Metal-Stabilized Phenoxonium Cation

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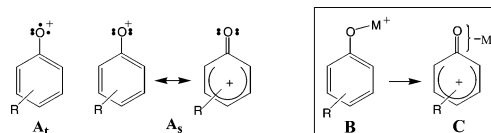Haim Rozenberg,[‡] and David Milstein*,[†]

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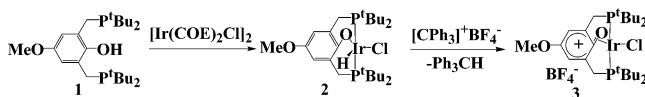Received September 17, 2003; E-mail: david.milstein@weizmann.ac.il

Phenoxonium cations (**A**, Scheme 1) play important roles in chemical and biochemical processes. They have been postulated as key intermediates in the oxidation of phenols and in biological oxidative coupling reactions, which lead to a variety of natural products and chemicals.[1] Ab initio calculations predicted a singlet ground state for the phenoxonium cation,[2] implying effective overlap between an empty oxygen p orbital and the arene π system, resulting in positive charge delocalization into the ring (**A$_s$**), whereas in the triplet ground state the positive charge resides only on the oxygen atom. Although too unstable to be isolated, they have been generated as transients by various methods[3] and their trapping reactions have led to synthetic methodologies.[3a–c,4] One of the most significant reactions thought to involve phenoxonium intermediates is the oxidative coupling of phenols. It is catalyzed by various metal (e.g., Cu, Co, Fe, Mn) complexes and metalloenzymes[1] and is involved in the biosynthesis of lignin and melanin.[1a,5] The industrially important Cu(II) complex-catalyzed oxidative polymerization of 2,6-dimethylphenol produces the major engineering plastics poly-(phenylene ether).[1a,b] Mechanistic and theoretical studies of the oxidative coupling and polymerization of phenols have invoked a two-electron transfer from a phenolate ligand to the metal (dinuclear Cu(II)) to form an oxo-coordinated singlet phenoxonium cation (i.e., with a positively charged ring) and a reduced metal center.[1a,6] However, such a process (**B→C**, Scheme 1) was never observed, and a phenoxonium cation, complexed via the C–O group, or free, has never been isolated, although η^5-oxocyclohexadienyl complexes are well-known.[7] We report here on such a process, including isolation, crystallographic characterization, and reactivity of a phenoxonium cation stabilized by metal coordination to the C=O bond.

Reaction of the phenolic ligand **1** with [Ir(cyclooctene)$_2$Cl]$_2$ in hot benzene afforded the fully characterized[8] phenoxy hydride complex **2** in 82% isolated yield, by an O–H activation process. When a red CH$_2$Cl$_2$ solution of **2** was treated with an equivalent amount of [Ph$_3$C]$^+$ BF$_4^-$, a color change to green took place and formation of the phenoxonuim complex **3** was observed by ^{31}P NMR spectroscopy; **3** was then isolated as a green solid in 69% yield (Scheme 2). The ^{31}P{^{1}H} NMR of **3** shows a high-field singlet at 6.46 ppm.[8] The presence of positive charge at the phenoxonuim ring causes dramatic downfield shifts of the aromatic carbon atoms in the ^{13}C{^{1}H} NMR spectrum. As most of the charge is localized at the ortho and para positions, the corresponding carbon atoms show a 20–40 ppm downfield shift compared with the neutral **2**. The *ipso*-carbon atom gives rise to a triplet at 83.27 ppm, indicating coordination to the iridium center. A similar upfield shift was observed for the *ipso*-carbon atom in the structurally related methylene arenium complexes.[9] Addition of acetonitrile to a solution of **3** in CH$_2$Cl$_2$ resulted in a color change from green to brown,
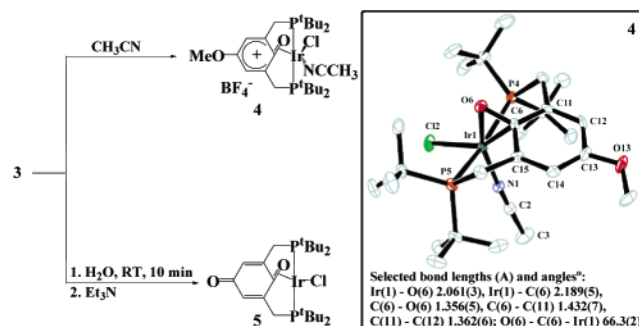
Scheme 1

Scheme 2

Scheme 3

Selected bond lengths (Å) and angles[a]:
Ir(1) - O(6) 2.061(3), Ir(1) - C(6) 2.189(5),
C(6) - O(6) 1.356(5), C(6) - C(11) 1.432(7),
C(11) - C(12) 1.362(6); O(6) - C(6) - Ir(1) 66.3(2)

and the CH$_3$CN adduct **4** was quantitatively formed (Scheme 3). Formation of **4** causes a further upfield shift of the ^{31}P{^{1}H} NMR signal, which now appears as a singlet at −13.71 ppm. The mild electron-donating properties of the acetonitrile ligand slightly decrease the positive charge in the aromatic ring, as evident from the upfield shifts of the *para-* and *ortho*-carbon atom signals in the ^{13}C{^{1}H} NMR spectrum as compared with those of **3**.

