Synthesis of Tungsten Oxo Fluoroalkoxide Complexes $\text{WO}(\text{OR})_3\text{L}$ as Precursors for Growth of WO_x Nanomaterials by Aerosol-Assisted Chemical Vapor Deposition.

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Abstract: Partially fluorinated oxo-alkoxide tungsten complexes bearing β -diketonate or ketoesterate ligands have been synthesized and their thermal and physical properties have been evaluated for Aerosol Assisted Chemical Vapor Deposition (AACVD) of WO_x . Volatility and thermal stability of the complexes have been shown to depend on the bidentate ligand and the degree of fluorination of the alkoxides. Growth of tungsten oxide from the precursor $\text{WO}(\text{OC}(\text{CH}_3)_2\text{CF}_3)_3(\text{tbac})$ (tbac = *tert*-butyl acetoacetate) has been demonstrated. Deposits grown at temperatures from 150 to 300 °C are amorphous thin films of substoichiometric WO_x . Deposition at temperatures from 350 to 500 °C produced either polycrystalline films or crystalline nanorods of $\text{W}_{18}\text{O}_{49}$.

1. INTRODUCTION

Tungsten oxide has found a wide range of applications due to its high work function, high transparency, chemical resistivity, and low price [1-4]. Tungsten oxide materials encompass a range of stable suboxide stoichiometries such as WO_2 , $\text{WO}_{2.5}$, $\text{W}_{18}\text{O}_{49}$, and $\text{W}_{20}\text{O}_{58}$, as well as the fully oxidized WO_3 [5-8]. Along with the variable stoichiometry, tungsten oxide has also been synthesized in numerous morphologies including thin films, nanorods, nanoplates and dendrimers [9-13]. Due to the available variations in its materials properties, tungsten oxide has found successful applications within organic electronics, photovoltaics, smart windows, catalysts, pseudocapacitors, and gas sensing devices [3, 4, 14-21].

Chemical vapor deposition (CVD) remains a highly advantageous deposition process due to its capacity for large area growth of highly conformal and uniform materials that are suitable for use in industrial applications [22]. This ability to control composition and morphology has been demonstrated for the CVD of WO_x , which produces nanoplates, nanorods or amorphous

thin films,[9, 23-27] with the materials characteristics dependent on deposition temperature and precursor choice. Although conventional CVD requires precursors with sufficiently high volatility for sublimation or evaporation, the volatility requirement can be circumvented by use of Aerosol-Assisted (AA)CVD. In AACVD, solutions of the precursor are volatilized by nebulization, which can promote high material growth rates and allow for deposition at a moderate temperature [28]. In precursor choice for AACVD, the need for volatility is replaced by the requirement of solubility in an appropriate solvent [28].

Two common precursors for CVD of tungsten oxide are $W(CO)_6$ and WCl_6 [29, 30]. However, both require coreactants, which can present challenges in control over stoichiometry and prevention of premature reactions in the gas phase [31, 32]. These precursors also produce toxic or corrosive byproducts such as CO and HCl. In contrast, single source precursors can provide control over the decomposition chemistry by careful choice of the ligand set, leading to deposition temperatures that are generally lower than those used in coreactant systems [33]. Single source precursors for deposition of WO_x include tungsten alkoxide complexes [25, 27, 34-37]. However, these complexes are air- and water-sensitive, which complicates their practical use. Modification of these complexes with chelating ligands has been reported to improve their stability and a series of these $WO(OR)_3L$ complexes has been demonstrated to serve as viable precursors for AACVD of WO_x films and nanostructures [9, 36, 38]. Fluorination of ligands has been shown to increase the volatility of complexes as a result of decreased intermolecular interactions due to the repulsion produced by the fluorine atoms [39, 40]. Following this strategy, fluorinated tungsten oxo-alkoxide complexes have been used as WO_x AACVD precursors [23, 37, 41, 42]. We now report the synthesis of a series of fluorinated oxo alkoxide complexes $WO(OR)_3L$ [$R = C(CH_3)_2(CF_3)$, $C(CH_3)(CF_3)_2$] that bear the chelating β -diketonate/ketoesterate ligands acetyl acetonate (acac), dipivaloylmethanate (dpm), ethyl acetoacetate (etac) and tert-butyl pivaloyl acetate (tbac) and demonstrate the use of $WO(OC(CH_3)_2(CF_3))tbac$ as a precursor for AACVD of WO_x films and nanorods.

2. EXPERIMENTAL

2.1 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 and toluene (Fisher Scientific) were purified using an MBraun MB-SP solvent purification system and stored over activated 3Å molecular sieves for at least 48 h prior to experiments. Diethylether and tetrahydrofuran were dried using sodium/benzophenone, distilled, and stored over activated 3Å molecular sieves for at least 48 h prior to experiments. Hexamethyldisiloxane, acetylacetone (Hacac), ethyl acetoacetate (Hetac), *tert*-butyl acetoacetate (Htbac, Sigma-Aldrich), dipivaloylmethane (Hdpm, Matrix Scientific), chloroform-*d*₃ and benzene-*d*₆ (Cambridge Isotopes) were stored over 4Å molecular sieves for at least 48 h before use. WCl₆ (Sigma-Aldrich) was used as received. WOCl₄,^[43] WO(OC(CH₃)₂CF₃)₄,^[41] and WO(OC(CF₃)₂CH₃)₄^[41] were synthesized and characterized according to literature procedures. NMR spectra were recorded on a Varian Mercury 300BB (300 MHz) spectrometer using residual protons from deuterated solvents for reference. The chemical shifts were referenced to the lock signal and reported on the CFCI₃ scale for ¹⁹F NMR spectra. Elemental analyses were performed by Robertson Microlit Laboratories (Ledgewood, NJ). Mass spectrometry was conducted on a Thermo Scientific Trace GC DSQ equipped with 70 eV electron ionization (EI), direct insertion probe (DIP) using chemical ionization (CI) with methane as the reagent gas. ESI mass spectrometry was obtained using a Bruker Daltonics Impact II-Qq-TOF instrument with electrospray as the source of ionization in positive mode. The operation parameters were: gas temperature 200 °C, drying gas 4L/min, nebulizer 1.0 bar, capillary voltage 4500 V in positive mode. The parent mass was further fragmented with a collision energy of 40 eV. The samples were injected using a syringe pump at a steady flow rate of 100 µL/min.

