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Partially Fluorinated Oxo-alkoxide Tungsten (VI) Complexes as Precursors for Deposition of WO$_x$ Nanomaterials$^\dagger$

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The partially fluorinated oxo-alkoxide tungsten (VI) complexes WO(OR)$_4$ [4; $R = C(CH_3)CF_3$, 5; $R = C(CH_3)(CF_3)_2$] have been synthesized as precursors for chemical vapour deposition (CVD) of WO$_x$ nanocrystalline material. Complexes 4 and 5 were prepared by salt metathesis between sodium salts of the fluoroalkoxides and WOCl$_4$. Crystallographic structure analysis allows comparison of the bonding in 4 and 5 as the fluorine content of the fluoroalkoxide ligands is varied. Screening of 5 as a CVD precursor by mass spectrometry and thermogravimetric analysis was followed by deposition of WO$_x$ nanorods.

Introduction

Tungsten oxide nanostructured materials have been studied for several applications, including gas sensing devices$^{1-3}$ and anodic charge injection layers for dye-sensitized solar cells (DSSCs).$^2, 4-6$ The interest in WO$_x$ nanomaterials for these applications is due to its strong and selective response to infrared (IR) light. Compared to the commonly used TiO$_2$, which responds to ultraviolet radiation (UV), the IR absorption by WO$_x$ nanocrystals provides better band gap matching with numerous low lying LUMO infrared absorbing organic dyes used in DSSCs.$^5$ Additional investigations have demonstrated that the photo-responses of WO$_x$ nanotubes are modified by absorption/desorption of small molecules, which facilitates use of this material in sensors.$^1, 2, 6$ In either application, it is observed that an increase in surface area-to-volume ratio of the WO$_x$ nanocrystals leads to significantly improved photosensitivity.$^5$ It is noted that the stoichiometry and crystalline phase is critical in determining the properties of the material.$^7, 8$

CVD has been employed for conformal and large surface area growth of WO$_x$ films$^9-11$ and with appropriate precursors and deposition conditions can enable growth of nanocrystalline materials under moderate reaction conditions. In addition to the possibility of controlling the properties of CVD materials through the structure and decomposition chemistry of precursors,$^{12-22}$ aerosol-assisted chemical vapour deposition (AACVD)$^{23-25}$ can be carried out in flexible reaction environments that are operated in a range of temperatures and pressures. With a higher mass transport rate of the precursor, the AACVD deposition rate could be several orders of magnitude higher than in CVD methods that rely on precursor volatilization or other techniques that have been used to synthesize WO$_x$.$^2, 3, 6, 7$

Tungsten oxide nanostructures can be prepared by CVD from the volatile carbonyl complex W(CO)$_6$, but a carbon...
nanotube template or a co-reactant was required. ACoVD of WO₃ nanorods from W(OPh)₆⁵,⁷ and W(CO)₆⁸ has also been reported. In addition, tungsten oxo complexes with ancillary aminoalkoxide ligands have been used to prepare WO₃ needles by hydrolysis but water is not compatible with some applications.⁹

Given the limited range of established precursors for WO₃ nanostructures, we sought to prepare molecular single source precursors that could be suitable for both conventional CVD and AACVD. Good candidates would possess adequate volatility and reactivity to enable oxide growth by CVD at moderate temperature, while being sufficiently soluble and stable in suitable solvents for AACVD. Incorporation of trifluoromethyl groups into sterically bulky alkoxide and beta-diketonate ligands of CVD precursors has been known to impart sufficient volatility.³²⁻³⁵ The partially fluorinated alkoxide precursor WO(OCH₂CF₃)₄ has been reported for atmospheric pressure CVD growth of WO₃, but the synthesis was described as problematic and the depositions produced films, in contrast to the nanorod growth reported here. The potential precursor compound WO[OC(CH₃)₂CF₃]₄ (4) was first mentioned as a decomposition product during cross-metathesis reactions of the corresponding tungsten alkylidyne and nitriles.³⁷ We now report an improved synthesis of 4 along with synthesis and characterization of the related volatile complex WO[OC(CF₃)₂CH₂]₄ (5). Aerosol assisted chemical vapour deposition (AACVD) from 5 results in WO₃ nanorod growth.

