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<td><strong>Author(s)</strong></td>
<td>Lau, MK; Chim, JLC; Wong, WT; Williams, ID; Leung, WH</td>
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Synthesis and molecular structures of monooxo aryl complexes of osmium(VI)

Man-Kit Lau, Joyce L.C. Chim, Wing-Tak Wong, Ian D. Williams, and Wa-Hung Leung

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Synthesis and molecular structures of monooxo aryl complexes of osmium(VI)

Man-Kit Lau, Joyce L.C. Chim, Wing-Tak Wong, Ian D. Williams, and Wa-Hung Leung

Abstract: Reaction of [OsO₄] with C₅H₅MgBr (C₅H₅ = 2-methylphenyl) followed by column chromatography afforded the reported osmium tetraaryl [Os(C₅H₅)₄] along with the oxo-osmium(VI) [OsO(C₅H₅)₄] (1) (13%) and the dioxo-osmium(VI) [OsO₂(C₅H₅)₂] (2) (25%) complexes. Treatment of [OsO₄] with C₅H₅MgBr (C₅H₅ = 2.5-dimethylphenyl) gave a mixture of [Os(C₅H₅)₄] (3) (34%) and [OsO(C₅H₅)₄] (4) (4%) while that with C₅H₅OMgBr (C₅H₅O = 4-methoxy-2-methylphenyl) afforded [OsO(C₅H₅O)₄] (5) in 20% yield. Oxidation of 3 with 3-chloroperbenzoic acid afforded 4 in good yield. The solid-state structures of 1 and 4 have been established by X-ray crystallography. Crystals of 1 are tetragonal with a = 13.080(1) Å and c = 6.6506(5) Å, V = 1137.9(1) Å³, Z = 2, and space group of P4/n; while those of 4 are tetragonal with a = 13.593(2) Å and c = 7.377(2) Å, V = 1363.0(5) Å³, Z = 4, and space group of P4/n.

The geometry around osmium in both complexes is square pyramidal with the oxo ligand occupying apical position. The Os—O and Os—C distances in 1 are 1.652(2) Å and 2.084(1) Å, respectively, while those in 4 are 1.688(7) and 2.088(4) Å, respectively. The cyclic voltammograms of the monooxo aryl osmium(VI) compounds show reversible Os(VI)/V couple at around −1.4 V vs. ferrocene/ferrocinium couple.

Key words: osmium(VI), oxo aryl complexes.

Résumé : La réaction du [OsO₄] avec du C₅H₅MgBr (C₅H₅ = 2-méthylphényle), suivie d’une chromatographie sur colonne permet d’isoler le tétraaryl-osmium attendu [Os(C₅H₅)₄], aux côtés de complexes oxo-osmium(VI) [OsO(C₅H₅)₄] (1) (13%) et dioxo-osmium(VI) [OsO₂(C₅H₅)₂] (2) (25%). Le réaction du [OsO₄] avec du C₅H₅MgBr (C₅H₅ = 2.5-diméthylphényle) conduit à un mélange de [Os(C₅H₅)₄] (3) (34%) et de [OsO(C₅H₅)₄] (4) (4%) alors que celle avec C₅H₅OMgBr (C₅H₅O = 4-méthoxy-2-méthylphényle) conduit au [OsO(C₅H₅O)₄] (5) avec un rendement de 20%.

L’oxydation du produit 3 par de l’acide 3-chloroperbenzoïque conduit au produit 4 avec un bon rendement. Les structures des composés 1 et 4 ont été déterminées à l’état solide par diffraction des rayons X. Les cristaux de 1 sont tétraédriques, groupe d’espace P4/n, avec a = 13.080(1) Å et c = 6.6506(5) Å, V = 1137.9(1) Å³ et Z = 2 alors que ceux du composé 4 sont tétraédriques, groupe d’espace P4/n, avec a = 13.593(2) Å et c = 7.377(2) Å et Z = 4 et V = 1363.0(5) Å³.

Dans chacun des complexes, la géométrie autour de l’osmium est de type pyramide carrée de laquelle le ligand oxo se trouve en position apicale. Les distances Os—O et Os—C dans le composé 1 sont respectivement de 1.652(2) et 2.084(1) Å alors que celles dans le composé 4 sont respectivement de 1.688(7) et 2.088(4) Å. Dans les voltampérammes cycliques des composés monooxo aryl osmium(VI), on observe le couple réversible Os(VI)/V aux environs de −1.4 V par rapport au couple ferrocène/ferrocénium.