2.2 Precursor Synthesis.

WO(OC(CH₃)₂CF₃)₃(acac) (1). In the glovebox, WO(OC(CH₃)₂CF₃)₄ (0.9153 mmol, 0.6226 g) was dissolved in diethyl ether (40 mL) and added to a Schlenk flask. Acetylacetone (Hacac) (1.1 mmol, 0.11 mL) was dissolved in diethyl ether (20 mL) and added to an addition funnel. This funnel was then attached to the Schlenk flask and placed on a Schlenk line. The WO(OC(CH₃)₂CF₃)₄ solution was chilled in an ice bath for 30 min. The acetylacetone solution was added dropwise, then the reaction flask was chilled for an additional 30 min before being allowed to stir for 18 h at room temperature. All volatiles were removed under vacuum to give a

waxy yellow liquid. The flask was placed in liquid nitrogen for 20 seconds to solidify the liquid and allowed to warm to room temperature. The crude product was sublimed at 300 mTorr at 45 °C for 18 h to afford a white solid. Yield: 0.23 g; 38 %. ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ 5.64 (s, 1H, $\text{OC}(\text{CH}_3)\text{CH}$), 2.05 (s, 3H, $\text{OC}(\text{CH}_3)\text{CH}$), 2.01 (s, 3H, $\text{OC}(\text{CH}_3)\text{CH}$), 1.61 (s, 6H, $\text{OC}(\text{CH}_3)_2\text{CF}_3$), 1.58 (s, 6H, $\text{OC}(\text{CH}_3)_2\text{CF}_3$), 1.48 (s, 6H, $\text{OC}(\text{CH}_3)_2\text{CF}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (500 MHz, CDCl_3 , 25 °C): δ 193.89 (s, $\text{OC}(\text{CH}_3)\text{CH}$), 184.57 (s, $\text{OC}(\text{CH}_3)\text{CH}$), 126.94 (q, $\text{OC}(\text{CH}_3)_2(\text{CF}_3)$, $J_{\text{C-F}} = 282.5$ Hz), 126.55 (q, $\text{OC}(\text{CH}_3)_2(\text{CF}_3)$, $J_{\text{C-F}} = 282.5$ Hz), 105.28 (s, $\text{OC}(\text{CH}_3)\text{CH}$), 85.43 (q, $\text{OC}(\text{CH}_3)_2(\text{CF}_3)$, $J_{\text{C-F}} = 30.0$ Hz), 83.17 (q, $\text{OC}(\text{CH}_3)_2(\text{CF}_3)$, $J_{\text{C-F}} = 30.0$ Hz), 27.27 (s, $\text{OC}(\text{CH}_3)\text{CH}$), 26.14 (s, $\text{OC}(\text{CH}_3)\text{CH}$), 22.56 (s, $\text{OC}(\text{CH}_3)_2(\text{CF}_3)$), 21.96 (s, $\text{OC}(\text{CH}_3)_2(\text{CF}_3)$). $^{19}\text{F}\{^{13}\text{C}\}$ NMR (282 MHz, CDCl_3 , 25 °C): δ -82.85 (s, 3F, $\text{OC}(\text{CH}_3)_2(\text{CF}_3)$), -83.07 (s, 6F, $\text{OC}(\text{CH}_3)_2(\text{CF}_3)$). Anal. Calc'd for $\text{WO}_6\text{C}_{17}\text{H}_{25}\text{F}_9$: C: 30.02; H: 3.70 %. Found: C, 30.16; H, 3.55 %.

$\text{WO}(\text{OC}(\text{CH}_3)_2\text{CF}_3)_3(\text{dpm})$ (2). Synthesis of $\text{WO}(\text{OC}(\text{CH}_3)_2\text{CF}_3)_3(\text{dpm})$ follows the same procedure as that for **1**. Starting with $\text{WO}(\text{OC}(\text{CH}_3)_2\text{CF}_3)_4$ (1.421 mmol, 1.006 g) and Hdpm (1.44 mmol, 0.30 mL), a yellow color was observed after mixing the two starting materials. Volatiles were removed to obtain a waxy yellow solid. The product was sublimed at 200-250 mTorr and 45 °C for 18 h to afford a white solid. Yield 0.29 g; 27 %. ^1H NMR (300 MHz, C_6D_6 , 25 °C): δ 5.83 (s, 1H, CH), 1.57 (m, 6H, $\text{C}(\text{CH}_3)_2\text{CF}_3$), 1.54 (m, 6H, $\text{C}(\text{CH}_3)_2\text{CF}_3$), 1.37 (m, 6H, $\text{C}(\text{CH}_3)_2\text{CF}_3$), 1.02 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.00 (s, 9H, $\text{C}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6 , 25 °C): δ 203.19 (s, $\text{OCC}(\text{CH}_3)_3\text{CH}$), 195.66 (s, $\text{OCC}(\text{CH}_3)_3\text{CH}$), 127.73 (q, $\text{OC}(\text{CH}_3)_2\text{CF}_3$, $J_{\text{C-F}} = 283.5$ Hz), 127.34 (q, $\text{OC}(\text{CH}_3)_2\text{CF}_3$, $J_{\text{C-F}} = 283.5$ Hz), 97.14 (s, CH), 85.42 (q, $\text{OC}(\text{CH}_3)_2\text{CF}_3$, $J_{\text{C-F}} = 30.0$ Hz), 83.32 (q, $\text{OC}(\text{CH}_3)_2\text{CF}_3$, $J_{\text{C-F}} = 29.25$ Hz), 41.57 (s, $\text{C}(\text{CH}_3)_3$), 40.98 (s, $\text{C}(\text{CH}_3)_3$), 28.68 (s, $\text{C}(\text{CH}_3)_3$), 27.94 (s, $\text{C}(\text{CH}_3)_3$), 23.08 (s, $\text{OC}(\text{CH}_3)_2\text{CF}_3$), 22.64 (s, $\text{OC}(\text{CH}_3)_2\text{CF}_3$), 22.24 (s, $\text{OC}(\text{CH}_3)_2\text{CF}_3$). $^{19}\text{F}\{^{13}\text{C}\}$ NMR (282 MHz, C_6D_6 , 25 °C): δ -82.56 (3F, $\text{C}(\text{CH}_3)_2\text{CF}_3$), -82.79 (6F, $\text{C}(\text{CH}_3)_2\text{CF}_3$). Anal. Calc'd for $\text{WO}_6\text{C}_{23}\text{H}_{37}\text{F}_9$: C, 36.14; H, 4.88. Found: C, 35.72; H, 4.60 %.