Experimental Details

General Procedures. All reactions were carried out under an atmosphere of dry nitrogen using either glovebox or standard Schlenk techniques. All chemicals used were of reagent grade. Methylene chloride, diethyl ether, hexane and toluene from Fisher Scientific were distilled and stored over reagent grade. Methylene chloride, diethyl ether, hexane and toluene were distilled and stored over 4 Å molecular sieves (4 Å) for at least 48 h prior to experiments. The orange colour of WOCl₄ was immediately turned bluish-grey to yellowish-brown after addition of the two starting materials. The reaction was run at room temperature for 12 h to yield a yellow-brown gummy residue. The residue was dissolved and stirred in hexane, the solvent was removed and the residue left under vacuum overnight. The light brown powder was sublimed between 85-90 °C (400 mTorr) to yield 0.54 g of a yellowish-white sublimate (52%). The compound was identified by comparison to literature data.³⁷ Single crystals suitable for X-ray structure determination were grown from toluene at -3 °C.

Synthesis of WO[OC(CF₃)₂CH₂]₄ (5). All reaction protocols were the same as for 4 above, starting with NaOC(CF₃)₂CH₂ (5.85 mmol, 1.19 g) dissolved in 20 mL DME and WOCl₄ (1.46 mmol, 0.500 g) dissolved in 10 mL DME. The orange colour of WOCl₄ immediately turned bluish, then pale yellow after addition. The reaction was run at room temperature for 12 h to yield a yellow-brown gummy solid, which was sublimed between 75 and 80 °C (400 mTorr) to yield a pale yellowish-white sublimate (0.57 g, 48%). H NMR (CD₂Cl₂, 25 °C): δ 1.52 (s, CH₂). ¹³C NMR (CD₂Cl₂, 25 °C): δ 123.75 (q, CF₃, J_C-H = 287.9 Hz), 87.06 (septet, C(CF₃)₂CH₂, J_C-F = 32.3 Hz), 15.76 (s, CH₃). ¹⁹F NMR (CD₂Cl₂, 25 °C): δ -76.25 (s, C(CF₃)₂CH₂). Anal. calcd for WO₅C₁₆H₁₂F₂₄: C, 20.78; H, 1.30. Found: C, 20.74; H, 1.44%. Crystals suitable for X-ray structure determination were grown by cooling a sample dissolved in a solvent mixture of toluene and DMSO to -3 °C.

Crystallographic Structure Determination of 4 and 5. X-Ray intensity data were collected at 100 K; 4 on a Bruker DUO diffractometer and 5 on a Bruker SMART diffractometer both using MoKα radiation (λ = 0.71073 Å) and an APEXII CCD area detector. Raw data frames were read by the program SAINT and integrated using 3D profiling algorithms. The resulting data were reduced to produce hkl reflections and their intensities and estimated standard deviations. The data were corrected for Lorentz and polarization effects and numerical absorption...
corrections were applied based on indexed and measured faces. The structure for 4 was solved and refined in SHELXTL6.1, using full-matrix least-squares refinement. The non-H atoms were refined with anisotropic thermal parameters and all of the H atoms were calculated in idealized positions and refined riding on their parent atoms. The complex 4 is located on a 2-fold rotational axis thus a half exists in the asymmetric unit. In the final cycle of refinement of 4, 2652 reflections (of which 2517 are observed with I > 2σ(I)) were used to refine 159 parameters and the resulting R, wR2 and S (goodness of fit) were 2.02%, 4.32% and 1.040, respectively. The structure for 5 was solved and refined in SHELXTL2013. In the final cycle of refinement of 5, 93014 reflections (of which 6573 are observed with I > 2σ(I)) were used to refine 457 parameters and the resulting R, wR2 and S (goodness of fit) were 2.23%, 5.82% and 1.081, respectively. The refinement was carried out by minimizing the wR2 function using F2 rather than F values. R1 is calculated to provide a reference to the conventional R value but its function is not minimized. The toluene molecules encountered in 5 were disordered and could not be modelled properly, thus the program SQUEEZE, a part of the PLATON package of crystallographic software, was used to calculate the solvent disorder area and remove its contribution to the overall intensity data.

