

Pentamethylcyclopentadienyl rhodium and iridium complexes containing oxinato ligands

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ABSTRACT

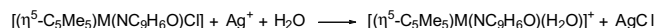
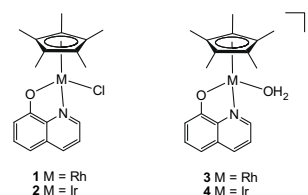
The neutral chloro complexes $[(\eta^5\text{-C}_5\text{Me}_5)\text{M}(\eta^2\text{-NC}_9\text{H}_6\text{O})\text{Cl}]$ as well as the cationic aqua complexes $[(\eta^5\text{-C}_5\text{Me}_5)\text{M}(\eta^2\text{-NC}_9\text{H}_6\text{O})(\text{H}_2\text{O})]^+$ ($\text{M} = \text{Rh}, \text{Ir}$) have been synthesized from the reaction of the dinuclear precursors $[(\eta^5\text{-C}_5\text{Me}_5)\text{MCl}_2]_2$ and 8-hydroxyquinoline. The single crystal X-ray structure analysis of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\eta^2\text{-NC}_9\text{H}_6\text{O})\text{Cl}]$ reveals for these complexes a piano-stool arrangement with the aromatic ligand, the chelating oxinato ligand and the terminal chloro or aqua ligand surrounding the metal center in a pseudo-tetrahedral fashion.

Keywords:

Rhodium, Iridium, Pentamethylcyclopentadienyl, Oxinato

8-Hydroxyquinoline, $\text{NC}_9\text{H}_6\text{OH}$ ("oxine"), reacts with many metal cations under deprotonation to give complexes in which the oxinato moiety $\text{NC}_9\text{H}_6\text{O}$ acts as η^2 -chelating ligand [1]. Oxinato complexes such as $\text{Mg}(\eta^2\text{-NC}_9\text{H}_6\text{O})_2$, $\text{Zn}(\eta^2\text{-NC}_9\text{H}_6\text{O})_2$ and $\text{Al}(\eta^2\text{-NC}_9\text{H}_6\text{O})_3$ are used since 1930s in classical analytical chemistry [2]. The oxinato ligand is also well known in organometallic complexes; however, while arene ruthenium and osmium complexes containing an oxinato ligand have been reported $[(\eta^6\text{-MeC}_6\text{H}_4\text{-Pr}^i)\text{Ru}(\eta^2\text{-NC}_9\text{H}_6\text{O})\text{Cl}]$ [3] and $[(\eta^6\text{-MeC}_6\text{H}_4\text{Pr}^i)\text{Os}(\eta^2\text{-NC}_9\text{H}_6\text{O})\text{Cl}]$ [4], to the best of our knowledge, the isoelectronic pentamethylcyclopentadienyl rhodium and iridium complexes are not known so far. We now report the synthesis and characterization of the neutral chloro complexes $[(\eta^5\text{-C}_5\text{Me}_5)\text{M}(\eta^2\text{-NC}_9\text{H}_6\text{O})\text{Cl}]$ and of the cationic aqua complexes $[(\eta^5\text{-C}_5\text{Me}_5)\text{M}(\eta^2\text{-NC}_9\text{H}_6\text{O})(\text{H}_2\text{O})]^+$ derived thereof.

The dinuclear pentamethylcyclopentadienyl complexes $[(\eta^5\text{-C}_5\text{Me}_5)\text{MCl}_2]_2$ ($\text{M} = \text{Rh}, \text{Ir}$) react in chloroform with potassium oxinate at room temperature to give the neutral chloro complexes $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\eta^2\text{-NC}_9\text{H}_6\text{O})\text{Cl}]$ (**1**) and $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\eta^2\text{-NC}_9\text{H}_6\text{O})\text{Cl}]$ (**2**). Both complexes **1** and **2**, isolated by precipitation with diethyl ether and purified by thin-layer chromatography, form air-stable, yellow to orange crystalline solids which are well soluble in dichloromethane or in chloroform [5].