Mots clés : osmium(VI), complexes oxo aryles.

[Traduit par la Rédaction]

Introduction

Organometallic oxides are of interest due to their relevance to the active intermediates in metal-catalyzed oxidations of organic compounds (1, 2). Some transition metal oxo alkyls, notably [Re(CH₃O₂)], are also used as stoichiometric and catalytic reagents for organic transformations (2). While oxo alkyls of oxophosphoryl early transition metals are well-documented, there are relatively few examples of the later transition-metal congeners. Wilkinson and co-workers (3, 4) first reported the synthesis of high-valent osmium aryls and oxo aryls by arylation of [OsO₄] with Grignard reagents ArMgBr (Ar = aryl). It was found that the ortho-methyl substituent in Ar has a significant effect on the nature of the arylation products. Thus, reaction of [OsO₄] with diortho-substituted mesMgBr (mes = 2,4,6-trimethylphenyl) afforded [OsO₂(mes)₂] (3) whereas interactions of [OsO₄] with monoortho-substituted or unsubstituted ArMgBr (e.g., Ar = 2-methylphenyl or phenyl) gave homoleptic Os(IV) aryls [Os(=Ar₄)] (4). However, to our knowledge, no oxo(tetraaryl)osmium(VI) complexes have been isolated al-


This paper is dedicated to Professor Brian R. James on the occasion of his 65th birthday.

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though oxo(tetraalkyl)osmium(VI) complexes have been prepared by alkylation of [OsO₄] (5) or oxo-osmium glycolates (6). In view of the low yield for the synthesis of [Os(C₅H₅)₂], we suspect that there may be other unidentified product(s) for the arylation of [OsO₄]. To this end, we set out to reinvestigate the reaction between [OsO₄] and ArMgBr, and to separate the products by column chromatography. We here describe the isolation, molecular structures, and electrochemistry of the first monooxo aryl complexes of osmium(VI).

**Experimental**

All manipulations, unless otherwise stated, were carried out in air. Solvents were purified, dried, and distilled prior to use. [OsO₄] was obtained from Strem Ltd. ArMgBr in Et₂O were prepared from commercially available aryl bromides and Mg.

Spectrometers used were as follows: IR spectra (in KBr discs) PerkinElmer 16 PC FT IR: mass spectra on a Finnigan TSQ 7000; UV–vis spectra Milton-Royal 3000 diode array; 300 MHz ¹H NMR spectra Bruker ALX 300 (chemical shifts in ppm relative to SiMe₄). Cyclic voltammetry was performed with a Princeton Applied Research (PAR) Model 273A potentiostat. The working and reference electrodes were glassy carbon and Ag/AgNO₃ (0.1 M in acetonitrile), respectively, and the scan rate was 100 mV s⁻¹. Formal potentials (E₁/₂) were measured in CH₂Cl₂ solutions with 0.1 M [n- NBu₄][PF₆] as supporting electrolyte and reported with reference to the ferrocenium/ferrocene couple (Fc⁺/Fc). Elemental analyses were performed by Medac Ltd, Surrey, U.K.

[OsO(C₅H₅)₂]²⁺ (1) and [OsO₂(C₅H₅)₂]²⁺ (2) (C₅H₅ = 2-methylphenyl)

These complexes were synthesized using a modification of the Wilkinson’s procedure. To a solution of [OsO₄] (1 g, 3.94 mmol) in THF (30 mL) at −78°C were added 7 equiv of 2-methylphenylmagnesium bromide (17.3 mL of a 1.6 M solution in Et₂O), and the mixture was stirred for 45 min. The resulting purple mixture was then warmed to room temperature, stirred for a further 2 h, and evaporated to dryness. The residue was extracted into CH₂Cl₂ in air and subjected to column chromatography (silica gel). Elution with hexane, CH₂Cl₂–hexane (1:4), and acetone afforded purple [Os(C₅H₅)₂]²⁺ (10%), orange 1 (13%), and green 2 (25%), respectively. Recrystallization of I from CH₂Cl₂–hexane led to isolation of orange blocks, which were suitable for X-ray diffraction.

