An improved route to osmium(IV) tetraaryl complexes

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ABSTRACT

Investigations into the reactivity, properties, and applications of osmium(IV) tetraaryl complexes have been hampered by their low yielding syntheses from volatile and toxic OsO₄ (typically $\leq 34\%$). Here we show that air-stable M(aryl)₄ compounds (M = Os, Ru; aryl = 2-tolyl, 2,5-xylyl) can be prepared in improved yields ($\leq 73\%$) starting from new, less hazardous (Oct₄N)₂[MX₆] precursors (M = Os, Ru; X = Cl, Br). This approach also facilitates the preparation of Os(mesityl)₄ (**Os3**), a complex comprising bulky 2,6-methyl substituted aryl ligands, for the first time (5% yield). We evaluate the X-ray crystal structures of Os(2,5-xylyl)₄ (**Os2**) and **Os3**, employing a "tetrahedrality" metric that shows **Os3** has a particularly distorted tetrahedral geometry compared to other Ru(aryl)₄ and Os(aryl)₄ materials. The ¹H NMR spectrum of **Os3** exhibits significantly broadened features at 298 K that split into distinct resonances at low temperatures, indicative of restricted rotation of the mesityl ligands around the Os-aryl σ -bond. Solution cyclic voltammograms of Os(aryl)₄ reveal that the potentials of their known reversible redox features can be fine-tuned by varying the number of ligand methyl substituents, and that **Os3** exhibits an additional 1+/2+ redox event not previously observed in this class of compounds. This work aims to help advance the potential application of these relatively underexplored organometallic complexes in established and emerging areas of molecular materials science, such as extended molecular frameworks and self-assembled monolayers, where analogous tetraphenylmethane and silane species (M = C, Si) have been frequently targeted.

INTRODUCTION

Homoleptic transition metal(IV) tetraaryl complexes, $M(\text{aryl})_4$, are an underexplored class of organometallic materials with distinct electrochemical, magnetic, and optical characteristics resulting from their tetrahedral coordination geometry.¹ Their properties complement and extend beyond those of their isostructural group 14 congeners, widely utilized as primary components of advanced molecular materials such as covalent- and metal-organic frameworks,^{2–5} polymers,⁶ self-assembled monolayers,^{7–10} and single-molecule electronic components.^{11,12} We anticipate that modular, isostructural $M(\text{aryl})_4$ units can provide new approaches, for example, to tune the electrochemical energy storage capacity, electrocatalytic function, and electrical conductivity/conductance of such materials, among other applications. Notable in this context, $\text{Cr}(\text{aryl})_4$ complexes have recently been shown to function as optically accessible molecular qubits for quantum information applications after spatial isolation through dispersion in a $\text{Sn}(\text{aryl})_4$ diluent matrix.¹³

Among the reported $M(\text{aryl})_4$ materials, $\text{Os}(\text{IV})$ ^{14–16} and $\text{Ru}(\text{IV})$ ^{15–17} compounds with ortho-methylated σ -aryl ligands are particularly robust. As stated by Wilkinson *et al.* their stability is consistent with a d^4 low-spin electronic configuration, with the ligand methyl groups serving to inhibit decomposition pathways including reductive elimination and *ortho*-hydrogen abstraction.¹⁵ These compounds can be purified using chromatography in air, and their aryl ligands can be chemically functionalized via different methods (including bromination,¹⁸ Suzuki coupling,¹⁸ and Friedel-Crafts acylation¹⁹). $\text{Os}(\text{aryl})_4$ also have a particularly rich redox chemistry which facilitated the early isolation of a stable paramagnetic $\text{Os}(\text{V})$ complex.²⁰ However, $\text{Os}(\text{aryl})_4$ are often obtained in poor yields (typically $\leq 34\%$, 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)²¹ and bisoxo(diaryl)osmium(VI)^{21,22} 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 new tetra-*n*-octylammonium hexahaloosmate(IV) precursors $(\text{Oct}_4\text{N})_2[\text{OsX}_6]$ (X = Cl, Br; **Figure 1**, bottom); our approach can also be used to prepare ruthenium homologues from tetra-*n*-octylammonium hexachlororuthenate(IV), $(\text{Oct}_4\text{N})_2[\text{RuCl}_6]$. Reactions of the appropriate aryl Grignard reagent with $(\text{Oct}_4\text{N})_2[\text{OsBr}_6]$ provide $\text{Os}(\text{2-tolyl})_4$ (**Os1**) and $\text{Os}(\text{2,5-xylyl})_4$ (**Os2**) in among the highest yields reported for any $M(\text{aryl})_4$ compound prepared to date (55–73%). From reactions with mesitylmagnesium bromide we obtain $\text{Os}(\text{mesityl})_4$ (**Os3**) in

5% yield, 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 (**Figures 2 and 3**) and explore the redox properties of **Os1-3** using solution electrochemistry (**Figure 4**).