$\text{WO}(\text{OC}(\text{CH}_3)_2\text{CF}_3)_3(\text{etac})$ (3). Synthesis of $\text{WO}(\text{OC}(\text{CH}_3)_2\text{CF}_3)_3(\text{etac})$ follows the same procedure as that for **1**. Starting with $\text{WO}(\text{OC}(\text{CH}_3)_2\text{CF}_3)_4$ (1.648 mmol, 1.1672 g) and Hetac (1.648 mmol, 0.2145 g), a yellow color was observed after mixing the two starting materials. Volatiles were removed leaving a yellow oil. The crude product was purified via trap

to distillation at 200-250 mTorr and 40 °C for 18 h to afford a whitish-yellow liquid. The liquid was put in a freezer in the glovebox. The product solidified and remained as a yellow solid. Yield 0.8206 g; 70 %. ^1H NMR (300 MHz, C_6D_6 , 25 °C): δ 4.94 (s, 1H, CH), 3.83 (q, 2H, OCH_2CH_3 , $J_{\text{H-H}} = 6$ Hz), 1.55 (m, 6H, $\text{C}(\text{CH}_3)_2\text{CF}_3$), 1.53 (q, 6H, $\text{C}(\text{CH}_3)_2\text{CF}_3$), 1.50 (s, 3H, $\text{C}(\text{CH}_3)$), 1.39 (m, 6H, $\text{C}(\text{CH}_3)_2\text{CF}_3$), 0.88 (s, 3H, CCH_2CH_3 , $J_{\text{H-H}} = 6$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6 , 25 °C): δ 180.13 (s, $\text{OCO}(\text{CH}_2)\text{CH}$), 172.34 (s, $\text{OCC}(\text{CH}_3)\text{CH}$), 126.98 (q, $\text{OC}(\text{CH}_3)_2\text{CF}_3$, $J_{\text{C-F}} = 283.5$ Hz), 126.49 (q, $\text{OC}(\text{CH}_3)_2\text{CF}_3$, $J_{\text{C-F}} = 282.8$ Hz), 92.12 (s, CH), 84.48 (q, $\text{OC}(\text{CH}_3)_2\text{CF}_3$, $J_{\text{C-F}} = 30.0$ Hz), 82.59 (q, $\text{OC}(\text{CH}_3)_2\text{CF}_3$, $J_{\text{C-F}} = 29.25$ Hz), 61.69 (s, $\text{OCH}_2(\text{CH}_3)$), 24.36 (s, $\text{C}(\text{CH}_3)$), 21.98 (s, $\text{OC}(\text{CH}_3)_2\text{CF}_3$), 21.68 (s, $\text{OC}(\text{CH}_3)_2\text{CF}_3$), 21.51 (s, $\text{OC}(\text{CH}_3)_2\text{CF}_3$), 13.61 (s, $\text{OC}(\text{CH}_3)$). $^{19}\text{F}\{^{13}\text{C}\}$ NMR (C_6D_6 , 25 °C): -82.58 (3F, $\text{C}(\text{CH}_3)_2\text{CF}_3$), -82.72 (6F, $\text{C}(\text{CH}_3)_2\text{CF}_3$). Anal. Calcd for $\text{WO}_7\text{C}_{20}\text{H}_{34}\text{F}_9$: C, 30.44; H, 3.83. Found: C, 30.32; H, 3.70 %.

$\text{WO}(\text{OC}(\text{CH}_3)_2\text{CF}_3)_3(\text{tbac})$ (4). Synthesis of $\text{WO}(\text{OC}(\text{CH}_3)_2\text{CF}_3)_3(\text{tbac})$ follows the same procedure as that for **1**. Starting with $\text{WO}(\text{OC}(\text{CH}_3)_2\text{CF}_3)_4$ (0.878 mmol, 0.622 g) and Htbac (0.85 mmol, 0.15 mL), a yellow color was observed after mixing the two starting materials. All volatiles were removed under vacuum to give a yellow product. The product was sublimed at 300 mTorr and 45 °C for 18 h to afford a whitish-yellow solid. Yield 0.412 g, 64 %. ^1H NMR (300 MHz, C_6D_6 , 25 °C): δ 4.88 (s, 1H, CH), 1.57 (q, 6H, $\text{C}(\text{CH}_3)_2\text{CF}_3$), 1.53 (m, 6H, $\text{C}(\text{CH}_3)_2\text{CF}_3$), 1.50 (s, 3H, $\text{C}(\text{CH}_3)$), 1.37 (m, 6H, $\text{C}(\text{CH}_3)_2\text{CF}_3$), 1.33 (s, 9H, $\text{C}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , 25 °C): δ 179.71 (s, $\text{OCOC}(\text{CH}_3)_3\text{CH}$), 172.34 (s, $\text{OCC}(\text{CH}_3)\text{CH}$), 126.53 (q, $\text{OC}(\text{CH}_3)_2\text{CF}_3$, $J_{\text{C-F}} = 283.5$ Hz), 126.26 (q, $\text{OC}(\text{CH}_3)_2\text{CF}_3$, $J_{\text{C-F}} = 282.8$ Hz), 93.42 (s, CH), 84.17 (q, $\text{OC}(\text{CH}_3)_2\text{CF}_3$, $J_{\text{C-F}} = 30.0$ Hz), 83.55 (s, $\text{OC}(\text{CH}_3)_3$), 82.74 (q, $\text{OC}(\text{CH}_3)_2\text{CF}_3$, $J_{\text{C-F}} = 29.25$ Hz), 28.00 (s, $\text{C}(\text{CH}_3)_3$), 25.09 (s, $\text{C}(\text{CH}_3)$), 22.37 (s, $\text{OC}(\text{CH}_3)_2\text{CF}_3$), 21.85 (s, $\text{OC}(\text{CH}_3)_2\text{CF}_3$). $^{19}\text{F}\{^{13}\text{C}\}$ NMR (C_6D_6 , 25 °C): -82.40 (3F, $\text{C}(\text{CH}_3)_2\text{CF}_3$), -82.61 (6F, $\text{C}(\text{CH}_3)_2\text{CF}_3$). Anal. Calcd for $\text{WO}_7\text{C}_{20}\text{H}_{34}\text{F}_9$: C, 32.40; H, 4.62. Found: C, 32.54; H, 4.11 %.

