Ir-Mediated Nucleophilic Ortho-Functionalization of Phenols: Syntheses, Structures, Scope, and Limitation

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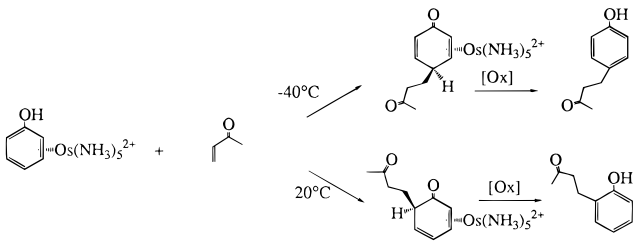
Treatment of [Cp*Ir(η^5-PhO)][BF_4] (**1**) with hydride, deuteride, and C-, N-, and S-centered nucleophiles affords the stable η^4-phenol tautomers of the type [Cp*Ir(η^4-exo-2-(Nu)-C_6H_5O)] (**2**−**6**) {Nu = nucleophile}. In all cases regiospecific nucleophilic addition occurs at the ortho-position relative to C=O with exo-stereochemistry. The X-ray molecular structure of the first neutral phenol tautomer [Cp*Ir(η^4-exo-2-(CH(COMe)$_2$)-C_6H_5O] (**4**) was determined and provides valuable crystallographic information for an organic phenol tautomer. Oxidation of the novel dienone iridium complexes [Cp*Ir(η^4-exo-2-(Nu)-C_6H_5O)] by iodine provided a different type of products depending dramatically on the nature and electron properties of the 2-exo-nucleophile. For instance R_3C-, RO-, and R_3P-centered nucleophiles gave the related ortho-functionalized phenols along with the starting material recycled in the form of [Cp*Ir-(μ-I)I]$_2$. In dramatic contrast N- and S-centered nucleophiles showed a retronucleophilic addition or C−Nu bond cleavage as demonstrated by complexes **5** and **6** to give the starting material identified spectroscopically and by X-ray structure as [Cp*Ir(η^5-PhO)][I] (**8**). In the latter, a rationale involving a one-electron oxidation process is proposed to explain the experimental results.

Aromatic systems are naturally activated to electrophilic substitution reactions. Friedel−Crafts alkylation is one of the greatest discoveries that allows the placement of a carbon substituent on an arene ring.[1] Yet this reaction is not without drawbacks; for instance, lack of selectivity, multiple alkylations, and carbocation rearrangements result in difficulty of product separation and consequently lower yields. Transition metal fragments coupled with the ability of an organometallic chemist to place these moieties at the aromatic systems modify profoundly the electronic properties of the arene rings and activate the π-hydrocarbon to nucleophilic substitution and addition reactions.[2−4] The chemistry of arene−metal complexes has been developed in the past 30 years, and their use in organic synthesis has been the focus of several reviews,[5] yet there is no organometallic procedure that allows *nucleophilic phenol functionalization*. The only known organometallic procedure that allows systematic *electrophilic phenol functionalization* was recently described by Harman and co-workers.[5c,6]

Scheme 1. Os-Mediated Electrophilic Phenol Functionalization



Harman has elegantly shown that the electron-rich moiety $Os(NH_3)_5^{2+}$ coordinates to a phenol ring in a dihapto fashion, rendering the aromatic π-system partially localized and activating the η^2-phenol to electrophilic addition reactions; subsequent decomplexation provides the functionalized free phenol (Scheme 1).

In this paper we report a convenient synthetic procedure that allows regiospecific *nucleophilic phenol functionalization* mediated by the $[Cp^*Ir]^{2+}$ moiety. Scheme 2 describes the general procedure, which in-

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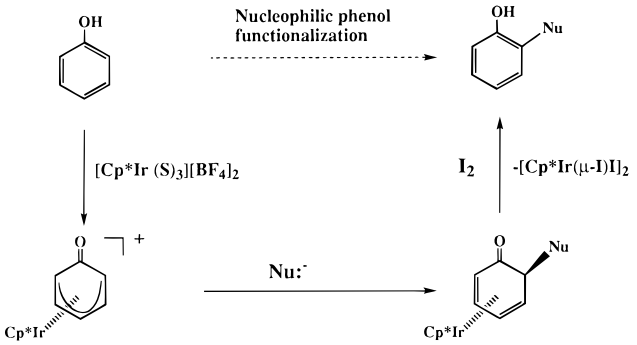
Scheme 2. Ir-Mediated Nucleophilic Phenol Functionalization



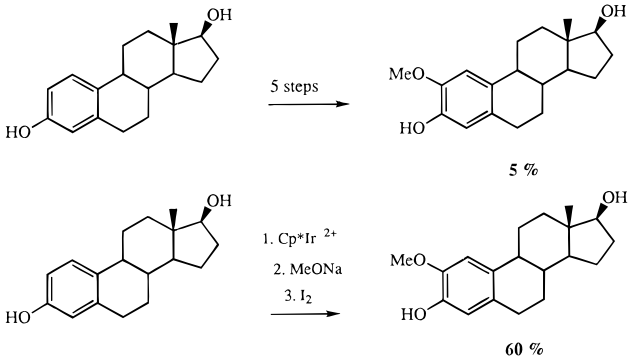
volves three steps: (a) Placement of the "Cp*Ir" moiety on the aromatic ring, followed by treatment with NEt_3 affords the (oxo-cyclohexadienyl)iridium complexes. (b) The latter react with a nucleophile (Nu) to give the stable η^4-dienone compounds. (c) Subsequent oxidative decomplexation by iodine provides the ortho-substituted phenols along with the starting organometallic material recycled in the form $[Cp^*Ir(\mu\text{-}I)I]_2$. The individual steps as well as the influence of the organometallic moiety on the nucleophilic addition sequence were thoroughly examined; we also isolated and characterized by X-ray analysis of the key intermediate "Cp*Ir(η^4-exo-2-Nu-dienone)" species.

In particular the stable complex [Cp*Ir(η^4-exo-2-(CH-(COMe)$_2$)-C_6H_5O] (**4**) is the first X-ray structure of a stable monocyclic phenol tautomer η^4-coordinated to a metal center. The reactivity of the (oxo-cyclohexadienyl)-iridium complexes toward carbon-, nitrogen-, and sulfur-centered nucleophiles as well as their influence on the demetalation step was examined, including a rationale to explain the experimental results.