Figure 1. Synthetic routes to Os(aryl)₄ complexes from reactions of aryl Grignard reagents with OsO₄ (previous work, top) or (Oct₄N)₂[OsX₆] (this work, bottom). Conditions: (i) HX, NH₄X (X = Cl, Br), ethanol (and FeCl₂ for X = Cl).^{23,24} Use of (Oct₄N)₂[OsX₆] mitigates 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.

EXPERIMENTAL SECTION

Materials and Instruments

All manipulations were carried out in oven-dried glassware under a nitrogen atmosphere using standard Schlenk line techniques. No special precautions were taken to exclude air or moisture during workup unless otherwise stated. Tetrahydrofuran and dichloromethane were sparged with nitrogen and dried using a two-column solvent purification system packed with alumina (Pure Process Technologies, Nashua, NH, USA). Grignard reagents were commercially available or prepared according to the general method described here, and titrated using a salicylaldehyde phenylhydrazine indicator to determine their concentration prior to use.²⁵ Additional notes on Grignard preparation can be found in the supporting information. Flash chromatography was performed using a Pure C-850 FlashPrep chromatography system and FlashPure EcoFlex flash cartridges (silica, irregular 40-63 μm particle size, 55-75 Å pore size; BUCHI Corporation, New Castle, DE, USA), or manually using Alfa Aesar silica gel 60 (215-400 mesh). (Oct₄N)₂[RuCl₆]²⁶ was prepared using established literature procedures. (NH₄)₂[OsCl₆]²³ and (NH₄)₂[OsBr₆]²⁴ were prepared using established literature procedures or

purchased from commercial suppliers. All other chemical reagents were commercially available and used without further purification.

^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded at room temperature on Varian VNMRS 500 (500 MHz), 400MR (400 MHz), VNMRS 600 (600 MHz), or Mercury 400 (400 MHz) NMR spectrometers, unless otherwise stated. ^1H NMR data recorded in CDCl_3 , CD_2Cl_2 , C_6D_6 , and toluene- d_8 is referenced to residual internal CHCl_3 (δ 7.26), CDHCl_2 (δ 5.32), $\text{C}_6\text{D}_5\text{H}$ (δ 7.16), and $\text{C}_6\text{D}_5\text{CD}_2\text{H}$ (δ 2.08) solvent signals.²⁷ $^{13}\text{C}\{^1\text{H}\}$ NMR data recorded in CDCl_3 is referenced to internal CDCl_3 (δ 77.16).²⁷ Variable-temperature NMR measurements were performed on a Varian VNMRS 600 (600 MHz) NMR spectrometer, with temperatures calibrated using a 4% CH_3OH in CD_3OD sample containing a trace of HCl .²⁸ Infrared spectra were obtained using an Agilent compact Cary 630 FTIR spectrometer fitted with a diamond ATR sampling module and KBr window. Mass spectrometry analyses were performed on an Agilent 6545 QTOF mass spectrometer fitted with an atmospheric pressure electrospray ionization source (Dual AJS ESI) at the University of Southern California (USC), or on a Waters Synapt G2-Si (ESI) or Waters GCT Premier (EI) at the Mass Spectrometry Lab, University of Illinois Urbana-Champaign. Microanalyses were carried out using a Thermo Flash 2000 CHNS Combustion Analyzer at USC, or on a Control Equipment Corp. CEC 440HA Elemental Analyzer at the Marine Science Institute, University of California Santa Barbara. Electrochemical measurements were performed under an argon atmosphere using a CHI760E bipotentiostat (CH Instruments, Austin, TX, USA) with anhydrous, nitrogen-sparged 0.1 M tetrabutylammonium hexafluorophosphate (NBu_4PF_6) dichloromethane solutions. We used a glassy carbon disc working electrode ($\varnothing = 3$ mm, CH Instruments), with Pt wire reference and counter electrodes. Glassy carbon electrodes were mechanically polished using an alumina slurry prior to use, Pt wires were cleaned by annealing in an oxyhydrogen flame. Analyte solutions were between 0.1-1 mM. Potentials are reported relative to $[\text{Cp}_2\text{Fe}]^+ / [\text{Cp}_2\text{Fe}]$, measured against internal Cp_2Fe or Cp^*Fe references as appropriate.