Growth of WO4 nanorods. Compound 5 was tested using a custom Aerosol-Assisted Chemical Vapour Deposition (AACVD) reactor. The solid precursor was dissolved in anhydrous diglyme at a concentration of 0.034 M and pumped into a nebulizer at a rate of 4 mL/h. Nitrogen (99.999% purity, 1000 sccm) was used as carrier gas and the reaction chamber pressure was maintained at 350 Torr. Indium Tin Oxide (ITO, 150 nm) coated borosilicate glass substrates were placed on a graphite susceptor and heated to 450 or 550 °C by a radio frequency (RF) induction heat generator. The reaction time was 150 min.

Characterization of WO4 nanorods. X-Ray photoelectron spectroscopy (XPS, Perkin Elmer PHI5100, PHI Versaprobe II), field emission scanning electron microscopy (FESEM, FEI Nova Nano 430), secondary ion mass spectrometry (ION TOF IV, ION TOF Inc., Chestnut Hill NY) and X-ray diffraction (XRD, Panalytical X’pert Pro) were used to identify the composition, thickness, morphology, and film crystallinity. The PHI5100 XPS used a non-monochromatized aluminum Ka X-ray source (hv = 1486.6 eV). XPS depth profiles and high resolution XPS were obtained using a monochromatic Al Ka X-ray source and charge neutralization employed (electron and Ar+ ions). Depth profiles were obtained using a 1 keV Ar+ ion beam. Static TOF SIMS data were obtained using a 25 keV Bi+ primary ion beam and electron beam charge neutralization. SIMS data were acquired before and after sputtering the samples with a dc Bi+ ion beam for 30s.

Results and Discussion

Precursor Design. A key strategy in mechanism-based precursor design for AACVD utilization is selection of ligands to fine tune electronic and steric properties of the complexes to induce sufficient solubility in a suitable solvent. Dual use in conventional CVD requires consideration of volatility as well. The neutral monomeric metal complexes of fluoroalkoxides are known to display better solvent solubilisation and higher volatilities than the oligomers that are often encountered in conventional metal alkoxide precursors. These effects can be attributed to Coulombic repulsive interactions caused by high electron density in the vicinity of the fluorides. Moreover, fluoroalkoxides are much bulkier than their hydrocarbon equivalents, and are thus able to effectively shield empty coordination sites and prevent oligomerization. The net effect is expected to be formation of monomeric complexes with sufficient solubility for AACVD applicability and volatility for conventional CVD. Another benefit that could be derived from fluoroalkoxide ligands is the increased acidity of the hydroxyl protons of their corresponding alcohols. For instance, (CH3)2COH has a pKa of approximately 9.0, which could be exploited to simplify the synthetic process through more favourable alcohol exchange or simple salt metathesis.

Synthesis. The synthetic route to 4 and 5 (Scheme 1) parallels a general salt metathesis method previously used by Schrock to isolate a similar compound. Addition of DME solutions of the sodium alkoxide salts 2 and 3 to suspensions of 1 in DME was carried out dropwise over 30 min at 0 °C. A series of colour changes observed during slow addition of the two starting materials signified sequential substitution at the tungsten. The brown gummy residues formed upon removal of volatiles from reaction mixtures were purified by sublimation. Complex 4 sublimed between 85 and 90 °C (400 mTorr) as a yellowish-white solid with an average yield of 52%, while complex 5 sublimed between 75 and 80 °C (400 mTorr) as a moist
yellowish solid with an average yield of 48%. Precursors 4 and 5 exhibit good solubility in organic solvents, especially in ethers (diethyl ether, THF, monoglyme, diglyme) in which their solubility is more than five-fold higher than the 0.01-0.02 M concentrations that are commonly utilized in AACVD.28, 49

NMR Characterization of 4 and 5. The $^1$H NMR and $^{19}$F NMR spectra of precursors 4$^{37}$ and 5 are consistent with the symmetry equivalence of the hydrogen and the fluorine substituents on the tert-butoxide ligands. The methyl groups of 4 and 5 give rise to singlets in the $^1$H NMR spectra, which exhibit no coupling to the fluorine atoms four bonds away. This is consistent with the $^{19}$F NMR spectra, which show singlet peaks for the CF$_3$ groups. In the $^{13}$C NMR spectra, $^1$C-$^{19}$F coupling is observed for the CF$_3$ carbons ($^1$J$_{CF}$ ≈ 285.6 Hz) and the tertiary carbons ($^3$J$_{CF}$ ≈ 29.9 Hz) of 4, whereas these were $^1$J$_{CF}$ ≈ 287.9 Hz and $^3$J$_{CF}$ ≈ 32.3 Hz, respectively in 5.

