Stable *o*-Quinone Methide Complexes of Iridium: Synthesis, Structure, and Reversed Reactivity Imparted by Metal Complexation

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o-Quinone methides are important intermediates in biochemistry and organic chemistry, partly because of their high reactivity: the simplest compound *o*-quinone methide (**1**) is unstable in condensed phases above approximately −100 °C. In contrast, here a general synthetic route to the first metal complex of *o*-quinone methide and complexes of several simple alkyl derivatives is reported. Coordination of 2-alkylphenols to $[Cp^*Ir(acetone)_3](BF_4)_2$ and subsequent deprotonation with Et_3N affords $(\eta^5\text{-}Cp^*)Ir[\eta^5\text{-}(2\text{-alkyl})oxodienyl](BF_4)$ complexes **5** in 85−90% yield. Deprotonation of **5** with KO-*t*-Bu gives 81−96% yields of neutral *o*-quinone methide complexes $Cp^*Ir\{\eta^4\text{-}C_6H_3R^1[=C(R^2)_2]O\}$ [$R^1 = R^2 = H$ (**6a**); $R^1 =$ Me, $R^2 = H$ (**6b**); $R^1 = H$, $R^2 =$ Me (**6c**); $R^1 = i$-Pr, $R^2 =$ Me (**6d**)], in which the Cp*Ir fragment is coordinated in η^4 fashion to the two carbon−carbon double bonds of the six-membered ring. The remarkable stability of the complexes allows characterization of their structure and reactivity. The X-ray molecular structure of **6d** and a series of 1D and 2D NMR studies on **6a** and **6c** are reported, showing the pronounced effects of Cp*Ir coordination to the *o*-quinone methide ligand, particularly a strong upfield ^{13}C chemical shift for the exocyclic carbon $[=C(R^2)_2]$ of the uncoordinated carbon−carbon double bond. Although stable under argon at room temperature, Cp*Ir-*o*-quinone methide complexes **6** exhibited unusual reactivity toward acids or electrophiles; for instance treatment of **6a** with 1 equiv of $HBF_4{\cdot}Et_2O$ or I_2 lead to the oxodienyl complexes $[Cp^*Ir(\eta^5\text{-}C_7H_7O)][BF_4]$ (**5a**) or $[Cp^*Ir(\eta^5\text{-}C_7H_6IO)][I]$ (**8**), respectively. Moreover, when complex **6a** was treated with methyl propynoate, a new *o*-quinone methide complex (**9**) was obtained as a result of a coupling reaction between the electrophilic alkyne and the exocyclic carbon ($=CH_2$) of complex **6a**. Finally, treatment of **6a** with *N*-methylmaleimide gave the tricyclic iridium complex (**11**) as a result of an unprecedented [2+3] cycloaddition with part of the *o*-quinone methide complex **6a**. The above reactions and ^{13}C NMR evidence show that in *o*-quinone methide complexes **6** the exocyclic carbon $[=C(R^2)_2]$ is nucleophilic, opposite of what is reported for free, electrophilic *o*-quinone methides. The difference in reactivity is attributed to the Cp*Ir unit, which modifies dramatically the electronic properties of the *o*-quinone methide ligand.

Introduction

Quinone methide (QM) exists in three isomeric forms (Scheme 1), *o*-QM (**1**), *m*-QM, and *p*-QM. The importance of *o*- and *p*-quinone methides in organic synthesis and their role in biochemistry have been reviewed.[1] Unlike benzoquinones, *o*-QM and *p*-QM derivatives are highly polarized compounds, usually observed with difficulty or postulated as reactive intermediates, because of facile reactions driven by the formation of aromatized phenol derivatives. *p*-Quinone methides have been discussed as intermediates in the chemistry

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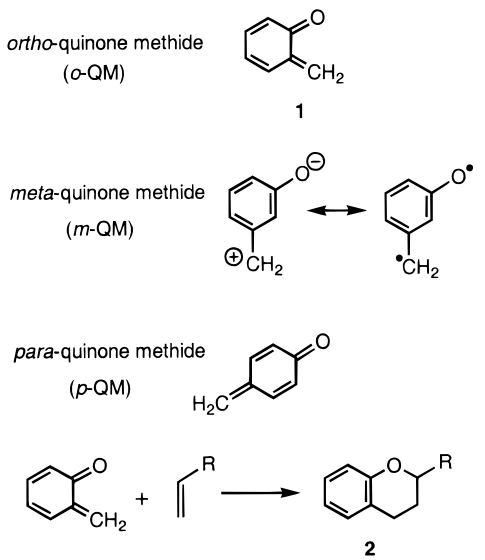
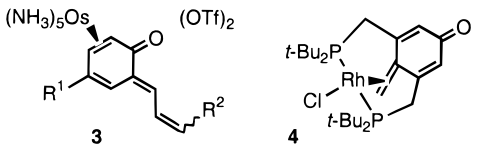
Scheme 1



of lignins[2] and have been used in organic synthesis[3] as electrophiles or electron acceptors. *o*-Quinone methides such as **1** are versatile reactive intermediates used in organic synthesis,[1b,c,4,5] acting as electrophilic enones toward nucleophiles, or as heterodiene 4π cycloaddition partners in inter- and intramolecular Diels−Alder [2+4] cycloadditions with alkenes to give various substituted chromans (**2**). Spectacular demonstrations of the potential of such cycloadditions are the total syntheses of carpanone,[5a,d] hexahydrocannabinols,[5e,g,i] and thielocin-A1β.[5j] *o*-Quinone methides are also believed to act as key intermediates in the action of several antitumor and antibiotic drugs. Due to their highly electrophilic character, they can act as alkylating agents of DNA.[1e,6] For example, it has been suggested that the active form of mitomycin C is an *o*-QM.[6a] The electrophilic reactivity of *o*-quinone methides has inspired their use in the design of new strategies to combat cancer.[6c]

However, despite this widening interest, examples of isolated *simple* quinone methides (i.e., those not bearing substituents on the exocyclic double bond) are scarce, and in fact in condensed phases the parent compound (**1**) has only been characterized spectroscopically at temperatures below −100 °C,[7] because it is extremely reactive. Most procedures used previously for *o*-QM preparation involve elimination or oxidation reactions of *o*-substituted phenols, either induced by heat or light. Evidence for the formation of highly reactive *o*-QMs comes indirectly from isolation of cycloadducts such as chromans **2** or, more directly, at room temperature from transient UV−vis spectroscopy or near 0 K from isolation in an argon matrix. These experimental procedures show how difficult it has been to isolate QMs.

Although many highly reactive π-systems (e.g., cyclobutadienes) have been stabilized by metal complexation, as far as we are aware, before this work there were only four known QM complexes. Two alkenyl-substituted *o*-quinone methide complexes (**3**) are known,[8a] but neither was of a simple QM and neither was characterized crystallographically. Further, one *p*-quinone methide complex (**4**) features two strongly coordinating tertiary phosphine groups which anchor the metal to the methylene unit,[8b,c] whereas the other reported one (not shown) is only coordinated to the metal through the exocyclic C−C double bond.[8d] Despite the fact that



almost nothing is known about the reactivity of QM complexes **3** and **4**, other than their reactions with strong electrophiles (e.g., triflic acid) or strong nucleophiles (e.g., CH_3Li), their isolation shows the rich potential of using metal complexation to stabilize reactive QM derivatives. In this paper we show how metal complexation not only allows isolation of QM derivatives but also turns an electrophilic system into a nucleophilic one.

