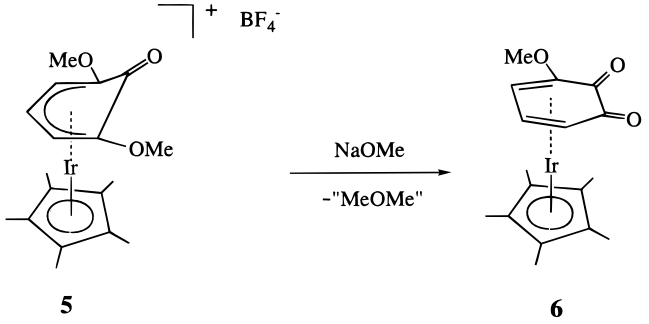
Scheme 3. Nucleophilic Ortho-Functionalization of Phenols



Scheme 4



in methanol to give the η^4-dienone compounds. (c) Subsequent oxidative decomplexation by iodine provides the ortho-substituted phenols, along with the starting organometallic material recycled in the form [Cp*Ir(μ-I)I]$_2$.

To direct the nucleophilic attack of NaOMe to the para-position of the complexed oxo-η^5-dienyl moiety, we chose to study the reactivity of the model complex [Cp*Ir(η^5-(2,6-dimethoxy)-C_6H_3O)][BF_4] (**5**). In this compound, the two ortho-positions are substituted; therefore, one might favor an attack elsewhere on the complexed oxo-η^5-dienyl fragment. Complex **5** was completely characterized by spectroscopic methods and elemental analysis. The ^{13}C NMR of **5** recorded in CD_3CN gave the expected signals, however, the C=O function of the η^5-oxo−dienyl unit appeared unexpectedly at 151.20 ppm. This value is low compared to those reported for the C=O functions of other oxo−dienyl iridium complexes, which usually appear in the range of 162−167 ppm. This unexpected result stimulated us to determine the X-ray structure of [Cp*Ir(η^5-(2,6-dimethoxy)-C_6H_3O)][BF_4] (**5**). Crystals of **5** were obtained by slow crystallization from a CH_3CN/Et_2O solution. Compound **5** crystallizes in the monoclinic space group $P2_1/n$; there are two independent molecules in the unit cell. Figure 2 shows a view of the cation [Cp*Ir(η^5-(2,6-dimethoxy)-C_6H_3O)]$^+$ with the atom-

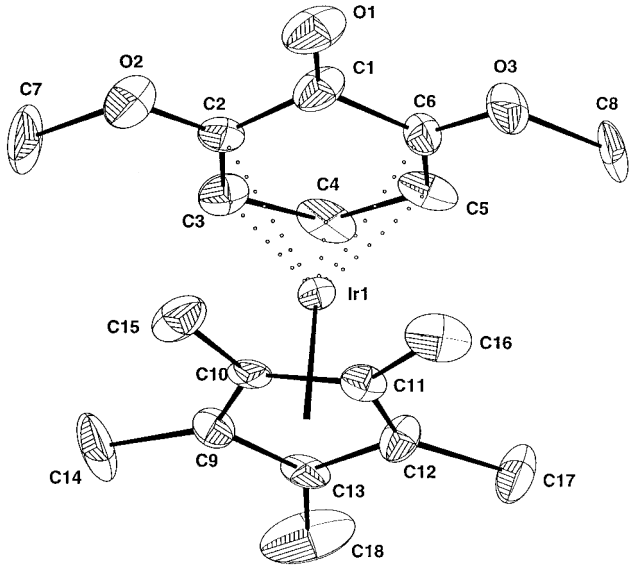
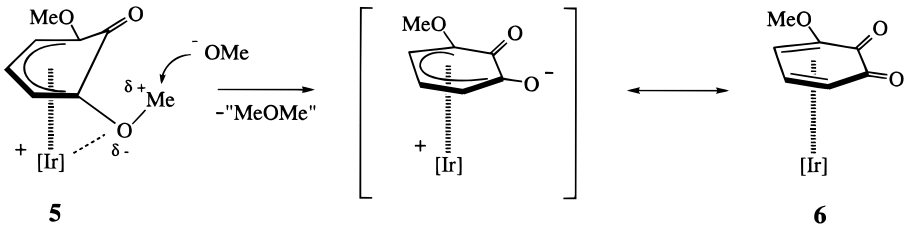