X-Ray Crystal Structures of 4 and 5. Single crystals suitable for X-ray diffraction were grown for compounds 4 and 5, and their geometries were determined to be monomeric in the solid state (Figures 1 and 2, Table 1). The coordination geometry of complex 4 was the expected square pyramidal geometry about the tungsten centre (Figure 1). The oxo ligand occupies the apical position with the four trifluorotertbutoxide ligands coordinating equatorially, and bent just slightly below the plane of the W(VI) to complete the square pyramid. The W–O bond distance for the terminal oxo ligand of 4 is 1.700(3) Å (Table 2), which is within the range found for similar tungsten complexes with terminal oxo ligands,50, 51 and is suggestive of multiple bonding. In oxoalkoxide compounds such as 4 and 5, competition from the equatorial alkoxides for the π-orbitals of the metal50, 52 lowers the W–O(oxo) bond order from its maximum value of three.51, 53 The slightly longer W–O terminal bond distance for 4 with respect to the 1.684(4) Å for its precursor WOCl$_4$54 (1) can be attributed to weaker π-bonding capability of the chlorides as compared to the trifluorotertbutoxide ligands in compound 4.

The molecular geometry of compound 5 determined by X-ray crystallography shows similarities to that of compound 4; however, 5 exhibits pseudo-octahedral geometry at the tungsten centre due to coordination of DMSO from the crystallization solvent trans to the oxo ligand (Figure 2). The bond angles between the equatorial ligands increase slightly in compound 5, approaching 90° as a result of the coordinated DMSO and the increased steric bulk in the equatorial ligands of 5. Moreover, there is slight increase in the W–O(alkoxide) bond distances with the increased fluorination of 5, which decreases π-donation from the coordinated fluoroalkoxide. The decreased π-donation from the hexafluorotertbutoxide in 5 is compensated by strong donation from the apical oxo ligand, as evidenced by the shorter W–O(oxo) bond distances of 1.690(3) Å in 5 as compared with 1.700(3) Å in 4 (Table 2).
Independent reflections
by residual masses of 13.6 and 14.2% for between 150 and 250 ºC through thermal vaporization precursors for CVD. The TGA/DTA traces of both complexes (TGA) and the differential thermal (DTA) analyses of (Table S†1). However, there is slight decomposition shown more readily in the low temperature range (<200 °C). The TGA traces of both complexes show substantial mass loss Table 1

<table>
<thead>
<tr>
<th>Identification code</th>
<th>4</th>
<th>5</th>
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<tr>
<td>Formula</td>
<td>C₆H₄F₂O₫W</td>
<td>C₆H₄F₂O₆W</td>
</tr>
<tr>
<td>Formula weight</td>
<td>708.20</td>
<td>1002.23</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>100(2)</td>
<td>100(2)</td>
</tr>
<tr>
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<td>Orthorhombic</td>
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<tr>
<td>Space group</td>
<td>C2/c</td>
<td>P2₁2₁2₁</td>
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<td>a(Å)</td>
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<td>10.612(3)</td>
</tr>
<tr>
<td>b(Å)</td>
<td>6.0103(6)</td>
<td>15.222(5)</td>
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<td>c(Å)</td>
<td>20.6144(19)</td>
<td>18.311(6)</td>
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<td>β(deg.)</td>
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<td>90</td>
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<td>4</td>
</tr>
<tr>
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<td>2958.0(15)</td>
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<tr>
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<td>2.251</td>
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<tr>
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<td>0.16x0.13x0.08</td>
<td>0.289x0.225x0.184</td>
</tr>
<tr>
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<td>5.121 mm⁻¹</td>
<td>4.163 mm⁻¹</td>
</tr>
<tr>
<td>Index range</td>
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<td>-13≤h≤13, -19≤k≤19, -23≤l≤23</td>
</tr>
<tr>
<td>Theta range for data coll.</td>
<td>2.13 to 27.50°</td>
<td>1.740 to 27.497°</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>2652 [R(int) = 0.0267]</td>
<td>6777 [R(int) = 0.0346]</td>
</tr>
</tbody>
</table>

Table 2: Selected Bond Distances (Å) and Angles (deg) for Compounds 4 and 5.