The cationic pentamethylcyclopentadienyl rhodium $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\eta^2\text{-NC}_9\text{H}_6\text{O})(\text{H}_2\text{O})]^+$ (**3**) and iridium $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\eta^2\text{-NC}_9\text{H}_6\text{O})(\text{H}_2\text{O})]^+$ (**4**) aqua complexes have been synthesized by reacting **1** and **2**, respectively, with silver tetrafluoroborate in aqueous solution or, alternatively, by the reaction of the triaqua complexes $[(\eta^5\text{-C}_5\text{Me}_5)\text{M}(\text{H}_2\text{O})_3]^{2+}$ ($\text{M} = \text{Rh}, \text{Ir}$) [6] with oxine in aqueous solution [7]. The cationic complexes **3** and **4** can be isolated as the tetrafluoroborate salts that form orange-red solids, well soluble in water, methanol, acetone and acetonitrile. Because of stability problems, satisfactory micro-analyses could not be obtained for (**3**) $[\text{BF}_4]$ and (**4**) $[\text{BF}_4]$. A single crystal X-ray structure analysis of (**3**) $[\text{BF}_4]$ confirmed the piano-stool geometry of **3** to be similar to that of **2** [8], however, due to low crystal quality, the structural data are not publishable.

The molecular structure of **2** was confirmed by X-ray crystallography. An ORTEP drawing [9] with the corresponding atom labeling scheme is shown in Fig. 1 together with selected bond lengths and

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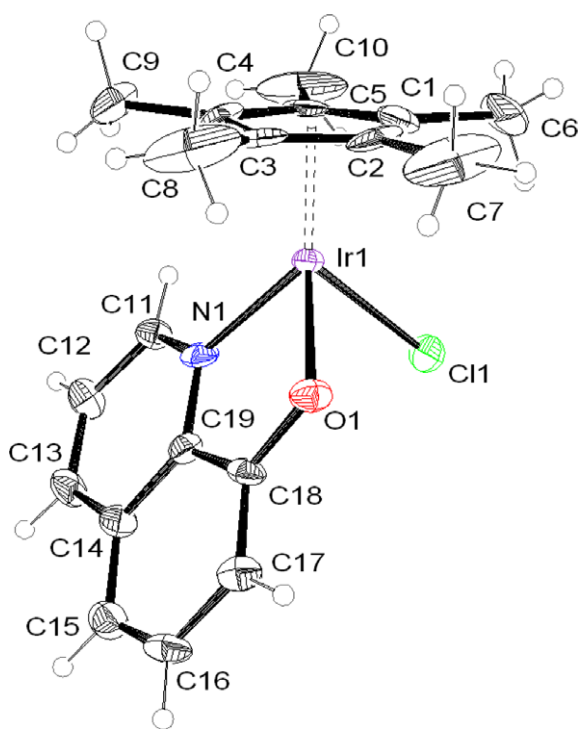


Fig. 1. Molecular structure of the complex **2** showing ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (°): Ir–Cl 2.386(2), Ir–N 2.088(7), Ir–O 2.091(6), O–C(18) 1.328(10), C(18)–C(19) 1.412(12), N–C(19) 1.353(11); Cl–Ir–N 85.2(2), Cl–Ir–O 84.6(2), O–Ir–N 77.8(3), O–C(18)–C(17) 123.9(9), O–C(18)–C(19) 118.1(8), N–C(19)–C(18) 115.6(8), O–C(18)–C(19)–N 3.0(13).

angles. Complex **2** shows a typical piano-stool geometry with the metal center being coordinated by the aromatic ligand, a terminal chloride and a chelating *N,O*-ligand, thus possessing metal-centered chirality. However, since none of the ligands contains chiral centers, complex **2** is obtained as a racemic mixture. The distance between the Ir atom and the center of the η^5 -C₅Me₅ ligand in **2** is 1.788(4) Å. The Ir–Cl, Ir–O and Ir–N distances are comparable to those reported in the related complexes containing a terminal chloride and a chelating *N,O*-ligand [(η^5 -C₅Me₅)Ir(η^2 -C₆H₅CH(Me)NCH₂C₆H₄O)Cl] [10,11] and [(η^5 -C₅Me₅)Ir(η^2 -NC₅H₄COO)Cl] [12].

