Electronic Supporting Information (ESI)

Tuning the Redox Profiles of Polyoxovanadate-alkoxide Clusters via Heterometal Installation: Toward Designer Redox Reagents

Lauren E. VanGelder[†], William W. Brennessel[†], and Ellen M. Matson*[†]

[†]Department of Chemistry, University of Rochester, Rochester, New York 14627

Corresponding author email: matson@chem.rochester.edu

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Experimental Details

General Considerations.

All manipulations were carried out in the absence of water and oxygen in a UniLab MBraun inert atmosphere glovebox under a dinitrogen atmosphere. Glassware was oven dried for a minimum of 4 hrs and cooled in an evacuated antechamber prior to use in the drybox. Anhydrous methanol was purchased from Sigma-Aldrich and stored over activated 4 Å molecular sieves purchased from Fisher Scientific. All other solvents were dried and deoxygenated on a Glass Contour System (Pure Process Technology, LLC) and stored over activated 3 Å molecular sieves purchased from Fisher Scientific. $Ti(OCH_3)_4$, $Zr(O^tBu)_4$, $Hf(O^tBu)_4$, and $^tBuNBH_4$ were purchased from Sigma-Aldrich and used as received. $VO(OCH_3)_3$ was synthesized according to literature precedent.[1] Complexes **1-V_6O_7** and **2-V_5FeClO_4** were prepared according to literature procedures.[2, 3]

^1H NMR spectra were recorded at 500 on Bruker DPX-500 spectrometer locked on the signal of deuterated solvents. All chemical shifts were reported relative to the peak of residual ^1H signal in deuterated solvents. $CDCl_3$ was purchased from Cambridge Isotope Laboratories, degassed by three freeze−pump−thaw cycles, and stored over activated 4 Å molecular sieves. Infrared (FT-IR, ATR) spectra of complexes were recorded on a Shimadzu IRAffinity-1 Fourier Transform Infrared Spectrophotometer and are reported in wavenumbers (cm^{-1}). Electronic absorption measurements were recorded at room temperature in anhydrous acetonitrile in a sealed 1 cm quartz cuvette with an Agilent Cary 60 UV-Vis spectrophotometer. Mass spectrometry analyses were performed on an Advion expression^L Compact Mass Spectrometer equipped with an electrospray probe operating in negative ion mode (−ve) with an ion-trap mass analyzer. Direct injection analysis was employed in all cases with a sample solution in acetonitrile. Single crystals were mounted on the tip of a thin glass optical fiber (goniometer head) and mounted on a Bruker SMART APEX II CCD platform diffractometer for a data collection at 100.0(5) K. The structures were solved using SHELXT-2014/5[4] and refined using SHELXL-2014/7.[5] Elemental analyses were performed on a PerkinElmer 2400 Series II Analyzer, at the CENTC Elemental Analysis Facility, University of Rochester.

Cyclic Voltammograms were recorded with a CH Instruments Inc. 410c time-resolved electrochemical quartz crystal microbalance. All measurements were performed in a three electrode system cell configuration that consisted of a glassy-carbon (ø = 3.0 mm) as working electrode, a Pt wire as the counter electrode, and an Ag/AgCl wire as the reference electrode. All electrochemical measurements were performed at room temperature in a N_2-filled glovebox. A 0.1 M $^nBu_4NPF_6$ solution in dry acetonitrile was used as the electrolyte solution. All redox events were referenced against ferrocenium/ferrocene (Fc^+/Fc) redox couple.

Group IV POV-alkoxide Syntheses:

*Synthesis of [Bu_4N] [$(VO)_5O(OCH_3)_{12}TiOCH_3$] (**4-$V_5TiOCH_3$**):*

In a glovebox, $VO(OCH_3)_3$ (0.450 g, 2.812 mmol) and 10 mL MeOH were charged in a 25 mL Teflon-lined Parr reactor. [Bu_4N][BH_4] (0.146 g, 0.568 mmol) in 4 mL MeOH was added to the solution. This mixture immediately turned dark green as gas evolved. $Ti(OCH_3)_4$ (0.098 g, 0.570 mmol) was added as a solid to the reaction mixture. The Parr reactor was sealed, and the mixture heated in an oven at 100 °C for 48 hours. The Parr reactor was allowed to cool to room temperature, then returned to the glove box. A brown solution resulted, and the solvent was removed under vacuum to give a red-brown solid. This solid was washed with toluene (10 mL, 3x), and any volatiles were removed under vacuum to yield **4-V_5TiOCH_3** as a brown solid (0.493 g, 0.472 mmol, 84%). X-ray quality crystals were grown by making a supersaturated solution of the product in hot MeOH, filtering the solution, and cooling to –30 °C for 24 hours. ^1H NMR (400 MHz, $CDCl_3$) δ = 1.03, 1.36, 3.14, 3.90, 13.16, 25.02 ppm. Elemental analysis Calcd (%) (MW = 1044.48): C, 33.35; H, 7.24; N, 1.34. Found: C, 33.18; H, 6.99; N, 1.31 %.