<table>
<thead>
<tr>
<th>Bond Parameter</th>
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<th>5</th>
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<tr>
<td>W1 – O1</td>
<td>1.700(3)</td>
<td>1.695(4)</td>
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<tr>
<td>W1 – O2</td>
<td>1.8995(18)</td>
<td>1.9274(5)</td>
</tr>
<tr>
<td>W1 – O3</td>
<td>1.8718(19)</td>
<td>1.888(5)</td>
</tr>
<tr>
<td>W1 – O2A</td>
<td>1.8995(18)</td>
<td>1.9274(5)</td>
</tr>
<tr>
<td>W1 – O3A</td>
<td>1.8718(19)</td>
<td>1.888(5)</td>
</tr>
<tr>
<td>O2 – W1 – O3</td>
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<td>86.2(2)</td>
</tr>
<tr>
<td>O3 – W1 – O2A</td>
<td>86.82(8)</td>
<td>89.3(2)</td>
</tr>
<tr>
<td>O2A – W1 – O3A</td>
<td>87.33(8)</td>
<td>89.2(2)</td>
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<tr>
<td>O3A – W1 – O2</td>
<td>86.82(8)</td>
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<tr>
<td>O1 – W1 – O2</td>
<td>98.70(6)</td>
<td>96.8(2)</td>
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<td>O1 – W1 – O3</td>
<td>109.74(7)</td>
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<td>O1 – W1 – O2A</td>
<td>98.70(6)</td>
<td>98.5(2)</td>
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<tr>
<td>O1 – W1 – O3A</td>
<td>109.74(7)</td>
<td>95.8(2)</td>
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Thermal Analysis of 4 and 5. The thermogravimetric (TGA) and the differential thermal (DTA) analyses of complexes 4 and 5 (Figure 3, Figure S-7) demonstrate similar thermal behaviour. Compound 5 volatilizes slightly more readily in the low temperature range (<200 °C). The TGA traces of both complexes show substantial mass loss between 150 and 250 °C through thermal vaporization (Table S-1). However, there is slight decomposition shown by residual masses of 13.6 and 14.2% for 4 and 5, respectively, which are constant above 300 °C. The DTA traces in Figure S-7 present large endotherms at about 105 °C and 100 °C for complexes 4 and 5, which represent the respective melting points of these compounds.

The phase changes prior to the onset of vaporization are a good indication of their volatility, which is desirable in precursors for CVD. The TGA/DTA traces of both 4 and 5 are compared to that of the starting material 1 (WOCl₄), which is also a common WO₃ deposition precursor. As compared to this material, fluorinated alkoxide derivatives of W₃O represent considerable improvement. They have cleaner evaporation as compared to their precursor 1, which predominantly undergoes thermal decomposition above 200 °C (Figure 3).
Mass Spectrometry of 4 and 5. Fragmentation patterns from mass spectrometry have been correlated with possible gas phase decomposition pathways in a CVD reactor, although it must be taken into consideration that the CVD process does not involve ionization. Selected fragments observed in the mass spectra of 4 and 5 in the positive-ion direct insertion probe chemical ionization (DIPCI) mode are summarized in Table 3.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ion</th>
<th>m/z</th>
<th>Rel. Abundance (%)</th>
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<tr>
<td>4</td>
<td>[M]+</td>
<td>708</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>[WO(OC(CH3)2CF3)2]+</td>
<td>581</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>[WO(OC(CH3)2CF2OH)H2O]+</td>
<td>489</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>[HOC(CH3)2CF3]+</td>
<td>129</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>[C(CH3)2CF3]+</td>
<td>111</td>
<td>12</td>
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<tr>
<td></td>
<td>[H2CCH2CF3]+</td>
<td>110</td>
<td>9</td>
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<tr>
<td></td>
<td>[HCCCH2CF3]+</td>
<td>109</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
<td>[M]+</td>
<td>924</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>[WOOC(OH)CF3]2]+</td>
<td>743</td>
<td>9</td>
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<td></td>
<td>[WO[OC(CF3)2OH]+]</td>
<td>579</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>[HOC4H8F8]+</td>
<td>183</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>[H2CCFCF3]+</td>
<td>164</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>[HCCFCF3]+</td>
<td>163</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>[H2C(CF3)3]</td>
<td>152</td>
<td>39</td>
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</table>

* Relative abundances were predicted by adjusting peak intensities relative to the highest peak normalized to 100%.