We recently communicated[9] a general and unprecedented synthetic procedure to make the first metal complex of the parent *o*-quinone methides (**1**), as well as complexes of simple alkylated derivatives, Cp*Ir-η^4-

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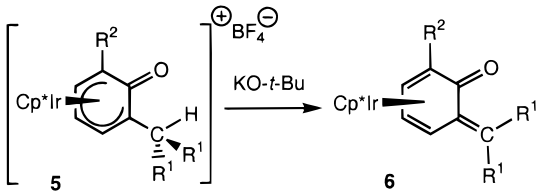
Scheme 2



a $R^1 = R^2 = H$
b $R^1 = H$, $R^2 = CH_3$
c $R^1 = CH_3$, $R^2 = H$
d $R^1 = CH_3$, $R^2 = CH(CH_3)_2$

o-quinone methide complexes **6** (Scheme 2). Unlike the parent molecule **1**, complex **6a** is thermally stable and can be stored indefinitely under argon. Significantly, the Cp*Ir fragment does *not* migrate to other double bonds of the *o*-QM ligand, such as the exocyclic ones, as seen recently for geometrically similar Ru and Os *o*-xylylene complexes.[10] Because these are the first known stable simple *o*-quinone methide complexes, full characterization of the series has been possible, including the X-ray molecular structure of complex **6d**. Here the full details of the preparation and structure of **6** are presented, along with new NMR data which permit understanding of the unique reactivity of the complexed *o*-QM ligand. Further new studies reported here show that the Cp*Ir fragment not only stabilizes the *o*-QM framework but also reverses its reactivity, allowing *electrophilic* functionalization and [3+2] cycloaddition to part of the *o*-QM system, reactions unknown on the free ligand.

Results and Discussion

Synthesis, Characterization, and NMR Analysis. We recently described a general procedure for nucleophilic phenol functionalization, promoted by the Cp*Ir moiety,[11] which allows efficient introduction of alkoxy groups onto tetralols and steroids[12] by way of nucleophilic attack on Cp*Ir-oxo-η^5-dienyl complexes. In contrast, it was found that cationic Cp*Ir-oxo-η^5-dienyl iridium complexes with an alkyl group at one end of the dienyl terminus (**5**, Scheme 2) undergo regioselective deprotonation at a benzylic position of the alkyl group to afford the related neutral η^4-*o*-quinone methide complexes **6**. Bases used include NaOMe in methanol or, better, a suspension of *t*-BuOK in CH_2Cl_2 for several hours at room temperature. The neutral η^4-*o*-quinone methide complexes **6** were obtained as yellow microcrystalline substances in yields of 81−96%. All compounds were recrystallized from hexane and were obtained as analytically pure materials, stable in the solid state under argon. The infrared spectra of these complexes recorded in KBr displayed two bands in the area 1595−1615 cm^{-1} (s) and 1631−1643 cm^{-1} (m) similar to what was found for *p*-quinone methide complexes.[8b−d] Infrared data for *o*-quinone complexes **3** were not reported,[8a] but the literature data for free *o*-QM (**1**) at −196 °C have been reported as 1656, 1565, and 1539 cm^{-1} [7a] and 1657 (s), 1604 (s), 1560 (s), and 1531 (s) cm^{-1}.[7c]

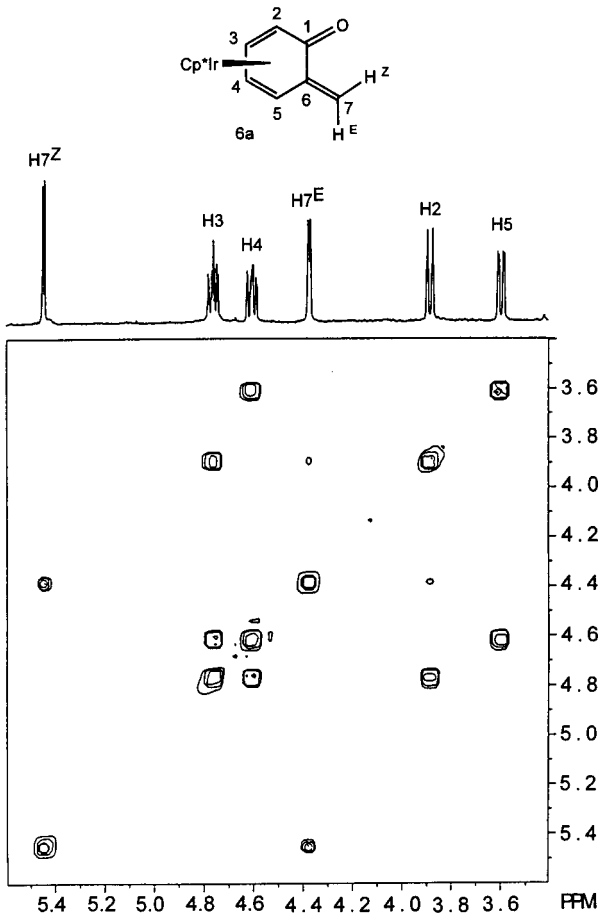


Figure 1. Section of a 250 MHz ^1H NMR COSY spectrum of complex **6a** in C_6D_6 at 298 K.

Because the parent *o*-QM molecule C_7H_6O (**1**) is unstable in condensed phases above −100 °C,[7c] NMR spectroscopic data are not available. Therefore we decided to fully examine by 2D NMR techniques the parent *o*-QM complex [Cp*Ir(η^4-C_7H_6O)] (**6a**), to understand its structure and reactivity. The upper part of Figure 1 shows part of the proton NMR spectrum of **6a** in C_6D_6; six multiplets in the region 3.6−5.6 ppm are visible. The two resonances at 4.38 and 5.43 ppm, showing a small mutual coupling $J_{H-H} = 2.5$ Hz, were ascribed to the geminal protons of the exocyclic double bond, $H7^E$ and $H7^Z$, respectively. An NOE difference spectrum in which the signal at 4.38 ppm ($H7^E$) was irradiated showed enhancement of the dd at 3.61 ppm, identifying the latter resonance as belonging to H5, the proton at the diene terminus closest to the exocyclic double bond. In the COSY spectrum (Figure 1), a strong cross-peak between the signal for H5 and the resonance at 4.61 ppm allowed the latter to be ascribed to H4. Similarly peaks at 4.77 and 3.89 ppm were assigned to H3 and H2, respectively. The upfield shifts of resonances for H2 and H5 relative to those of H3 and H4 resemble the trends observed in NMR spectra of numerous η^4-diene complexes of transition metals, wherein the protons at the diene termini are more shielded than those at internal positions.[13]

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Interestingly a small long-range coupling between H2 and $H7^E$ was identified by homonuclear decoupling. Finally the anisotropy of the carbonyl group is shown by the fact that chemical shift of $H7^Z$ is larger than that of $H7^E$ and that of H2 is larger than that of H5. Similar trends are seen in the spectral data of the other complexes **6b**−**d**.