General Synthesis of $(\text{Oct}_4\text{N})_2[\text{OsX}_6]$ Complexes ($X = \text{Cl}, \text{Br}$)

This method is adapted from the synthesis of $(\text{Oct}_4\text{N})_2[\text{RuCl}_6]$.²⁶ A solution of tetra-*n*-octylammonium bromide in 2-propanol was added to an aqueous solution of $(\text{NH}_4)_2[\text{OsX}_6]$ in deionized water. After 1 h, deionized water was added and the precipitate collected via filtration in air. The solid was rinsed with deionized water (3 x ~20 mL) and dried under vacuum overnight.

$(\text{Oct}_4\text{N})_2[\text{OsCl}_6]$

Tetra-*n*-octylammonium bromide (1.470 g, 2.69 mmol), 2-propanol (50 mL), (NH₄)₂[OsCl₆] (0.577 g, 1.31 mmol), and deionized water (45 mL, then 10 mL) yielded a yellow powder (1.521 g, 87% yield). ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 0.87 (t, 12H, *J* = 6.8 Hz), 1.21-1.33 (m, 24H), 1.37 (m, 8H), 1.49 (m, 8H), 1.77 (m, 8H), 3.23 (m, 8H). ¹³C{¹H} NMR (CDCl₃, 125 MHz): δ (ppm) 13.83, 22.38, 24.30, 27.56, 28.88, 29.38, 31.52, 69.04. Anal. Calc. for C₆₄H₁₃₆N₂Cl₆Os: C, 57.59; N, 2.10; H, 10.27%. Found: C, 57.64; N, 2.04; H, 10.22%.

(Oct₄N)₂[OsBr₆]

Tetra-*n*-octylammonium bromide (1.088 g, 1.99 mmol), 2-propanol (35 mL), (NH₄)₂[OsBr₆] (0.701 g, 0.99 mmol), and deionized water (35 mL, then 20 mL). The resulting solid was rinsed with 2-propanol, dissolved in CH₂Cl₂, then filtered through a plug of sand. Solvent removal provided the analytically pure material as a red-brown powder (1.048 g, 66%). ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 0.87 (t, 12H, *J* = 5.7 Hz), 1.22-1.35 (m, 24H), 1.39 (m, 8H), 1.50 (m, 8H), 1.77 (m, 8H), 3.22 (m, 8H). ¹³C{¹H} NMR (CDCl₃, 125 MHz): δ (ppm) 13.38, 21.92, 24.40, 27.76, 28.45, 29.08, 31.09, 69.70. HR-MS (ESI) *m/z*: 466.5352 ([Oct₄N]⁺ calc. for C₃₂H₆₈N: 466.5352), 590.5464 ([OsBr₅][−] calc. for OsBr₅: 590.5491). Anal. Calc. for C₆₄H₁₃₆N₂Br₆Os: C, 47.94; N, 1.75; H, 8.55%. Found: C, 47.80; N, 1.99; H, 8.33%.

General Synthesis of M(aryl)₄ Complexes from (Oct₄N)₂[MX₆] (M = Os, Ru; X = Cl, Br)

A solution of the appropriate aryl Grignard reagent in THF was added dropwise to a stirred suspension of (Oct₄N)₂[MX₆] in THF. The mixture was stirred at room temperature for 2 h, then nitrogen-sparged methanol (1 mL) was added. The solvent was removed *in vacuo*. The resulting solid was dissolved in CH₂Cl₂, packed onto Celite and purified by automated flash chromatography in air (silica; hexanes/CH₂Cl₂, 1:0→4:1).