The molecular ions were observed only in small amounts (< 10%) for both complexes 4 and 5. The fragmentation patterns in the mass spectra provide evidence of loss of fluoroalkoxide fragments to give rise to [WO(OC(CH3)2CF3)2]+ and [WO(OC(CF3)2CH3)]+ with peaks at m/z 581 and 743 from 4 and 5, respectively. This is supported by the presence of high intensity peaks at m/z 127 and 129 corresponding to [OC(CH3)2CF3]+ and [HOC(CH3)2CF3]+ from 4 and at m/z 181 and 183 corresponding to [OC4H8F8]+ and [HOC4H8F8]+ from 5. The resulting residues undergo subsequent C–O bond cleavage, releasing fluorocarbon fragments to produce peaks for [WO(OC(CH3)2CF3)2(3OH)(H2O)]+ and [WO(OC(CF3)2CH3)2(OH)]+ at m/z 489 and 579 in compounds 4 and 5, respectively. These results are consistent with the observation of loss of isobutylene and water upon pyrolysis of M(OStBu)3 (M = Ti, Zr, Hf) complexes by Tilley. A related pathway during fragmentation of 4 and 5 would generate hydroxide ligands in the fragment ions, as well as the fluoroisobutylene ions [H2CCH2CF3]+ and [H2C2CC(CF3)2]+, which are observed as moderately intense peaks at m/z 110 and 164 in the mass spectra of 4 and 5, respectively. Under positive-ion chemical ionization conditions, the hydroxide ligands are likely to be protonated to form aquo ligands, as observed.

Apparent loss of a fluoroalkyl group to generate an oxo ligand has also been observed during the metathesis of nitriles by EtC≡W(OCH2CF3). If fragments observed in the DIPCI-MS are indicative of the gas phase decomposition of compounds 4 and 5, then successive cleavage of W–O and O–C bonds is a viable pathway for decomposition of 4 and 5 to form WOx films under CVD conditions.

Materials Characterization. The grown tungsten oxide materials have a dark-blue colour. As the deposition temperature increases the materials become non-transparent and contain more carbon impurity. The XPS of as-grown material shows 36.0, and 41.9 at% carbon contamination on surfaces of materials grown at 450, and 550 °C, respectively. Additional XPS data were collected after 10 min and 20 min of 500 eV Arion sputtering to remove surface contamination. Comparison of composition data between 10 min and 20 min sputtering shows preferred sputtering. After sputtering, more tungsten, and less oxygen and carbon were detected, however, the maximum composition difference between sputtering time difference was 4.2 at%. Data from XPS after 10 min Ar ion sputtering (Figure 4 and Table 4) clearly show the material grown by AACVD was tungsten oxide with incorporated carbon. The XPS W 4f, O 1s, and C 1s peaks were deconvoluted after Shirley baseline subtraction. The XPS multiplex survey in Figure 4 is consistent with 4f5/2 and 4f7/2 doublets of tungsten in the W6+ and W5+ oxidation states. Metallic tungsten (W) and tungsten carbide (WC) components were not observed. Carbon peak deconvolution yields signals for free carbon and carbon bonded to oxygen with BE values at 284.4 eV and 285.4 eV, respectively. The O 1s peak with a BE at 530.7 eV is correlated to WOx and a smaller peak with a BE at 531.7 eV arises from oxygen bound to carbon. Minor signals from indium and tin are attributed to exposed portions of the ITO substrates. No fluorine peaks were detected in the XPS detection limit, 1 at%, either before or after sputtering. Further, XPS depth profiles (Figure S8, Supporting Information) indicate that there is no F present throughout the deposited layer. The oxygen to tungsten ratio increases from 2.56 to 2.94 upon increasing the deposition temperature from 450 to 550 °C. These data suggest that the grown material consists mostly of substoichiometric WOx with lesser amounts of a C-O containing material, for example, amorphous carbon with chemisorbed oxygen.
Figure 4. XPS scan for the film grown from $\mathbf{5}$ at 550 °C, and multiplex survey of W 4f, O 1s, and C 1s (Inset: Dashed lines and thin solid lines are deconvoluted peaks).

TOF SIMS spectra (Figures S-9 to S-12, Supporting Information) are consistent with the XPS data. Ions of the form WO$_x$ $^\pm$, such as WO$_3$$^-$, are observed indicating that WO$_x$ has been deposited. Before and after sputtering of the surface, the intensity of the F $^-$ ion is negligible indicating that there is little, or no, incorporation of F in the deposit.