Results and Discussion

We recently discovered that oxo-η^5-dienyl complexes can be used as precursors to promote *nucleophilic phenol functionalization*.[7] In fact such complexes are attacked smoothly with a nucleophile such as a phosphine or methoxide MeO^- specifically at the ortho-position, leading to only a single dienone iridium complex. Surprisingly and intriguingly no nucleophilic addition occurs at the carbon atom of the ketonic function; the formation of the novel dienone species is accompanied by reduction of the metal oxidation state from Ir(III) to Ir(I). Our method (Scheme 2) has been shown also to be efficient for ortho-functionalization of complex organic molecules such as tetralols and steroids. For instance 2-methoxyestradiol is obtained from β-estradiol in 60% yield and only in three steps,[7b] compared to the conventional organic procedure, which affords the same compound in 5% overall yield and via five steps (Scheme 3). 2-Methoxyestradiol is an anticancer agent and possesses important physiological properties.[8]

Scheme 3



Scheme 4. Synthesis of the Birch Complex Analogues

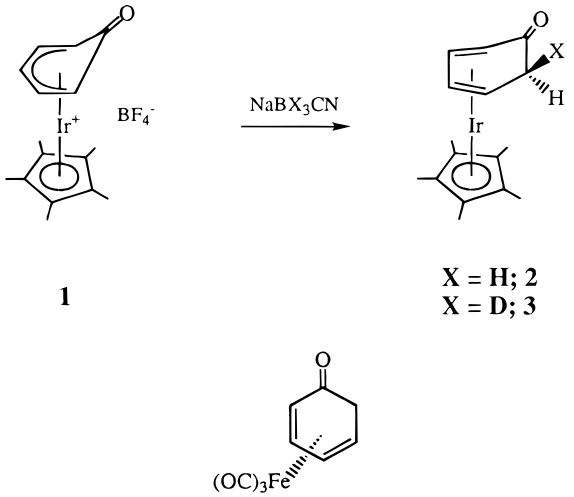


Figure 1. Birch complex.

Extension of this nucleophilic functionalization reaction (Scheme 2) to other kinds of nucleophiles allows a better comprehension of the factors that stabilize the key intermediate molecule and should influence the selectivity and yield, and further it determines the scope and limitations of this reaction relative to the only known electrophilic phenol functionalization reaction reported recently in the literature. Therefore the reactivity of [Cp*Ir(η^5-C_6H_5O][BF_4] (**1**) with hydrides and C-, N-, and S-centered nucleophiles is presented here.

Reaction of [Cp*Ir(η^5-C_6H_5O)][BF_4] (1) with Hydride and Deuteride Sources and Formation of the Birch Complex Analogues [Cp*Ir(η^4-C_6H_5(X)O] {X = H (2); D (3)}. Among the most known organometallic compounds in the literature is the Birch complex[9] [$(CO)_3$Fe(η^4-C_6H_6O)] (Figure 1). The synthesis and reactivity of this compound have been well investigated in the literature; however to our knowledge there exist no other analogous complexes in which the phenol tautomer is stabilized through η^4-coordination to a metal center. We have found that treatment of [Cp*Ir(η^5-C_6H_5O][BF_4] (**1**) with $NaBH_3CN$ for 48 h affords the Birch complex analogue [Cp*Ir(η^4-C_6H_6O)] (**2**) in 60% yield. Interestingly the synthesis of complex **2** is easy and straightforward and is obtained in 54% yield via two steps starting from phenol, and this should be

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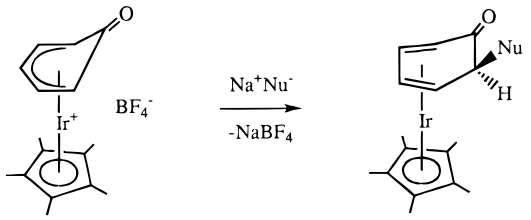
Scheme 5. Synthesis of the Dienone−Ir Complexes 4−6



1

Nu⁻=$(CH_3CO)_2CH^-$ **4**

Nu⁻= N⁻ **5**

Nu⁻=PhS^- **6**

compared to the preparation of the complex [$(CO)_3$Fe-(η^4-C_6H_6O)], which requires four steps starting from anisole and is obtained in 26% yield.[9b]

The ^{1}H NMR of complex **2** recorded in $CDCl_3$ shows the presence of six multiplets in the area 2−6 ppm, while the methyl protons of η^5-Cp* appear at 2.07 ppm. The ^{13}C NMR of **2** recorded in $CDCl_3$ is in accord with the proposed formula, and it shows the presence of a singlet at 188 ppm attributed to the dienone C═O function of such complexes.[7] Although the Birch complex [$(CO)_3$Fe(η^4-C_6H_6O)] is an effective phenylating agent of aromatic amines,[10] we did not examine the reactivity of our dienone complex **2**. On the other hand when [Cp*Ir(η^5-C_6H_5O)][BF_4] (**1**) was treated with $NaBD_3CN$ followed by reaction workup, the novel deuterated dienone complex [Cp*Ir(η^4-C_6H_5DO)] (**3**) was isolated. The ^{1}H and ^{13}C NMR data of complex **3** are in accord with the proposed formula. The structure of **3** was also confirmed by comparison with the ^{1}H NMR spectrum of [Cp*Ir(η^4-C_6H_6O)] (**2**), which displays a doublet of doublets for H_{2endo} at 2.63 ppm ($J_{HexoHendo}$ = 16 Hz) and a doublet for H_{2exo} at 3.80 ppm. The latter signal was not observed for complex **3**; therefore, we deduced that the addition of deuterium anion (D^-) occurs regiospecifically at the C-2 position and exo relative to the organometallic moiety "Cp*Ir". This result was also confirmed by an X-ray molecular structure obtained for the analogous dienone complex [Cp*Ir(η^4-exo-2-(CH-($COMe)_2$)-C_6H_5O] (**4**) (vide infra).

Reaction of [Cp*Ir(η^5-C_6H_5O)][BF_4] (1) with Acetylacetonate and Formation of the Complex [Cp*Ir(η^4-exo-2-(CH(COMe)$_2$)-C_6H_5O] (4). The complex [Cp*Ir(η^5-C_6H_5O)][BF_4] (**1**) reacted smoothly with a slurry of freshly prepared acetylacetone anion from acetylacetone and sodium methoxide in CH_2Cl_2 for 12 h and afforded after reaction workup a light yellow complex [Cp*Ir(η^4-exo-2-(CH(COMe)$_2$)-C_6H_5O)] (**4**) in 72% yield (Scheme 5) identified by ^{1}H and ^{13}C NMR analysis and X-ray structural determination. For instance the ^{1}H NMR of **4** recorded in C_6D_6 displayed five multiplets attributed to the dienone protons in the area 2.5−5.0 ppm, while the two methyl groups of the coordinated acetylacetone unit appeared at 1.87 and 2.13 ppm, respectively. We also note the CH moiety between the two carbonyl function appeared at 3.6 ppm, while the methyl protons of η^5-Cp* resonated at 1.63 ppm. The ^{13}C NMR data were in accord with the proposed formula, and all the expected signals were assigned; however, we note the presence of a singlet at 194.7 ppm attributed to the dienone C═O function, which is a characteristic for this novel class of iridium−dienone complexes.[7] To ascertain the structure of this complex, an X-ray study of suitable crystals of **4** was undertaken.