Supplementary material

CCDC-726878 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]

Acknowledgements

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- [5] Synthesis of the chloro complexes [(η^5 -C₅Me₅)M(η^2 -NC₉H₆O)Cl]: To a solution of [(η^5 -C₅Me₅)MCl₂]₂ (0.082 mmol) in chloroform (8 mL), 2 equiv. of NC₉H₆OK [3] (0.163 mmol) was added, and the reaction mixture was stirred for 2 h at room temperature. Then the solution was evaporated under high vacuum. The orange solid was washed by diethyl ether (3 × 2 mL), isolated by decanting and evaporated to dryness. The product was purified by the thin-layer chromatography (dichloromethane: acetone 50:50) and dried *in vacuo*. [(η^5 -C₅Me₅)Rh(η^2 -NC₉H₆O)Cl] (**1**) yield: 68 % (47 mg). ¹H NMR (CD₂Cl₂): δ 1.70 (s, 15 H, C₅(CH₃)₅), 6.79 (d, *J* = 8 Hz, 1H, C₉H₆), 6.84 (d, *J* = 8 Hz, 1H, C₉H₆), 7.32 (t, *J* = 8 Hz, 1H, C₉H₆), 7.38 (m, 1H, C₉H₆), 8.09 (d, *J* = 8 Hz, 1H, C₉H₆), 8.54 (d, *J* = 4 Hz, 1H, C₉H₆). ¹³C {¹H} NMR (CD₂Cl₂): δ 5.51–8.56 (5 C, C₅(CH₃)₅), 93.08–93.16 (5 C, C₅(CH₃)₅), 109.36 (1 CH, C₉H₆), 114.11 (1 CH, C₉H₆), 122.02 (1 CH, C₉H₆), 130.30 (1 CH, C₉H₆), 130.72 (1 C, C₉H₆), 137.46 (1 CH, C₉H₆), 145.46 (1 C, C₉H₆), 146.07 (1 CH, C₉H₆), 167.99 (1 C, C₉H₆). MS (ESI) *m/z* = 382 [1–Cl]⁺. Anal. Cal. for C₁₉H₂₁ClNOIr: C, 54.63; H, 5.07; N, 3.35. Found: C, 54.91; H, 5.15; N, 3.26%. [(η^5 -C₅Me₅)Ir(η^2 -NC₉H₆O)Cl] (**2**) yield: 67 % (56 mg). ¹H NMR (400 MHz, CD₂Cl₂): δ 1.70 (s, 15 H, C₅(CH₃)₅), 6.79 (d, *J* = 8 Hz, 1H, C₉H₆), 6.83 (d, *J* = 8 Hz, 1H, C₉H₆), 7.34 (d, *J* = 8 Hz, 1H, C₉H₆), 7.35 (m, 1H, C₉H₆), 8.06 (d, *J* = 8 Hz, 1H, C₉H₆), 8.54 (d, *J* = 4 Hz, 1H, C₉H₆). ¹³C {¹H} NMR (CD₂Cl₂): δ 8.67 (5 C, C₅(CH₃)₅), 84.89–84.94 (5 C, C₅(CH₃)₅), 110.62 (1 CH, C₉H₆), 114.74 (1 CH, C₉H₆), 122.25 (1 CH, C₉H₆), 130.61 (1 CH, C₉H₆), 131.10 (1 C, C₉H₆), 137.72 (1 CH, C₉H₆), 146.17 (1 C, C₉H₆), 146.21 (1 CH, C₉H₆), 169.33 (1 C, C₉H₆). MS (ESI) *m/z* = 472 [2–Cl]⁺. Anal. Cal. for C₁₉H₂₁ClNOIr: C, 45.01; H, 4.17; N, 2.76. Found: C, 44.74; H, 4.22; N, 2.68%.
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- [7] Preparation of the aqua complexes [(η^5 -C₅Me₅)M(η^2 -NC₉H₆O)(H₂O)][BF₄]: (a) From the chloro complexes **1** and **2**: A mixture of [(η^5 -C₅Me₅)M(η^2 -NC₉H₆O)Cl] (0.163 mmol) (**1** or **2**) and two equivalents of silver sulfate (0.326 mmol) in deionised water (10 mL) was stirred at room temperature in the dark for 2 h. After this time, the resulting orange solution was filtered through celite. Then NaBF₄ saturated solution was added until the appearance of a yellow precipitate. The suspension was centrifuged, the solid was dissolved in 5 mL of acetonitrile, and the solution was filtered through celite. After evaporation of the solvent, the tetrafluoroborate salt was obtained as an orange-red powder. (b) From the