$\text{WO}(\text{OC}(\text{CF}_3)_2\text{CH}_3)_3(\text{acac})$ (5). Synthesis of $\text{WO}(\text{OC}(\text{CF}_3)_2\text{CH}_3)_3(\text{acac})$ follows the same procedure as that for **1**. Starting with $\text{WO}(\text{OC}(\text{CH}_3)(\text{CF}_3)_2)_4$ (0.797 mmol, 0.736 g) and Hacac (0.9 mmol, 0.09 mL), a yellow color was observed after mixing the two starting materials. Volatiles were removed to obtain a yellow solid. The product began to sublime at room temperature at 150 mTorr. After 24 h, the sublimation temperature was raised to 45 °C to yield a

yellow solid. Yield 0.407 g; 61 %. ^1H NMR (300 MHz, C_6D_6 , 25 °C): δ 4.90 (s, 1H, CH), 1.70 (m, 3H, $\text{C}(\text{CF}_3)_2\text{CH}_3$), 1.67 (m, 6H, $\text{C}(\text{CF}_3)_2\text{CH}_3$), 1.46 (s, 3H, CH_3), 1.41 (s, 3H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , 25 °C): δ 196.15 (s, $\text{OC}(\text{CH}_3)\text{CH}$), 183.32 (s, $\text{OC}(\text{CH}_3)\text{CH}$), 122.98 (q, $\text{OC}(\text{CF}_3)_2(\text{CH}_3)$, $J_{\text{C-F}} = 286.5$ Hz), 122.90 (q, $\text{OC}(\text{CF}_3)_2(\text{CH}_3)$, $J_{\text{C-F}} = 286.5$ Hz), 122.50 (q, $\text{OC}(\text{CF}_3)_2(\text{CH}_3)$, $J_{\text{C-F}} = 286.5$ Hz), 106.93 (s, CH), 85.94 (m, $\text{OC}(\text{CF}_3)_2(\text{CH}_3)$, $J_{\text{C-F}} = 30.8$ Hz), 84.13 (m, $\text{OC}(\text{CF}_3)_2(\text{CH}_3)$, $J_{\text{C-F}} = 30.8$ Hz), 26.88 (s, $\text{C}(\text{CH}_3)$), 25.09 (s, $\text{C}(\text{CH}_3)$), 15.55 (s, $\text{OC}(\text{CF}_3)_2(\text{CH}_3)$), 15.25 (s, $\text{OC}(\text{CF}_3)_2(\text{CH}_3)$). $^{19}\text{F}\{^{13}\text{C}\}$ NMR (282 MHz, C_6D_6 , 25 °C): δ -76.88 (s, 6F, $\text{C}(\text{CF}_3)_2\text{CH}_3$), -77.09 (q, 6F, $\text{C}(\text{CF}_3)_2\text{CH}_3$, $J_{\text{F-F}} = 8.46$ Hz), -77.43 (q, 6F, $\text{C}(\text{CF}_3)_2\text{CH}_3$, $J_{\text{F-F}} = 8.46$ Hz). Anal. Calc'd for $\text{WO}_6\text{C}_{23}\text{H}_{28}\text{F}_{18}$: C, 24.25; H, 1.92. Found: C, 24.44; H, 1.68 %.

$\text{WO}(\text{OC}(\text{CF}_3)_2\text{CH}_3)_3(\text{dpm})$ (6). Synthesis of $\text{WO}(\text{OC}(\text{CF}_3)_2\text{CH}_3)_3(\text{dpm})$ follows the same procedure as that for **1**. Starting with $\text{WO}(\text{OC}(\text{CF}_3)_2\text{CH}_3)_4$ (0.797 mmol, 0.736 g) and Hacac (0.9 mmol, 0.09 mL), a yellow color was observed after mixing the two starting materials. Volatiles were removed to obtain a yellow solid. The product was sublimed at 150 mTorr and 40 °C to yield a yellow solid. Yield 0.407 g; 61 %. ^1H NMR (500 MHz, CDCl_3 , 25 °C): δ 6.19 (s, 1H, CH), 1.96 (6H, $\text{C}(\text{CH}_3)(\text{CF}_3)_2$), 1.94 (3H, $\text{C}(\text{CH}_3)(\text{CF}_3)_2$), 1.33 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.26 (s, 9H, $\text{C}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3 , 25 °C): δ 205.48 (s, $\text{OCC}(\text{CH}_3)_3\text{CH}$), 195.63 (s, $\text{OCC}(\text{CH}_3)_3\text{CH}$), 123.41 (q, $\text{OC}(\text{CF}_3)_2(\text{CH}_3)$, $J_{\text{C-F}} = 287.28$ Hz), 123.01 (q, $\text{OC}(\text{CF}_3)_2(\text{CH}_3)$, $J_{\text{C-F}} = 289.8$ Hz), 100.39 (s, CH), 86.50 (m, $\text{OC}(\text{CF}_3)_2(\text{CH}_3)$), 84.56 (m, $\text{OC}(\text{CF}_3)_2(\text{CH}_3)$, $J_{\text{C-F}} = 30.24$ Hz), 42.05 (s, $\text{C}(\text{CH}_3)_3$), 41.42 (s, $\text{C}(\text{CH}_3)_3$), 28.86 (s, $\text{C}(\text{CH}_3)_3$), 27.68 (s, $\text{C}(\text{CH}_3)_3$), 16.20 (s, $\text{OC}(\text{CF}_3)_2(\text{CH}_3)$), 15.94 (s, $\text{OC}(\text{CF}_3)_2(\text{CH}_3)$). $^{19}\text{F}\{^{13}\text{C}\}$ NMR (282 MHz, C_6D_6 , 25 °C): δ -76.70 (s, 6F, $\text{C}(\text{CF}_3)_2\text{CH}_3$), -76.94 (m, 6F, $\text{C}(\text{CF}_3)_2\text{CH}_3$, $J_{\text{F-F}} = 11.3$ Hz), -77.08 (m, 6F, $\text{C}(\text{CF}_3)_2\text{CH}_3$). Anal. Calc'd for $\text{WO}_6\text{C}_{23}\text{H}_{28}\text{F}_{18}$: C, 29.82; H, 3.05. Found: C, 29.94; H, 2.83 %.