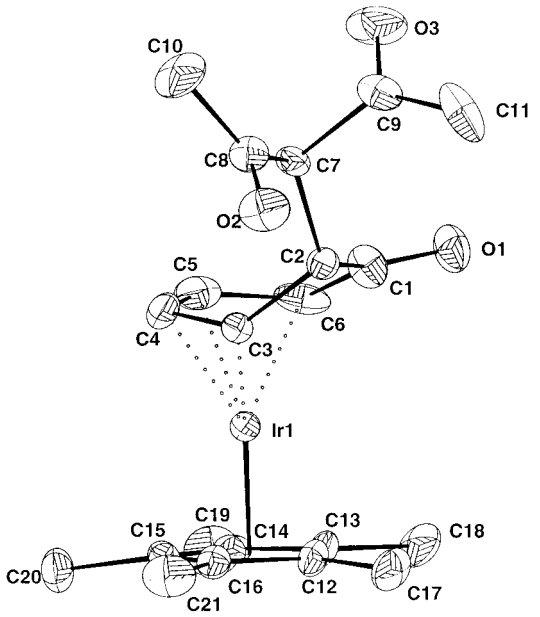


Figure 2. X-ray molecular structure of [Cp*Ir(η^4-exo-2-(CH(COMe)$_2$)-C_6H_5O)] (**4**) with atom-numbering system.

X-ray Molecular Structure of [Cp*Ir(η^4-exo-2-(CH(COMe)$_2$)-C_6H_5O)] (4). Suitable crystals of [Cp*Ir-(η^4-2-exo-(CH(COMe)$_2$)-C_6H_5O)] (**4**) were obtained by cooling a saturated solution of **4** in Et_2O/hexane. The compound crystallizes in the triclinic unit cell, space group $P\bar{1}$. There are two independent molecules in the asymmetric unit. Refinement details are discussed in the Experimental Section. Figure 2 shows the structure of the first neutral phenol tautomer [Cp*Ir(η^4-exo-2-(CH(COMe)$_2$)-C_6H_5O] with the atom-numbering system; crystallographic data collection parameters and selected bond lengths and angles are listed in Tables 1 and 2.

The structure reveals that the acetyl−acetone radical is indeed attached at C-2, with exo-stereochemistry relative to the organometallic moiety "Cp*Ir". The distances from the metal to the centers of the π-bonded carbons is 1.74(1) Å for the diene and 1.83(1) Å for the η^5-Cp* ligand. Further, the "Cp*Ir" moiety is coordinated to only four carbons of the ring. Loss of aromaticity is manifested by the irregularity of the C−C bond distances; the length of the uncoordinated bond C1−C2 is 1.51(2) Å, while the C1−O1 bond distance is 1.23-(2) Å, which is characteristic of a C═O double bond of a ketonic function. The dihedral angle "hinge" across C3−C6 is 39° and slightly bigger than that reported for the only known cationic phenol tautomer complex [Cp*Ir-(η^4-exo-2-(PMe_3)-C_6H_5O)]$^+$ with θ = 36.5°.[7c] As mentioned in the previous paragraph, the only well-known η^4-phenol tautomer complex is the Birch compound Fe-$(CO)_3$(η^4-2,4-cyclohexadien-1-one);[9,10] further, there is no X-ray structure for this type of η^4-dienone compound.[11] On the other hand, it should be borne in mind that the free dienone ligands are unstable and tautomerize

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Table 1. Crystal Data and Structure Refinement

	4	**8**
empirical formula	$C_{21}H_{27}O_3Ir$	$[C_{16}H_{20}OIr][I]\cdot{}^1/_2CH_3CN$
fw	523.7	568
cryst system	triclinic	triclinic
space group	P-1	P-1
a, Å	10.972(1)	7.514(9)
b, Å	12.751(2)	16.459(12)
c, Å	14.731(2)	16.633(9)
α, deg	84.32(1)	118.46(6)
β, deg	79.75(1)	100.11(7)
γ, deg	81.75(1)	91.72(8)
V, Å^3	2001.2(3)	1765(3)
Z	4	4
ρ (calcd), g/cm^3	1.74	2.14
μ(Mo Kα), cm^{-1}	66.6	92.6
crystal size, mm	0.12 × 0.18 × 0.30	0.20 × 0.20 × 0.20
T, °C	20	20
λ (MoKα), Å	0.710 69	0.710 69
scan type	*ω*/2*θ*	*ω*/2*θ*
scan range, deg	0.8 + 0.345 tan *θ*	0.8 + 0.345 tan *θ*
octants collected	0,14; −16,16; −19,19	0,8; −19,19−19,19
no. of reflns collected	101 34	6708
no. of ind reflns	9634 (R_{int} = 0.0206)	6187 (R_{int} = 0.04)
data used	4658 $(F_o)^2 > 3\sigma(F_o)^2$	3988 $(F_o)^2 > 3\sigma(F_o)^2$
R^a	0.0472	0.0675
$R_w{}^b$	0.0560	0.0729
$\Delta\rho_{min}$ (e/Å^3)	−1.59	−2.55
$\Delta\rho_{max}$ (e/Å^3)	2.45	2.59

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

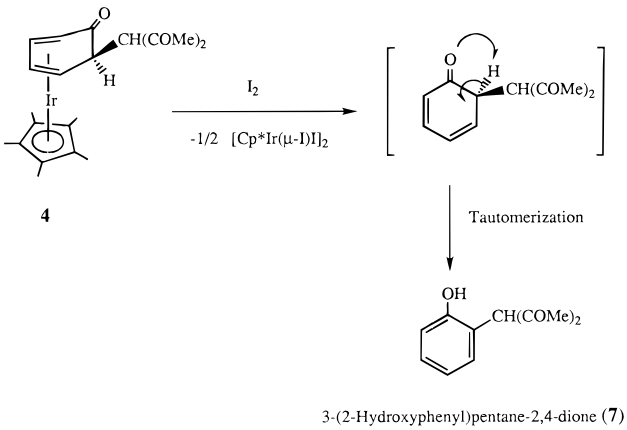
Table 2. Selected Bond Distances (Å) and Angles (deg) for 4

