An improved route to osmium(IV) tetraaryl complexes

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Abstract

Air-stable, redox-active osmium(IV) tetraaryl complexes can be prepared in yields ≤76% from the novel precursor $(Oct_4N)_2[OsBr_6]$, facilitating the synthesis of $Os(mesityl)_4$ for the first time. This complex exhibits a distorted tetrahedral geometry and three reversible redox events including a 1+/2+ feature not previously observed in this family of materials.

Homoleptic transition metal(IV) tetraaryl complexes, M(aryl)$_4$, are an underexplored class of organometallic materials with distinct electrochemical, magnetic, and optical properties resulting from their tetrahedral coordination geometry.[1] Os(IV)[2–4] and Ru(IV)[3–5] compounds with ortho-methylated σ-aryl ligands are particularly robust (consistent with a stable d^4 low-spin electronic configuration), where the methyl groups provide steric protection from decomposition pathways such as reductive elimination and *ortho*-hydrogen abstraction.[3] They can be purified using chromatography in air, and their aryl ligands can be chemically functionalized via different methods (including bromination,[6] Suzuki coupling,[6] and Friedel-Crafts acylation[7]). The osmium compounds have a particularly rich redox chemistry which facilitated the early isolation of a stable paramagnetic Os(V) complex.[8] However, Os(aryl)$_4$ complexes are often obtained in poor yields (typically ≤34%, see **SI, Table S2**) from reactions of aryl Grignard reagents with OsO_4 (aryl = 2-tolyl, 2,5-xylyl, 2,4-xylyl, 4-fluoro-2-tolyl, and phenyl). Given the high toxicity of OsO_4, and additional purification complications caused by the presence of monooxo(tetraaryl)osmium(VI)[9] and bisoxo(diaryl)osmium(VI)[9,10] side products (**Figure 1**, top), the development of new, high-yielding preparative approaches using alternative starting reagents is desirable.

In this work we report an improved synthetic route to osmium(IV) tetraaryl complexes starting from novel tetra-*n*-octylammonium hexahaloosmate(IV) precursors ($(Oct_4N)_2[OsX_6]$; X = Cl, Br; **Figure 1**, bottom); our approach can also be used to prepare ruthenium homologues from tetra-*n*-octylammonium hexachlororuthenate(IV). Reactions of the appropriate aryl Grignard reagent with $(Oct_4N)_2[OsBr_6]$ provide Os(2-tolyl)$_4$ (**Os1**) and Os(2,5-xylyl)$_4$ (**Os2**) in the highest yields reported for any M(aryl)$_4$ compound prepared to date (≥75%). Analogous reactions using mesitylmagnesium bromide provide Os(mesityl)$_4$ (**Os3**) in ≤21%, a previously inaccessible complex comprising sterically demanding and electron rich 2,6-dimethyl substituted aryl ligands. We unambiguously determine the structure of **Os2** and **Os3** via single-crystal X-ray diffraction (**Figure 2**) and explore the redox properties of **Os1-3** using solution electrochemistry (**Figure 3**).