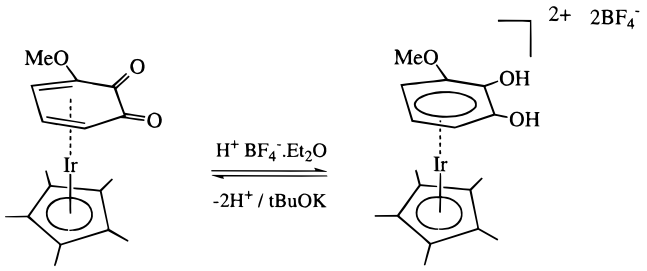
Figure 2. X-ray molecular structure of [Cp*Ir(η^5-(2,6-dimethoxy)-C_6H_3O]$^+$ (cation of **5**) with atom-numbering system. Selected bond distances (Å) and angles (deg): Ir1−C2 = 2.31(2), Ir−C3 = 2.22(2), Ir1−C4 = 2.17(2), Ir1−C5 = 2.27(2), Ir1−C6 = 2.37(2), Ir1−C9 = 2.17(2), Ir1−C10 = 2.17(2), Ir1−C11 = 2.19(2), Ir1−C12 = 2.16(2), Ir1−C13 = 2.20(2); C2−C1−C6 = 113.6(19), C2−C1−O1 = 122.3(24), C6−C1−O1 = 123.3(24), C3−C4−C5 = 122.2(23).

Scheme 5. Proposed Mechanism for the Formation of [Cp*Ir(η^4-(3-methoxy)-*o*-benzoquinone] (6)



[Ir] = Cp*Ir

Scheme 6



6 **7**

numbering system, and crystallographic data collection parameters are listed in Table 1.

The structure shows that the Cp*Ir unit is coordinated to only five carbons of the oxo−dienyl unit with Ir(1)−C(2−6)(average) = 2.27 Å, while the Ir(1)−C(1) bond distance is 2.58 Å. Another important feature of this structure is the C(1)−O(1) bond distance of 1.24(3) Å, which is longer than those reported for the analogous iridium oxo−dienyl complexes [Cp*Ir(η^5-(3,5-dimethyl)-C_6H_3O)][BF_4] (**8**) {d(C(1)−O(1)) = 1.23 Å} and [Cp*Ir-(η^5-$C_{18}H_{23}O_2$)][BF_4] (**9**) {d(C(1)−O(1)) = 1.19 Å}. The dihedral angle θ between the C(1)−C(2)−C(6) plane and the rest of the oxo−dienyl unit is 14°; this angle θ is smaller than that reported for **8** (θ = 19°) and **9** (θ = 23°). In conclusion, the X-ray data show that the ketonic character of C═O in **5** is less pronounced relative to the analogous iridium complexes **8** and **9**;[19,20] therefore, the X-ray data are in accord with ^{13}C NMR values obtained in solution for complex **5**.

Treatment of complex **5** by NaOMe in methanol gave, after reaction workup, the 3-methoxy-*o*-benzoquinone iridium complex [Cp*Ir(η^4-(3-methoxy)-$C_6H_3O_2$)] (**6**), isolated in 62% yield. Complex **6** is presumably obtained via (a) attack of the MeO− at the methyl group of one the methoxy groups and not on the complexed oxo−dienyl moiety, and (b) subsequent loss of "MeOMe" provides the substituted 3-methoxy-*o*-benzoquinone iridium complex **6** (Scheme 4). This unexpected chemical transformation that leads to **6** could be attributed to the cationic nature of Cp*Ir which enhances the attack at the methyl group (−CH_3) by stabilizing the intermediate complex formed during the nucleophilic reaction (Scheme 5).

The *o*-benzoquinone iridium compound **6** reacted in a similar way to the *p*-benzoquinone complex [Cp*Ir-(η^4-*p*-benzoquinone)] (**4**). Thus, treatment of **6** with an excess of HBF_4·Et_2O produced the related catechol iridium complex [Cp*Ir(η^6-(3-methoxy)-$C_6H_5O_2$)][BF_4]$_2$ (**7**) quantitatively (Scheme 6). The latter is deprotonated by tBuOK and provided the starting material **6**. This acid−base reaction occurs reversibly without showing any sign of decomposition for the organometallic complexes **6** and **7**. Once again, the nature of the Cp*Ir^{2+} fragment plays an important role in stabilizing these sensitive π-cyclic hydrocabon ligands.