	Bond Lengths		
Ir(1)−Cp*$_{centroid}$	1.83	Ir(1)−C(3−6)$_{centroid}$	1.74
Ir(1)−C(3)	2.16(1)	Ir(1)−C(4)	2.14(1)
Ir(1)−C(5)	2.11(1)	Ir(1)−C(6)	2.16(1)
C(1)−O(1)	1.23(1)	C(2)−C(7)	1.55(1)
C(1)−C(2)	1.51(2)	C(2)−C(3)	1.52(2)
C(3)−C(4)	1.42(2)	C(4)−C(5)	1.39(3)
C(5)−C(6)	1.49(3)	C(1)−C(6)	1.48(2)
	Bond Angles		
C(3)−Ir(1)−C(4)	38.6 (6)	C(3)−Ir(1)−C(5)	66.3(6)
C(3)−Ir(1)−C(6)	74.9(5)	C(1)−C(2)−C(3)	107.5(11)
C(2)−C(1)−C(6)	114.2(13)	C(2)−C(3)−C(4)	119.0(13)
C(2)−C(1)−O(1)	121.3(14)	C(7)−C(2)−C(3)	110.8(10)
C(8)−C(7)−C(9)	105.7(11)	O(2)−C(8)−C(10)	123.4(14)

rapidly to the related phenols; however, it has been reported that they can be generated by vacuum pyrolysis and were partially characterized.[12] Therefore the Cp*Ir moiety not only stabilizes the phenol tautomer "(CH(COMe)$_2$)-C$_6$H$_5$O" through η^4-coordination but also allows the first determination of an X-ray structure of an organic phenol tautomer.

Oxidative Demetalation of [Cp*Ir(η^4-exo-2-(CH(COMe)$_2$)-C$_6$H$_5$O)] (4) and Formation of 3-(2-Hydroxyphenyl)pentane-2,4-dione (7). When a CH_3CN solution of **4** was exposed to iodine and the mixture was stirred for 5 min, a red solution resulted. Reaction workup and analysis of the reaction mixture by ^{1}H NMR suggested the formation of the novel phenol 3-(2-hydroxyphenyl)pentane-2,4-dione (**7**) and [Cp*Ir(μ-I)I]$_2$ (Scheme 6), as indicated by a singlet at 1.84 ppm, which

Scheme 6. Oxidative Demetalation of Complex 4 and Formation of the Free Functionalized Phenol 7



3-(2-Hydroxyphenyl)pentane-2,4-dione (**7**)

corresponds to the methyl protons of the η^5-Cp* unit.[13] The novel phenol **7** was sublimed at P = 0.2 mmHg, T = 30−35 °C to give white needles in 85% yield. The free ortho-functionalized phenol 3-(2-hydroxyphenyl)pentane-2,4-dione (**7**) was fully characterized by elemental analysis and spectroscopic methods and has a sharp melting point of 79 °C. The ^{1}H NMR of **7** recorded in CD_2Cl_2 showed the expected four multiplets of the aromatic ring in the area 6.80−7.30 ppm, while the phenolic proton appeared at low field at 16.85 ppm. Finally two singlets at 5.20 and 1.88 ppm are attributed to the methine (CH) and methyl groups of the acetyl−acetone radical in the ortho-position. Recently the synthesis of 3-(4-hydroxyphenyl)pentane-2,4-dione (**9**), which is the para-isomer of **7**, was reported. The para-substituted phenol (**9**) was prepared in three steps starting with para-iodo phenol and obtained in 45% overall yield. The authors reported that such phenols are valuable intermediates for liquid crystals.[14] The physical properties of our novel ortho-phenol analogous to molecule **9** have not yet been investigated.

The formation of the novel phenol is no doubt the result of keto−enol tautomerism of the free cyclohexadienone intermediate to give the more stable substituted phenol species **7** (see Scheme 6). It should be mentioned that the only known organometallic method that allows activation and functionalization of *phenols toward electrophiles* was illustrated by Harman using the Os(NH$_3$)$_5^{2+}$ unit. The Os system is completely different from the Ir one because the electron-rich Os(NH$_3$)$_5^{2+}$ moiety blocks one of the double bonds of the arene and activates the free diene part to an electrophilic addition reaction.[6a]

Reaction of [Cp*Ir(η^5-C$_6$H$_5$O)][BF$_4$] (1) with Piperidine and Thiophenol Anions and Formation of the Complexes [Cp*Ir(η^4-exo-2-(N(CH$_2$)$_5$)-C$_6$H$_5$O] (5) and [Cp*Ir(η^4-exo-2-(SPh)-C$_6$H$_5$O] (6). In a method similar to the preparation of **4** the oxo-dienyl iridium complex [Cp*Ir(η^5-C$_6$H$_5$O)][BF$_4$] (**1**) reacted with a slurry of the piperidine anion in THF or with thiophenol anion in CH_2Cl_2 for several hours. Reaction workup allowed the isolation of complex [Cp*Ir(η^4-exo-2-(N(CH$_2$)$_5$)-C$_6$H$_5$O] (**5**) and that of complex [Cp*Ir(η^4-exo-2-(SPh)-C$_6$H$_5$O] (**6**) in 68% and 57% yields, respectively

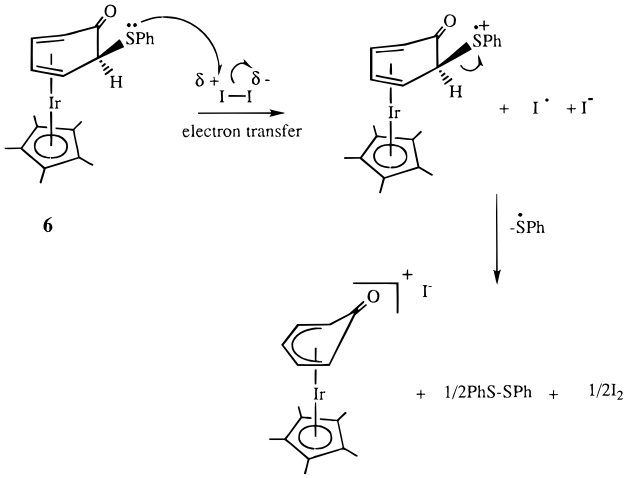
(11) X-ray structures of η^4-dienone complexes are rare in the literature, see: Wulff, W. D.; Bax, B. M.; Brandvold, T. A.; Chan, K. S.; Gilbert, A. M.; Hsung, R. P.; Mitchell, J.; Clardy, J. *Organometallics* **1994**, *13*, 102. Pavkovic, S. F.; Zaluzec, E. J. *Acta Crystallogr.* **1989**, *C45*, 18. However in these two examples the η^4-dienone is a part of a complex organic molecule and therefore cannot be compared to this work, where an X-ray structure of a monocyclic η^4-phenol tautomer [Cp*Ir(η^4-2-exo-(CH(COMe)$_2$)-C$_6$H$_5$O)] (**4**) is presented.

(12) Lasne, M. C.; Ripoll, J. L. *Tetrahedron. Lett.* **1980**, *21*, 463.

(13) Gill, D. S.; Maitlis, P. M. *J. Organomet. Chem.* **1975**, *87*, 359.