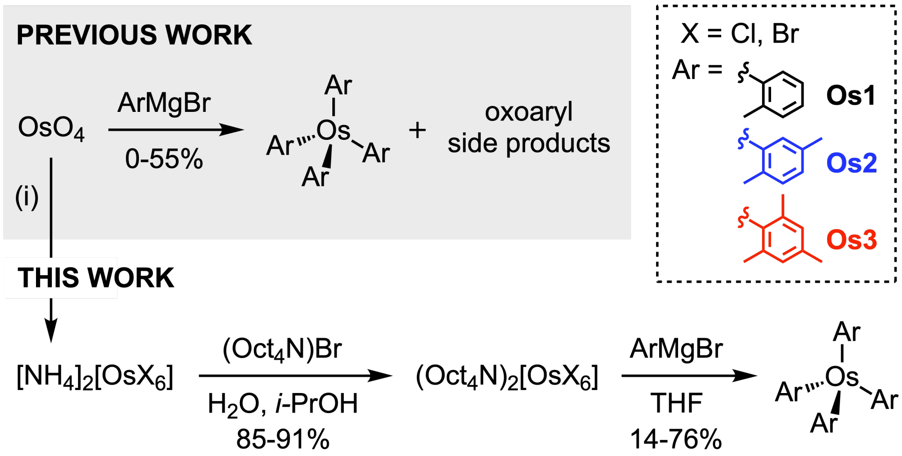

Figure 1. Synthetic routes to Os(aryl)$_4$ complexes from reactions of aryl Grignard reagents with OsO_4 (previous work, top) or $(Oct_4N)_2[OsX_6]$ (this work, bottom). Conditions: (i) HX, NH_4X (X = Cl, Br), ethanol (and $FeCl_2$ for X = Cl).[11,12] Use of $(Oct_4N)_2[OsX_6]$ avoids the formation of osmium(VI) oxoaryl side products, provides higher yields of Os(aryl)$_4$, and facilitates the formation of Os(mesityl)$_4$ (**Os3**) for the first time.

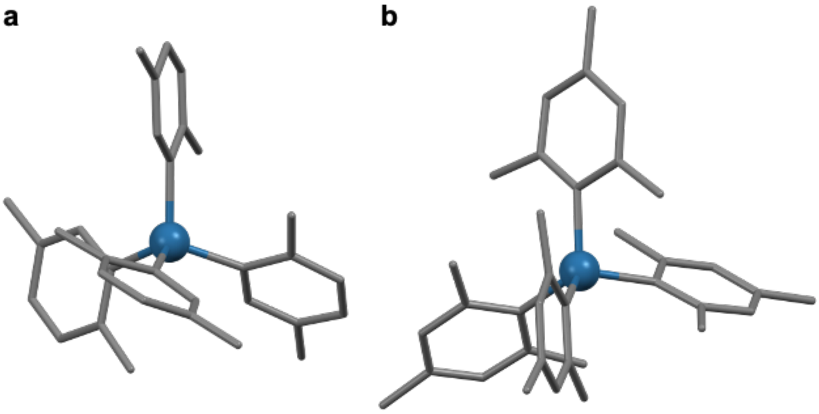

Figure 2. X-ray crystal structures of **(a) Os2** and **(b) Os3**. Hydrogen atoms are omitted for clarity (Os = teal, C = grey). Selected structural parameters are provided in **Table 1** and in the **SI, Table S7**, **S8**, and **S13**.

In developing this method, we considered approaches that might reduce or eliminate the formation of osmium(VI) oxoaryl side products. These are reported to originate from the incomplete substitution of OsO_4 rather than through air oxidation in solution or during chromatographic purification.[9] We reasoned that oxoaryl side products could be avoided simply by using alternative oxygen-free osmium precursors, and looked for inspiration from the materials used to prepare analogous ruthenium(IV) tetraaryl complexes. These include $(Et_4N)[RuCl_5(THF)]$,[4] $(Et_4N)[RuCl_5(MeCN)]$,[4] $Ru_2(\mu\text{-}O_2CMe)_4$,[4] $RuCl_3(tht)_3$,[5] and $Ru(acac)_3$[13,14] (tht = tetrahydrothiophene, acac = acetylacetonate). Unfortunately, yields of the Ru(aryl)$_4$

products are also low, and methods involving some of these precursors are reportedly difficult to reproduce (**SI, Table S1**).[4,5] Given that the use of multinuclear, Ru(II), or Ru(III) species also have the potential to increase the complexity of reactions,[4] and noting that the mononuclear pentachlororuthenate salts have not been utilized since the first synthetic reports of Ru(aryl)$_4$ species, we sought alternative easily accessible M(IV) compounds. Remarkably, several members of the family of $(NH_4)_2[MX_6]$ salts (M = Os, Ru; X = Cl, Br) are commercially available or readily synthesized using verified protocols,[11,12] but have not yet been explored as precursors to M(aryl)$_4$ compounds.

