

Preliminary communication

 η^4 -quinone, η^5 -semiquinone and η^6 -hydroquinone complexes of pentamethylcyclopentadienyl iridium. X-ray molecular structure of $[\text{Cp}^* \text{Ir}(\eta^4\text{-1,4 benzoquinone})]$ Jean Le Bras^a, H. Amouri^{a,*}, Jacqueline Vaissermann^b^a *École Nationale Supérieure de Chimie de Paris, URA CNRS 403, 11, Rue Pierre et Marie Curie, Paris Cedex 05, 75231, France*^b *Laboratoire de Chimie de Métaux de Transition, URA CNRS 419, Université Pierre et Marie Curie, 4 Place Jussieu, Paris Cedex 05, 75252, France*

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Abstract

Treatment of hydroquinone with $[\text{Cp}^* \text{Ir}(\text{solvent})_3][\text{BF}_4]_2$ (**1**) in acidic medium afforded the stable π -bonded complex $[\text{Cp}^* \text{Ir}(\eta^6\text{-hydroquinone})][\text{BF}_4]_2$ (**2**) in high yield. Complex **2** can be easily deprotonated by a base to give the related $[\text{Cp}^* \text{Ir}(\eta^5\text{-semiquinone})][\text{BF}_4]$ (**3**) and $[\text{Cp}^* \text{Ir}(\eta^4\text{-quinone})]$ (**4**) compounds identified by spectroscopic methods. Complex **4** reacts with an excess of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ to give the starting material **2** quantitatively. Interestingly, these chemical transformations occur with facile reversible changes of the oxidation state from Ir(III) to Ir(I). Further the X-ray molecular structure of **4** is reported. © 1998 Elsevier Science S.A.

Keywords: Pentamethylcyclopentadienyl iridium; Hydroquinone; Semiquinone; Quinone

1. Introduction

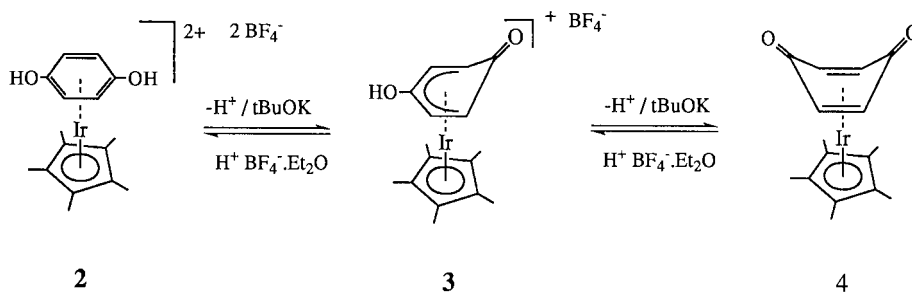
While π -complexes of η^4 -duroquinone (duroquinone = 2,3,5,6-Tetramethyl-1,4-benzoquinone) and the related η^5 -semi-duroquinone and η^6 -hydro-duroquinone complexes are well known and extensively investigated [1–5], those of the simple η -benzoquinone derivatives have attracted less attention. This, in part, is due to the instability of such π -complexes. For instance, $(\eta^6\text{-hydroquinone})\text{Cr}(\text{CO})_3$ is reported to be a heat and air sensitive compound and is identified spectroscopically but cannot be isolated as pure solid [6]. Recently, however, Sun et al. [7] reported the synthesis of $[\eta^6\text{-hydroquinone} \text{Mn}(\text{CO})_3][\text{PF}_6]$ via arene displacement reaction from $[(\eta^6\text{-acenaphthene})\text{Mn}(\text{CO})_3]^+$ and hydroquinone. Here, we report a high yield synthesis of $[\text{Cp}^* \text{Ir}(\eta^6\text{-hydroquinone})][\text{BF}_4]_2$ (**2**) from direct treatment of the solvated iridium complex $[\text{Cp}^* \text{Ir}(\text{solvent})_3][\text{BF}_4]_2$ (**1**) with hydroquinone.

