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Direct functionalisation of σ-aryl ligands: preparation of homoleptic functionalised aryls of osmium(IV)†

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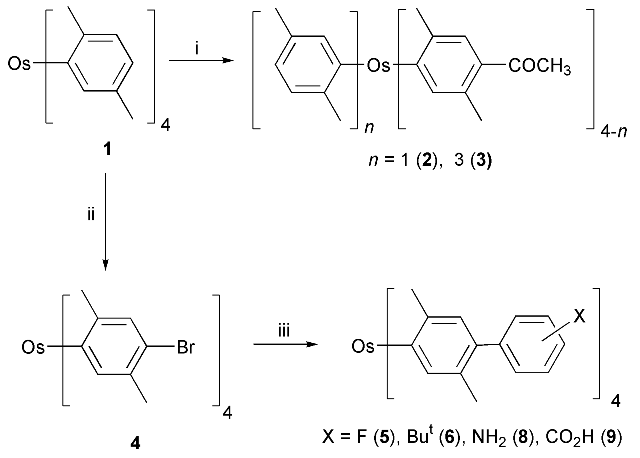
The osmium(IV) tetraaryl complex $[Os(C_8H_9)_4]$ (C_8H_9 = 2,5-dimethylphenyl) reacts with pyridinium tribromide in the presence of Fe powder to give $[Os(C_8H_8Br)_4]$, which undergoes Suzuki coupling with arylboronic acids to afford a series of homoleptic functionalised aryls of osmium(IV).

Transition metal complexes of σ-aryl ligands bearing reactive functional groups are of interest because they may serve as structure building units for organometallic polymers that exhibit interesting electrical, magnetic or catalytic properties.[1] There are, however, relatively few reports on chemical functionalisation of σ-aryl ligands. Functionalised arylmetal complexes have been previously prepared by using mercury transmetallation reagents[2] or oxidative addition of aryl halides to low-valent metal centres.[3] Recently Roper and Wright and their coworkers reported the direct functionalisation of aryl[4] and 2-(2′-pyridyl)phenyl[5] groups σ-bound to ruthenium and osmium, demonstrating that these metal aryls are sufficiently inert to undergo a wide range of transformations. This prompted us to investigate the functionalisation of homoleptic aryls of osmium(IV), which are known to be remarkably stable.[6] The use of homoleptic functionalised aryls of osmium as metalloligands is of interest because of their tetrahedrally directing property, and the fact that they can be readily oxidised to paramagnetic Os^V species.[7] We here report on the acylation and bromination of an osmium tetraaryl, and the Suzuki cross-coupling reactions of the resulting osmium bromoaryl complex.

The osmium tetraaryl complex $[Os(C_8H_9)_4]$ **1** (C_8H_9 = 2,5-dimethylphenyl) was synthesised by alkylation of $[OsO_4]$ with C_8H_9MgBr in diethyl ether, as described elsewhere.[6,8] Scheme 1 summarises the reactions that lead to functionalisation of the aryl groups in **1**.

As reported previously, the electron-rich σ-aryl groups in osmium tetraaryls are prone to electrophilic attack, *e.g.* Friedel–Crafts acylation.[9] Thus, treatment of **1** with MeCOCl in the presence of Al_2Cl_6 afforded a mixture of $[Os(C_8H_8COMe)_3(C_8H_9)]$ **2** and $[Os(C_8H_8COMe)(C_8H_9)_3]$ **3** in 40 and 30% yield, respectively. The solid-state structure of complex **2** is shown in Fig. 1.‡ The geometry around Os in **2** is approximately tetrahedral (average C–Os–C′ angle of 109.5°) and the average Os–C distance is 1.99(1) Å. The MeCO group in each aryl ligand is situated at the *para* position relative to Os, indicative of the *para*-directing property of the Os centre. Bromination of **1** by pyridinium tribromide in the presence of Fe powder afforded the tetrabromide compound $[Os(C_8H_8Br)_4]$ **4** in 52% yield. Fig. 2 shows the molecular structure of **4**.‡ The geometry around Os in **4** is approximately tetrahedral [average C–Os–C′ angle of 109.5°] and the average Os–C distance of 2.00(2) Å. Complex **4** in CH_2Cl_2 exhibits a reversible Os^V–Os^{IV} couple at 0.45 V *vs*.. the ferrocenium–ferrocene couple, which is about 0.21 V more anodic than that for complex **1**[7] due to the inductive effect of the bromo substitutents.