$\text{WO}(\text{OC}(\text{CF}_3)_2\text{CH}_3)_3(\text{etac})$ (7). Synthesis of $\text{WO}(\text{OC}(\text{CF}_3)_2\text{CH}_3)_3(\text{etac})$ follows the same procedure as that for **1**. Starting with $\text{WO}(\text{OC}(\text{CH}_3)(\text{CF}_3)_2)_4$ (1.262 mmol, 1.1663 g) and Hetac (1.272 mmol, 0.1656 g), a yellow color was observed after mixing the two starting materials. Volatiles were removed to obtain a yellow liquid. The product was vacuum distilled at 200-250 mTorr and 65 °C for 18 h to afford a yellow liquid. The liquid was put in a freezer in the glovebox, whereupon it solidified. Compound **7** was obtained as a yellow solid. Yield 0.2272 g; 21 %. ^1H NMR (300 MHz, C_6D_6 , 25 °C): δ 4.84 (s, 1H, CH), 3.83 (q, 2H, OCH_2CH_3 ,

$J_{\text{H-H}} = 6$ Hz), 1.67 (m, 3H, C(CH₃)(CF₃)₂), 1.64 (m, 6H, C(CH₃)(CF₃)₂), 1.43 (s, 3H, C(CH₃)), 0.82 (s, 3H, CCH₂CH₃, $J_{\text{H-H}} = 6$ Hz). ¹³C{¹H} NMR (75 MHz, C₆D₆, 25 °C): δ 178.67 (s, OCOC(CH₂CH₃)CH), 172.50 (s, OCC(CH₃)CH), 123.40 (q, OC(CF₃)₂(CH₃), $J_{\text{C-F}} = 286.5$ Hz), 123.20 (q, OC(CF₃)₂(CH₃), $J_{\text{C-F}} = 286.5$ Hz), 122.87 (q, OC(CF₃)₂(CH₃), $J_{\text{C-F}} = 286.5$ Hz), 95.17 (s, CH), 85.77 (m, OC(CF₃)₂(CH₃), $J_{\text{C-F}} = 30.75$ Hz), 84.16 (m, OC(CF₃)₂CH₃), $J_{\text{C-F}} = 30$ Hz), 62.74 (s, OCH₂CH₃), 23.40 (s, C(CH₃)), 15.25 (s, OC(CF₃)₂(CH₃)), 15.09 (s, OC(CF₃)₂(CH₃)), 13.32 (s, OCH₂CH₃). ¹⁹F{¹³C} NMR (282 MHz, C₆D₆, 25 °C): δ -77.11 (6F, C(CF₃)₂(CH₃)), -77.20 (m, 6F, C(CF₃)₂(CH₃)), -77.22 (m, 6F, C(CF₃)₂(CH₃)). Anal. Calcd for WO₇C₂₀H₃₄F₉: C, 24.79; H, 2.08. Found: C, 24.67; H, 2.36 %.

WO(OC(CF₃)₂CH₃)₃(tbac) (8). Synthesis of WO(OC(CF₃)₂CH₃)₃(tbac) follows the same procedure as that for **1**. Starting with WO(OC(CF₃)₂CH₃)₄ (1.247 mmol, 1.152 g) and Htbac (1.3 mmol, 0.21 mL), a yellow color was observed after mixing the two starting materials. Following removal of the volatiles under vacuum, a yellow product was obtained. The yellow product was sublimed at 50 °C at 200 mTorr for 18 h to produce a yellow solid. Yield 0.573 g, 51 %. ¹H NMR (300 MHz, C₆D₆, 25 °C): δ 4.75 (s, 1H, CH), 1.70 (m, 3H, C(CF₃)₂CH₃), 1.59 (m, 6H, C(CF₃)₂CH₃), 1.41 (s, 3H, CH₃), 1.25 (s, 9H, C(CH₃)₃). ¹³C{¹H} NMR (75 MHz, CDCl₃, 25 °C): δ 177.81 (s, OCOC(CH₃)₃CH), 172.38 (s, OCC(CH₃)CH), 123.04 (q, OC(CF₃)₂(CH₃), $J_{\text{C-F}} = 288.8$ Hz), 122.82 (q, OC(CF₃)₂(CH₃), $J_{\text{C-F}} = 287.25$ Hz), 122.73 (q, OC(CF₃)₂(CH₃), $J_{\text{C-F}} = 286.5$ Hz), 96.71 (s, CH), 85.53 (s, OC(CH₃)₃), 85.28 (m, OC(CF₃)₂(CH₃), $J_{\text{C-F}} = 31.5$ Hz), 84.16 (m, OC(CF₃)₂(CH₃), $J_{\text{C-F}} = 30.8$ Hz), 27.63 (s, C(CH₃)₃), 24.15 (s, C(CH₃)), 15.80 (s, OC(CF₃)₂(CH₃)), 15.53 (s, OC(CF₃)₂(CH₃)). ¹⁹F{¹³C} NMR (282 MHz, C₆D₆, 25 °C): δ -76.71 (6F, C(CF₃)₂(CH₃)), -77.01 (m, 6F, C(CF₃)₂(CH₃)), -77.04 (m, 6F, C(CF₃)₂(CH₃)). Anal. Calcd for WO₇C₂₀H₂₅F₁₈: C, 26.60; H, 2.79. Found: C, 26.76; H, 2.21 %.

2.3 AACVD of WO_x from **4**.

Indium tin oxide (ITO, 150 nm) coated borosilicate glass and silicon with native silicon dioxide (Si/SiO₂, n-type, <100>) were cut into squares of approximately 1 cm² and cleaned in boiling acetone, methanol, and water for 3 min each. The substrates were placed on a SiC coated graphite susceptor heated by a radio frequency (RF) induction heat generator within a custom AACVD reactor and held under vacuum for 18 hours. The down-flow vertical impinging jet reactor has been detailed previously [44, 45]. Compound **4** was dissolved in anhydrous diglyme

at a concentration of 0.034 M, loaded into a Hamilton 10 mL gastight syringe and pumped into the nebulizer, vibrating at 1.44MHz, at a rate of 4 mL h⁻¹. High purity nitrogen (99.999% purity, 1000 sccm) was used as a carrier gas and the reactor pressure was maintained at 350 Torr. The reaction time was 150 min.