Our initial attempts to prepare Ru(2-tolyl)$_4$ (**Ru1**) by the addition of 6-8 equivalents of 2-tolylmagnesium bromide to $(NH_4)_2[RuCl_6]$ proved unsuccessful due to the low solubility of the metal salt in THF and diethyl ether (coordinating solvents commonly used for Grignard reactions). However, following cation exchange to increase solubility of the anion in common organic solvents, the analogous reaction using $(Oct_4N)_2[RuCl_6]$[15] provided **Ru1** in 35% yield (**SI, Figure S1**). This yield is comparable to those from previously reported routes (**SI, Table S1**). We readily adapted this cation exchange protocol to prepare the novel Os(IV) starting materials $(Oct_4N)_2[OsCl_6]$ and $(Oct_4N)_2[OsBr_6]$ in 85% and 91% yield, respectively (**Figure 1**, bottom). **Os1** (X = Cl, 30%; X = Br, 75%) and **Os2** (X = Cl, 44%; X = Br, 76%) could be isolated in high yields following reactions between these salts and the appropriate arylmagnesium bromide (see **SI, Table S2** for a summary of previous work). Further demonstrating the advantage of this approach, reaction of mesitylmagnesium bromide with $(Oct_4N)_2[OsX_6]$ provided the novel **Os3** complex as a green-black solid (X = Cl, 14%; X = Br, 21%). Previous attempts by others to prepare Os(aryl)$_4$ complexes with bulky 2,6-disubstituted aryl ligands from OsO_4, such as **Os3** or Os(2,6-xylyl)$_4$, resulted only in the formation of OsO_2(aryl)$_2$ complexes.[3,10,16] **Os1-3** and **Ru1** were worked up in air and purified by chromatography without any signs of decomposition.

The solid-state structures of **Os2** and **Os3** were determined by single-crystal X-ray diffraction and compared to analogous tetrahedral compounds (**Figure 2**, **Table 1** and **SI, Tables S7-S20**). While M-C bond lengths (**Os2** = 2.008(4) Å, **Os3** = 2.037(3) Å) appear to increase for Os(IV) compounds as the aryl ligands become more electron-donating (phenyl < 2-tolyl < 2,5-xylyl < cyclohexyl < mesityl; **Table 1**), the same trend is not observed for the Ru(IV) analogues. The range of angles between aryl planes does not appear to correlate with the number of ortho-substituents or the electronic character of the aryl ligand (**Table 1** and **SI, Table S7;** see **SI, Figure S2** for structural parameter definitions). However, we note that **Os2** has the largest difference between minimum and maximum aryl plane angles for all compounds surveyed here (36.77°; **Table 1**).

Table 1. Selected average and calculated structural parameters for different compounds.

compound	M-C (Å) [a]	aryl plane range (°) [b]	*T*-value [c]	identifier [d]	reference
Os(mesityl)$_4$ (**Os3**)	2.037(3)	18.96	8.02	2024176	this work
Os(cyclohexyl)$_4$	2.029	-	5.18	1135690	[3]
Os(2-tolyl)$_4$ (**Os1**)	1.997	7.51	4.38	1135692	[3]
Os(4-Br-2,5-xylyl)$_4$	2.000(2)	24.87	1.60	164949	[6]
Os(phenyl)$_4$	1.995	24.40	1.32	1153940	[3]
Os(2,5-xylyl)$_4$ (**Os2**)	2.008(4)	36.77	1.11	2024175	this work
Ru(mesityl)$_4$ (**Ru3**)	2.01(1)	17.22	7.42	1191069	[5]
Ru(cyclohexyl)$_4$	2.019	-	4.02	1153943	[3]
Ru(2-tolyl)$_4$ (**Ru1**)	1.995	12.53	3.53	1161553	[4]
Ru(4-MeO-2-tolyl)$_4$	1.986	26.19	2.45	1032104	[13]
Ru(4-Br-2,5-xylyl)$_4$	1.984	24.97	2.17	1032108	[13]
Ru(2,4,5-trimethylphenyl)$_4$	1.985(10)	20.99	0.86	1510576	[14]
C(phenyl)$_4$	1.551	5.98	1.95	191149	[17]

[a] Average bond length, provided with pooled estimated standard deviations (ESDs) in parentheses for all structures with associated ESDs. M = Os, Ru, C. [b] Difference between minimum and maximum aryl plane angles. [c] *T*-value (tetrahedricity) = a measure of the mean absolute deviation of a set of C–M–C angles from their ideal tetrahedral values (109.5°). *T*-value = 0 indicates no deviation. Calculated using **Equation S1**. [d] CCDC Deposition Number.