**Characterization data for 1**

FT IR (KBr, cm⁻¹): 986 (Os=O). FAB-MS m/z: 572 (M⁺). ¹H NMR (300 MHz, CDCl₃) δ: 2.32 (s, 12H, CH₂), 5.96 (d, J = 7.6 Hz, 4H, H₄), 6.87 (t, J = 7.6 Hz, 4H, H₅), 6.96 (t, J = 7.6 Hz, 4H, H₆), 7.27 (d, J = 7.6 Hz, 4H, H₇), E₁/₂ (V): −1.41 [Os(VI/V)]. Anal. calcd. for C₂₈H₂₄O⁻: C 59.0, H 4.9; found: C 58.3, H 4.9.

**Characterization data for 2**

FT IR (KBr, cm⁻¹): 912, 956 (Os=O). FAB-MS m/z: 407 [M + 1]⁺. UV–vis (CH₂Cl₂) λ_max (nm) (ε_max (M⁻¹ cm⁻¹)): 248 (23 000), 350 (8700). ¹H NMR (300 MHz, CDCl₃) δ: 2.57 (s, 6H, CH₃), 7.04–7.13 (m, 4H, H₄ and H₅), 7.19 (d, J = 7.8 Hz, 2H, H₆), 7.40 (d, J = 7.8 Hz, 2H, H₇), E₁/₂ (V): −1.14 [Os(VI/V)]. Anal. calcd. for C₁₄H₁₀O₂Os: C 41.6, H 3.5; found: C 41.3, H 3.9.

[Os(C₅H₅)₂]³⁺ (3) and [OsO₂(C₅H₅)₂]⁴⁺ (4)

To a solution of [OsO₄] (0.5 g, 2.0 mmol) in Et₂O (20 mL) at −78°C were added 7 equiv of 2,5-dimethylphenylmagnesium bromide (11.5 mL of a 1.2 M solution in Et₂O, 14 mmol) dropwise under nitrogen. The resulting reddish-brown mixture was warmed to room temperature, stirred for 2 h, and evaporated to dryness. The dark yellow sticky residue was extracted into CH₂Cl₂, filtered through a Celite pad, and subjected to column chromatography (silica gel). Elution with hexane and hexane–Et₂O (7:3) afforded purple 3 (34%) and orange 4 (2%), respectively.

**Characterization data for 3**

FAB-MS m/z: 612 (M⁺). ¹H NMR (300 MHz, CDCl₃) δ: 2.22 (s, 12H, CH₂), 2.27 (s, 12H, CH₂), 6.57 (d, J = 8.5 Hz, 4H, H₄), 6.68 (d, J = 8.5 Hz, 4H, H₅), 7.67 (s, 4H, H₆), E₁/₂ (V): −1.48 [Os(VI/V)]. Anal. calcd. for C₂₆H₂₀O⁻: C 62.9, H 5.9; found: C 63.0, H 6.0.

**Characterization data for 4**

FT IR (KBr, cm⁻¹): 986 (Os=O). FAB-MS m/z: 572 (M⁺). UV–vis (CH₂Cl₂) λ_max (nm) (ε_max (M⁻¹ cm⁻¹)): 248 (22 000), 350 (8250). ¹H NMR (300 MHz, CDCl₃) δ: 1.99 (s, 12H, CH₂), 2.25 (s, 12H, CH₂), 5.78 (s, 4H, H₄), 6.75 (d, J = 7.5 Hz, 4H, H₅), 7.13 (d, J = 7.5 Hz, 4H, H₆), E₁/₂ (V): −1.35 [Os(VI/V)]. Anal. calcd. for C₂₆H₂₀O⁻: C 59.0, H 4.9; found: C 58.3, H 4.9.

**Preparation of 4 from 3**

To a solution of 3 (0.5 g, 0.08 mmol) in CH₂Cl₂ (10 mL) was added 1.5 equiv of 3-chloroperoxycarboxylic acid or t-BuOOH at room temperature. The reaction mixture was stirred for 2 h, evaporated to dryness, and subjected to column chromatography (silica gel). The product was eluted with hexane and recrystallized from CH₂Cl₂–hexane to give orange crystals (80% yield), which was identified as 4 by ¹H NMR spectroscopy and mass spectrometry. Recrystallization of 4 from CH₂Cl₂–hexane afforded orange blocks, which were suitable for X-ray diffraction study.