2.4 Materials Characterization

The elemental composition of the deposits was determined by X-ray photoelectron spectroscopy (XPS, ULVAC-PHI XPS). The deposits were sputtered with Ar⁺ at 2kV for 2 min. and oxygen was used as an internal standard set at 530.5 eV. CasaXPS software was used to deconvolute the XPS peaks. The Shirley base line was subtracted before peak fitting. The XPS spectra of the W 4f core level were fitted into peak doublets with parameters of spin-orbit separation ΔE_P ($4f_{5/2}$ – $4f_{7/2}$) = 2.18 eV. The intensity ratio of the W $4f_{7/2}$ and W $4f_{5/2}$ peak doublet was set to 4:3. Field emission scanning electron microscopy (FESEM, FEI Nova NanoSEM 430) was used to image the surface of the deposits. Crystallinity was measured by X-ray diffraction (XRD, Panalytical X'pert Pro).

3. RESULTS AND DISCUSSION

3.1 Precursor design

Oxygen-bound ligands such as oxo, alkoxide, β -diketonate and β -ketoesterate moieties have found use in single source precursors for the deposition of metal oxides because the pre-existing metal oxygen bonding can facilitate conversion of the precursor to the oxide material during deposition [25, 34-36]. We have previously demonstrated that oxo alkoxide complexes of the type $WO(OR)_4$ ($R = C(CH_3)_2CF_3$ and $C(CF_3)_2CH_3$) and the dioxo derivative $WO_2(OR)_2L$ ($R = C(CF_3)_2CH_3$, $L = DME$) are low temperature precursors to WO_x films and nanorods, consistent with incorporation of the terminal oxo moieties into the deposits [23, 41, 42].

Based on these results, the $WO(OR)_4$ framework was the starting point for the design of precursors for this study. Bulky alkoxide ligands were chosen to minimize the tendency of $WO(OR)_4$ complexes to dimerize and to facilitate decomposition of the alkoxide ligands by dissociation of weak C-O bonds to 3° or 2° alkyl groups [9, 46]. The bidentate β -diketonate or ketoesterate ligand was chosen to increase stability of the complex to air and moisture through

additional occupancy of the coordination sphere. We have previously compared β -ketoesterate ligands to β -diketonates in related series of precursors of the type $\text{WO}(\text{OR})_3\text{L}$ ($\text{R} = \text{Me}, \text{Et}, \text{'Pr}, \text{'Bu}$ and Np , $\text{L} = \text{acac}, \text{dpm}$ and tbac) and determined that the β -ketoesterates offer the advantage of facile fragmentation pathways involving the ester group,[38] a conclusion also reached in other studies [47].

Although the use of AACVD makes the volatility of the precursors less important than solubility for our growth experiments, we also consider volatility of the complexes to facilitate their possible use in conventional bubbler systems. In order to improve volatility, intermolecular interactions were lessened through the use of sterically bulky substituents, both in the alkoxides and in the β -diketonate/ketoesterate ligand [48]. Unsymmetrical complexes were used to decrease crystallinity, in an attempt to further increase volatility. An additional contribution to the volatility comes from fluorination of the alkoxide ligands, which has also been shown to increase the volatility of related metal complexes[39, 40, 49] by the introduction of non-bonding p electrons on fluorine, which cause repulsive interactions. The hydrophobic aspect of the fluoroalkoxides also provides an additional degree of stability for the metal center against hydrolysis [39, 40]. This further decreases the sensitivity to moisture that these complexes commonly possess. Although both fluorinated alkoxide ligands and β -diketonates/ketoesterates have been individually shown to be beneficial in single source metal oxide precursors, to our knowledge, these features have not been explored in tandem.

3.2 Synthesis

The oxo-alkoxide tungsten complexes, $\text{WO}(\text{OC}(\text{CH}_3)_2\text{CF}_3)_4$ and $\text{WO}(\text{OC}(\text{CF}_3)_2\text{CH}_3)_4$ react with one equiv of the β -diketone or β -ketoester (Hacac, Hdpm, Hetac, and Htbac) dropwise in an ice bath followed by warming to room temperature for 18 h to form the $\text{WO}(\text{OR})_3\text{L}$ complexes ($\text{R} = \text{C}(\text{CH}_3)_2\text{CF}_3, \text{C}(\text{CF}_3)_2\text{CH}_3$) as seen in Scheme 1. The byproducts formed are the fluoroalcohols which are subsequently removed under vacuum with the solvent. Compounds **1-8** were solids that could be purified by sublimation.

Scheme 1. Synthesis of compounds **1-8**.

3.3 NMR Characterization

The ¹H NMR, ¹³C NMR, and ¹⁹F NMR spectra of **1-6** are consistent with the *mer* isomers shown in Scheme 1. The ¹H NMR spectra of the trifluoro-*tert*-butoxide ligands in complexes **1-4** exhibit three distinct alkoxide signals resulting from the CH₃ groups of R¹. For the two -OR¹ ligands that are trans to each other, the methyl groups of a single alkoxide are inequivalent with each other but each has an enantiotopic methyl on the other alkoxide. The third alkoxide methyl signal is from the equivalent CH₃ groups on the unique -OR¹ ligand. The ¹⁹F NMR spectra of complexes **5-8** reflect the same symmetry relationships, resulting in three distinct peaks from the CF₃ groups of the hexafluoro-*tert*-butoxide ligands. These characteristics of the alkoxide ligand signals are also reflected in the ¹³C NMR spectra. The integrations of the ¹H NMR spectra indicate that only one β-diketonate/ketoesterate is bound to the complex.

3.4 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was utilized to examine the thermal properties of compounds **1-8**. The thermal profiles in Figures 1a and 1b suggest that the complexes that bear β-diketonate ligands (**1**, **2**, **5**, and **6**) sublime cleanly at atmospheric pressure before any

decomposition occurs. Despite the increased bulk of the β -diketonate ligands, compounds **2** and **6** appear to have a higher sublimation temperature. Compounds **3**, **4**, and **8**, which bear a β -ketoesterate ligand, appear to undergo slight decomposition concomitant with sublimation leaving residual masses of 7.60, 23.3 and 7.53 % respectively. Compounds **4** and **8**, which have a tbac ligand, undergo their initial mass drop at lower temperatures than the other complexes. Although it is not clear if the lower onset temperature reflects greater volatility or more facile decomposition (or both), these results are consistent with the *tert*-butyl substituent allowing a more accessible decomposition pathway. The residual masses from **3**, **4**, and **8** are lower than the calculated value for complete decomposition to WO_3 , which has been seen previously with the TGA of $\text{WO}(\text{O}^t\text{Bu})_3\text{tbac}$ [38]. The fluorinated complexes **1-8** exhibit different thermal properties from their non-fluorinated analogs. The thermogravimetric analyses of the related nonfluorinated series $\text{WO}(\text{OR})_3\text{L}$ ($\text{R}=\text{Me}$, Et, ^iPr , Np, $\text{L}=\text{acac}$, dpm, tbac), show significant residual masses ranging from about 18-60 % [38]. The TGA trace of $\text{WO}(\text{O}^t\text{Bu})_3\text{tbac}$ also indicates that decomposition occurs at 100 °C, while its fluorinated derivatives **4** and **8** decompose at 135 °C [50]. This further confirms that the fluorinated alkoxide ligands not only promote greater volatility compared to their non-fluorinated counterparts, but also offer a degree of stability.