Os(2-tolyl)₄ (Os1)

From (Oct₄N)₂[OsCl₆]: 2-Tolylmagnesium bromide in THF (0.66 mL, 0.9 M, 0.60 mmol), (Oct₄N)₂[OsCl₆] (0.113 g, 0.085 mmol), and THF (10 mL) provided a black solid (0.014 g, 30%). From (Oct₄N)₂[OsBr₆]: 2-Tolylmagnesium bromide in THF (2.40 mL, 0.9 M, 2.16 mmol), (Oct₄N)₂[OsBr₆] (0.494 g, 0.31 mmol), and THF (10 mL) provided a black solid (0.124 g, 73%). Spectroscopic data was consistent with previous reports.^{15,29} ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 2.30 (s, 12H), 6.79 (m, 8H), 6.94 (m, 8H). ¹H NMR (toluene-*d*₈, 400 MHz): δ (ppm) 2.30 (s, 12H), 6.60 (m, 8H), 6.78 (m, 4H), 7.04 (d, 4H). ¹H NMR (benzene-*d*₆, 400 MHz): δ (ppm) 2.34 (s, 12H), 6.64 (m, 8H), 6.81 (m, 4H), 7.09 (d, 4H). HR-MS (EI) *m/z*: 556.1805 ([M]⁺ calc. for C₂₈H₂₈Os: 556.1806).

Os(2,5-xylyl)₄ (Os2)

From (Oct₄N)₂[OsCl₆]: 2,5-Xylylmagnesium bromide in THF (0.55 mL, 1.04 M, 0.57 mmol), (Oct₄N)₂[OsCl₆] (0.108 g, 0.08 mmol), and THF (10 mL) afforded a black powder (0.020 g, 40%). From (Oct₄N)₂[OsBr₆]: **(A)** 2,5-Xylylmagnesium bromide in THF (2.5 mL, 0.53 M, 1.33 mmol), (Oct₄N)₂[OsBr₆] (0.293 g, 0.18 mmol), and THF (4 mL) provided a black powder (0.069 g, 61%). **(B)** 2,5-Xylylmagnesium bromide in THF (24.77 mL, 0.87 M, 21.55 mmol), (Oct₄N)₂[OsBr₆] (4.921 g, 3.07 mmol), and THF (100 mL) afforded a black powder (1.032 g, 55%). From OsO₄: A solution of 2,5-xylylmagnesium bromide in THF (14 mL, 0.5 M, 7 mmol) was added dropwise to a stirred suspension of OsO₄ (0.250 g, 0.98 mmol) in THF (10 mL) at −78°C under nitrogen. The resulting reddish-brown mixture was allowed to warm to room temperature and stirred for 2 h, then nitrogen-sparged methanol (1 mL) was added. The solvent was removed *in vacuo* to provide the crude product. This was found by ¹H NMR to consist of a mixture of **Os2** and OsO(2,5-xylyl)₄²¹ in an approximate 2:1 ratio. The resulting crude material was dissolved in hexanes, packed onto Celite and purified by automated flash chromatography in air (silica; hexanes/diethyl ether, 1:0→99:1) to provide **Os2** as a black solid (0.039 g, 6%). The low isolated yield is due to challenging separation from the closely eluting OsO(2,5-xylyl)₄²¹ species.

Crystals suitable for X-ray diffraction were grown by cooling a solution of **Os2** in *n*-hexane to −20°C (red-brown plate-like crystals). Spectroscopic data was consistent with previous reports.^{18,21} ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 2.24 (s, 12H), 2.28 (s, 12H), 6.59 (d, 4H, *J* = 7.5 Hz), 6.69 (d, 4H, *J* = 7.5 Hz), 6.72 (s, 4H). HR-MS (ESI/Q-TOF) *m/z*: 612.2433 ([M]⁺ calc. for C₃₂H₃₆Os: 612.2432).

Os(mesityl)₄ (Os3) and OsO₂(mesityl)₂

Mesitylmagnesium bromide in THF (2.88 mL, 0.94 M, 2.71 mmol), (Oct₄N)₂[OsBr₆] (0.618 g, 0.39 mmol), and THF (10 mL) provided **Os3** (0.014 g, 5%) as a green-black solid from selected fractions of the black band eluting with hexanes/CH₂Cl₂ (9:1). Crystals suitable for X-ray diffraction were grown by cooling a solution in *n*-hexane to −20°C (green-black needles). ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 2.11 (br s, 24H), 2.36 (s, 12H), 6.47 (br s, 8H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ (ppm) 20.20, 126.23, 127.64, 138.10 (only 4 of 6 expected resonances observed). HR-MS (ESI/Q-TOF) *m/z*: 668.3066 ([M]⁺ calc. for C₃₆H₄₄Os: 668.3058). OsO₂(mesityl)₂ was obtained as a green solid from fractions of the green band eluting with hexanes/CH₂Cl₂ (4:1) (0.022 g, 12%). Crystals suitable for X-ray diffraction were grown by slow evaporation of a *n*-hexane/CH₂Cl₂ solution (dark green needles). Spectroscopic