Moreover, the $^{13}C\{^1H\}$ NMR data for **6** obtained in toluene-d_8 or benzene-d_6 at room temperature were consistent with the proposed structures. In particular, the most downfield resonance in the area 185−195 ppm was readily ascribed to the C═O group. However, to fully characterize the effects of metal complexation on the *o*-QM ligand, all the carbon resonances in the spectrum of **6a** and **6c** were identified using HMQC and HMBC experiments. In both complexes, there was a strict correspondence between the chemical shifts of the methine carbons and the protons attached to them. For example, for **6a** in C_6D_6 the chemical shifts for ring protons H5, H2, H4, and H3 were δ 3.61, 3.89, 4.61, and 4.77 ppm, while the carbons to which these protons are attached resonated at δ 49.48, 59.43, 68.29, and 70.37 ppm, respectively. In η^4-diene complexes, not only the proton but also the carbon nuclei at the termini are typically shifted upfield relative to nuclei at the internal positions.[13] Finally, HMQC data for **6a** clearly assigned the carbon resonance at 104.86 ppm to the terminal carbon of the exocyclic double bond (C7), and HMBC data allowed the signal at 142.41 to be ascribed to the internal or ring carbon of the exocyclic double bond (C6). For the series **6a**−**d**, the carbons of the exocyclic double bond resonated in the range 103−128 ppm (exocyclic carbon ═CR_2, C7) and 130 to 142 ppm (ring carbon C6).

The upfield chemical shift of the exocyclic carbon is completely unlike the shift expected for the β-carbon of an enone such as **1**, but rather is reminiscent of the shift of the carbon β to the alkoxy group in electron-rich alkenes such as vinyl ethers ROCH═CH_2.[14] Similarly, in the case of **6a** the proton chemical shift of $H7^E$ (4.38 ppm), which unlike that of $H7^Z$ should be unaffected by anisotropy of the carbonyl group, is at least 1 ppm upfield of that expected for a proton at the β position of an enone and is more like that observed for a nucleus at the β position of a vinyl ether.[15] Vinyl ethers function as nucleophilic alkenes,[16] and as described below, **6** reacts as a *nucleophile* at the exocyclic carbon, unlike uncomplexed quinone methides, which show electrophilic reactivity at the exocyclic carbon characteristic of an enone.

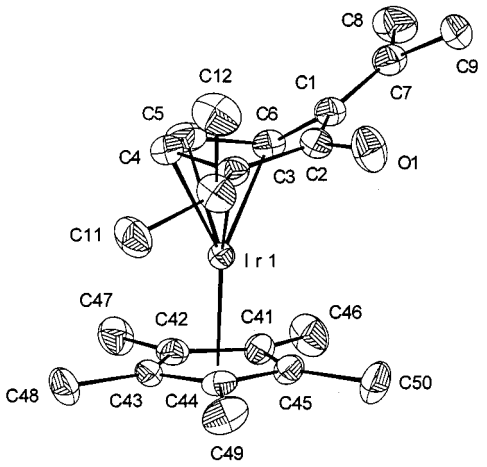

Figure 2. X-ray molecular structure of complex [Cp*Ir (η^4-$C_{12}H_{16}O$)] (**6d**). ORTEP view shows thermal ellipsoids at 30% probability. Depicted is one of two independent molecules, without hydrogens for clarity.

X-ray Molecular Structure of Complex 6d. Despite the high solubility of complexes **6** even in hexane, crystals of complex **6d** suitable for an X-ray single-crystal analysis were obtained from that solvent. The compound crystallizes in a triclinic unit cell, space group *P*1; a brief description of the solution of the structure is provided in the Experimental Section, and full details of the structure are in the Supporting Information. The bonding and molecular geometry of **6d** are shown in an ORTEP diagam in Figure 2. Selected bond lengths and angles are listed in Table 1. The structure of **6d** clearly shows the lack of aromaticity in the six-membered ring and coordination of Cp*Ir to four ring carbons. In the six-membered ring, the C−C bond distances are irregular; the length of the uncoordinated bond C(1)−C(2) is 1.49(1) Å, while the C(2)−O(1) bond distance is 1.23(1) Å, which is characteristic of a C═O double bond and in the range expected for substituted quinones. Further, the C(1)−C(7) bond distance is 1.34(1) Å, slightly shorter than that reported for the C═C double bond in duroquinone [cf. 1.352(8)].[17] The distances from the metal to the centers of the π-bonded carbons is 1.76 Å for the *o*-QM ligand and 1.84 Å for the η^5-C_5Me_5 ligand. The uncoordinated part of the *o*-QM ligand is bent away from the metal, shown by the dihedral angle of the "hinge" across C(3)−C(6), 33°. To our knowledge, this is the first X-ray structure of an *o*-QM complex reported in the literature. Having elucidated the geometric and electronic structure of such η^4-*o*-quinone methide complexes, we started to investigate their reactivity.

Reactions of Cp*Ir-Stabilized *o*-QM Complex 6a. The electrophilic character of *o*-quinone methides has been widely demonstrated.[1,4] Such intermediates have important biological uses.[1e,6] For instance, they have been suggested as alkylating agents generated in vivo from appropriately substituted quinones in bioreductive activation processes.[6] The electrophilicity of *o*-QM and

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Table 1. Selected Crystallographic Data and Collection Parameters for Complex 6d

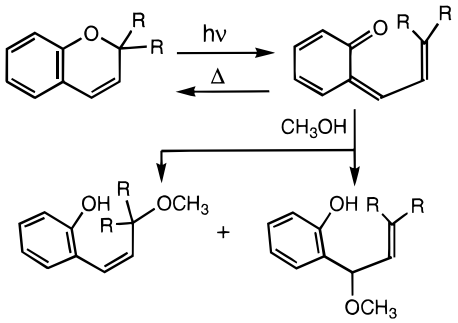
fw	503.7
a (Å)	10.238(3)
b (Å)	11.674(2)
c (Å)	18.209(9)
α (deg)	72.72(3)
β (deg)	75.24(3)
γ (deg)	87.50(2)
V (Å^3)	2008(1)
Z	4
cryst syst	triclinic
space group	*P*1
linear abs coeff μ (cm^{-1})	66.3
density ρ (g cm^{-3})	1.67
diffractometer	CAD4 Enraf-Nonius
radiation	Mo Kα (λ = 0.71069 Å)
scan type	$\omega/2\theta$
scan range (deg)	0.8 + 0.345 tan θ
θ limits (deg)	1−28
temp of measurement	room temp
octants collected	0,13; −15, 15; −23, 24
no. of data collected	10 217
no. of unique data collected	9679 (R_{int} = 0.0244)
no. of unique data used for refinement	6522 $(F_o)^2 > 3\sigma(F_o)^2$
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.0420
$R_w{}^a = [\sum w(\|F_o\| - \|F_c\|)^2/\sum wF_o{}^2]^{1/2}$	0.0487
extinction param	89
no. of variables	434
$\Delta\rho_{min}$ (e Å^{-3})	−1.89
$\Delta\rho_{max}$ (e Å^{-3})	1.60

[a] $w = w'$ [1 − ((×f4F_o×f4 −×f4F_c×f4×f4)/6$\sigma(F_o)$)^2]^2 with $w' = 1/\sum_{r=1}A_rT_r(X)$ with 3 coefficients, 7.62, −2.62, and 5.02, for a Chebyshev series, for which X is F_o/F_o(max).