Figure 1. Thermogravimetric analysis of compounds a) **1-4** and b) **5-8**

3.5 Mass Spectrometry

Ionization during mass spectrometry has been shown to correlate with the possible decomposition pathways that occur during CVD [51-54]. However, care during interpretation of the data is warranted because mass spectrometry detects ionized species while [53, 54] thermal decomposition during CVD is more likely to produce neutral fragments. Selected ions observed during direct insertion probe chemical ionization mass spectrometry (DIPCI-MS) of compounds **2-6** appear in Table 1. All four compounds give rise to an ion that can be attributed to loss of the chelating ligand from the parent complex, while loss of the alkoxide is observed for compounds **2**, **4**, and **5**. For β -ketoesterate complexes **4** and **8**, the base peak is the loss of the chelating ligand while for the β -diketonate complexes **2** and **5**, the base peak is loss of an alkoxide. This greater lability of the β -ketoesterate ligands is consistent with structural data on similar tungsten complexes in which β -diketonate ligands have shorter bonds (and thus stronger bonding) to tungsten than β -ketoesterates [38]. There is also little or no $[M-OR]^+$ peak for the β -ketoesterates **4** and **8**. This is due in part to the higher lability of the β -ketoesterate ligand and in part to the tendency of the tbac ligand to undergo cleavage of the *tert*-butyl group on the ester substituent. Loss of *tert*-butyl groups from both **4** and **8** can be seen in the intense peaks corresponding to $[M-OR-C_4H_9]^+$. This is consistent with the TGA data in which β -ketoesterates **4** and **8**, which contain *tert*-butoxides, have lower decomposition onset temperatures than **3**, which has an ethyl ester.

MO(OR) ₃ L	$[M-OR]^+$ <i>m/z</i> (%)	$[M-L]^+$ <i>m/z</i> (%)	$[M-OR-C_4H_9+H]^+$ <i>m/z</i> (%)
WO(OC(CH ₃) ₂ CF ₃) ₃ dpm (2)	673 (100)	581 (23.0)	n. o.
WO(OC(CH ₃) ₂ CF ₃) ₃ tbac (4)	611 (17.8)	581 (100)	555 (90.1)
WO(OC(CF ₃) ₂ CH ₃) ₃ acac (5)	661 (100)	743 (11.7)	n. o.
WO(OC(CF ₃) ₂ CH ₃) ₃ tbac (8)	n. o.	743 (53.00)	663 (100)

Table 1. Selected observed ions in positive ion DIPCI mass spectra of **2**, **4**, **5**, and **8**.

In order to investigate the compounds even further, complexes **1**, **4**, **5**, and **8** were analyzed using tandem ESI mass spectrometry (Table 2). The molecular ion observed during ESI-MS was either $[M+K]^+$, the adduct of the complex with potassium ion or $[M+Na]^+$, the sodium analog. These ions were isolated and further analyzed using MS/MS. For complex **5**, no fragmentation of the parent ion could be detected under these conditions. The other three complexes (**1**, **4** and **8**) produce fragments that can be identified as loss of the protonated β -

diketonate/ β -ketoesterate ligand HL and the fluorinated alkene (A_f in Table 2) derived from the alkyl fragment of an alkoxide. Loss of HL and A_f from **1**, **4**, and **8** suggests that all three complexes share features of their decomposition mechanisms. These fragments are consistent with a pathway in which a hydrogen on an alkoxide undergoes nucleophilic attack by a neighboring β -diketonate/ β -ketoesterate (Scheme 2), a step invoked in decomposition of related metal alkoxide complexes [38, 55]. The additional fragments observed for **4** and **8** suggest a decomposition pathway enabled by the *tert*-butyl acetoacetate ligand. These fragments can be identified as loss of C_4H_8 (alkene A in Table 2) with or without loss of the alcohol (HOR) corresponding to an alkoxide ligand. These fragments are consistent with the *tert*-butyl substituent on the β -ketoesterate ligand undergoing deprotonation by the adjacent ester group to produce the loss of C_4H_8 (A). The newly formed carboxylic acid could then protonate a neighboring alkoxide to form the corresponding alcohol. This mechanism is outlined in Scheme 3. In addition to the $[M-A_f-HL+H]^+$ fragment type similar to what is seen in **4** and **8**, tandem mass spectrometry of compound **1** also produced fragments that were identified as loss of ROH and A_f ($C_4H_5F_3$), loss of protonated acetoacetate ligand $[M+H-HL]^+$ (15%, not listed in Table 2), and the base peak from a more substantial fragmentation to $[WO(OH)_2(OR)]^+$.

Table 2. Selected observed ions in positive ion ESI MS/MS of M^+ for **1**, **4** and **8**.

$MO(OR)_3L$	$[M-A+K]^+$ <i>m/z</i> (%)	$[M-HOR-A+K]^+$ <i>m/z</i> (%)	$[M-A_f-HL+K]^+$ <i>m/z</i> (%)	$[M-A_f-HOR+K]^+$ <i>m/z</i> (%)	$[WO(OH)_2(OR)]^+$ <i>m/z</i> (%)
1 ^b	n. o. ^d	n. o.	471.01 (64) ^e	465.00 (29) ^f	360.99 (100)
4 ^{a,b}	721.04 (9.75)	592.99 (25.2)	508.98 (100)	n. o.	n. o.
8 ^{a,c}	882.95 (100)	700.94 (7.08)	616.92 (2.20)	n. o.	n. o.

^aA = C_4H_8 . ^b $A_f = C_4H_5F_3$. ^c $A_f = C_4H_2F_6$. ^dn. o. = not observed. ^eProton, not potassium adduct.

^fSodium, not potassium adduct.