The tetrabromide **4** has proved to be a good starting material for metal-catalysed cross-coupling reactions. For example, complex **4** underwent Suzuki coupling with $4\text{-}XC_6H_4B(OH)_2$ in



Scheme 1 *Reagents and conditions*: i, MeCOCl, Al_2Cl_6, CH_2Cl_2, −40 °C; ii, pyridinium tribromide, Fe powder, CH_2Cl_2, room temp; iii, 6 equivalents of arylboronic acids, $[Pd(PPh_3)_4]$, K_2CO_3, dmf, 110 °C.

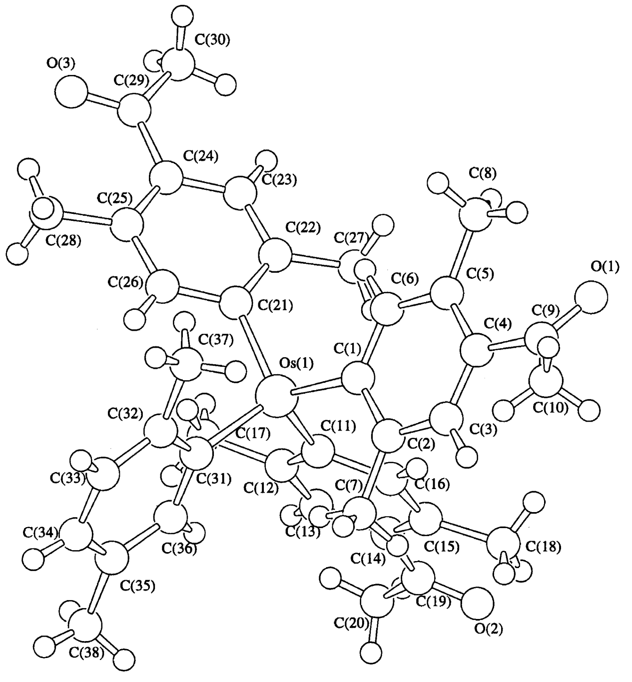


Fig. 1 Molecular structure of $[Os(C_8H_8COMe)_3(C_8H_9)]$ **2**. Selected bond lengths (Å) and angles (°): Os(1)–C(1) 2.011(9), Os–C(11) 1.975(9), Os(1)–C(21) 1.991(8), Os(1)–C(31) 1.985(10); C(1)–Os(1)–C(11) 107.9(3), C(1)–Os(1)–C(21) 111.7(3), C(1)–Os(1)–C(31) 110.7(4), C(11)–Os(1)–C(21) 108.0(4), C(11)–Os(1)–C(31) 110.0(4), C(21)–Os(1)–C(31) 108.5(4).

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† Electronic supplementary information (ESI) available: preparations of osmium tetraaryl complexes. See http://www.rsc.org/suppdata/cc/b1/b104075h/

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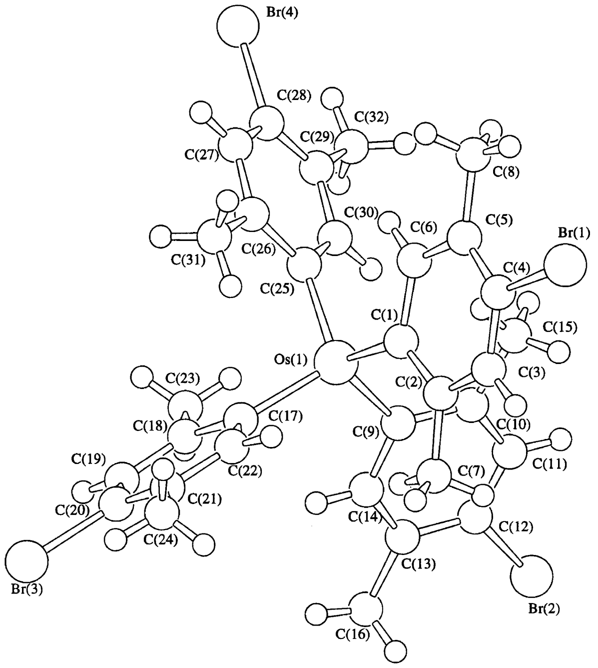

Fig. 2 Molecular structure of $[Os(C_8H_8Br)_4]$ **4**. Selected bond lengths (Å) and angles (°): Os(1)–C(1) 1.98(2), Os(1)–C(9) 2.01(2), Os(1)–C(17) 2.03(2), Os(1)–C(25) 1.98(1); C(1)–Os(1)–C(9) 107.3(6), C(1)–Os(1)–C(17) 111.6(6), C(1)–Os(1)–C(25) 109.5(6), C(9)–Os(1)–C(17) 110.8(6), C(9)–Os–C(25) 110.3(6), C(17)–Os(1)–C(25) 107.4(6).