The data also suggest that there is incorporation of carbon and hydrocarbon species in the film especially in the surface region; in the spectra W$_x$C$_y$H$_z$ $^\pm$ ions, e.g. [WC$_4$H$_6$]$^-$ are observed.

As shown in the SEM images in Figure 5, the tungsten oxide deposited at 450 and 550 °C consists of whisker-type nanorod structures. It is apparent from this plan-view SEM image that the nanorod structure in the sample grown at 450 °C shows multiple bundles of several nanorods each, while growth at 550 °C produces unbundled nanorods that are considerably longer and smaller diameter. The nanorods grown at 550 °C are up to 3 µm in length and 20 to 50 nm in diameter, while the nanorods in the bundles grown at 450 °C are ~ 0.3 µm in length and 50 to 100 nm in diameter. The cross-sectional SEM images in Figure 5 show that the height of nanorods grown at 450 and 550 °C are 0.3 (±0.02) µm and 2.7 (±0.3) µm, respectively. The XRD spectra in Figure 6 indicate that materials grown at both temperatures possess the W$_{18}$O$_{49}$ monoclinic crystal structure. It was observed that the underlying ITO substrate did not recrystallize or undergo preferential texturing during material depositions. The diffraction peak at 23.5 ° 2θ corresponds to the W$_{18}$O$_{49}$ (010) plane, which indicates that the nanorods grow in the [010] direction. This is expected since the {010} planes are the close-packed planes and have the highest surface energy.$^{71-73}$

Table 4. XPS Atomic Compositional Data of Materials Grown from $\mathbf{5}$.

<table>
<thead>
<tr>
<th>Deposition Temperature (°C)</th>
<th>W (atom %)</th>
<th>O (atom %)</th>
<th>C (atom %)</th>
<th>In (atom %)</th>
<th>Sn (atom %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>23.2</td>
<td>62.7</td>
<td>11.8</td>
<td>2.1</td>
<td>0.2</td>
</tr>
<tr>
<td>550</td>
<td>19.1</td>
<td>60.8</td>
<td>17.0</td>
<td>2.9</td>
<td>0.2</td>
</tr>
</tbody>
</table>

$^a$Data were obtained after 10 min Ar ion sputtering.

Figure 5. Plan-view and cross-sectional SEM images of materials grown from $\mathbf{5}$ at (a) 450, and (b) 550 °C.

Figure 6. XRD spectra of materials grown from $\mathbf{5}$ at 450 and 550 °C.
Boettcher has reported growth of nanorod structures by vapour transport\textsuperscript{24} with the same nanorod orientation and similar morphology and stoichiometry to the structure grown using compound 5 at 550 °C (Figure 5b). Nanorod growth was attributed to the formation of oxygen-deficient planar defects nucleating and serving as preferential sites for 1D growth. Although their films were grown at higher temperature and on a reducing substrate (W-coated Si vs. ITO), a similar mechanism may be operative here. Additional studies to address the growth mechanism from 5 are planned.

**Conclusions**

We have successfully synthesized monomeric neutral oxo-fluoroalkoxide tungsten (VI) complexes $\text{WO(OR)}_4$ \textsuperscript{4} ($R = \text{C(CH}_3)_2\text{CF}_3$, 5, $R = \text{C(CF}_3)_2\text{CH}_3$) by reacting the sodium salts of the bulky fluoroalkoxide ligands with WOCl\textsubscript{4}. Sublimation of the crude products yields clean solids that can be subsequently crystallized to yield high purity products. Data from crystallographic structure determination indicate increased strength of the apical W-O bond from 4 to 5 as the donor strength of the equatorial fluoroalkoxide ligands decreases with increasing fluorine content. Pre-screening using TGA/DTA suggests both complexes are sufficiently volatile to be promising single source precursors for CVD of WO\textsubscript{3} thin films. High temperature AACVD film growth with complex 5 demonstrated growth of WO\textsubscript{3} nanorods without an oxygen-containing co-reactant.

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**Notes and references**

Graphical Abstract:

Volatile partially fluorinated tungsten (VI) oxo-alkoxides yield tungsten oxide nanorods upon chemical vapour deposition.