In conclusion, we have reported the high-yield syntheses of *p*- and *o*-benzoquinone complexes of pentamethylcyclopentadienyl iridium complexes **4** and **6**. The X-ray molecular structure of the *p*-benzoquinone compound **4** was determined. The solution and chemical behavior of these complexes were studied. In particular, reversible protonation/deprotonation reactions were observed without decomposition of the organometallic complexes. We also demonstrated the remarkable stability of these [Cp*Ir(η^6-arene)][BF_4]$_2$ due to the ability of the Cp*Ir^{2+} moiety to stabilize these sensitive ligands (hydroquinone catechol). Complexes of this type are rare in the literature. Finally, we have found that oxidation of the *p*- and *o*-benzoquinone iridium complexes by iodine provides the free ligand along with the starting material recycled in the form of [Cp*Ir(μ-I)I]$_2$. These results are significant since it shows that functionalization of this type of sensitive ligand promoted by a Cp*Ir fragment is possible and may occur in a fashion similar to that described recently by us for the regioselective nucleophilic phenol reactions (Scheme 3).[19,20]

Experimental Section

General Procedures. All manipulations were carried out under an 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 freshly used in the preparation of NaOMe solutions. All reagents obtained from commercial sources were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 250 MHz instrument. ^{1}H NMR chemical shifts are reported in parts per million referenced to the residual solvent proton resonance. Infrared spectra were obtained on a Bruker IR 45 spectrometer from samples prepared on KBr disks or in Nujol. All absorptions are expressed in wavenumbers (cm^{-1}). Elemental analyses were performed by the Microanalytical Laboratory of the University of Paris VI.

Synthesis of [Cp*Ir(η^6-hydroquinone)][BF_4]$_2$ (2). A solution of $AgBF_4$ (400 mg, 2.05 mmol) in THF (10 mL) was added to [Cp*IrCl_2]$_2$ (400 mg, 0.50 mmol) in acetone (20 mL) to rapidly give a white preciptate of AgCl. The reaction mixture was stirred for 15 min, then the yellow orange solution of [Cp*Ir(acetone)$_3$][BF_4]$_2$ (**1**) was filtered into a dry Schlenk tube which was kept under argon. To this orange-yellow solution was then added hydroquinone (230 mg, 2.1 mmol) in THF (15 mL), and the mixture was stirred for 1 h, during which the solution becomes yellowish-green. The solvents were removed under vacuum, and the residue was dried. The yellow solid material was dissolved in CH_3CN (20 mL), and addition of an excess of HBF_4·Et_2O caused a rapid decolorization. The reaction was allowed to continue for 15 min, then the solution was concentrated under vacuum. Subsequent addition of Et_2O (30 mL) provoked the precipitation of a white microcrystalline solid. The precipitate was separated, washed 3 times with Et_2O, and dried under vacuum. Overall yield: 570 mg (93%). IR (Nujol, cm^{-1}): ν(O−H) 3100−3300, ν(B−F) 1065. ^{1}H NMR (250 MHz, TFA-d_1): δ 2.16 (s, 15H, −Cp*), 6.76 (s, 4H, aromatic protons), −OH (not observed). ^{13}C{^{1}H} NMR (62.87 MHz, TFA-d_1): δ 9.21 (−CH_3, −Cp*), 85.00 (C═C, aromatic carbons), 105.96 (C═C, −Cp*), 137.94 (C−O). Anal. Calcd for $C_{16}H_{21}B_2F_8IrO_2$: C, 31.42; H, 3.40. Found: C, 32.30; H, 3.57.

Synthesis of [Cp*Ir(η^5-semiquinone)][BF_4] (3). This complex was obtained pure by slow recrystallization of [Cp*Ir-(η^6-hydroquinone)][BF_4]$_2$ (**2**) from CH_3CN/Et_2O. Crystals of **3** were formed after 2−3 days. This period of time is sufficient to allow a complete monodeprotonation of complex **2**. IR (KBr, cm^{-1}): ν(O−H) 3250−3400, ν(C═O) 1629, ν(B−F) 1065. ^{1}H NMR (CD_3CN, 250 MHz): δ 2.10 (s, 15H, η^5-Cp*), 5.15 (d, J_{H-H} = 7.5 Hz, 2H arene protons), 5.95 (d, J_{H-H} = 7.5 Hz, 2H arene protons). Anal. Calcd for $C_{16}H_{21}BF_4IrO_2$: C, 36.67; H, 3.82. Found: C, 36.62; H, 3.87.

