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Redox Chemistry of the Homoleptic Aryl $Os(2\text{-}MeC_6H_4)_4$: Synthesis and Characterization of the First Osmium(V) Organometallic $[Os(2\text{-}MeC_6H_4)_4][CF_3SO_3]$

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Oxidation of $Os(2\text{-}MeC_6H_4)_4$ in CH_2Cl_2 gives the remarkably stable osmium(V)tetra-aryl salts, $[Os(2\text{-}MeC_6H_4)_4][Y]$, ($Y = BF_4^-$, $CF_3SO_3^-$); 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 aryls[4] 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 $Os(2\text{-}MeC_6H_4)_4$[5] in CH_2Cl_2 and tetrahydrofuran (thf) with cp_2Fe (cp = cyclopentadiene) as internal standard are shown in Figure 1. In CH_2Cl_2, there are two reversible one-electron waves at +0.33 V [Os(IV/V)] and −1.96 V [Os(IV/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 $Os(2\text{-}MeC_6H_4)_4$ at +0.7 V at a platinum gauze electrode with $Bu^n{}_4NPF_6$ supporting electrolyte gave dark purple solutions in either thf or CH_2Cl_2. 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 $Os(2\text{-}MeC_6H_4)_4$ and either $AgBF_4$ or $AgCF_3SO_3$. However, oxidation in CH_2Cl_2 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,

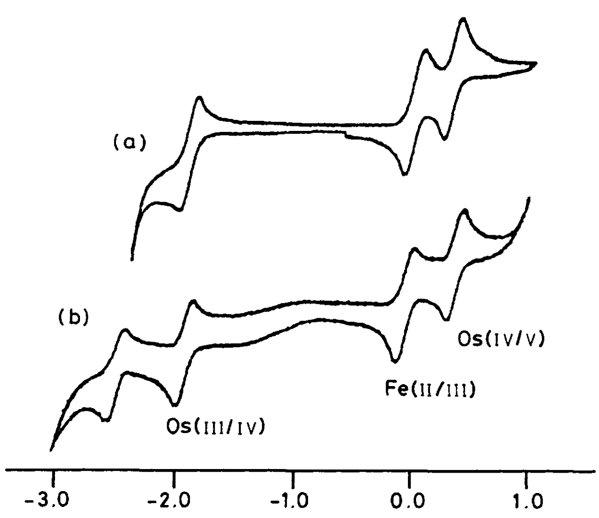

Figure 1. Cyclic voltammograms of $Os(2\text{-}MeC_6H_4)_4$ in (a) CH_2Cl_2, and (b) thf, with cp_2Fe as internal reference (0.00 V) and $Bu^n{}_4NPF_6$ as supporting electrolyte. Platinum wire working, silver pseudo-reference, and tungsten wire electrodes were employed at 20 °C with a scan rate of 50 mV s^{-1}.

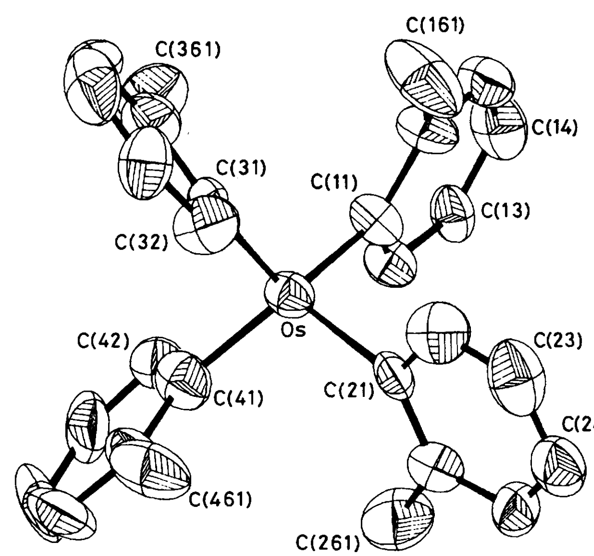

Figure 2. View of the cation in $[Os(2\text{-}MeC_6H_4)_4][CF_3SO_3]$ with atom-labelling scheme. Selected distances and angles: Os–C(11) 1.99(4), Os–C(21) 1.99(4), Os–C(31) 1.99(4), Os–C(41) 2,00(4) Å; C(11)–Os–C(41) 114(2), C(21)–Os–C(31) 115(1), C(11)–Os–C(21) 101(2), C(31)–Os–C(41) 102(2), Os–C(*n*1)–C(*n*6) 120—124(3), Os–C(*n*1)–C(*n*2) 117—120(3)°.