data was consistent with previous reports.²² ¹H NMR (CDCl₃, 500 MHz): δ (ppm) 2.34 (s, 12H), 2.54 (s, 6H), 7.00 (s, 4H). ¹H NMR (C₆D₆, 400 MHz): δ (ppm) 2.27 (s, 6H), 2.35 (s, 12H), 6.74 (s, 4H). IR (ATR): ν (cm⁻¹) 950, 917 (Os=O).

Ru(2-tolyl)₄ (Ru1)

From (Oct₄N)₂[RuCl₆]: 2-Tolylmagnesium bromide in THF (4.75 mL, 0.9 M, 4.28 mmol), (Oct₄N)₂[RuCl₆] (0.253 g, 0.20 mmol), and THF (10 mL) yielded a red-brown powder (0.034 g, 36%). Spectroscopic data was consistent with previous reports.¹⁶ ¹H NMR (CDCl₃, 600 MHz): δ (ppm) 2.13 (s, 12H), 6.90 (d, 4H, J = 5.8 Hz), 7.00 (m, 8H), 7.20 (d, 4H, J = 6.2 Hz). HR-MS (ESI/Q-TOF) m/z : 466.1243 ([M]⁺ calc. for C₂₈H₂₈Ru: 466.1234).

X-Ray Crystallography

X-ray intensity data were collected at 100 K on a Bruker APEX DUO 3-circle platform diffractometer, equipped with an APEX II CCD detector, using MoK α radiation (λ = 0.71073 Å, TRIUMPH curved-crystal monochromator) from a fine-focus tube. The structures were solved by intrinsic phasing and refined on F^2 using the Bruker SHELXTL Software Package and ShelXle.^{30–33} All non-hydrogen atoms were refined anisotropically. Further crystallographic details can be obtained from the Cambridge Crystallographic Data Centre (CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: (+44) 1223–336–033; e-mail: deposit@ccdc.cam.ac.uk) on quoting the deposition no. CCDC 2024175, 2024176, 2119165.

RESULTS AND DISCUSSION

In developing this synthetic 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 OsO₄ rather than through air oxidation in solution or during chromatographic purification.²¹ 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 (Et₄N)[RuCl₅(THF)],¹⁶ (Et₄N)[RuCl₅(MeCN)],¹⁶ Ru₂(μ -O₂CMe)₄,¹⁶ RuCl₃(tht)₃,¹⁷ and Ru(acac)₃.^{34,35} (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**).^{16,17} We therefore sought alternative easily accessible M(IV) compounds, noting that multinuclear, Ru(II), or Ru(III) species increase the complexity of reactions (potentially involving disproportionation reactions to form Ru(IV))¹⁶ and that the

mononuclear pentachlororuthenate salts have not been utilized since the first synthetic reports of Ru(aryl)₄ compounds. Remarkably, several members of the family of (NH₄)₂[MX₆] salts (M = Os, Ru; X = Cl, Br) are commercially available or readily synthesized using verified protocols,^{23,24} but have not yet been explored as precursors to M(aryl)₄ compounds.