To simplify comparisons of C-M-C angles we employ a “tetrahedricity”-value (*T*-value), the root-mean-square deviation of a set of C–M–C angles from their ideal tetrahedral values (109.5°). This is calculated for **Os1-3**, **Ru1**, and related compounds using **Equation S1**, where a *T*-value = 0 indicates no deviation. An analogous “octahedricity” metric has been utilized in the structural characterization of metal polypyridyl complexes,[18–20] and related analyses have been performed for coordination environments in solid-state materials.[21,22] We observe that *T*-values decrease in the order **M3** > M(cyclohexyl)$_4$ > **M1** for both series of Os and Ru compounds (**Table 1**), suggesting that a greater tetrahedral distortion is required to accommodate aryl ligands of increased steric bulk. This analysis supports the view that steric constraints due to 2,6-dimethyl substituents contribute to the lower synthetic yields of **Os3** compared to **Os2** and **Os1** (**SI, Table S2**), given that the four mesityl groups of **Os3** are arranged in a particularly distorted tetrahedral geometry (*T*-value = 8.02, C-Os-C angles between 98.4-117.2°). In contrast, complexes with 2,5-xylyl ligands adopt a more ideal tetrahedral structure compared to **M1** and materials with simple phenyl substituents (**Table 1**). For example, **Os2** (*T*-value = 1.11, C-Os-C angles between 108.6-110.9°) is more tetrahedral than **Os1** (*T*-value = 4.38), Os(phenyl)$_4$ (*T*-value = 1.32), or C(phenyl)$_4$ (*T*-value = 1.95). In the **SI, Figure S3**, we present space-filling models that show the 2,6-dimethyl substituents of **Os3** provide additional steric shielding around the Os center compared with **Os1** and **Os2**. We hypothesize that 2,6-substituted aryl ligands may impart an increased chemical or electrochemical stability to such complexes, which have been shown to undergo rapid reactions with different Lewis bases.[23]

We studied the redox properties of **Os1-3** using cyclic voltammetry in CH_2Cl_2 with 0.1 M NBu_4PF_6 as the supporting electrolyte. The results are summarized in **Table 2** and **Table S21**, with representative overlaid cyclic voltammograms shown in **Figure 3**. Voltammograms for **Os3** at different scan rates are shown in **SI, Figure S4**. **Os1-3** exhibit two reversible, one-electron transfers ($i_{pa}/i_{pc} \approx 1$, $i_p \propto V_s^{1/2}$), in broad agreement with previous reports.[8,9] These 0/1+ and 1−/0 events have previously been assigned to the Os^{4+}/Os^{5+} and Os^{3+}/Os^{4+} redox couples, respectively. We observe an additional 1+/2+ oxidation event for **Os3** at +1.117 V which may be metal Os^{5+}/Os^{6+} or ligand-based. Using the equilibrium potentials for the 0/1+ feature of **Os1-3**, we find that Os(aryl)$_4$ complexes are approximately ~22 mV easier to oxidize for every methyl substituent added. This is compared to ~50 mV/methyl group for ferrocene analogues.[24] Using these values, we estimate the 0/1+ equilibrium potential of Os(2,3,4,5,6-pentamethylphenyl)$_4$ (**Os5**) to be around −0.02 mV vs. $[Cp_2Fe]^+/[Cp_2Fe]$, with a total range of ~350 mV between the mono-substituted and permethylated complexes (4-20 methyl substituents). This compares to ~500 mV between ferrocene and decamethylferrocene (0-10 methyl substituents).

Table 2. Selected electrochemical data for Os(aryl)$_4$ complexes.[a]

entry	compound	solvent	$E_{1/2}$ (V)				reference
			2−/1−	1−/0	0/1+	1+/2+	
1 [b]	Os(2-tolyl)$_4$ (**Os1**)	THF	−2.47	−1.89	+0.41	-	[8]
2 [b]		CH_2Cl_2	-	−1.96	+0.33	-	[8]
3		CH_2Cl_2	-	−1.961	+0.326	-	this work
4 [c]	Os(2,5-xylyl)$_4$ (**Os2**)	CH_2Cl_2	-	−1.48 [d]	+0.24	-	[9]
5		CH_2Cl_2	-	−2.008	+0.244	-	this work
6	Os(mesityl)$_4$ (**Os3**)	CH_2Cl_2	-	−2.028	+0.153	+1.117	this work

[a] Scan rate = 0.1 V s^{-1}; NBu_4PF_6 supporting electrolyte; working electrode: glassy carbon; reference electrode, counter electrode: Pt. Potentials measured with internal Cp^*_2Fe (−0.532 V vs $[Cp_2Fe]^+/[Cp_2Fe]$),[24] reported relative to $[Cp_2Fe]^+/[Cp_2Fe]$. See **SI, Table S22** for additional electrochemical data. [b] Scan rate = 0.05 V s^{-1}; working electrode: Pt; reference electrode: Ag; counter electrode: W. Potentials measured with internal Cp_2Fe. [c] Reference electrode: $Ag/AgNO_3$ (0.1 M in acetonitrile). Potentials measured with internal Cp_2Fe. [d] The reported potential of the 1−/0 redox event is significantly shifted compared to other measurements for these compounds.