[OsO(C₅H₅)₂O₄]²⁻ (5)

To a solution of [OsO₄] (0.5 g, 2.0 mmol) in Et₂O (20 mL) at −40°C was added 7 equiv of 4-methoxy-2-methylphenylmagnesium bromide (20.6 mL of a 0.67 M solution in Et₂O), and the mixture was slowly warmed to room temperature and stirred for 2 h. The solvent was pumped off and the residue was extracted into CH₂Cl₂ in air. Column chromatography (silica gel, eluant: CH₂Cl₂–Et₂O (1:5)) followed by recrystallization from CH₂Cl₂–hexane afforded a brown solid. Yield: 0.25 g, 20%. FAB-MS m/z: 693 [M + 1]⁺. FT IR (KBr, cm⁻¹): 982 (Os=O). UV–vis (CH₂Cl₂) λ_max (nm) (ε_max (M⁻¹ cm⁻¹)): 254 (26 700), 350 (11 700). ¹H NMR (300 MHz, CDCl₃) δ: 2.28 (s, 12H, CH₂), 3.76 (s, 12H, OCH₃), 5.77 (d, J = 8.8 Hz, 4H, H₄), 6.41 (d, J = 8.8 Hz, 4H, H₅),

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Table 1. Crystallographic data for [OsO{(C₄H₇)}₂] (1) and [OsO{(C₆H₆)}₂] (4).

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<td>P4/n</td>
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<tr>
<td>a (Å)</td>
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<td>13.593(2)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>6.6505(5)</td>
<td>7.377(2)</td>
</tr>
<tr>
<td>V (Å³)</td>
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<td>1363.0(5)</td>
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<tr>
<td>Z</td>
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<td>wR₂ (F²) (all data)</td>
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<td>—</td>
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<tr>
<td>Residual density (e Å⁻³)</td>
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<td>-0.549–1.153</td>
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X-ray crystallography

Pertinent crystallographic data and other experimental details for complexes 1 and 4 are summarized in Table 1. Data for 1 and 4 were collected on a Bruker CCD diffractometer and a Siemens P4 diffractometer, respectively, at room temperature using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data were corrected for Lorentz and polarization effects. Absorption corrections were semiempirical based on ψ-scan data. Structures 1 and 4 were solved by direct methods and refined by full-matrix least-squares on F and F², respectively. Hydrogen atoms were included and fixed in their idealized positions (C-H 0.95 Å). Calculations were carried out using the teXsan (7) (for 1) and SHELXL (8) (for 4) crystallographic software packages. Complete listings of bond lengths and angles, final atomic coordinates of non-hydrogen atoms with thermal parameters, and anisotropic thermal parameters are included as supplementary material.²

Results and Discussion

Synthesis

The preparations of osmium oxo aryl complexes are summarized in Scheme 1. Wilkinson and co-workers (4a) first reported the synthesis of [Os{(C₄H₇)}₄] by the reaction of [OsO₄] with C₅H₅MgBr. The osmium tetraaryl was obtained in 29% yield after extraction into light petroleum and subsequent recrystallization under nitrogen. However, we found that when the reaction mixture was exposed to air and then chromatographed (silica gel) in air, in addition to [Os{(C₄H₇)}₄], the oxo-osmium species [OsO{(C₆H₆)}₂] (1) and [OsO₂{(C₆H₆)}₂] (2) species were isolated in 13 and 25% yield, respectively. The relative yields of [Os{(C₄H₇)}₄], 1, and 2 for the reaction were, however, found to be dependent on reaction conditions, workup procedure, and some unknown factors that have not been optimized yet. It appears that the oxo complexes 1 and 2 were derived directly from reaction of [OsO₄] with C₅H₅MgBr, instead of via aerobic oxidation of [Os{(C₄H₇)}₄], because [Os{(C₄H₇)}₄], 1, and 2 are all air stable in solution and under chromatographic conditions. Like [Os{(C₄H₇)}₄] (3a), complex 1 exhibits a symmetric ¹H NMR spectrum featuring a single ortho-methyl resonance at δ 2.32 at room temperature, indicating that the 2-methylphenyl ligands are free to rotate around the Os—C bonds at the NMR timescale. The UV–vis spectrum of 1 in CH₂Cl₂ displays absorption bands at ca. 350 (εmax = 8700 M⁻¹ cm⁻¹) and 248 nm (εmax = 23 000 M⁻¹ cm⁻¹). The former band is tentatively attributed to a charge transfer transition due to the Os=O moiety while the latter probably arises from an intraligand transition because a similar absorption was also found for [Os{(C₆H₆)}₂]. The IR Os—O