Crystals of **4** were obtained from a CH$_2$Cl$_2$ solution layered with hexane. The X-ray structure of **4** (Scheme 3)[10] reveals a unique η^2 coordination mode of the metal center to the C=O double bond in a quinonoid compound. As we are unaware of other examples of crystallographically characterized metal complexes of η^2 bound quinones, we compare the relevant distances around the third row metal center with those in η^2-coordinated ketones and ketenes (sp-hybridized system). The M−C bond distance of 2.189(5) Å in **4** is longer than that in Ir ketene complexes[11] (1.971(4)−1.982(12) Å) and slightly longer than that in the pentaammineosmium(II) acetone complex (2.126(11) Å).[12] The M−O bond length of 2.061(3) Å is slightly shorter than that in coordinated ketenes (2.090(3)−2.099-(8) Å) and compares well with the one in the Os acetone complex (2.057(7) Å). The C−O bond length of 1.356(5) Å indicates strong coordination of this bond to the iridium center.[13] This distance is close to the corresponding one in the Os acetone complex (1.322-(13) Å). These observations point toward the η^2 coordination character for the two neighboring third row metals. For comparison,

metal−oxygen and carbon−oxygen bond lengths in mid-row tungsten η^2 ketone complexes show values between 1.933(4)−1.970(6) Å and 1.379(8)−1.397(11) Å, respectively, indicating a metallacycle coordination mode in these complexes.[14] The carbon−carbon bond alternation in the aromatic ring in **4** is typical for metal-stabilized arenium compounds.[9] Most of the positive charge is localized at the *ortho*- and *para*-carbon atoms as evidenced by the C(11)−C(12) and C(14)−C(15) bond distances of 1.362(6) and 1.319(6) Å, respectively, being shorter than the rest of the distances in the ring. The bond angles inside the ring are nearly equal to 120°, suggesting that the structure of **4** is better described in terms of the C=O double-bond coordination to the Ir(I) center rather than in terms of a three-centered Ir(III) metallacycle. The X-ray structure also shows that all six carbon atoms are located in the same plane with the coordinated oxygen atom pushed out of the plane by approximately 10°. In the η^5-oxocyclohexadienyl complexes of Ir, the carbon atom itself is removed out of plane, indicating nonaromaticity.[7c] A slight deviation of the oxygen atom with respect to the ring plane has also been observed in chelated η^1-coordinated Pd(II) anthraquinone complexes.[15] Due to steric constrains, the acetonitrile ligand occupies the position trans to the coordinated C=O bond.

While phenoxonium cations are implicated in chemical and biochemical processes,[1] they have never been isolated. As previously demonstrated with the elusive methylene arenium species, metal complexation to the exocyclic double bond provides a useful tool for stabilizing such a species without direct metal interaction with the aromatic π-system.[16] However, while η^2 metal complexation to a C=C double bond is well-known, no examples of such coordination to C=O bonds in quinonoid compounds have been reported. Complexes **3** and **4** are, therefore, the first examples of metal-stabilized phenoxonium compounds, which also involve the unprecedented η^2 C=O quinonoid coordination mode. Various coordination modes in quinonoid compounds have been explored. Metal complexes of bidentate *o*-quinone derivatives have received considerable attention due to their unique electronic and magnetic properties.[17] In addition, π-metal complexes of *p*-quinones were studied with regard to their application in new materials design and in catalysis.[18,19] Recently, metal coordination to a quinone methide-type oxygen atom was demonstrated to trigger DNA alkylation.[20]

The positive charge delocalization within the aromatic ring is further evidenced by the chemical reactivity of the phenoxonium complex **3**. Thus, addition of water to a solution of **3** in dioxane results in quantitative hydrolysis of the methoxy group in the para position within a few minutes at room temperature. For comparison, removal of the methoxy group in anisol requires activation by strong Lewis acids.[21,22] Addition of NEt$_3$ results in instantaneous deprotonation of the phenolic proton to give the iridium quinone complex **5** (Scheme 3). The ^{31}P{^{1}H} NMR spectrum of **5** exhibits a singlet at 23.72 ppm. The ^{13}C{^{1}H} NMR spectrum shows the *ipso*-carbon signal as a triplet at 71.86 ppm, indicating an η^2 metal coordination mode and disappearance of the positive charge at the former phenoxonium ring. The quinonoid *para*-carbon atom appears as a triplet at 188.35 ppm, which corresponds well with organic carbonyl signals in quinones. The strong IR band at 1644 cm^{-1} further confirms the formation of a neutral quinonoid moiety.

In summary, we have reported the first example of a phenoxonium cation stabilized by an unprecedented η^2 metal coordination to the quinonoid C=O double bond. The X-ray structure and the spectroscopic data confirm the positive charge delocalization within

the aromatic ring. The phenoxonium cation undergoes facile Me−O bond cleavage, resulting in the corresponding *p*-quinone complex while maintaining the unprecedented η^2 coordination mode of a quinonoid C=O bond.

Supporting Information Available: Experimental details for compounds **1**−**5** and crystal data for complex **4** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) X-ray structure data for **4**: 2[C$_{25}$H$_{45}$O$_2$P$_2$ClIr(NCCH$_3$) + (CH$_2$Cl$_2$) + (BF$_4$)], yellow parallelogram, $P2(1)/n$, a = 24.726 (5) Å, b = 11.704 (2) Å, c = 26.129 (5) Å, β = 106.53 (3)°, V = 7250 (2) Å^3, F_w = 1759.98, Z = 4, $R_1(I > 2\sigma I)$ = 0.036.

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