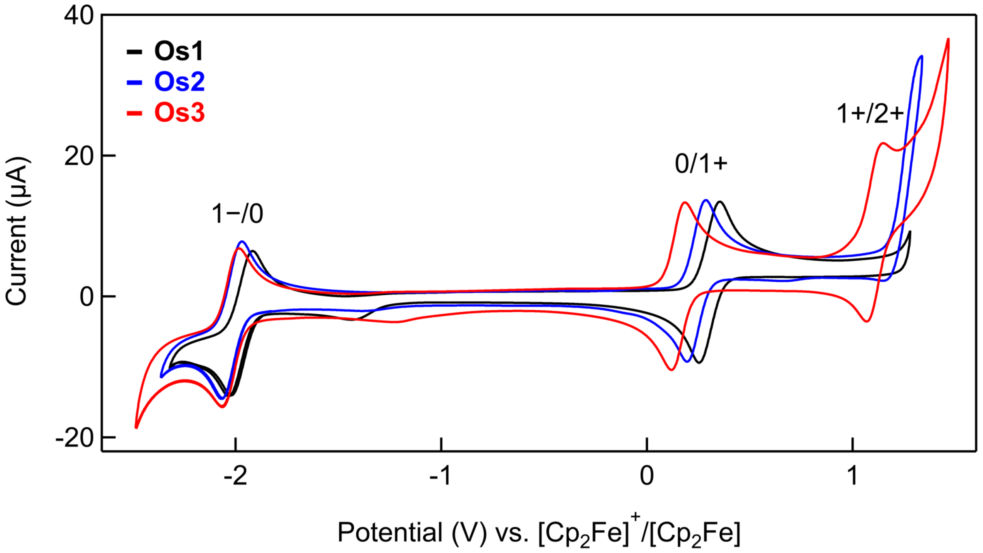

Figure 3. Overlaid cyclic voltammograms for Os(2-tolyl)$_4$ (**Os1**, black), Os(2,5-xylyl)$_4$ (**Os2**, blue), and Os(mesityl)$_4$ (**Os3**, red) in 0.1 M NBu_4PF_6–CH_2Cl_2. Potentials are reported relative to FcH/[FcH]$^+$, corrected for iR_u. Scan rate = 0.1 V s^{-1}. Redox features are shifted to cathodic potentials with increasing numbers of methyl substituents, and a second oxidation event is observed for **Os3**.

CONCLUSION

In conclusion, we have shown that synthetic yields of Os(aryl)$_4$ complexes can be significantly improved using the novel starting material $(Oct_4N)_2[OsBr_6]$, even facilitating the preparation of previously inaccessible compounds such as **Os3**. $(Oct_4N)_2[OsBr_6]$ is relatively non-hazardous, straightforward to prepare, and convenient to handle, avoiding the direct use of volatile and toxic OsO_4 in reactions with aryl Grignard reagents. By quantifying the degree of tetrahedral distortion in these materials using a tetrahedricity metric, we show how their geometry is altered by varying the degree of substitution at the aryl ligands. Solution electrochemical studies of **Os1-3** suggest that the redox potentials of such compounds, with 20 possible substituent positions, can be precisely and systematically tuned. It is hoped that this study will help increase the utility of this fascinating family of complexes in established and emerging areas of molecular materials science.

ASSOCIATED CONTENT

Electronic Supplementary Information (ESI) available: Experimental procedures, characterization data (^1H and $^{13}C\{^1H\}$ NMR, high-resolution mass spectrometry or elemental analysis) for all new compounds, X-ray crystal structure data for **Os2** and **Os3,** and solution electrochemical data for **Os1-3**. CCDC 2024175, 2024176.

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Notes

The authors declare no competing interests.

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