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex 6d

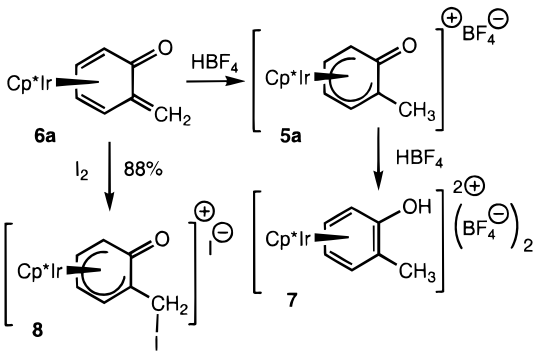
C(1)−C(2)	1.49(1)	Ir(1)−C(3)	2.193(8)	C(2)−C(1)−C(6)	109.7(7)
C(2)−C(3)	1.48(1)	Ir(1)−C(4)	2.143(9)	C(1)−C(2)−C(3)	114.7(7)
C(3)−C(4)	1.44(1)	Ir(1)−C(5)	2.122(9)	C(2)−C(3)−C(4)	121.4(8)
C(4)−C(5)	1.43(1)	Ir(1)−C(6)	2.169(8)	C(1)−C(6)−C(5)	120.6(8)
C(5)−C(6)	1.42(1)	Ir−C(41)	2.179(8)	O(1)−C(2)−C(3)	121.0(9)
C(1)−C(6)	1.46(1)	Ir−C(42)	2.220(7)	O(1)−C(2)−C(1)	124.3(8)
C(2)−O(1)	1.23(1)	Ir−C(43)	2.246(7)		
C(1)−C(7)	1.34(1)	Ir−C(44)	2.208(7)		
		Ir−C(45)	2.180(8)		

Scheme 3



its derivatives has been exploited in several synthetic applications.[4] Padwa and co-workers have shown in a series of papers that *o*-quinone methide intermediates (Scheme 3) generated by photolysis of a pyran can be trapped by nucleophilic solvents such as MeOH to give methyl ether addition products or return to the original pyran structure.[4a−c] Similarly, Wan and co-workers have generated reactive *o*-quinone methides through flash photolysis[1f,4e,f] and found products from nucleophilic addition of alcohols or water at the exocyclic carbon. Moore and co-workers have shown that (trimethylsilyl)methyl-1, 4-benzoquinone can be converted to reactive electrophilic *o*-quinone methides which are subsequently trapped by various nucleophiles.[4d] *In these addition reactions the o-quinone methide intermediates are electrophilic species, reacting at the exocyclic carbon*.

Scheme 4

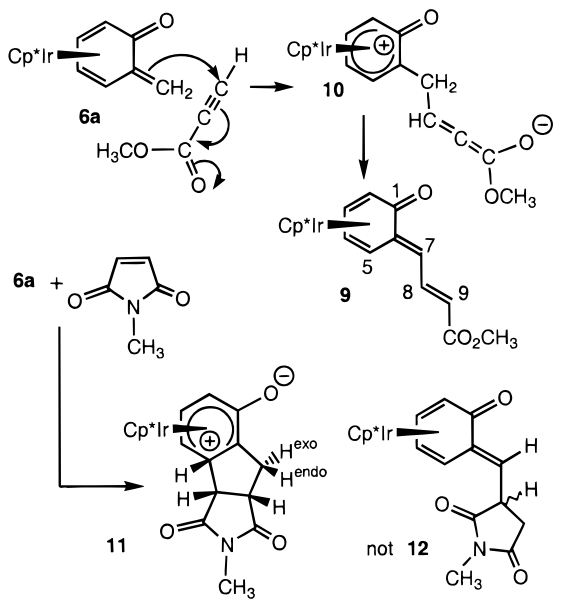


In contrast, metal-stabilized *o*-quinone methide **6a** reacts as a base or nucleophile (Scheme 4). Thus, protonation of complex **6a** by $HBF_4{\cdot}Et_2O$ afforded primarily the oxo-dienyl compound **5a**; however in the presence of an excess of $HBF_4{\cdot}Et_2O$ the dicationic species **7** was obtained. The monoprotonation of **6a** at *carbon* by strong acid thus contrasts the protonation of *p*-quinone methide complex **4** at *oxygen*.[8c] All subsequent reactions of **6** described in this paper show how the *o*-QM system is activated to reactions with other electrophiles at the exocyclic carbon. Attempted oxidation of **6a** in diethyl ether by iodine did not liberate the free *o*-quinone methide ligand (**1**), but rather the novel oxo-dienyl complex **8** was obtained as deep red microcrystalline solid in 88% yield (Scheme 4). Analytic and spectroscopic data are in accord with the proposed formula. The ^{13}C NMR data of **8** recorded in CD_3CN showed the presence of a peak at 162.44 ppm attributed to the C═O group, while the $-CH_2-I$ unit exhibited a high-field signal at −4.43 ppm, characteristic of an sp^3 carbon substituted by an iodine atom.[18] The reactivity of **6a** at the exocyclic carbon of the methylene group (Scheme 4) can be compared with the behavior of enol acetates or enol silyl ethers, which undergo electrophilic iodination[16a,b] or similar reactions at the more electron-rich carbon β to the oxygenated substituent.

We reasoned that the nucleophilic reactivity of the exocyclic carbon of **6a** could be used to make carbon−carbon bonds by using electron-poor alkenes and alkynes as electrophiles or cycloaddition partners. With the electron-poor alkyne methyl propynoate, within 2 days at room temperature formation of coupling product **9** (Scheme 5, 46% yield) as a single stereoisomer is observed. The structure of **9** was secured by a combination of NOESY and gradient COSY, HMQC, and HMBC experiments. The presence of four one-proton multiplets between δ 3.90 and 4.80 suggested the maintenance of the *o*-QM core in **9**, and these four proton resonances could be correlated with four carbon resonances in the range δ 49.76−69.21 ppm, data similar to those exhibited by **6**. The carbonyl carbon of the complexed *o*-QM core (C1) resonated at δ 181.51, with an HMBC cross-peak to a one of the *o*-QM protons at δ 4.11 ppm,

(18) Reference 14a, pp 149−154.

Scheme 5



ascribed to H5. The existence of the $=CH^7-CH^8=CH^9-CO_2CH_3$ side chain in **9** was implicated by a downfield doublet of doublets (J = 12.6 and 14.9 Hz) centered at δ 8.05 ppm, attributed to the central proton H8, β to the $-CO_2CH_3$ group, coupled to signals at 6.31 (d, J = 12.6 Hz, H7) and 5.84 ppm (dd, J = 0.6 and 14.9 Hz, H9). The 14.9 Hz coupling of H8 and H9 suggests a trans-configured double bond in the side chain, and a NOESY cross-peak between H8 and the *o*-QM core proton resonating at δ 4.11 (ascribed to H5) secured the geometry of the double bond between the side chain and the six-membered ring.