Our initial attempts to prepare Ru(2-tolyl)₄ (**Ru1**) through the addition of 6-8 equivalents of 2-tolylmagnesium bromide to (NH₄)₂[RuCl₆] proved unsuccessful due to the low solubility of the metal salt in THF and diethyl ether (coordinating solvents commonly used for Grignard reactions). Following cation exchange to increase the solubility of the anion in common organic solvents, and to eliminate possible quenching of Grignard reagent with the protic ammonium cations, the analogous reaction using (Oct₄N)₂[RuCl₆]²⁶ provided **Ru1** in 36% 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 new Os(IV) starting materials (Oct₄N)₂[OsCl₆] and (Oct₄N)₂[OsBr₆] in 87% and 66% yield, respectively (**Figure 1, bottom**). Reactions between (Oct₄N)₂[OsX₆] and the appropriate arylmagnesium bromide provided **Os1** (X = Cl, 30%; X = Br, 73%) and **Os2** (X = Cl, 40%; X = Br, 61%) in among the highest yields for any M(aryl)₄ species reported to date (see **SI, Table S2** for a summary of previous work). Notably, to achieve consistently high yields, (Oct₄N)₂[OsBr₆] samples of analytically purity must be used. We also find that this preparative approach can be scaled, facilitating the synthesis of **Os2** in >1 g quantities (55% yield). **Os1-3** and **Ru1** were all worked up in air and are readily purified by chromatography. We anticipate their chemical stability will prove useful in isolating derivatized or heteroleptic analogues in the future. While M(aryl)₄ species have previously been directly purified by recrystallisation techniques, this process is inhibited when using (Oct₄N)₂[MX₆] reagents. A viscous crude reaction product is obtained after solvent removal which limits full extraction of reaction products into hexanes. In line with previous reports, we find that isolated M(aryl)₄ are readily crystallized from solution.

The higher yields of Os(aryl)₄ obtained from (Oct₄N)₂[OsBr₆] compared to (Oct₄N)₂[OsCl₆] suggest that the nature of the metal halide plays a critical role in the formation of these complexes. Noting trends observed for related materials, the Os-Br bonds in (Oct₄N)₂[OsX₆] should have lower heterolytic bond energies than Os-Cl.^{36,37} We hypothesize that this, in combination with the greater steric crowding around the M(IV) center in [OsBr₆]²⁺ compared to [OsCl₆]²⁺, increases the rate of loss of the larger bromide ions and subsequent coordination of σ -aryl ligands to the Os center via a dissociative mechanism. While the focus of this initial study is on Os(aryl)₄ complexes, we anticipate that reactions from

precursors such as (Oct₄N)₂[RuBr₆] (containing Ru-Br rather than Ru-Cl bonds) would also provide improved yields of Ru(aryl)₄ complexes compared to (Oct₄N)₂[RuCl₆].

To further demonstrate the potential of our synthetic approach we next targeted the preparation of **Os3**, a previously inaccessible bulky 2,6-disubstituted Os(aryl)₄ complex. Previous reactions of OsO₄ with mesitylmagnesium bromide resulted only in the isolation of OsO₂(mes)₂,^{15,22} and with 2,6-xylylmagnesium bromide yielded only OsO₂(2,6-xylyl)₂.³⁸ In contrast, the reaction of mesitylmagnesium bromide with (Oct₄N)₂[OsBr₆] provided **Os3** as a green-black solid in 5% yield in addition to OsO₂(mes)₂ (12%).²² Though the ¹H and ¹³C{¹H} NMR spectra of these complexes are somewhat ambiguous, each showing only resonances attributable to mesityl ligands, their identity could be verified through single-crystal X-ray diffraction (**Figure 2b** and **SI, Figure S2**) and IR spectroscopy. Of all the osmium compounds described here, only OsO₂(mes)₂ exhibits IR spectral features attributable to Os=O (**SI, Figure S5**). Given that (Oct₄N)₂[OsBr₆] contains no oxo groups, we propose that OsO₂(mes)₂ forms through incomplete substitution of the [OsBr₆]²⁻ ion, followed by hydrolysis/oxygen abstraction during reaction workup in air or chromatographic purification. OsO₂(aryl)₂ species were not isolated during analogous reactions with less bulky ligands in the formation of **Os1-2**. Accordingly, we attribute the low yield of **Os3** to the steric constraints of incorporating four 2,6-dimethylated aryl ligands around the metal(IV) center (see discussion below). Analogous ruthenium complexes comprising bulky ligands are also reported in relatively lower yields; Ru(mesityl)₄ and Ru(2,6-xylyl)₄ were prepared in 13-21% yield¹⁶ compared to 24-48% for Ru(aryl)₄ complexes with a single 2-methyl substituent (**SI, Table S1**). Additional evidence for the steric congestion around the osmium center in **Os3** is provided by its ¹H NMR spectrum. This reveals significantly broadened *ortho*-CH₃ and *meta*-H resonances (**SI, Figure S12**), indicative of restricted rotation of the mesityl ligand around the Os-aryl σ-bond at room temperature. Variable temperature NMR studies reveal that the Gibbs free energy of activation (Δ*G*[‡]) for **Os3** is ~47 kJ mol⁻¹, compared to ~50 kJ mol⁻¹ for Ru(mes)₄ (**Ru3**; see the **SI, Figure S16** and **Table S24**). This result is in agreement with the noted trend that the longer the M-C bond length, the lower the value of Δ*G*[‡] (**Os3**_(Os-C) = 2.037(3) Å, **Ru3**_(Ru-C) = 2.01(1) Å; see discussion below and **Table 1**).³⁹