Synthesis of [Cp*Ir(η^4-*p*-benzoquinone)] (4). To a suspension of [Cp*Ir(η^6-hydroquinone)][BF_4]$_2$ (**2**) (100 mg, 0.16 mmol) in CH_2Cl_2 (10 mL) was added 50 mg (0.44 mmol) of tBuOK, and the reaction was left for 2 h. During this period of time, the reaction mixture became yellow and clear. The solution was filtered through Celite, and the filtrate was reduced under vacuum. Addition of Et_2O (20 mL) afforded an off-white precipitate. The solid was separated, washed with Et_2O, and then dried under vacuum. Yield: 60 mg (84%). IR (Nujol, cm^{-1}): ν(C═O) 1567, 1537. ^{1}H NMR (CD_3CN, 250 MHz): δ 2.04 (s, 15H, η^5-Cp*), 4.87 (s, 4H, olefinic protons). $^{13}C\{^1H\}$ NMR (62.87 MHz, CD_3CN): δ 9.0 (−CH_3, −Cp*), 74.2 (C═C, dienone carbons), 96.4 (C═C, −Cp*), 160.5 (C═O). Anal. Calcd for $C_{16}H_{19}IrO_2\cdot 2H_2O$: C, 36.67; H, 3.82. Found: C, 36.62; H, 3.87.

Synthesis of [Cp*Ir(η^5-(2,6-dimethoxy)-C_6H_3O)][BF_4] (5). A solution of $AgBF_4$ (200 mg, 1.03 mmol) in 6 mL of acetone was added to [Cp*$IrCl_2$]$_2$ (200 mg, 0.25 mmol) in 15 mL of acetone to rapidly give a white precipitate of AgCl. The reaction mixture was stirred for 15 min, then the orange-yellow solution of [Cp*Ir(acetone)$_3$][BF_4]$_2$ was filtered into a dry Schlenk tube kept under argon. To this orange-yellow solution was then added 2,6-dimethoxyphenol (154 mg, 1 mmol) in 9 mL THF, and the mixture was stirred for 1 h, during which a white precipitate starts to form. The reaction mixture was reduced under vacuum, and subsequent addition of Et_2O (50 mL) affords a white precipitate. Our target compound **5** was obtained by treating the white precipitate obtained in the first step with NEt_3 (200 μL) in 15 mL of acetone for 15 min. Then the light yellow solution was reduced under vacuum, and subsequent addition of Et_2O (40 mL) afforded a white precipitate. This compound was washed several times with Et_2O and dried under vacuum. Overall yield: 81% (230 mg). IR (KBr disk, cm^{-1}): ν(C═O) 1631, ν(B−F) 1055. ^{1}H NMR (CD_3CN, 250 MHz): δ 2.02 (s, 15H, −Cp*), 3.70 (s, 6H, −OMe), 5.80 (t, J_{H-H} = 6 Hz, 1H, dienyl proton), 6.25 (d, J_{H-H} = 6 Hz, 2H, dienyl protons). $^{13}C\{^1H\}$ NMR (62.87 MHz, CD_3CN): δ 9.41 (CH_3, −Cp*), 58.17 (−OMe), 73.35 (C═C, dienyl carbon), 78.16 (C═C, dienyl carbon), 98.61 (C═C, −Cp*), 128.86 (C−OMe, dienyl), 151.20 (C═O). Anal. Calcd for $C_{18}H_{24}BF_4IrO$: C, 38.11; H, 4.20. Found: C, 37.91; H, 4.32.