(14) Cativiela, C.; Serrano, J. L.; Zurbano, M. M. *J. Org. Chem.* **1995**, *60*, 3074.

Scheme 7. Proposed Mechanism for the Retronucleophilic Addition and Formation of PhS−PhS



6 8

(Scheme 5). Both compounds were obtained as yellow microcrystalline solids and are analytically pure as confirmed by elemental analysis and spectroscopic data (see Experimental Section). For instance the ^{13}C NMR data of **5** and **6** were very informative, showing in addition to the signs of η^4-diene and Cp* carbons the presence of a singlet at 189.6 ppm for **5** and at 187.0 for **6** attributed to the dienone C═O function of the η^4-dienone iridium complex, in analogy with the ^{13}C shifts seen in NMR spectra of other phenol tautomer iridium complexes.[7] Surprisingly this novel class of complexes is intriguingly stable and can been stored indefinitely in Schlenk tubes under argon. Therefore the pentamethylcyclopentadienyl iridium "Cp*Ir" is a very stabilizing moiety and allows the stabilization of intermediates such as phenol tautomers. In this respect we recently reported the isolation and full characterization of the first stable *o*-quinone methide as a π-complex of Cp*Ir.[15]

Treatment of a CH_3CN solution of complex **5** or **6** with iodine did not afford the related functionalized phenols as expected and previously observed with complex **4**, but instead a *nondemetalative oxidation reaction was observed involving "C−Nu" bond cleavage* (Nu = S-, N-centered nucleophile) and providing the starting material oxo-dienyl iridium [Cp*Ir(η^5-C_6H_5O)][I] (**8**) with iodide as a counteranion. Complex **8** was identified by ^1H NMR spectroscopy and X-ray structure analysis. Sublimation of the residue of the oxidation of complex **6** gave the known disulfide compound PhS−SPh. The latter may arise from a oxidative redox reaction involving a one-electron transfer process. Scheme 7 shows a plausible mechanism for the formation of the complex **8** and the disulfide compound PhS−SPh (**10**) from oxidation of **6** by iodine. In this mechanism the first step involves activation of the Cp*Ir(η^4-exo-2-SPh-dienone) function by removal of an electron, followed by C−SPh bond cleavage to give complex **8**; finally subsequent radical coupling affords iodine and the disulfide compound PhS−SPh.

(15) Amouri, H.; Besace Y.; Vaissermann J.; Le Bras, J. *J. Am. Chem. Soc.* **1998**, *120*, 6171.

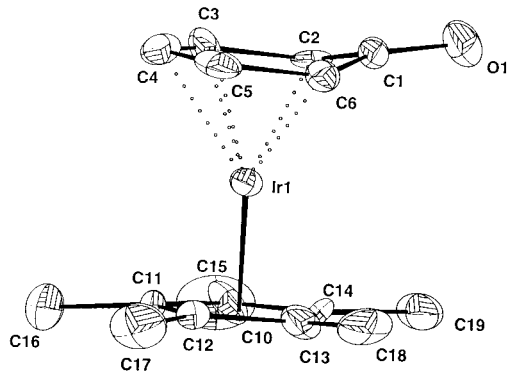


Figure 3. X-ray molecular structure of [Cp*Ir(η^5-C_6H_5O]$^+$ with atom-numbering system.

Grotjahn and Vollhardt have recently reported that the CpCo-complexed polycyclic dienes undergo a nondemetalative oxidation to the related CpCo-propellanes.[16] The authors suggested the intermediacy of CpCo-stabilized(η^5-dienyl) cations, in which the mechanism of oxidation is probably the formation of a radical cation through a one-electron-transfer reaction. Further it has been shown that one-electron oxidation of (η^6-C_6H_6)Fe(η^4-exo-5-(R)-cyclohexadiene) complexes bearing a 5-exo-substituent takes place by $PhC^+PF_6^-$.[17] At low temperature (−40 °C) a 17-electron radical cation species was detected by ESR, while at room temperature cleavage of the bond to the 5-exo-substituent predominated, leading to the dienyl cation starting material [(η^6-C_6H_6)Fe(η^5-C_6H_7)][PF_6]. We feel that in our system a scenario similar to the above examples is probably occurring, where at room temperature the dienone complex Cp*Ir(η^4-dienone-SPh) (**6**) undergoes a one-electron oxidation process and subsequent cleavage of the bond to the −SPh-substituent provides the cationic oxo-η^5-dienyl iridium [Cp*Ir(η^5-C_6H_5O)][I] (**8**). Therefore the I_2-oxidation of these novel Cp*Ir-stabilized (η^4-exo-2-Nu-dienone) complexes depends dramatically on the nature of the 2-exo-nucleophile substituent and does not lead systematically to the related *ortho-functionalized phenol*.

X-ray Molecular Structure of [Cp*Ir(η^5-C_6H_5O)][I] (8). Crystals of **8** were obtained by slow crystallization from CH_3CN/Et_2O solution. Compound **8** crystallizes in the triclinic space group $P\bar{1}$; there are two independent molecules in the asymmetric unit; refinement details are discussed in the Experimental Section. Figure 3 represents a view of the cation [Cp*Ir(η^5-C_6H_5O)]$^+$ with the atom-numbering system; crystallographic data collection parameters and selected bond lengths and angles are listed in Tables 1 and 3. The structure shows that the "Cp*Ir" unit is coordinated to only five carbons of the phenyl ring. The distances from the metal to the centers of the π-bonded carbons are 1.73 Å for the phenoxide ligand and 1.80 Å for the η^5-C_5Me_5 ligand, while the bond distance d_{Ir-C1} is 2.50 Å. Loss of aromaticity in the bonded phenoxo unit is manifested by the irregularity of the arene C−C bond lengths. Another important feature of this structure is described by the distance d_{C1-O1} = 1.23 Å, typical of a

(16) Grotjahn D. B.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1990**, *112*, 5653.
(17) Mandon, D.; Toupet, L.; Astruc, D. *J. Am. Chem. Soc.* **1986**, *108*, 1320.