*Synthesis of [Bu_4N] [$(VO)_5O(OCH_3)_{12}ZrOCH_3$] (**5-$V_5ZrOCH_3$**):*

In a glovebox, $VO(OCH_3)_3$ (0.450 g, 2.812 mmol) and 10 mL MeOH were charged in a 50 mL Teflon-lined Parr reactor. [Bu_4N][BH_4] (0.146 g, 0.568 mmol) in 4 mL MeOH was added to the solution. This mixture immediately turned dark green as gas evolved. $Zr(O^tBu)_4$ (0.222 mL, 0.570 mmol) was added to the reaction mixture. The Parr reactor was sealed, and the mixture heated in an oven at 100 °C for 48 hours. The Parr reactor was allowed to cool to room temperature, then returned to the glove box. A blue-green solution resulted, which was concentrated to half of its original volume and cooled to –30 °C for 24 hours. Blue-green crystals of **5-V_5ZrOCH_3** (0.293 g, 0.270 mmol, 48%) formed directly from this solution. These crystals were used for X-ray analysis. ^1H NMR (400 MHz, $CDCl_3$) δ = 1.01, 1.35, 3.20, 3.95, 13.50, 25.56 ppm. Elemental analysis Calcd (%) (MW = 1087.83): C, 32.02; H, 6.95; N, 1.29 %. Found: C, 31.73; H, 6.76; N, 1.18 %.

*Synthesis of [Bu_4N] [$(VO)_5O(OCH_3)_{12}HfOCH_3$] (**6-$V_5HfOCH_3$**)*

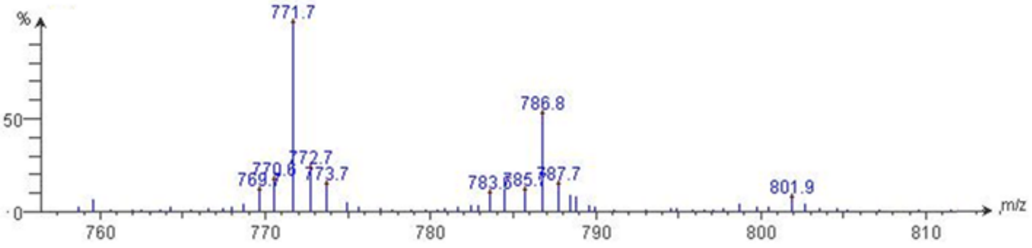
In a glovebox, $VO(OCH_3)_3$ (0.450 g, 2.812 mmol) and 10 mL MeOH were charged in a 50 mL Teflon-lined Parr reactor. [Bu_4N][BH_4] (0.146 g, 0.568 mmol) in 4 mL MeOH was added to the solution. This mixture immediately turned dark green as gas evolved. $Hf(O^tBu)_4$ (0.230 mL, 0.570 mmol) was added to the reaction mixture. The Parr reactor was sealed, and the mixture heated in an oven at 100 °C for 48 hours. The Parr reactor was allowed to cool to room temperature, then returned to the glove box. A blue-green solution resulted, which was concentrated to half of its original volume and cooled to –30 °C for 24 hours. Blue-green crystals of **6-V_5HfOCH_3** (0.237 g, 0.202 mmol, 36%) formed directly from this solution. These crystals were used for X-ray analysis. ^1H NMR (400 MHz, $CDCl_3$) δ = 1.00, 1.39, 3.24, 3.99, 13.90, 26.06 ppm. Elemental analysis Calcd (%) (MW = 1175.10): C, 29.64; H, 6.43; N, 1.19. Found: C, 29.81; H, 6.57; N, 1.21 %