Coupling of the *o*-QM complex **6** with the electrophilic alkyne may be initiated by nucleophilic attack of the terminal carbon of the exocyclic alkene unit on the terminal carbon of the alkyne, generating zwitterionic oxo-dienyl intermediate **10** (Scheme 5). Proton transfer from the side chain of the oxo-dienyl cation (cf. deprotonation of **5** to give **6**) to the enolate would give the observed product. Many nucleophilic additions to electrophilic alkynes apparently follow a similar course.[19]

Furthermore (Scheme 5), **6a** reacts with *N*-methylmaleimide in several days to give at least 40% of **11**, some of which precipitated from benzene or toluene solutions of sufficient concentration. Proton NMR data for **11** were quite different from those for complexes **6** or **9**, in which the *o*-QM nucleus was present, suggesting that a profound structural change had taken place: singlets for Cp* and *N*-CH_3 protons were accompanied by eight one-proton multiplets, one of which appeared quite far upfield at δ 0.76 ppm (dd, J = 9.9, 11.5 Hz). COSY data showed that this upfield doublet of doublets was coupled to a doublet (J = 11.5 Hz) and a doublet of doublets at 2.26 (J = 7.0 and 9.9 Hz). HMQC data placed protons resonating at δ 0.76 and 3.58 ppm on the same carbon (δ 30.24 ppm), which could be consistent with **12**, the product of conjugate addition of the nucleophilic exocyclic carbon of **6a** on the maleimide double bond, followed by proton transfer to regenerate the *o*-QM core. However, it was difficult to see how the difference in chemical shifts of the protons resonating at 0.76 and 3.58 ppm could be caused simply by anisotropy of the nearby amide carbonyl or by the *o*-QM system, when rotation about the single bond shown in **12** between the QM core and the new maleimide-derived substituent presumably would be unhindered. Moreover, structure **12** would seem to require observation of five resonances for the protons of the six-membered ring and the exocyclic carbon, probably in the range δ 3.5−5 ppm, whereas only three such resonances remained unaccounted. Ultimately, all data proved consistent with structure **11**, which features the eight protons of the former π-systems of the *o*-QM and maleimide units on seven contiguous carbons, completely in accord with COSY data. Therefore, the signals at 0.76 and 3.58 ppm are assigned to the methylene protons in the newly formed five-membered carbocyclic ring. Phased NOESY data indicate that all protons at the three ring junctions are mutually cis and that the ring-junction proton resonating at 2.26 ppm is close to the proton resonating at 0.76 ppm, placing the latter proton and the three ring-junction protons on the same side of the tricyclic framework, as shown. In corroboration, NOESY correlation between the proton resonating at 3.58 and the three ring-junction protons was not observed. On the basis of steric arguments, we assume that *N*-methylmaleimide adds to **6a** exo with respect to the large Cp*Ir fragment, but endo with respect to the five- and six-membered rings of the maleimide and *o*-QM π-systems.[20] The reasons for the large chemical shift difference between the two resonances of the methylene unit are not completely clear, but the tricyclic framework of **11** is undoubtedly rather rigid, perhaps holding H^{exo} under the deshielding influence of the nearby imide carbonyl and keeping H^{endo} under the shielding influence of the metal fragment.[21] Finally, the carbon chemical shifts for the zwitterionic oxydienyl ligand are reasonable, considering known data for [Cp*M(η^5-cyclohexadienyl)]$^+$ salts (M = Ir and Rh)[13a] and the substituent effects of alkoxy groups on carbon shifts in spectra of Fe−diene complexes.[13c]

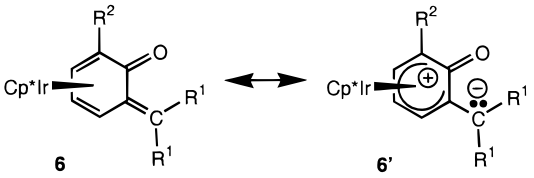
The cycloadduct **11** is formally the result of an unusual [3+2] cycloaddition with part of the quinone methide π-system. The closest precedent for this reaction is a formal [3+2] cycloaddition of *p*-quinone methides with alkenes catalyzed by Lewis acids, in which aryl-substituted alkenes capable of bearing a developing positive charge were the best.[3b] In contrast, the reaction here involves an *o*-QM derivative and an electron-poor alkene.

In summary, all results show that complex **6a** has a nucleophilic exocyclic carbon, unlike free *o*-quinone methides, which feature an electrophilic exocyclic carbon. The apparent role of the Cp*Ir fragment is to stabilize the mesomeric form **6′**. In this limiting struc-

(19) (a) Winterfeldt, E. In *Chemistry of Acetylenes*; Viehe, H. G., Ed.; M. Dekker: New York, 1969; Chapter 4, pp 267−334. (b) Bergmann, E. D.; Ginsburg, D.; Pappo, R. *Org. React.* **1959**, *10*, 179−555, especially pp 519−522. (c) For a discussion of the mechanism with focus on the structure of possible intermediates, see: Lavallée, J.-F.; Berthiaume, G.; Deslongchamps, P.; Grein, F. *Tetrahedron Lett.* **1986**, *27*, 5455−5458.

(20) The preference for endo orientation of the maleimide and the *o*-QM complex π-systems is reminiscent of the endo selectivity of the Diels−Alder reaction. March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley: New York, 1992; pp 843 and 851−852.

(21) For references to the magnetic anisotropy of the Cp*Ir fragment, see Amouri, H.; Le Bras, J.; Vaissermann, J. *Organometallics* **1998**, *17*, 5850−5857, and ref 13a.



ture the exocyclic carbon acquires a greater electron density than in the free ligand, reflected in the upfield ^{13}C chemical shifts in the range 103−128 ppm and in the reactivity toward electrophiles (H^+, I^+, or $HC{\equiv}CCO_2CH_3$) or an electron-poor cycloaddition partner (*N*-methylmaleimide). Both the NMR chemical shift data and reactivity patterns are completely unlike those expected for the β-carbon of an enone, but similar to those for the β-carbon of an electron-rich alkoxy-substituted alkene $ROCH{=}CH_2$.

Conclusions

The first complexes of *simple o*-quinone methides (**6**) reported here can be prepared in one step from oxo-dienyl complexes **5**, which in turn are readily prepared from the appropriate 2-substituted phenols and [Cp*Ir(acetone)$_3$][BF_4]$_2$. Overall yields are high. Because unique stability and reactivity are imparted on the quinone methide ligand by the Cp*Ir fragment, reactions of **6a** forming carbon−carbon bonds in both unprecedented electrophilic addition and [3+2] cycloaddition are possible. Future efforts will utilize the unusual reactivity in new routes to highly substituted oxo-dienyl complexes and polycyclic organic products.

Experimental Section

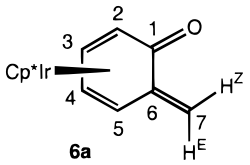
General Comments. All manipulations were carried out under argon atmosphere using Schlenk techniques. Solvents were purified and dried prior to use by conventional distillation techniques. MeOH was distilled from Na. All reagents obtained from commercial sources were used without further purification. ^1H NMR were recorded on Bruker AM 200, 250, or 400 MHz or Varian INOVA 500 MHz instruments. NMR chemical shifts are reported in parts per million referenced to solvent proton resonances [^1H, $C_6D_5CD_2H$, 2.09; C_6D_5H, 7.16; CHD_2CN, 1.95; $(CHD_2)COCD_3$, 2.05; $CHDCl_2$, 5.32; ^{13}C, $C_6D_5\mathit{C}D_3$, 20.39; C_6D_6 128.62; $\mathit{C}D_3CN$, 1.29; $\mathit{C}D_3CO\mathit{C}D_3$, 29.6; CD_2Cl_2, 53.73].