Complex **2** can be deprotonated by the appropriate base to give the related η^5 -semiquinone (**3**) and the η^4 -quinone (**4**) iridium complexes. Treatment of **4** by $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ gave back quantitatively the parent complex $[\text{Cp}^* \text{Ir}(\eta^6\text{-hydroquinone})][\text{BF}_4]_2$ (**2**). These deprotonation/protonation reactions were found to be reversible for the iridium series. Further, the X-ray structure of $[\text{Cp}^* \text{Ir}(\eta^4\text{-quinone})]$ (**4**) was determined and showed that the quinone ligand adopts a boat conformation.

2. Results and discussions

Placement of the ‘ $\text{Cp}^* \text{Ir}$ ’ moiety at the arene ring was accomplished in acetone/THF by treating $[\text{Cp}^* \text{Ir}(\text{acetone})_3][\text{BF}_4]_2$ (**1**) prepared in situ with an excess of hydroquinone for 1 h. Reaction workup afforded a yellow microcrystalline compound which was subsequently treated by $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ in CH_3CN for 10 min and produced a white microcrystalline complex in 90% overall yield. This complex was identified analyti-

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Scheme 1.

cally and by infrared and NMR spectroscopy¹ as $[\text{Cp}^* \text{Ir}(\eta^6\text{-hydroquinone})][\text{BF}_4]_2$ (**2**). The ¹H NMR of **2** recorded in CD₃CN and in presence of HBF₄·Et₂O (to suppress H⁺ dissociation, vide infra) displayed a singlet at 6.80 ppm attributed to the aromatic protons, while the η⁵-Cp* showed a singlet at 2.20 ppm, the ¹H NMR spectrum also shows a signal at 9.30 ppm attributed to the exchange of the phenolic protons of **2** with the H⁺ from HBF₄·Et₂O. The tendency of **2** to lose its phenolic proton is not surprising since the $[\text{Cp}^* \text{Ir}]^{2+}$ fragment increases dramatically the acidity of the η⁶-hydroquinone relative to that of the free molecule and as observed previously for the related phenol complex $[\text{Cp}^* \text{Ir}(\eta^6\text{-phenol})][\text{BF}_4]_2$ [8,9]. Further, the analogous dicationic cobalt complex $[\text{Cp}^* \text{Co}(\eta^6\text{-hydroquinone})][\text{BF}_4]_2$ was also found to deprotonate easily in solution even during recrystallization [10,11]. This behavior stimulated us to study the properties and stability of complex **2** in acidic and basic medium.

When a CD₃CN solution of $[\text{Cp}^* \text{Ir}(\eta^6\text{-hydroquinone})][\text{BF}_4]_2$ (**2**) was exposed to an excess of tBuOK, a rapid yellow color was formed. The ¹H NMR of the sample shows the total disappearance of **2** and the formation of the related η⁵-semiquinone and η⁴-quinone iridium complexes (**3–4**) (Scheme 1). When the reaction was allowed to continue, complete deprotonation occurred, yielding exclusively the η⁴-quinone complex $[\text{Cp}^* \text{Ir}(\eta^4\text{-quinone})]$ (**4**). The latter can be prepared quantitatively and isolated as a light yellow microcrystalline solid.¹ Crystals of **4** were obtained by crystallization from CH₃CN/Et₂O solution. Although several X-ray structures of η⁴-duroquinone complexes were reported in the literature, those of the simple η⁴-1,4 benzoquinone are rare. Complex **4** crystallizes with two

molecules of water in the orthorhombic space group *Pbca*.² Fig. 1 shows Cameron view of **4**. In this structure the Cp* Ir fragment is indeed coordinated to only four carbons of the quinone ligand whereby the distances from the metal to the centers of the π-bonded carbons is 1.69 Å for the quinone and 1.81 Å for the η⁵-C₅Me₅. Further, the quinone ligand acquires a boat-like conformation with the dihedral angles across C2–C6 and C3–C5 of almost 16°. These angles are smaller than those reported for neutral and cationic rhodium complexes of η⁴-duroquinone which lie in the range of 20–28° [1,3].

When complex **4** was protonated by HBF₄·Et₂O in CH₃CN the parent complex **2** was recovered in quantitative yield. The protonation/deprotonation reactions were found to be reversible without showing any minor decomposition of the iridium complexes. At this stage, a brief comment on these π-complexes of iridium is adequate. The remarkable stability of these complexes **2–4** is no doubt related to the nature of the 'Cp* Ir' moiety which helps to stabilize the different coordination modes η⁴-, η⁵- and η⁶- of the quinone family ligands. We also note that the reversible deprotonation/protonation reactions occur via changes of the oxidation states from Ir(III) to Ir(I) and inversely. Further, our synthetic approach to this class of π-complexes is simple and different than that described in the literature, which often involves the preparation of η⁴-duroquinone compounds as the starting material [1–5].