Synthesis of [Cp*Ir(η^4-(3-methoxy)-*o*-benzoquinone] (6). A methanolic solution of NaOMe (1 mmol) {freshly prepared from NaH (40 mg; 60%) in distilled methanol (5 mL)} was added to a solution of **5** (100 mg, 0.175 mmol) in 10 mL of MeOH. The reaction mixture was stirred fo 12 h at room temperature, then the solvent was removed completely and dried under vacuum. The residue was then extracted with 20 mL of CH_2Cl_2 and filtered under argon into a dry Schlenk tube. The solvent was removed under vacuum, affording a yelllow microcrystalline solid in 62% yield (50 mg). IR (KBr disk, cm^{-1}): ν(C═O) 1555.8. ^{1}H NMR (CD_3CN, 250 MHz): δ 1.85 (s, 15H, −Cp*), 3.55 (s, 3H, −OMe), 4.96 (d, J_{H-H} = 6 Hz, 1H, dienone proton), 5.29 (t, J_{H-H} = 6 Hz, 1H, dienone proton), 5.88 (d, J_{H-H} = 6 Hz, 1H, dienone proton). $^{13}C\{^1H\}$ NMR (62.87 MHz, CD_3CN): δ 8.71 (CH_3, −Cp*), 56.87 (−OMe), 69.76 (C═C, dienone carbon), 73.04 (C═C, dienone carbon), 74.76 (C═C, dienone carbon), 94.23 (C═C, −Cp*), 121.91 (C−OMe, dienone), 155.17 (C═O), 160.91 (C═O). Anal. Calcd for $C_{17}H_{21}O_3Ir\cdot CH_2Cl_2$: C, 39.27; H, 4.18. Found: C, 38.37; H, 4.64.

Synthesis of [Cp*Ir(η^6-(3-methoxy)catechol][BF_4]$_2$ (7). To a solution of **6** (40 mg, 0.08 mmol) in 5 mL of CH_3CN was added 100 μL of $HBF_4\cdot Et_2O$, and the reaction mixture was stirred for 20 min, then filtered through Celite. The solvent was concentrated under vacuum, and addition of Et_2O (15 mL) afforded a white precipitate, which was separated and washed several times with Et_2O and dried under vacuum. The catechol complex [Cp*Ir(η^6-(3-methoxy)catechol][BF_4]$_2$ (**7**) is extremely moisture sensitive, and therefore, microanalysis could not be obtained. IR (KBr disk, cm^{-1}): ν(−OH) 3250−3500, ν(B−F) 1084. ^{1}H NMR (CD_3CN, 250 MHz): δ 2.10 (s, 15H, −Cp*), 4.05 (s, 3H, −OMe), 4.22 (b, 2H, −OH), 6.27 (t, J_{H-H} = 7.5 Hz, 1H, aromatic protons), 6.63 (d, J_{H-H} = 7.5 Hz, 2H, aromatic protons). $^{13}C\{^1H\}$ NMR (62.87 MHz, CD_3CN): δ 9.25 (CH_3, −Cp*), 60.1 (−OMe), 76.33 (C═C, aromatic carbon), 86.94 (C═C, dienyl carbon), 101.79 (C═C, −Cp*), 129.60 (C−OMe, aromatic), not observed (C−OH).

X-ray Crystallography of [Cp*Ir(η^4-*p*-benzoquinone)] (4) and [Cp*Ir(η^5-(2,6-dimethoxy)-C_6H_3O][BF_4] (5). Suitable crystals of **4** and **5** were obtained by recrystallization from a CH_3CN/Et_2O solution. The selected crystal of complex **4** or **5** was glued on the top of a glass stick. Accurate cell dimensions and 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 for **4** are listed (Table 1). The data were corrected for Lorentz and polarization effects. Computations were performed by using the PC version of CRYSTALS.[23] Scattering factors and corrections for anomalous dispersion were taken from ref 24. The structure of compound **4** was solved by standard Patterson and Fourier technics and refined by full-matrix least-squares 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. The structure of complex **5** was solved by direct methods (SHELXS).[25] The asymmetric unit consists of two independent moleules. Refinements were carried out by full-matrix least-squares with anisotropic thermal parameters for all atoms except the boron atoms of the two BF_4^- anions. These anions show some disorder, and refinements were performed using restraints on B−F bond lengths and F−B−F bond angles. As a consequence, a relatively high value of $\Delta\rho$ was observed for BF_4^- anions and the hydrogen atoms were not introduced.

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Supporting Information Available: Tables of fractional parameters (Tables S1 and S5) and anisotropic displacement parameters (Tables S2 and S6) for **4** and **5** and bond lengths and angles (Tables S3 and S4) for **5** (7 pages). Ordering information is given on any current masthead page.

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