Table 3. Selected Bond Distances (Å) and Angles (deg) for 8

Bond Lengths			
Ir(1)−Cp*$_{centroid}$	1.80	Ir(1)−C(2−6)$_{centroid}$	1.73
Ir1−C2	2.21 (2)	Ir1−C6	2.24(2)
Ir−C3	2.21 (2)	Ir1−C10	2.15(2)
Ir1−C4	2.21(2)	Ir1−C11	2.16(2)
Ir1−C5	2.21(2)	Ir1−C12	2.19(2)
Ir1−C13	2.23(2)	Ir1−C14	2.15(2)
Bond Angles			
C(2)−C(1)−C(6)	112.6(15)	C(6)−C(1)−O(1)	121.5(16)
C(2)−C(1)−O(1)	125.1(17)	C(3)−C(4)−C(5)	119.9(18)

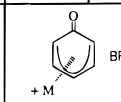
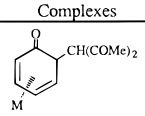
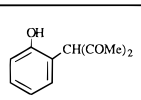
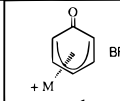
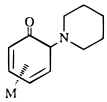
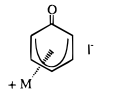
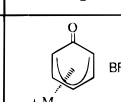
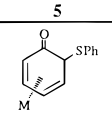
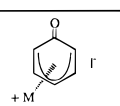
C═O function. This bond distance is shorter than that reported for the analogous rhodium, ruthenium, and iron derivatives [Cp*Rh(η^5-PhO)][BF_4], [Cp*Ru(η^5-PhO)·2PhOH], and [Cp*Fe(η^5-PhO)] with d_{C-O} = 1.25, 1.28, and 1.25 Å, respectively.[18−20] The dihedral angle θ between the plane C2−C1−C6 and the rest of the ring in **8** is 21°; this angle θ is greater than that reported for the iron (θ = 1.55°), ruthenium (θ = 4°), and rhodium (θ = 14°) complexes. In conclusion, we note that the η^5-phenoxide moiety coordinated to the iridium center in **8** (transition metal of third row) adopts a specific geometry relative to the other metal series (Fe, Ru, and Rh) where the ketonic character of the carbonyl group C═O is more pronounced.

Concluding Remarks

In this paper we described the reactivity of [Cp*Ir(η^5-PhO)][BF_4] (**1**) with hydride, deuteride, and C-, N-, and S-centered nucleophiles. In all cases regiospecific nucleophilic addition occurs at the ortho-position relative to C═O with exo-stereochemistry, leading to a novel class of stable η^4-cyclohexadienone complexes of general formula [Cp*Ir(η^4-2-exo-(Nu)-C_6H_5O)]. In this respect, pentamethylcyclopentadienyl iridium "Cp*Ir" is a very stabilizing entity and therefore provides stable phenol tautomers through η^4-coordination. The X-ray molecular structure of the first neutral phenol tautomer [Cp*Ir(η^4-2-exo-(CH(COMe)$_2$)-C_6H_5O] (**4**) was determined. The latter represents the key intermediate for the Ir-mediated phenol functionalization reaction.

Oxidation of the novel dienone iridium complexes [Cp*Ir(η^4-exo-2-Nu-C_6H_5O)] depends dramatically on the nature and electron properties of the exo-2-nucleophile. For instance R_3C-, RO-, and R_3P-centered nucleophiles gave the related ortho-functionalized phenol along with the starting material recycled in the form [Cp*Ir(μ-I)I]$_2$, as shown by Scheme 2. In dramatic contrast N- and S-centered nucleophiles showed a retronucleophilic addition or C−Nu bond cleavage, as demonstrated by complexes **5** and **6**. In the latter case the proposed mechanism involves a one-electron oxidation process. Therefore oxidation of Cp*Ir(I) to [Cp*Ir(μ-I)I]$_2$ and formation of the related functionalized phenols does not occur. Table 4 shows the reactants and products of the nucleophilic phenol functionalization reaction.

Table 4. Reactants and Products of the Oxidative Step

Phenol Starting material	oxo-η^5-dienyl-Ir Complex	η^4-dienones Complexes	Products of oxydation
	 **1**	 **4**	 **7**
	 **1**	 **5**	 **8**
	 **1**	 **6**	 **8**

M = Cp*Ir

We hope that we have demonstrated to the reader that the chemistry exhibited by the Cp*Ir system has many important applications in organic syntheses and displays a rich chemistry on the mechanistic level. We also draw attention to the fact that the functionalized organic molecules are obtained along with the starting material recycled in the form [Cp*Ir(μ-I)I]$_2$. This at least would compensate the inconvenience of using a fairly expensive transition metal in organic syntheses. Further, the isolation of the key intermediate η^4-dienone complex [Cp*Ir(η^4-2-exo-(CH(COMe)$_2$)-C_6H_5O] (**4**) is significant, since it represents the first example of the proposed ultimate intermediate for the *nucleophilic phenol functionalization* promoted by the Cp^*Ir^{2+} moiety, which to our knowledge represents the only available organometallic procedure in the literature. Efforts are currently directed to render this reaction catalytic.

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 used freshly in preparation of NaOMe solutions. All reagents obtained from commercial sources were used without further purification. ^1H and ^{13}C NMR were recorded on a Bruker AM 250 MHz instrument. ^1H NMR chemical shifts are reported in parts per million referenced to 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^4-C_6H_6O] (2). A solution of [Cp*Ir(η^5-C_6H_5O)][BF_4] (**1**) (190 mg, 0.37 mmol) in CH_3CN (10 mL) was added to $NaBH_3CN$ (120 mg, 1.87 mmol) kept in a dry Schlenk tube under argon. The reaction mixture was stirred for 48 h, and then the solvent was removed under vacuum. The residue was extracted by ether (100 mL) and filtered through Celite. The solvent was evaporated under vacuum to afford a light yellow semicrystalline substance identified as complex **2**. Yield: 93 mg, 60%. ^1H NMR (250 MHz, $CDCl_3$): δ 5,20 (t, 1H, J_{H-H} = 5.2 Hz, H_5), 4.87 (t, 1H, J_{H-H} = 5.2 Hz, H_4), 3.80 (d, 1H, J_{H-H} = 16 Hz, H_{2exo}), 3.42 (d, 1H, J_{H-H} = 5.2 Hz, H_6), 2.78 (t, 1H, J_{H-H} = 5.2 Hz, H_3), 2.63 (dd, 1H, J_{H-H} = 16; 5.2 Hz, H_{2endo}), 2.07 (s, 15H, Me−Cp). ^{13}C NMR (62.89 MHz,

(18) Le Bras, J.; Amouri, H.; Besace Y.; Vaissermann J.; Jaouen, G. *Bull. Soc. Chim. Fr.* **1995**, *132*, 1073.
(19) Koelle, U.; Wang M. J.; Raabe, G. *Organometallics* **1992**, *10*, 2573.
(20) Moulines, F.; Djakovitch, L.; Delville-Desbois, M.-H.; Robert, F.; Gouzerh, P.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1995**, 463.

$CDCl_3$): δ 188.0 (s, C_1=O), 90.0 (s, Cp), 70.1 (s, C_5), 68.0 (s, C_4), 57.3 (s, C_6), 33.5 (s, C_2), 31.7 (s, C_3), 10.2 (s, Me−Cp). IR (CH_2Cl_2, cm^{-1}): ν(C=O) 1626, ν(C−H_{endo}) 2919, ν(C−H_{exo}) 2836.