[Cp*Ir(η^5-2-Me-C_6H_4O)][BF_4] (5a). A solution of $AgBF_4$ (780 mg, 4 mmol) in acetone (20 mL) was added to [Cp*IrCl_2]$_2$ (796 mg, 1 mmol) in acetone (30 mL). A white precipitate formed rapidly. The reaction mixture was stirred for 15 min, then the resulting orange 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 added *o*-cresol (540 mg, 5 mmol) in CH_2Cl_2 (20 mL), and the mixture was stirred for 12 h, during which time the solution was decolorized and a white precipitate was obtained. The reaction mixture was treated with NEt_3 (200 μL) for 1 h before the light yellow solution was concentrated under vacuum. Subsequent addition of Et_2O (40 mL) afforded a white precipitate, which was washed several times with Et_2O and dried under vacuum, leaving **5a** (896 mg, 86%): IR (KBr, cm^{-1}) ν(C=O) 1620, ν(B−F) 1055; ^1H NMR (CD_3CN, 250 MHz) δ 1.71 (s, 3 H, -CH_3), 2.09 (s, 15 H, η^5-Cp*), 5.53 (d, 1 H, dienyl C−H), 6.26 ppm (m, 3 H, dienyl C−H); $^{13}C\{^1H\}$ NMR (62.89 MHz, CD_3CN) δ 163.71 (C=O), 103.76 (*C*−Me, dienyl), 99.97, 99.94 [$C_5(CH_3)_5$], 95.14, 83.64, 80.55, 14.14 (CH_3−), 9.73 ppm [$C_5(\mathit{C}H_3)_5$]. Anal. Calcd for $C_{17}H_{22}BF_4IrO$ (521.38): C, 39.16; H, 4.25. Found: C, 39.06; H, 4.41.

[Cp*Ir(η^5-2,6-(Me)$_2$-C_6H_3O)][BF_4] (5b). This compound was prepared in a fashion similar to that used for **5a** and isolated as a white microcrystalline solid in 90% yield: IR (KBr, cm^{-1}) ν(C=O) 1622, ν(B−F) 1050; ^1H NMR (CD_3CN, 250 MHz) δ 1.73 (s, 6 H, $-CH_3$), 2.00 (s, 15 H, η^5-Cp*), 6.01 (m, 1 H, dienyl C−H), 6.24 ppm (m, 2 H, dienyl C−H); $^{13}C\{^1H\}$ NMR (62.89 MHz, CD_3CN) δ 164.34 (C=O), 99.09 [$C_5(CH_3)_5$], 96.07 (C−Me, dienyl), 94.72, 82.31, 14.38 (CH_3−), 9.29 ppm [$C_5(\mathit{C}H_3)_5$]. Anal. Calcd for $C_{18}H_{24}BF_4IrO{\cdot}H_2O$ (553.42): C, 39.06; H, 4.74. Found: C, 38.96; H, 5.05.

[Cp*Ir(η^5-2-*i*-Pr−C_6H_4O)][BF_4] (5c). This complex was prepared in a similar way to that used for **5a** and isolated as an off-white microcrystalline solid in 88% yield: IR (KBr, cm^{-1}) ν(C=O) 1620, ν(B−F) 1060; ^1H NMR (CD_3CN, 250 MHz) δ 1.08 (d, J = 6.8 Hz, 3 H, $-CH_3$), 1.20 (d, J = 6.8 Hz, 3 H, $-CH_3$), 2.08 (s, 15 H, η^5-Cp*), 2.55 (septet, J = 6.8 Hz, 1 H, $H\mathit{C}Me_2$), 5.52 (d, J = 6.8 Hz, 1 H), 6.17 (t, J = 1.5, 5.5 Hz, 1 H), 6.31 (t, J = 5.5 Hz, 1 H), 6.33 ppm (dd, J = 1.5, 5.5 Hz, 1 H); $^{13}C\{^1H\}$ NMR (62.89 MHz, CD_3CN) δ 162.73 (C=O), 108.24 (*C*−*i*-Pr), 100.02 [$C_5(CH_3)_5$], 95.31, 93.36, 83.16, 80.87, 27.83, 19.88, 10.07 [$C_5(\mathit{C}H_3)_5$], 9.16 ppm. Anal. Calcd for $C_{19}H_{26}BF_4IrO{\cdot}H_2O$ (567.45): C, 40.22; H, 4.97. Found: C, 40.03; H, 5.49.

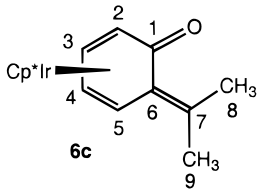
{Cp*Ir[η^5-2,6-(*i*-Pr)$_2$-C_6H_3O]}[BF_4] (5d). This compound was prepared in a manner similar to that used for complex **5a** and isolated as an off-white microcrystalline solid in 85% yield: IR (KBr, cm^{-1}) ν(C=O) 1622, ν(B−F) 1055; ^1H NMR (CD_3CN, 250 MHz) δ 1.11 (d, J = 7 Hz, 6 H, $-CH_3$), 1.22 (d, J = 7 Hz, 6 H, $-CH_3$), 2.02 (s, 15 H, η^5-Cp*), 2.58 (septet, J = 7 Hz, 2 H, $HCMe_2$), 6.05 (t, J = 5.5 Hz, 1 H), 6.23 ppm (d, J = 5.5 Hz, 2 H); $^{13}C\{^1H\}$ NMR (62.89 MHz, CD_3CN) δ 162.02 (C=O), 106.85 (*C*−*i*-Pr), 99.39 [$C_5(CH_3)_5$], 92.73, 81.14, 28.37, 21.05, 20.30, 10.13 ppm [$C_5(\mathit{C}H_3)_5$]. Anal. Calcd for $C_{22}H_{32}BF_4IrO{\cdot}H_2O$ (609.53): C, 43.35; H, 5.62. Found: C, 43.53; H, 5.63.



[Cp*Ir(η^4-C_7H_6O)] (6a). To a solution of [Cp*Ir(η^5-2-Me-C_6H_4O)][BF_4] (**5a**) (180 mg, 0.34 mmol) in CH_2Cl_2 (20 mL) was added *t*-BuOK (152 mg, 1.12 mmol). The resulting light yellow solution was stirred for 1 h before the reaction mixture was concentrated under vacuum. Extraction of the residue by hexane (50 mL), concentration of the hexane solution, and storage of the residue under vacuum afforded **6a** as a pale yellow semicrystalline material (120 mg, 81%): ^1H NMR (C_6D_6, 500 MHz, assignments made by GCOSY) δ 1.64 (s, 15 H, η^5-Cp*), 3.61 (dd, J = 1.4, 5.4 Hz, 1 H, H5), 3.87 (ddd, J = 0.8, 0.9, 5.4 Hz, 1 H, H2), 4.38 (ddd, J = 0.4, 0.8, 2.1 Hz, 1 H, H7^E), 4.63 (ddd, J = 0.9, 3.6, 5.4 Hz, 1 H, H4), 4.78 (ddd, J = 1.4, 3.6, 5.4 Hz, 1 H, H3), 5.43 ppm (d, J = 2.1 Hz, 1 H, H7^Z); ^1H NMR (C_6D_6, 250 MHz) δ 1.62 (s, 15 H, η^5-Cp*), 3.61 (dd, J = 1.3, 5.3 Hz, 1 H, H5), 3.89 (dd, J = 5.5 Hz, 1 H, H2), 4.38 (d, J = 1.8 Hz, 1 H, H7^E), 4.61 (m, 1 H, H4), 4.77 (m, 1 H, H3), 5.45 ppm (d, J = 1.8 Hz, 1 H, H7^Z); $^{13}C\{^1H\}$ NMR (125.7 MHz, benzene-d_6, assignments made by GCOSY, GHMQC, GHMBC) δ 187.79 (C1, C=O), 142.41 (C6), 104.86 (C7, exocyclic C), 90.23 [$C_5(CH_3)_5$], 70.37 (C3), 68.29 (C4), 59.43 (C2), 49.48 (C5), 10.52 ppm [$C_5(\mathit{C}H_3)_5$]; $^{13}C\{^1H\}$ NMR (62.89 MHz, toluene-d_8) δ 187.20 (C=O), 141.61, 104.27, 89.32 [$C_5(CH_3)_5$], 69.47, 67.50, 58.44, 48.38, 9.81 ppm [$C_5(\mathit{C}H_3)_5$]. Anal. Calcd for $C_{17}H_{21}IrO$ (433.57): C, 47.09; H, 4.88. Found: C, 46.89; H, 5.12.