addition of diethyl ether, and cooling.[6]† Although they are air stable as solids or in CH_2Cl_2 or MeCN solutions for prolonged periods, the compounds are rapidly reduced to Os(2-$MeC_6H_4)_4$ 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, d^3). The triflate salt has a single broad line at *ca.* $g = 2$ in the e.s.r. spectrum in frozen CH_2Cl_2 at 77 K.

$$\mathrm{Os(2\text{-}MeC_6H_4)_4 + AgY \xrightarrow{CH_2Cl_2} [Os(2\text{-}MeC_6H_4)_4]^+[Y]^- + Ag^0}$$
$$\mathrm{Y = BF_4,\ CF_3SO_3} \qquad (1)$$

A view of the structure of the $[Os(2\text{-}MeC_6H_4)_4]$ cation, determined by *X*-ray crystallography,‡ is shown in Figure 2. The cation has approximate 4 symmetry. The C–Os–C angles are very similar to those in $Os(2\text{-}MeC_6H_4)_4$,[5] while the Os–C distances are also very similar to those in both $Os(2\text{-}MeC_6H_4)_4$ and in $O(C_6H_5)_4$;[5] these results show quite strikingly that the one electron change has little effect on the geometry.

Present results show that $[Os(2\text{-}MeC_6H_4)_4]^+$ is a strong oxidant; treatment of the BF_4^- salt with $NaBPh_4$, PMe_2Ph, or TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy radical) in CH_2Cl_2, or MeLi in Et_2O, results in immediate reduction to $Os(2\text{-}MeC_6H_4)_4$. Further studies on related homoleptic aryls are now in progress.

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† Correct elemental analyses were obtained. $[Os(2\text{-}MeC_6H_4)_4][BF_4]$: m.p. 201—202 °C; yield 95%; $\mu_{eff} = 1.1(2)\ \mu_B$ (Evans' method in MeCN, 22 °C); $\Lambda_M = 120\ ohm^{-1}\ cm^2\ mol^{-1}$ (0.01 M in MeCN, 20 °C). $[Os(2\text{-}MeC_6H_4)_4][CF_3SO_3]$: m.p. 173—174 °C; yield 71%; $\mu_{eff} = 1.6(2)\ \mu_B$; $\Lambda_M = 117\ ohm^{-1}\ cm^2\ mol^{-1}$.

‡ *Crystal data*: $[C_{28}H_{28}Os]^+[CF_3O_3S]^-$, $M = 703.77$, monoclinic, $a = 27.175(2)$, $b = 12.501(1)$, $c = 8.208(1)$ Å, $\beta = 98.96(9)°$, $U = 2754.4$ Å^3, space group $P2_1/n$, $Z = 4$, $D_c = 1.70$ g cm^{-3}, μ(Mo-K_α) = 45.42 cm^{-1}, $F(000) = 1380$. 5460 Reflections measured ($-32 \leqslant l \leqslant 32, 0 \leqslant k \leqslant 14, 0 \leqslant l \leqslant 9, 1.5 \leqslant \theta \leqslant 25°$; CAD4 diffractometer Mo-K_α radiation, $\lambda = 0.71069$ A), 4833 unique, 3085 observed [$I > 3\sigma(I)$]. Structure solved *via* heavy atom method, full matrix least squares, non-hydrogens anisotropic, hydrogens in idealised positions, riding model; 318 parameters, weights $\omega = \sigma^2(F_o) + 0.04\ F_o{}^2]^{-1}$, $R = 0.043$, $R_w = 0.049$.

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.

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