¹ Spectroscopic data for new compounds. **2**: IR (Nujol, cm⁻¹): ν(O–H) 3100–3300, ν(B–F) 1065. ¹H NMR (CD₃CN/HBF₄·Et₂O, 250 MHz) δ 9.30 (s, acidic protons –OH), 6.80 (s, 4H, arene protons), 2.20 (s, 15H, η⁵-Cp*). Anal. for **2** Calc.: C, 31.42; H, 3.40. Found: C, 32.20; H, 3.57. **3**: IR (KBr, cm⁻¹): ν(O–H) 3250–3400, ν(C=O) 1531, ν(B–F) 1065. ¹H NMR (CD₃CN, 250 MHz) δ 5.95 (d, *J*_{H–H} = 8 Hz, 2H arene protons), 5.15 (d, *J*_{H–H} = 8 Hz, 2H arene protons), 2.10 (s, 15H, η⁵-Cp*). **4**: IR (Nujol, cm⁻¹): ν(C=O) 1567, 1537. ¹H NMR (CD₃CN, 250 MHz) δ 4.87 (s, 4H, quinone protons), 2.04 (s, 15H, η⁵-Cp*).

² X-ray data collection was carried out on a suitable crystal using a Nonius CAD4 diffractometer equipped with graphite monochromated Mo Kα radiation. Crystal data for **4**: Orthorhombic, space group *Pbca*, with *a* = 14.032(2) Å, *b* = 15.578(4) Å, *c* = 14.474(3) Å, α = β = γ = 90°, *V* = 3163.7(2) Å³, *Z* = 8, *D*_{calc} = 1.98 g cm⁻³, μ = 84.2 cm⁻¹, θ range = 2°–21°, 192 variables refined with 3819 independent reflections to *R* = 0.0326, *R*_w = 0.0347 and GOF = 1.03. Computations were performed by using the PC version of CRYSTALS [12]. Scattering factors and corrections for anomalous dispersion were taken from Ref. [13]. The structure 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.

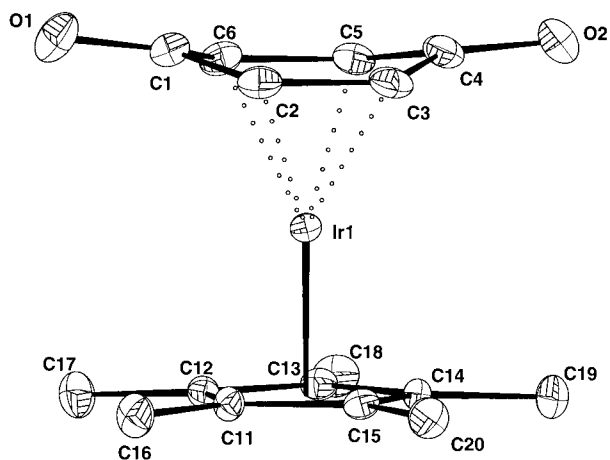


Fig. 1. Cameron view of the structure of $[\text{Cp}^*\text{Ir}(\eta^4\text{-1,4-benzoquinone})]$ (**4**) showing the atom numbering system. Note that the quinone ligand adopts a boat like conformation. Selected bond distances (Å) and angles ($^\circ$): Ir1–C2 = 2.188(6), Ir1–C3 = 2.182(6), Ir1–C5 = 2.192(6), Ir1–C6 = 2.218(6), C1–O1 = 1.252(8), C4–O2 = 1.260(8), C2–C1–C6 = 111.9(6), C3–C4–C5 = 112.0(6).

In this communication, we reported high yield syntheses of stable η^6 -hydroquinone, η^5 -semiquinone and η^4 -quinone complexes of $[\text{Cp}^*\text{Ir}]^{2+}$. The solution behavior and reversible chemical transformations between complexes **2** and **4** stimulate us to study their redox and electrochemical behavior. These investigations as well as their reactivity toward nucleophiles will be the subject of future full paper.

Acknowledgements

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