[Cp*Ir(η^4-C_8H_8O)] (6b). In a manner similar to that used for **6a**, [Cp*Ir(η^5-2,6-$Me_2C_6H_3O$)][BF_4] (**5b**) (150 mg, 0.28 mmol) and *t*-BuOK (103 mg, 0.92 mmol) were used to make **6b** as a yellow microcrystalline solid (110 mg, 88%): ^1H NMR (C_6D_6, 250 MHz) δ 1.50 (s, 3 H, $-CH_3$), 1.62 (s, 15 H, η^5-Cp*), 3.58 (dd, J = 1.5, 5.5 Hz, 1 H, H^d), 4.33 (d, J = 1.3 Hz, 1 H,

H^e, $=CH_2$), 4.51 (dd, J = 3.8, 5.5 Hz, 1 H, H^c), 4.72 (dd, J = 1.5, 3.8 Hz, 1 H, H^b), 5.43 ppm (d, J = 1.3 Hz, 1 H, H^f, $=CH_2$); $^{13}C\{^1H\}$ NMR (62.89 MHz, toluene-d_8) δ 186.55 (C=O), 141.36 (C=), 103.34 ($=CH_2$), 89.10 [$C_5(CH_3)_5$], 73.41, 67.33, 64.71, 48.77, 17.67 (s, CH_3), 9.39 ppm [$C_5(CH_3)_5$]. Anal. Calcd for $C_{18}H_{23}IrO$ (447.59): C, 48.30; H, 5.18. Found: C, 48.65; H, 5.47.

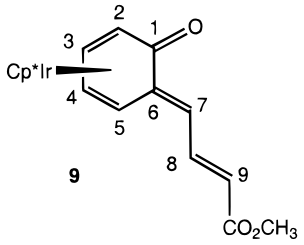


[Cp*Ir(η^4-$C_9H_{10}O$)] (6c). In a manner similar to that used for **6a** and **6b**, **5c** (150 mg, 0.27 mmol) and *t*-BuOK (103 mg, 0.92 mmol) were used to make **6c** as a yellow microcrystalline solid (126 mg, 95%): ^1H NMR (benzene-d_6, 500 MHz) δ 1.73 (s, 15 H, η^5-Cp*), 1.93 (s, 3 H, CH_3 *E* to carbonyl, C9), 2.71 (s, 3 H, CH_3 *Z* to carbonyl, C8), 3.64 (dd, J = 1.2, 5.3 Hz, 1H, H5), 3.80 (dd, J = 0.7, 5.2 Hz, 1 H, H2), 4.76 (ddd, J = 0.7, 3.4, 5.2 Hz, 1 H, H4), 4.83 ppm (ddd, J = 1.2, 3.4, 5.2 Hz, 1 H, H3); $^{13}C\{^1H\}$ NMR (125.7 MHz, benzene-d_6, assignments made by GCOSY, GHMQC, GHMBC) δ 193.07 (C1, C=O), 133.42 (C6), 128.07 (C7, exocyclic C), 90.24 [$C_5(CH_3)_5$], 69.30 (C3), 67.05 (C4), 59.61 (C2), 43.33 (C5), 21.94 (C9), 21.27 (C8), 10.90 ppm [$C_5(CH_3)_5$]; $^{13}C\{^1H\}$ NMR (62.89 MHz, toluene-d_8) δ 192.13 (C1, C=O), 132.60 (C6), C7 probably obscured by solvent resonances, 89.61 [$C_5(CH_3)_5$], 68.69, 66.38, 59.02, 42.86, 30.29, 23.17, 10.22 ppm [$C_5(CH_3)_5$]. Anal. Calcd for $C_{19}H_{25}IrO$: C, 49.44; H, 5.46. Found: C, 49.35; H, 5.55.

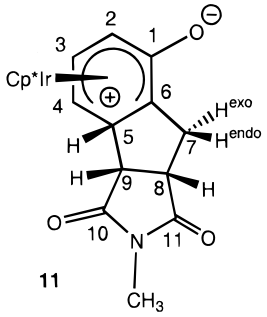
[Cp*Ir(η^4-$C_{12}H_{16}O$)] (6d). As was done for **6a**, **5d** (220 mg, 0.37 mmol) and *t*-BuOK (141 mg, 1.26 mmol) afforded **6d** as yellow crystals (180 mg, 96%): ^1H NMR (benzene-d_6, 250 MHz) δ 1.0 [d, J = 7.5 Hz, 3 H, $-CH(CH_3)(CH_3)$], 1.50 [d, J = 7.5 Hz, 3 H, $-CH(CH_3)(CH_3)$], 1.62 (s, 15 H, η^5-Cp*), 1.95 [s, 3 H, $=C(CH_3)(CH_3)$], 2.58 (septet, J = 7.5 Hz, 1 H, $-CHMe_2$), 2.72 [s, 3 H, $=C(CH_3)(CH_3)$], 3.45 (dd, J = 1.3, 4.3 Hz, 1 H), 4.61 (dd, J = 3.8, 4.3 Hz, 1 H), 4.99 ppm (dd, J = 1.3, 3.8 Hz, 1 H); $^{13}C\{^1H\}$ NMR (62.89 MHz, toluene-d_8) δ 186.70 (C=O), 130.68 (C=), 110.67 ($=CMe_2$), 89.51 [$C_5(CH_3)_5$], 70.01, 66.47, 50.15, 44.56, 28.42 ($CH_3-C=C$), 22.46 ($CH_3-C=C$), 21.46 (*C*H), 21.13 (CH_3-CH), 20.73 (CH_3-CH), 9.86 ppm [$C_5(CH_3)_5$]. Anal. Calcd for $C_{22}H_{31}IrO$ (503.70): C, 52.46; H, 6.20. Found: C, 52.39; H, 6.30.