Synthesis of [Cp*Ir(η^4-C_6H_5DO] (3). Complex **3** was prepared in a manner similar to that of complex [Cp*Ir(η^4-C_6H_6O] (**2**), but using $NaBD_3CN$ instead of $NaBH_3CN$. Yield: 62%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 5.22 (t, 1H, J_{H-H} = 5.2 Hz, H_5), 4.87 (t, 1H, J_{H-H} = 5,2 Hz, H_4), 3.43 (d, 1H, J_{H-H} = 5.2 Hz, H_6), 2.78 (t, 1H, J_{H-H} = 5.2 Hz, H_3), 2.63 (m, 1H, H_{2endo}), 2.05 (s, 15H, Me−Cp). IR (CH_2Cl_2, cm^{-1}): ν(C=O) 1630, ν(C−H_{endo}) 2917, ν(C−H_{exo}) 2122.

Synthesis of [Cp*Ir(η^4-2-exo-(CH(COMe)$_2$)-C_6H_5O] (4). Acetylacetone (5 mL, 4.87 mmol) was added to a suspension of NaOMe (530 mg, 9.81 mmol) in CH_2Cl_2 (10 mL), and the mixture was stirred for 1 h. Later a suspension of [Cp*Ir(η^5-C_6H_5O)][BF_4] (**1**) (500 mg, 0.98 mmol) in CH_2Cl_2 (20 mL) was added to the freshly prepared acetylacetone anion, and the mixture was stirred for 12 h. To this mixture was added CH_2Cl_2 (70 mL), and the resulting mixture was then filtered through Celite.The filtrate was dried under vacuum, and the residue was extracted by diethyl ether (120 mL) which was evaporated to dryness to yield a yellow microcrystalline substance. Complex **4** was recrystallized from hexane (2 mL), yield 370 mg, 72%. ^{1}H NMR (250 MHz, C_6D_6): δ 4.77 (t, 1H, J_{H-H} = 5.0 Hz, H_5), 4.36 (t, 1H, J_{H-H} = 5.0 Hz, H_4), 3.75 (dd, 1H, J_{H-H} = 9.3; 5.0 Hz, H_2), 3,64 (d, 1H, J_{H-H} = 9.3 Hz, C*H*(COMe)$_2$), 3.54 (d, 1H, J_{H-H} = 5.0 Hz, H_6), 3.09 (t, 1H, J_{H-H} = 5.0 Hz, H_3), 2.13 (s, 3H, Me−CO), 1.87 (s, 3H, Me−CO), 1.63 (s, 15H, Me−Cp). ^{13}C NMR (62.89 MHz, C_6D_6): δ 202.5 (s, CO−Me), 201.6 (s, CO−Me), 194.7 (s, C_1=O), 89.9 (s, Cp), 77.6 (s, *C*H(COMe)$_2$), 69.8 (s, C_5), 65.8 (s, C_4), 56.1 (s, C_6), 44.2 (s, C_2), 36.6 (s, C_3), 30.9 (s, Me−CO), 28.8 (s, Me−CO), 10.0 (s, Me−Cp). IR (KBr-disk, cm^{-1}): ν(C=O) 1696; 1652; 1631.3. Anal. Calcd for $C_{21}H_{27}IrO_3$: C, 48.54; H, 5.24. Found: C, 48.61; H, 5.17.

Synthesis of [Cp*Ir(η^4-2-exo-(N(CH$_2$)$_5$)-C_6H_5O] (5). Piperidine (1 mL, 1.01 mmol) was added to a suspension of NaH (120 mg, 5 mmol) in THF (10 mL). The mixture was stirred for 90 min, and then a suspension of [Cp*Ir(η^5-C_6H_5O)][BF_4] (**1**) (500 mg, 0.98 mmol) in THF (20 mL) was added to the freshly prepared piperidine anion. The reaction mixture was allowed to stir for 12 h, then THF (70 mL) was added, the mixture was filtered through Celite, and the filtrate was evaporated under vacuum. The residue was extracted by diethyl ether (150 mL), which was evaporated under vacuum to yield a yellow microcrystalline solid and recrystallized in pentane (2 mL). Yield: 340 mg, 68%. ^{1}H NMR (250 MHz, C_6D_6): δ 4.82 (t, 1H, J_{H-H} = 5.1 Hz, H_5), 4.59 (t, 1H, J_{H-H} = 5.1 Hz, H_4), 3.72 (d, 1H, J_{H-H} = 5.1 Hz, H_6), 3.39 (d, 1H, J_{H-H} = 5.1 Hz, H_2), 3.01 (t, 1H, J_{H-H} = 5.1 Hz, H_3), 2.95 (m, 2H, CH_α−N or CH_β−N), 2.66 (m, 2H, CH_α−N or CH_β−N), 1.68 (s, 15H, Me−Cp), 1.60 (m, 4H, C*H*$_2$−CH$_2$−N), 1.36 (m, 2H, C*H*$_2$−CH$_2$−CH$_2$−N). ^{13}C NMR (62.89 MHz, C_6D_6): δ 189.6 (s, C_1=O), 89.5 (s, Cp), 69.8 (s, C_5), 67.2 (s, C_4), 65.6 (s, C_2), 57.8 (s, C_6), 52.0 (s, CH$_2$−N), 38.7 (s, C_3), 26.9 (s, *C*H$_2$−CH$_2$−N), 25.3 (s, *C*H$_2$−CH$_2$−CH$_2$−N), 10.0 (s, Me−Cp). IR (KBr-disk, cm^{-1}): ν(C=O) 1626. Anal. Calcd for $C_{21}H_{30}IrON$: C, 49.98; H, 5.99. Found: C, 50.05; H, 6.09.