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 S9-S22**). We observe no clear correlation between M-C bond lengths and aryl substituents across the series, but note that the sterically bulky, 2,6-

dimethylated **M3** complexes have considerably longer M-C bond lengths than compounds with only single *ortho*-methyl aryl substituents. The range of angles between aryl planes also does not appear to correlate with the number of *ortho*-substituents or the electronic character of the aryl ligand (**Table 1** and **SI, Table S9**; see **SI, Figure S3** 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**).

Figure 2. X-ray crystal structures of (a) **Os2** and (b) **Os3** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity (Os = teal, C = grey). Selected structural parameters are provided in **Table 1** and in the **SI, Tables S9-10** and **S15**.

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

compound	M-C (Å) <i>a</i>	aryl plane range (°) <i>b</i>	<i>T</i> -value <i>c</i>	identifier <i>d</i>	reference
Os(mesityl) ₄ (Os3)	2.037(3)	18.96	8.02	2024176	this work
Os(cyclohexyl) ₄	2.029	-	5.18	1135690	15
Os(2-tolyl) ₄ (Os1)	1.997	7.51	4.38	1135692	15
Os(4-Br-2,5-xylyl) ₄	2.000(2)	24.87	1.60	164949	18
Os(phenyl) ₄	1.995	24.40	1.32	1153940	15
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	17
Ru(cyclohexyl) ₄	2.019	-	4.02	1153943	15
Ru(2-tolyl) ₄ (Ru1)	1.995	12.53	3.53	1161553	16
Ru(4-MeO-2-tolyl) ₄	1.986	26.19	2.45	1032104	34
Ru(4-Br-2,5-xylyl) ₄	1.984	24.97	2.17	1032108	34
Ru(2,4,5-trimethylphenyl) ₄	1.985(10)	20.99	0.86	1510576	35
C(phenyl) ₄	1.551	5.98	1.95	191149	40

^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 (tetrahedrity) = 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 straightforward “tetrahedrity”-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 “octahedrity” metric has been utilized in the structural characterization of metal polypyridyl complexes,^{41–43} and related, yet somewhat more involved analyses have previously been performed for molecular complexes,^{44,45} as well as for coordination environments in solid-state materials.^{46,47} 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. 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°). This analysis further supports the view that steric constraints due to 2,6-dimethyl substituents contribute to the lower synthetic yield of **Os3** compared to **Os1-2** (**SI**, **Table S2**). 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°) has a more ideal tetrahedral geometry than **Os1** (T -value = 4.38), Os(phenyl)₄ (T -value = 1.32), or C(phenyl)₄ (T -value = 1.95).

In **Figure 3**, 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**. It is reasonable to consider whether such 2,6-substituted aryl ligands may accordingly impart an increased chemical or electrochemical stability to such complexes. Interestingly, preliminary reactivity studies following Arnold *et al.*⁴⁸ reveal that black hexane solutions of **Os3** rapidly change color to yellow upon addition of an excess of PMe₃ (consistent with the formation of the corresponding osmium(II) η^6 -biaryl complex), demonstrating that the additional steric shielding imparted by the mesityl ligands does not provide sufficient protection against attack by small nucleophiles.

Figure 3. Space filling models of (a) **Os1**¹⁴ and (b) **Os3**, viewed along each Os-C axis, illustrating the additional steric shielding conferred by the second *ortho*-methyl group in **Os3** (Os = teal, C = grey, H = white).