Protonation of 6a To Give [Cp*Ir(η^5-C_7H_7O][BF_4] (5a) and [Cp*Ir(η^6-C_7H_8O][BF_4]$_2$ (7). One equivalent of $HBF_4\cdot Et_2O$ was added to a CD_3CN solution of complex **6a**, and the reaction was followed by ^1H NMR spectroscopy. The spectrum showed the total disappearance of the starting material and the formation of the new monocationic species **5a**. Further treatment with $HBF_4\cdot Et_2O$ (excess) afforded the related dicationic species **7**. Complex **7** can be also prepared by protonation of the oxo-dienyl iridium complex **5a**. ^1H NMR (CD_3CN, 250 MHz) for complex **7**: δ 2.20 (s, 15 H, η^5-Cp*), 2.23 (s, 3 H, $-CH_3$), 6.90 (m, 1 H, arene proton), 7.00 ppm 3 H, arene protons); $^{13}C\{^1H\}$ NMR (62.89 MHz, CD_3CN) δ 141.04 (C−OH), 105.20 (C−Me, dienyl), 103.20 [$C_5(CH_3)_5$], 99.01, 96.92, 93.25, 85.33, 13.50 (CH_3-), 9.85 ppm [$C_5(CH_3)_5$].

[Cp*Ir(η^5-C_7H_6IO][I] (8). An ether solution of iodine (excess) was added to a yellow solution of complex **6a** (50 mg, 0.12 mmol) in ether to give rapidly an orange precipitate. The solvent was removed, and the orange precipitate was washed several times with diethyl ether, then dried under vacuum, to yield **8** as an orange microcrystalline solid (70 mg, 88%): ^1H NMR (CD_3CN, 250 MHz) δ 2.11 (s, 15 H, η^5-Cp*), 3.79 (d, J = 8.8 Hz, 1 H, C*H*HI), 4.06 (d, J = 8.8 Hz, 1 H, CH*H*I), 5.68 (d, J = 7 Hz, 1 H), 6.29 (m, 1 H, dienyl−CH), 6.35 (t, J = 5.5 Hz, 1 H), 6.52 ppm (dd, J = 1.5, 5.5 Hz, 1 H); $^{13}C\{^1H\}$ NMR (CD_3CN, 62.89) δ 162.44 (C=O) 100.73 [$C_5(CH_3)_5$], 95.98, 95.67, 94.63, 84.76, 81.17, 9.94 [$C_5(CH_3)_5$], -4.43 ppm ($-CH_2I$). Anal. Calcd for $C_{17}H_{21}I_2IrO$ (687.37): C, 29.70; H 3.08. Found: C, 29.59; H, 3.29.



Reaction of Methyl Propynoate and 6a To Give [Cp*Ir(η^4-$C_{11}H_{10}O_2$)] (9). To a solution of complex **6a** (93 mg, 0.21 mmol) in benzene-d_6 (5 mL) was added methyl propynoate (0.125 mL, 5 equiv), and the reaction was left stirring for 2 days, during which the color changed from yellow to goldish-green. The solution was evaporated and the residue washed with hexane, then extracted with a benzene−hexane mixture (1:2) and dried under vacuum, leaving **9** (50 mg, 46%): IR (KBr, cm^{-1}) ν(CO ester) 1709, ν(CO of *o*-QM) 1650, ν(C=C) 1559; ^1H NMR (500 MHz, toluene-d_8, assignments made by GCOSY, GHMQC, GHMBC) δ 1.57 (s, 15 H, Cp*), 3.48 (s, 3 H, CH_3O), 3.90 (dd, J = 0.9, 5.5 Hz, 1 H, H2), 4.11 (slightly broad d, J = 5.4 Hz, 1 H, H5), 4.66 (ddd, J = 0.9, 4.0, 5.4 Hz, 1 H, H4), 4.80 (ddd, J = 1.3, 4.0, 5.5 Hz, 1 H, H3), 5.84 (dd, J = 0.6, 14.9 Hz, 1 H, H9), 6.31 (d, J = 12.6 Hz, 1 H,.H7), 8.05 ppm (dd, J = 12.6, 14.9 Hz, 1 H, H8); $^{13}C\{^1H\}$ NMR (125.7 MHz, benzene-d_6) δ 181.51 (C1, ring C=O), 167.74 (ester C=O), 139.05 (C8), 120.13 (C9), 113.51 (C7), 90.35 [$C_5(CH_3)_5$], 71.62 (C3), 69.21 (C4), 61.76 (C2), 50.67 (CH_3O), 49.76 (C5), 9.66 ppm [$C_5(CH_3)_5$] (resonance for C6 not clearly identified). Anal. Calcd for $C_{22}H_{25}IrO_3$ (517.64): C, 48.73; H, 4.87. Found: C, 47.49; H, 5.03.



Reaction of *N*-Methylmaleimide and 6a To Give [Cp*Ir(η^5-$C_{12}H_{11}NO_3$)] (11). To a solution of complex **6a** (100 mg, 0.23 mmol) in benzene-d_6 (5 mL) was added *N*-methylmaleimide (125 mg, 1.12 mmol), and the reaction mixture was left to stir under argon. After 15 min a color change from yellow to orange was observed with formation of a light precipitate. The reaction was left for 2 days, then filtered. The orange filtrate was evaporated under vacuum and washed with hexane, then the residue was dried under vacuum to give **11** as a solid (70 mg, 46%). Analysis by ^1H NMR spectroscopy suggested that the product was about 90% pure. Compound **11** decomposed in solution during attempted recrystallization: IR (KBr, cm^{-1}) ν(CO) 1698 (sharp); ^1H NMR (C_6D_6, 500 MHz, in reaction mixture with excess *N*-methylmaleimide) δ 0.77 (dd, J = 9.9, 11.5 Hz, 1 H, $H7^{endo}$), 1.47 (s, 15 H, Cp*), 2.13 (t, J = 6.9 Hz, 1 H, H9), 2.27 (dd, J = 7.0, 9.9 Hz, 1 H, H8), 2.77 (dd, J = 5.3, 5.6 Hz, 1 H, H5), 2.87 (s, 3 H, CH_3N), 3.59 (d, J = 11.5 Hz, 1 H, $H7^{exo}$), 3.97 (dd, J = 5.4, 5.9 Hz, 1 H, H4), 4.62 (ddd, J = 1.0, 5.9, 5.9 Hz, 1 H, H3), 5.11 ppm (d, J = 5.9 Hz, 1 H, H2); $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz) δ 176.6 and 179.2 (C10 and C11), 162.8 (C1), 91.4 [$C_5(CH_3)_5$], 87.2 (C3),

72.3 (C2), 57.0 (C8), 55.2 (C5), 53.9 (C4), 40.1 (C9), 32.2 (C6), 30.4 (C7), 25.6 (*C*H*3*N), 10.1 ppm [$C_5(CH_3)_5$]. Anal. Calcd for $C_{22}H_{26}IrNO_3 \cdot C_5H_5NO_2$ (655.76): C, 49.45; H, 4.76; N, 4.27. Found: C, 49.97; H, 5.20; N, 5.00.

X-ray Crystal Structure Determination for 6d. Suitable crystals of **6d** were obtained from a saturated solution in hexane at 7 °C. The selected crystal of complex **6d** 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[22] and provided the best structural resolution for **6d**. Complete crystallographic data and collection parameters for **6d** are listed in the Supporting Information. 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 asymmetric unit of complex **6d** consists of two independent molecules. The structure of compound **6d** 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 complex **6d**.

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Supporting Information Available: Crystallographic information for **6d**, NMR spectra for **6a** and **6c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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