Synthesis of [Cp*Ir(η^4-2-exo-(SPh)-C_6H_5O] (6). Thiophenol (5 mL, 4.87 mmol) was added to a suspension of NaOMe (530 mg, 9.81 mmol) in CH_2Cl_2 (10 mL), and the reaction mixture was stirred for 1 h. Then a suspension of [Cp*Ir(η^5-C_6H_5O)][BF_4] (**1**) (500 mg, 0.98 mmol) in CH_2Cl_2 (20 mL) was added to the freshly prepared thiophenol anion, and the reaction mixture was stirred for 12 h. Later CH_2Cl_2 (70 mL) was added, the mixture was filtered through Celite, and the filtrate was evaporated to dryness. The residue was extracted by diethyl ether (150 mL), which was evaporated under vacuum, providing a light yellow microcrystalline substance, recrystallized in hexane (2 mL). Yield: 300 mg, 57%. ^{1}H NMR (250 MHz, C_6D_6): δ 7.94 (d, 2H, J_{H-H} = 13.2 Hz, H_{ortho}(arene)−S), 7.05 (t, 2H, J_{H-H} = 13.2 Hz, H_{meta}(arene)−S), 6.95 (t, 1H, J_{H-H} = 13.2 Hz, H_{para}(arene)−S), 4.73 (t, 1H, J_{H-H} = 5.0 Hz, H_5), 4.45 (t, 1H, J_{H-H} = 5.0 Hz, H_4), 4.12 (d, 1H, J_{H-H} = 5.0 Hz, H_2), 3.69 (d, 1H, J_{H-H} = 5.0 Hz, H_6), 3.10 (t, 1H, J_{H-H} = 5.0 Hz, H_3), 1.62 (s, 15H, Me−Cp). ^{13}C NMR (62.89 MHz, C_6D_6): δ 187.0 (s, C_1=O), 139.7 (s, C_{ipso}(arene)−S), 132.1 (s, C_{ortho}(arene)−S), 129.0 (s, C_{meta}(arene)−S), 126.5 (s, C_{para}−S), 89.8 (s, Cp), 70.9 (s, C_5), 66.1 (s, C_4), 57.0 (s, C_6), 47.9 (s, C_2), 37.4 (s, C_3), 9.9 (s, Me−Cp). IR (KBr-disk, cm^{-1}): ν(C=O) 1635. Anal. Calcd for $C_{22}H_{25}IrOS$: C, 49.88; H, 4.75. Found: C, 49.91; H, 4.78.

Oxidation of Complex [Cp*Ir(η^4-2-exo-(CH(COMe)$_2$)-C_6H_5O)] (4) and Formation of 2-(CH(COMe)$_2$)-C_6H_5OH (7). Complex [Cp*Ir(η^4-2-exo-(CH(COMe)$_2$)-C_6H_5O)] (**4**) (320 mg, 0.61 mmol) was dissolved in CH_3CN (5 mL), and then a solution of iodine (170 mg, 0,67 mmol) in CH_3CN (4 mL) was added dropwise. The reaction mixture was stirred for 5 min, then the solvent was removed under vacuum. The residue was extracted by MeOH (8 mL), providing a red precipitate identified as [Cp*Ir(μ-I)I]$_2$ (350 mg, 98%). The supernatant phase was dried under vacuum, and the residue was sublimed at (0.2 mmHg, 30−35 °C), providing light yellow needles identified as the free substituted **7**. The free phenol (**7**) should be kept under argon. Yield: 85% (100 mg). ^{1}H NMR (250 MHz, CD_2Cl_2): δ 16.85 (s, 1H, OH), 7.30 (td, 1H, J_{H-H} = 7.5; 1.5 Hz, Ar), 7.08 (dd, 1H, J_{H-H} = 7.5; 2.0 Hz, Ar), 6.96 (m, 2H, Ar), 5.20 (s, 1H, C*H*(COMe)$_2$), 1.88 (s, 6H, CH_3−CO). ^{13}C NMR (62.89 MHz, CD_2Cl_2): δ 192.3 (s, C=O), 153.7 (s, C−OH), 131.9 (s, Ar), 129.6 (s, Ar), 122.1 (s, Ar), 120.6 (s, Ar), 115.1 (s, Ar), 107.4 (s, *C*H(COMe)$_2$), 23.3 (s, CH_3−CO). IR (KBr-disk, cm^{-1}): ν(O−H) 3416, ν(C=O) 1630. Melting point: 79.0 °C. Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29. Found: C, 68.69; H, 6.27.

Oxidation of Complex [Cp*Ir(η^4-2-exo-(SPh)-C_6H_5O] (6) and formation of [Cp*Ir(η^5-C_6H_5O)][I] (8) and PhS−SPh (10). Complex [Cp*Ir(η^4-2-exo-(N(CH$_2$)$_5$)-C_6H_5O)] (**5**) (300 mg, 0.59 mmol) was dissolved in CH_3CN (5 mL), and then a solution of iodine (170 mg, 0,67 mmol) in CH_3CN (4 mL) was added dropwise. The reaction mixture was stirred for 5 min. Later the solution was dried under vacuum, and the residue was extracted by THF (10 mL), providing a white precipitate, which was separated and washed with THF (5 mL) and recrystallized in acetonitrile/ether. Yield: 74% (240 mg). ^{1}H NMR (250 MHz, $(CD_3)_2CO$): δ 6.73 (t, 1H, J_{H-H} = 5.2 Hz, H_4), 6.60 (dd, 2H, J_{H-H} = 5.2; 7.5 Hz, H_3, H_5), 5.77 (d, 2H, J_{H-H} = 7.5 Hz, H_2, H_6), 2.37 (s, 15H, Me−Cp).

Spectroscopic Data for PhS−SPh (10). ^{1}H NMR (250 MHz, (CD_3Cl_3): δ 7.27 (bm, phenyl protons). Melting point: 58.0 °C. Anal. Calcd for $C_{12}H_{10}S_2$: C, 66.05; H, 4.58. Found: C, 65.83; H, 4.48.

X-ray Crystallography of [Cp*Ir(η^4-2-exo-(CH(COMe)$_2$)-C_6H_5O)] (4) and [Cp*Ir(η^5-C_6H_5O][I] (8). Suitable crystals of [Cp*Ir(η^4-2-exo-(CH(COMe)$_2$)-C_6H_5O)] (**4**) were obtained from a saturated solution of **4** in Et_2O/hexane at 7 °C, while for complex **8**, crystals were obtained by recrystallization from CH_3CN/Et_2O. The selected crystal of complex **4** or **8** 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 on a Nonius CAD4 diffractometer equipped with graphite-monochromated Mo Kα radiation. No significant variations were observed in the intensities of two checked reflections during data collection. An absorption correction was applied using the program DIFABS[21] and provided the best structural resolution with T_{min} = 0.94 and T_{max} = 1 for **4** and T_{min} = 0.95 and T_{max} = 1 for **8**. Complete crystallographic data and collection parameters for

(21) Walker, N. Stuart, D. *Acta Crystallogr.* **1983,** *A39*, 159.

4 and **8** are listed in Table 1. The data were corrected for Lorentz and polarization effects. Computations were performed by using the PC version of CRYSTALS.[22] Scattering factors and corrections for anomalous dispersion were taken from ref 23. The asymmetric unit of complex **4** or **8** consists of two independent molecules. The structure of compound **4** or **8** was solved by standard Patterson and Fourier techniques 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. Fractional parameters, anisotropic thermal parameters, and all bond lengths and angles are given in the Supporting Information for complexes **4** and **8**.

(22) Watkin, D. J.; Carruthers, J. R.; Betteridge P. W. *Crystals User Guide*; Chemical Crystallography Laboratory, University of Oxford: Oxford, U.K., 1988.

(23) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, Vol. IV, 1974.

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Supporting Information Available: Fractional parameters, anisotropic thermal parameters and bond lengths and angles for **4** and **8** (9 pages). Ordering information is given on any current masthead page.

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