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Redox Chemistry of the Homoleptic Aryl Os(2-MeC₆H₄)₄: Synthesis and Characterization of the First Osmium(v) Organometallic [Os(2-MeC₆H₄)₄][CF₃SO₃]

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Oxidation of Os(2-MeC₆H₄)₄ in CH₂Cl₂ gives the remarkably stable osmium(v)tetra-aryl salts, [Os(2-MeC₆H₄)₄][Y], (Y = BF₄⁻, CF₃SO₃⁻); the triflate salt has been characterized by X-ray crystallography.

Osmium(v) compounds are rare, only a few halo-substituted derivatives being known;¹⁻³ no organometallic species have been reported before. Continuing studies of the chemistry of transition metal homoleptic aryls⁴ have now led to the high yield synthesis of the first organometallic compound of osmium(v).

Results of cyclic voltammetry studies on the homoleptic aryl Os(2-MeC₆H₄)₄⁵ in CH₂Cl₂ and tetrahydrofuran (thf) with cp₂Fe (cp = cyclopentadiene) as internal standard are shown in Figure 1. In CH₂Cl₂, there are two reversible one-electron waves at +0.33 V [Os(IV/V)] and -1.96 V [Os(V/III)]. These processes occur at slightly higher potentials (+0.41 and -1.89 V respectively) in thf; an additional reduction wave at -2.47

V in this solvent may be metal [Os(III/II)] or ligand based. Bulk electrolysis of maroon Os(2-MeC₆H₄)₄ at +0.7 V at a platinum gauze electrode with Bu₄NPF₆ supporting electrolyte gave dark purple solutions in either thf or CH₂Cl₂. Only the latter solution was stable, but in thf the maroon colour of the starting material quickly reappeared once the applied potential was removed. The success of preparative scale reactions is also solvent dependant: thus, in thf no reaction was observed between Os(2-MeC₆H₄)₄ and either AgBF₄ or AgCF₃SO₃. However, oxidation in CH₂Cl₂ immediately gave a deposit of metallic silver [equation (1)] and a dark purple solution from which crystals of the osmium(v) tetra-aryl salts were isolated in 70-95% yields after filtration,

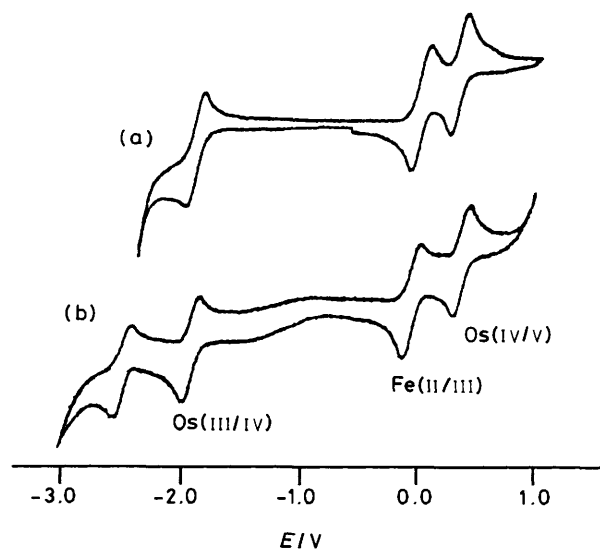


Figure 1. Cyclic voltammograms of Os(2-MeC₆H₄)₄ in (a) CH₂Cl₂, and (b) thf, with cp₂Fe as internal reference (0.00 V) and Bu₄NPF₆ as supporting electrolyte. Platinum wire working, silver pseudo-reference, and tungsten wire electrodes were employed at 20 °C with a scan rate of 50 mV s⁻¹.

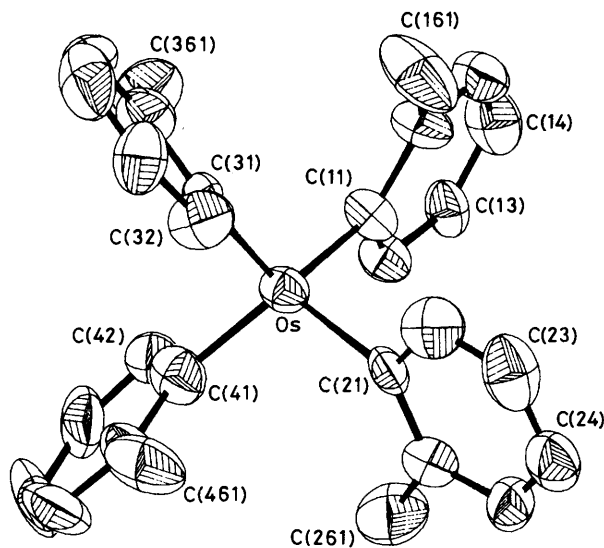
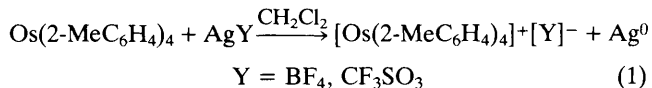