²Crystal data for 1 and 4 may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada DUD No. 3276. For information on obtaining material electronically go to http://www.nrc.ca/cisti/arm/unpub_e.shtml. This supplementary material has also been deposited with the Cambridge Crystallographic Centre (deposition nos. 148 810 and 148 809, respectively), and can be obtained on request from: The Director, Cambridge Crystallographic Centre, University Chemical Laboratory, 12 Union Road, Cambridge, CB2 1EZ, U.K.
Scheme 1.

\[
\text{[OsO}_4\text{]} \xrightarrow{7 \text{ArMgBr}} \text{chromatography} \quad \begin{array}{c}
\text{Ar} \\
\text{CH}_3
\end{array} \quad \begin{array}{c}
\text{Ar} \\
\text{CH}_3
\end{array} \\
\text{H}_3\text{C} \\
\text{H}_3\text{O} \\
\text{H}_3\text{O}
\]

(10%) 1 (13%) 2 (25%)

3 (34%) 4 (4%)

5 (20%)

The stretching frequency for 1 was observed at 990 cm\(^{-1}\), which is comparable to that for [OsO(CH\(_3\))\(_4\)] (994 cm\(^{-1}\)) (6a) but is lower than that for [OsO(CH\(_3\)SiMe\(_3\))\(_4\)] (1054 cm\(^{-1}\)) (5b). Complex 2, which presumably has a similar tetrahedral geometry as [OsO\(_2\)(mes)\(_2\)] (4a), exhibits \(\nu\text{OsO}_3\text{Ar}\) at 1000 and 980 cm\(^{-1}\). Neither 1 nor 2 reacted with oxygen abstractors such as tertiary phosphines and Si\(_2\)Cl\(_4\). Attempts to reduce 2 by cobaltocene led to recovery of the starting material.

To further investigate the substituent effect of Ar on the arylation of [OsO\(_4\)], disubstituted phenyl Grignard were used as the alkylation agents. Treatment of [OsO\(_4\)] with 7 equiv of 2,5-dimethylphenylmagnesium bromide (C\(_6\)H\(_5\)MgBr) in Et\(_2\)O afforded purple [Os(C\(_6\)H\(_5\))\(_2\)] (3) (33%) and orange [OsO(C\(_6\)H\(_5\))\(_4\)] (4) (4%), which were separated by column chromatography. On the other hand, reaction of [OsO\(_4\)] with 4-methoxy-2-methylphenylmagnesium bromide (C\(_6\)H\(_4\)OMgBr) in Et\(_2\)O gave the oxo-Os(VI) compound [OsO(C\(_6\)H\(_4\))\(_2\)] (5) as the sole isolable product in 20% yield. Complexes 3–5 are soluble in common organic solvents including hexanes, ether, and methanol. They are air-stable in solution and could be chromatographed in air without decomposition. It appears that the presence of the 5-methyl substituent in the aryl group enhances the production of Os(IV) tetraaryl while the 4-methoxy substituent favors oxo-Os(VI) formation although the origin of such a substituent effect is not well understood. The \(^1\)H NMR spectrum of 3 shows two singlets at \(\delta\) 2.22 and 2.27 due to the ortho- and meta-methyl protons. Oxidation of 3 with [Ag(C\(_2\)F\(_5\)SO\(_4\))] afforded the osmium(V) species [Os(C\(_6\)H\(_5\))\(_2\)]\(^+\), which exhibits an isotropic EPR signal at \(g = 2.04\) at \(-120^\circ\) C. A similar \(g\) value was found for the structurally characterized osmium(V) complex [Os(C\(_6\)H\(_5\))\(_3\)][CF\(_3\)SO\(_4\)] (3b, 9). Treatment of 3 with single-oxygen donors such as 3-chloroperoxybenzoic acid and \(t\)-BuOOH gave 4 in good yield. Figure 1 shows a spectral trace for the reaction of 3 with \(t\)-BuOOH in CH\(_2\)Cl\(_2\). Upon addition of ca. 1 equiv of \(t\)-BuOOH, the d-d bands for 3 centered at 447, 579, and 662 nm disappeared and concomitantly an absorption at 352 nm attributable to the charge transfer band for 4 appeared. The observation of isobestic points at ca. 325 and 420 nm suggests that the oxo transfer from \(t\)-BuOOH to 3 is a clean, single-step process. The charge transfer band for methoxy-substituted 5 (385 nm) was found at a longer wavelength relative to those for 4 (352 nm) and 1 (350 nm). The \(^1\)H NMR spectrum of 4 shows two singlets at \(\delta\) 1.99 and 2.25 due to the meta- and ortho-methyl protons while the methyl and methoxy proton signals for 5 were observed at \(\delta\) 2.28 and 3.76, respectively. The IR Os—O stretching frequencies for 4 and 5 (982 and 986 cm\(^{-1}\), respectively) are comparable to that for 1.