Scheme 2. Proposed MS decomposition mechanism of compounds **1**, **4** and **8** to produce the observed ion $[\text{M}-\text{A}_f-\text{HL}+\text{K}]^+$ where $\text{A}_f = \text{C}_4\text{H}_5\text{F}_3$.

Scheme 3. Proposed MS decomposition mechanism of compounds **4** and **8** to produce observed ions $[\text{M}-\text{A}+\text{K}]^+$ and $[\text{M}-\text{HOR}-\text{A}+\text{K}]^+$ where $\text{A} = \text{C}_4\text{H}_8$.

3.6 AACVD of WO_x From **4**

Compound **4** was chosen as a precursor for deposition studies due to the previous success with low temperature deposition from its non-fluorinated analog $\text{WO}(\text{O}^t\text{Bu})_3\text{tbac}$. Diglyme solutions of precursor **4** were used to successfully deposit tungsten oxide by AACVD at deposition temperatures of 150, 200, 250, 300, 350, 400, 450, and 500 °C on both silicon <100> and ITO coated silicate substrates. The deposited films had a blue color and as the deposition temperature increased, the color of the deposits took on a darker blue color and became less transparent.

The composition of the films deposited from precursor **4** was determined by X-ray photoelectron spectroscopy (XPS). The peaks observed for tungsten, oxygen, and carbon for deposits grown from 150 to 500 °C can be seen in Figure 2a-c. The presence of fluorine was not detected in any of the deposits. The elemental fractions can be seen in Figure 3a and the O:W ratios for each deposit are shown in Figure 3b. The O:W ratio at 150 °C is 2.16, indicating a substoichiometric tungsten oxide. The O:W ratio steadily increases with increasing deposition temperature to reach a maximum ratio of 2.75. Small amounts of carbon (0-5 at. %) were detected in deposits grown at low temperature (150-350 °C), while material from higher temperature depositions (400, 450, and 500 °C), contained increasing carbon contaminations of 9, 15, and 21 at. %, respectively. The C 1s binding energies (BEs) for these samples grown at relatively high temperatures were at 284.3 ± 0.3 eV, consistent with amorphous carbon on the film surface rather than carbon bound to tungsten or oxygen [9]. Deconvolution of the W 4f peaks for the deposits grown at 250, 350, and 450 °C indicated the presence of two oxidation states with a greater preference for the higher valent W^{6+} tungsten state (59%, 78% and 87%, respectively) as temperature increases. The W 4f_{7/2} BEs for W^{6+} (35.6 ± 0.3 eV) were similar for films deposited at different temperatures. Also, the deconvoluted W 4f spectra did not contain obvious peaks for tungsten metal or tungsten carbide, consistent with the absence of peaks for tungsten-bound carbon in the C 1s XPS.

Figure 2. XPS for a) W 4f, b) O 1s, and c) C 1s peaks observed from deposits grown at temperatures 150-500 °C.

Figure 3. a) Overall W, O, and C elemental fractions derived from XPS data and b) the O:W atomic ratio variation vs. deposition temperature for deposits grown from precursor **4**.

Scanning electron microscopy was used to observe the morphology of the films grown from precursor **4** (Figure 3). The tungsten oxide samples grown from 150-300 °C show a low textured film structure with no observable features. Beginning with deposits grown at 350 °C a grain-like morphology appears, with a highly textured grain-like surface and less distinguishable unique grains observed in the deposit grown at 400 °C. The material grown at 450 °C contained nanorods and nanosheets with thicknesses of 75 – 95 nm while deposits grown at 500 °C consisted of bundled nanorods with thicknesses of 30 – 50 nm.

Figure 4. Plane view SEM images of films grown on Si <100> at a) 350, b) 400, c) 450 and d) 500 °C from precursor **4** dissolved in diglyme with N₂ carrier gas.

XRD was used to determine the crystallinity of the deposits. As seen in Figure S27 the WO_x deposits grown from 150 – 300 °C are X-ray amorphous, with only ITO reflections observed. As shown in Figure 5, deposits grown at 350 °C and above show a major diffraction peak at 23.0° 2θ that can be identified as the (010) plane for the $\text{W}_{18}\text{O}_{49}$ monoclinic crystalline phase. The $\text{W}_{18}\text{O}_{49}$ crystalline phase is a substoichiometric tungsten oxide phase that is commonly observed as nanorods [56-58]. $\text{W}_{18}\text{O}_{49}$ also has been shown to preferentially grow along [010] direction which gives rise to the nanorods formed during the higher temperature depositions. Nanosheets and polycrystalline films of $\text{W}_{18}\text{O}_{49}$ have been reported, however they are less common due to the preferential growth along the [010] direction [59, 60]. It has been suggested that high oxygen vacancies along the (010) plane of $\text{W}_{18}\text{O}_{49}$ play a role in this anisotropic growth [24, 61, 62].

Figure 5. Powder X-ray diffraction patterns of deposits grown from **4**.

4. Conclusion

Tungsten oxo complexes bearing partially fluorinated alkoxides and β -diketonate/ketoesterate ligands have been synthesized. Investigation of their thermal properties using thermogravimetric analysis indicated that complexes **1**, **2**, **5**, **6**, and **7** sublime completely before decomposition while **3**, **4**, and **8** undergo partial decomposition concomitant with sublimation. Mass spectrometry of **4** was consistent with a decomposition pathway beginning with loss of the β -ketoesterate and trifluoroisobutene ($\text{C}_4\text{H}_5\text{F}_3$) or loss of an alkoxide and isobutene (C_4H_8). Compound **4** has been used as a precursor for AACVD of WO_x . Tungsten oxide was successfully deposited at temperatures of 150–500 °C. The deposits had oxygen:tungsten ratios from 2.2 to 2.8, as determined by XPS. Significant carbon incorporation was only observed in deposits grown at 300 °C and above. Scanning electron microscopy images show thin films grown from 150–300 °C, polycrystalline films at 350 and 400 °C, and crystalline nanorods at 450 and 500 °C. Powder X-ray diffraction confirms that deposits grown at temperatures of 350 °C and above contain the crystalline phase of $\text{W}_{18}\text{O}_{49}$.

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6. Supplementary Material

Supplementary material available: ^1H , ^{13}C , and ^{19}F NMR spectra of **1–8**, XPS of fluorine 1s region for deposits grown from 150–500 °C, SEM images of deposits grown from 150 – 300 °C, and XRD patterns of materials grown from 150–300 °C.

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