Figure 2. View of the cation in [Os(2-MeC₆H₄)₄][CF₃SO₃] with atom-labelling scheme. Selected distances and angles: Os-C(11) 1.99(4), Os-C(21) 1.99(4), Os-C(31) 1.99(4), Os-C(41) 2.00(4) Å; C(11)-Os-C(41) 114(2), C(21)-Os-C(31) 115(1), C(11)-Os-C(21) 101(2), C(31)-Os-C(41) 102(2), Os-C(n1)-C(n6) 120-124(3), Os-C(n1)-C(n2) 117-120(3)°.

addition of diethyl ether, and cooling.^{6†} Although they are air stable as solids or in CH₂Cl₂ or MeCN solutions for prolonged periods, the compounds are rapidly reduced to Os(2-MeC₆H₄)₄ on dissolution in thf. In the former solvents they behave as 1:1 electrolytes and have magnetic moments consistent with a single unpaired electron (*i.e.*, low spin Os^V, d³). The triflate salt has a single broad line at *ca.* *g* = 2 in the e.s.r. spectrum in frozen CH₂Cl₂ at 77 K.



A view of the structure of the [Os(2-MeC₆H₄)₄]⁺ cation, determined by X-ray crystallography,‡ is shown in Figure 2.

† Correct elemental analyses were obtained. [Os(2-MeC₆H₄)₄][BF₄]: m.p. 201–202 °C; yield 95%; μ_{eff} = 1.1(2) μ_B (Evans' method in MeCN, 22 °C); Λ_M = 120 ohm⁻¹ cm² mol⁻¹ (0.01 M in MeCN, 20 °C). [Os(2-MeC₆H₄)₄][CF₃SO₃]: m.p. 173–174 °C; yield 71%; μ_{eff} = 1.6(2) μ_B; Λ_M = 117 ohm⁻¹ cm² mol⁻¹.

‡ *Crystal data*: [C₂₈H₂₈Os]⁺[CF₃O₃S]⁻, *M* = 703.77, monoclinic, *a* = 27.175(2), *b* = 12.501(1), *c* = 8.208(1) Å, β = 98.96(9)°, *U* = 2754.4 Å³, space group *P*2₁/*n*, *Z* = 4, *D*_c = 1.70 g cm⁻³, μ(Mo-*K*α) = 45.42 cm⁻¹, *F*(000) = 1380. 5460 Reflections measured (-32 ≤ *l* ≤ 32, 0 ≤ *k* ≤ 14, 0 ≤ *h* ≤ 9, 1.5 ≤ θ ≤ 25°; CAD4 diffractometer Mo-*K*α radiation, λ = 0.71069 Å), 4833 unique, 3085 observed [*I* > 3σ(*I*)]. Structure solved *via* heavy atom method, full matrix least squares, non-hydrogens anisotropic, hydrogens in idealised positions, riding model; 318 parameters, weights ω = σ²(*F*_o) + 0.04 *F*_o²)⁻¹, *R* = 0.043, *R*_w = 0.049.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

The cation has approximate 4 symmetry. The C–Os–C angles are very similar to those in Os(2-MeC₆H₄)₄,⁵ while the Os–C distances are also very similar to those in both Os(2-MeC₆H₄)₄ and in O(C₆H₅)₄;⁵ these results show quite strikingly that the one electron change has little effect on the geometry.

Present results show that [Os(2-MeC₆H₄)₄]⁺ is a strong oxidant; treatment of the BF₄⁻ salt with NaBPh₄, PMe₂Ph, or TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy radical) in CH₂Cl₂, or MeLi in Et₂O, results in immediate reduction to Os(2-MeC₆H₄)₄. Further studies on related homoleptic aryls are now in progress.

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