Crystal structures

Complexes 1 and 4 have been unambiguously characterized by X-ray crystallography. The corresponding molecular structures with selected bond lengths and angles are shown in Figs. 2 and 3. Complex 1 is isostructural with the previously reported Re(VI) analogue [ReO(C\(_2\)H\(_5\))\(_4\)], which also exhibits a fourfold molecular symmetry (10). The geometry around osmium in 1 and 4 is pseudo-square pyramidal with the o xo ligand occupying the apical position. The Os atoms are situated above the C4 plane with the O-Os-C angles of 110.4(4) and 110.82(12)° for 1 and 4, respectively. (cf. Can. J. Chem. Vol. 79, 2001

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Fig. 2. Molecular structure of [OsO(C₂H₅)₃] (1). Selected bond lengths and angles are: Os(1)—O(1) 1.652(2) and Os(1)—C(1) 2.084(1) Å; O(1)-Os(1)-C(1) 110.04(4), C(1)-Os(1)-C(1*) 82.59(3), and C(1)-Os(1)-C(1*) 137.91(8)*.

Fig. 3. Molecular structure of [OsO(C₄H₇)₃] (4). Selected bond lengths and angles are: Os(1)—O(1) 1.688(7) and Os(1)—C(1) 2.088(4) Å; O(1)-Os(1)-C(1) 110.82(12), C(1)-Os(1)-C(1B) 82.74(8), and C(1)-Os(1)-C(1A) 138.4(2)*.

Fig. 4. Cyclic voltammogram of [OsO(C₄H₇)₃] (4) in CH₂Cl₂ at a glassy carbon electrode. Scan rate = 100 mV s⁻¹.

Electrochemistry
The formal potentials for the osmium aryl complexes have been determined by cyclic voltammetry in CH₂Cl₂. The tetraaryl complex 3 exhibits reversible couples at 0.24 and −1.48 V vs. Cp₂Fe⁴⁺, which are assigned to the metal-centered Os(V/IV) and Os(IV/III) couples, respectively. The E₁/₂ ([Os(V/IV)]) for 3 is less anodic than that for [Os(C₆H₅)₃] (0.33 V) due to inductive effect of meta-methyl substituents in the aryl groups. The cyclic voltammogram of 4 (Fig. 4) shows a reversible reduction couple at −1.35 V, which is assigned to the Os(VI/V) couple. Similarly, the Os(VI/V) couples for 1 and 5 were observed at −1.41 and −1.37 V, respectively. An irreversible oxidation wave at 0.93 V, which is tentatively assigned to the Os(VII/VI) oxidation, was also found for 5. For comparison, the Os(VI/V) couple for [Os(O)₂(CH₃SiMe₃)₃] was observed at 1.19 V vs. Ag/AgCl (5b). The dioxo-osmium(VI) complex 2 exhibits the Os(VI/V) couple at −1.14 V, which is similar to that for [OsO₂(mes)₂] (−1.28 V) (4b). In general, the E₁/₂ ([Os(VI/V)]) of [OsO(aryl)₃] are more negative than those for [OsO₂(aryl)₂], indicating that the σ-aryl is very strong donor ligands.

Conclusions
In summary, we found that depending on the nature of aryl ligand, reaction of [OsO₄] with aryl magnesium bromide produced a mixture of osmium(IV) tetraaryl, oxo(tetraaryl)osmium(VI), and dioxo(diaryl)osmium(VI) complexes, which could be separated by column chromatography. It appears that the presence of the 5-methyl substituent in the aryl ligand enhances the formation of Os(IV) tetraaryl while the 4-methoxy substituent favors the formation of [OsO(aryl)₃]. Oxidation of [Os(C₆H₅)₃] with 3-chloroperoxybenzoic acid gave [OsO(C₆H₅)₃] in good yield. The oxo(tetraaryl)osmium(VI) complexes exhibit reversible Os(V/IV) couples at ca. −1.4 V while the Os(V/IV) couples for dioxo(diaryl)osmium(VI) occur at ca. −1.1 V vs. Cp₂Fe⁴⁺.

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References