We studied the redox properties of **Os1-3** using cyclic voltammetry in CH₂Cl₂ with 0.1 M NBu₄PF₆ as the supporting electrolyte. The results are summarized in **Table 2** and **Table S23**, with representative overlaid cyclic voltammograms shown in **Figure 4**. 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.^{20,21} These 0/1+ and 1-/0 events have previously been assigned to the Os⁴⁺/Os⁵⁺ and Os³⁺/Os⁴⁺ redox couples, respectively. Interestingly, we observe an additional 1+/2+ oxidation event for **Os3** at +1.117 V which may be metal Os⁵⁺/Os⁶⁺ or ligand-based.²⁰ Using the equilibrium potentials

for the 0/1+ feature of **Os1-3**, we find that these 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.⁴⁹ Extrapolating from 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. [Cp₂Fe]⁺/[Cp₂Fe], 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	-	20
2 ^b		CH ₂ Cl ₂	-	-1.96	+0.33	-	20
3		CH ₂ Cl ₂	-	-1.961	+0.326	-	this work
4 ^c	Os(2,5-xylyl) ₄ (Os2)	CH ₂ Cl ₂	-	-1.48 ^d	+0.24	-	21
5		CH ₂ Cl ₂	-	-2.008	+0.244	-	this work
6	Os(mesityl) ₄ (Os3)	CH ₂ Cl ₂	-	-2.028	+0.153	+1.117	this work

^a Scan rate = 0.1 V s⁻¹; NBu₄PF₆ supporting electrolyte; working electrode: glassy carbon; reference electrode, counter electrode: Pt. Potentials measured with internal Cp*₂Fe (-0.532 V vs [Cp₂Fe]⁺/[Cp₂Fe]),⁴⁹ reported relative to [Cp₂Fe]⁺/[Cp₂Fe]. See **SI, Table S23** 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 Cp₂Fe. ^c Reference electrode: Ag/AgNO₃ (0.1 M in acetonitrile). Potentials measured with internal Cp₂Fe. ^d The reported potential of the 1-/0 redox event is significantly shifted compared to other measurements for these compounds.

Figure 4. 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 NBu₄PF₆-CH₂Cl₂. Potentials are reported relative to FcH/[FcH]⁺, corrected for *iR_u*. Scan rate = 0.1 V s⁻¹. Redox features are shifted to more negative potentials with increasing numbers of methyl substituents, and a second oxidation event is observed for **Os3**.

CONCLUSIONS

We have shown that synthetic yields of Os(aryl)₄ complexes can be significantly improved using the new starting material (Oct₄N)₂[OsBr₆], even facilitating the preparation of previously inaccessible compounds such as **Os3**. (Oct₄N)₂[OsBr₆] is non-hazardous, straightforward to prepare, and convenient to handle, avoiding the direct use of volatile and toxic OsO₄ in reactions with aryl Grignard reagents. By quantifying the degree of tetrahedral distortion in these materials using a straightforward tetrahedrality 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 readily tuned. The reversible redox properties of **Os1-3**,²⁰ the stability of M(aryl)₄ complexes with different metal centers,¹ and the potential for direct functionalization of their σ -aryl ligands^{18,19} draw intriguing parallels with metallocenes, the well-established and broadly utilized prototypical family of organometallic complexes. It is hoped that this work will help facilitate further studies of this fascinating class of tetrahedral

materials towards applications where such organometallic complexes have already demonstrated utility, for example in sensing, catalysis, or as components of extended molecular systems such as polymers or supramolecular assemblies.^{50,51}

ASSOCIATED CONTENT

Electronic Supplementary Information (ESI) available: Additional synthetic information, infrared spectra, ¹H and ¹³C{¹H} NMR spectra for all new compounds, X-ray crystal structure data for **Os2**, **Os3**, and OsO₂(mes)₂ (CCDC 2024175, 2024176, 2119165), details of tetrahedrality calculations and additional structural information for the compounds detailed in **Table 1**, and solution electrochemical data for **Os1-3**.

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Notes

The authors declare no competing financial interest.

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Air-stable osmium(IV) tetraaryl complexes are obtained in the highest yields reported for any $\text{M}(\text{aryl})_4$ compound prepared to date ($\leq 73\%$) using the new precursor $(\text{Oct}_4\text{N})_2[\text{OsBr}_6]$. Our approach avoids the use of toxic OsO_4 in reactions with aryl Grignard reagents and facilitates the synthesis of $\text{Os}(\text{mesityl})_4$ (**Os3**) for the first time. **Os3** exhibits a distorted tetrahedral geometry and three reversible redox events, including a $1+/2+$ feature not previously observed in this family of materials.