triaqua complexes: A mixture of [(η^5 -C₅Me₅)MCl₂]₂ (0.082 mmol) and two equivalents of silver sulfate (0.163 mmol) in deionised water (10 mL) was stirred at room temperature in the dark for 2 h. After this time, the yellow solution was filtered from the AgCl precipitate and added to solid 8-hydroxyquinoline (0.163 mmol). The solution obtained was then stirred for 2 h in the dark at room temperature. During this period the solution turned orange to red. The product was precipitated by adding a saturated solution of NaBF₄. The suspension was centrifuged, the solid was dissolved in 5 mL of dry acetonitrile and filtered through celite. After evaporation of the solvent, the tetrafluoroborate salt was obtained as an orange-red powder. [(η^5 -C₅Me₅)Rh(η^2 -NC₉H₆O)(H₂O)][BF₄] (**3**)[BF₄] yield: 84% (67 mg) (a), 81% (65 mg) (b). ¹H NMR (D₂O): δ 1.68 (s, 15 H, C₅(CH₃)₅), 7.00 (d, *J* = 8 Hz, 1H, C₉H₆), 7.12 (d, *J* = 8 Hz, 1H, C₉H₆), 7.41 (t, *J* = 8 Hz, 1H, C₉H₆), 7.64 (dd, *J* = 4 Hz, 1H, C₉H₆), 8.38 (d, *J* = 8 Hz, 1H, C₉H₆), 9.01 (d, *J* = 4 Hz, 1H, C₉H₆). ¹³C {¹H} NMR (D₂O): δ 8.04 (5 C, C₅(CH₃)₅), 94.77–94.86 (5 C, C₅(CH₃)₅), 113.70 (1 CH, C₉H₆), 114.46 (1 CH, C₉H₆), 123.16 (1 CH, C₉H₆), 130.18 (1 CH, C₉H₆), 130.61 (1 C, C₉H₆), 139.40 (1 CH, C₉H₆), 143.52 (1 C, C₉H₆), 148.82 (1 CH, C₉H₆), 164.20 (1 C, C₉H₆). MS (ESI) *m/z* = 382 [3–H₂O]⁺. [(η^5 -C₅Me₅)Ir(η^2 -NC₉H₆O)(H₂O)][BF₄] (**4**)[BF₄] yield: 88% (83 mg) (a), 90% (85 mg) (b). ¹H NMR (D₂O): δ 1.67 (s, 15 H, C₅(CH₃)₅), 7.02 (d, *J* = 8 Hz, 1H, C₉H₆), 7.11 (d, *J* = 8 Hz, 1H, C₉H₆), 7.45 (t, *J* = 8 Hz, 1H, C₉H₆), 7.61 (dd, *J* = 4 Hz, 1H, C₉H₆), 8.38 (d, *J* = 8 Hz, 1H, C₉H₆), 8.98 (d, *J* = 4 Hz, 1H, C₉H₆). ¹³C {¹H} NMR (D₂O): δ 8.10 (5 C, C₅(CH₃)₅), 87.29 (5 C, C₅(CH₃)₅), 114.82 (1 CH, C₉H₆), 115.11 (1 CH, C₉H₆), 123.49 (1 CH, C₉H₆), 130.57 (1 CH, C₉H₆), 130.92 (1 C, C₉H₆), 139.79 (1 CH, C₉H₆), 144.17 (1 C, C₉H₆), 149.40 (1 CH, C₉H₆), 165.58 (1 C, C₉H₆). MS (ESI) *m/z* = 472 [4–H₂O]⁺.
- [8] Orange crystals of **2** (0.18 × 0.12 × 0.11 mm) suitable for X-ray diffraction analysis were grown from solution of **2** in dichloromethane. Crystal data for **2**: C₁₉H₂₁ClIrNO, orthorhombic space group *P* na21 (No. 33), cell parameters *a* = 15.285(3), *b* = 8.335(2), *c* = 13.626(3) Å, *V* = 1736.0(7) Å³, *T* = 173(2) K, *Z* = 4, *D_c* = 1.940 g cm⁻³, *F*(000) 976, λ (Mo Kα) = 0.71073 Å, 3078 reflections measured, 2428 unique (*R_{int}* = 0.0539) which were used in all calculations. The structure was solved by direct method (SHELXS-97) and refined (SHELXL-97) [13] by full-matrix least-squares methods on *F*² with 214 parameters. *R*₁ = 0.0266 (*I* > 2σ(*I*)) and *wR*₂ (all data) = 0.0513, GOF = 0.0869; max/min residual density 3.274/–1.089 eÅ⁻³ located at less than 1 Å from the iridium atom.
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