the presence of $[Pd(PPh_3)_4]$ and K_2CO_3 to afford the respective homoleptic osmium biaryl $[Os(C_8H_8–C_6H_4X)_4]$ (X = F **5**, Bu^t **6**).§ Complexes **5** and **6** are highly soluble, lipophilic materials, which could be obtained as analytically pure dark solids after chromatography and recrystallisation. Oxidation of **5** with $AgBF_4$ gave a blue species, presumably $[Os(C_8H_8–C_6H_4F)_4]^+$, which exhibits an isotropic EPR signal at 77 K at $g = 2.025$ characteristic of Os^V species.[7] It appears that the Pd-catalysed cross coupling reaction involved oxidative addition of the aryl bromide ligand with Pd(0) followed by reductive elimination of the biaryl. The stoichiometric reaction between **4** and $[Pd(PPh_3)_4]$ afforded a blue solid analysed as $[Os(C_8H_8Br)_3\{C_8H_8PdBr(PPh_3)_2\}]$ **7**. Similarly, Pd-catalysed coupling of **4** with $3\text{-}H_2NC_6H_4B(OH)_2$ and $4\text{-}HO_2CC_6H_4B(OH)_2$ afforded the tetraamine $[Os(C_8H_8–C_6H_4NH_2)_4]$ **8**, which seems to contain a very small amount of unknown impurity since the N analysis is not satisfactory at the moment, and the tetracarboxylic acid $[Os(C_8H_8–C_6H_4CO_2H)_4]$ **9**, respectively. Complex **9** is soluble both in organic solvents and in aqueous medium (pH $\geqslant$ 10), indicative of the inertness of the Os–C σ bonds. The homoleptic functionalised aryls of osmium can be used as starting materials for preparations of organometallic oligomers/polymers. For example, cyclic voltammetry indicated that complex **8** could be polymerised on a graphite electrode by anodic oxidation. A preliminary result showed that homo-coupling of the tetrabromide **4** by $[Ni(cod)_2]$ (cod = cycloocta-1,5-diene) yielded oligomers of **1**.[10]

In summary, we have demonstrated that the aryl groups in osmium tetraaryl complex **1** could be functionalised by electrophilic attack, *e.g.* acylation and bromination, without cleavage of the Os–C σ bonds. Suzuki coupling of the osmium bromoaryl complex with arylboronic acids provides convenient access to a wide range of homoleptic functionalized aryls of osmium, which can be used as starting materials for organoosmium oligomers/polymers.

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Notes and references

‡ *Crystal data*: for **2**: $C_{38}H_{42}O_3Os\cdot\frac{1}{2}C_6H_{12}$, $M = 779.03$, triclinic, space group $P\bar{1}$ (no. 2), $a = 12.424(2)$, $b = 17.168(3)$, $c = 9.184(2)$ Å, $\alpha = 91.71(2)$, $\beta = 106.76(1)$, $\gamma = 95.82(2)°$, $U = 1862.3(6)$ Å^3, $T = 298$ K, $Z = 2$, $D_c = 1.389$ g cm^{-3}, μ(Mo-Kα) = 3.456 mm^{-1}. 5289 reflections measured, 5016 unique ($R_{int} = 0.033$). The final R and $R_w(F)$ were 0.042 and 0.044, respectively, on 3843 reflections with $I > 1.5\sigma(I)$.

For **4**: $C_{32}H_{32}Br_4Os$, $M = 926.42$, monoclinic, space group $C2/c$ (no. 15), $a = 37.556(8)$, $b = 9.256(6)$, $c = 18.856(7)$ Å, $\beta = 97.13(3)°$, $U = 6503(4)$ Å^3, $T = 298$ K, $Z = 8$, $D_c = 1.892$ g cm^{-3}, μ(Mo-Kα) = 8.867 mm^{-1}. 6205 reflections measured, 6101 unique ($R_{int} = 0.071$). The final R and $R_w(F)$ were 0.067 and 0.051, respectively, on 3117 reflections with $I > 1.5\sigma(I)$. Empirical absorption corrections (on ψ-scans) were applied for **2** and **4**.

CCDC reference numbers 164948 and 164949. See http://www.rsc.org/suppdata/cc/b1/b104075h/ for crystallographic data in CIF or other electronic format.

§ *Typical procedure* for Suzuki coupling of **4** with arylboronic acids: to a solution of **4** (100 mg, 0.1 mmol) in *N,N*-dimethylformamide (20 cm^3) were added 6 equivalents of arylboronic acid, K_2CO_3 (83 mg, 0.6 mmol) and $[Pd(PPh_3)_4]$ (12 mg). The reaction mixture was heated at 110 °C for 2 h, evaporated to dryness *in vacuo*, and extracted with CH_2Cl_2. The products were purified by column chromatography [silica gel, eluent: CH_2Cl_2–hexane (1 : 5)] and further recrystallised from hexane (yield: 40–60%).

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