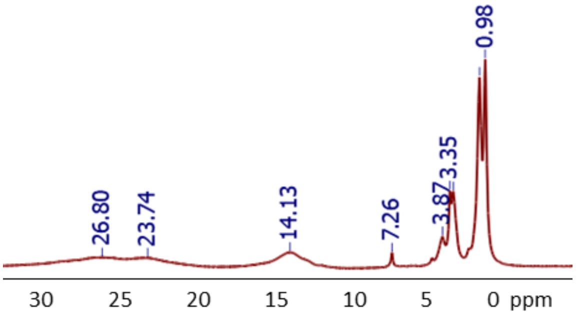
Table S1. Crystallographic parameters for molecular structures of **4-V_5TiOCH_3**, **5-V_5ZrOCH_3** and **6-V_5HfOCH_3**

Compound	**4-V_5TiOCH_3** **CCDC 1587541**	**5-V_5ZrOCH_3** **CCDC 1587540**	**6-V_5HfOCH_3** **CCDC 1587539**
Empirical formula	$C_{29}H_{75}O_{19}V_5Ti$	$C_{29}H_{75}O_{19}V_5Zr$	$C_{29}H_{75}O_{19}V_5Hf$
Formula weight	1044.50	1087.82	1075.09
Temperature / K	100.0(5)	100.0(5)	100.0(5)
Wavelength / Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_{1/c}$	$Pna2_1$	$Pna2_1$
Unit cell dimensions	a = 11.5947(17) Å b = 18.157(3) Å c = 23.178(3) Å α = 90° β = 103.2149(18)° γ = 90°	a = 21.402(2) Å b = 18.960(2) Å c = 11.5527(12) Å α = 90° β = 90° γ = 90°	a = 21.282(6) Å b = 18.958(6) Å c = 11.572(4) Å α = 90° β = 90° γ = 90°
Volume / $Å^3$	4750.3(12) $Å^3$	4687.9(8) $Å^3$	4669(2) $Å^3$
Z	4	4	4
Reflections collected	51687	134612	88214
Independent reflections	8626	15660	12086
Completeness (theta)	100.0% (25.242°)	100.0% (31.506°)	100.0% (28.700°)
Goodness-of-fit on F^2	1.009	1.020	1.044
Final R indices [I>2sigma(I)]	$R1$ = 0.0692	$R1$ = 0.0439	$R1$ = 0.0551
Largest diff. peak and hole	0.526 and -0.693 e.$Å^{-3}$	1.066 and -0.803 e.$Å^{-3}$	3.557 and -1.204 e.$Å^{-3}$

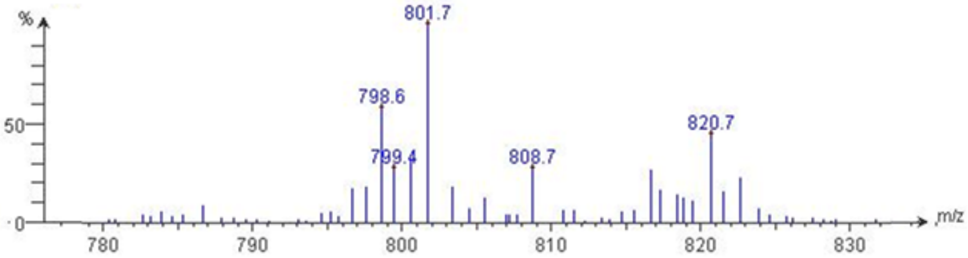
Figure S1. ESI-MS (negative mode) and 1H NMR ($CDCl_3$) of synthetic efforts to access **3-V_5TiCl**

$2\ TiCl_3(thf)_3 + 3\ VO(OCH_3)_3 \xrightarrow[MeOH]{}$





$1\ TiCl_3(thf)_3 + 5\ VO(OCH_3)_3 \xrightarrow[MeOH]{}$



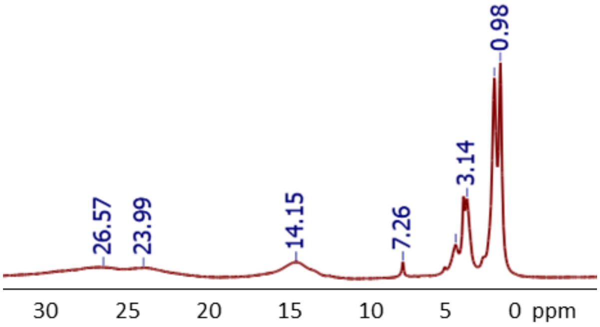


Figure S2. ESI-MS (negative mode) and 1H NMR (CD_3CN) of synthetic efforts to access **3-V_5TiCl**

$1\ TiCl_3(thf)_3 + 5\ VO(OCH_3)_3 \xrightarrow[\text{toluene}]{}$

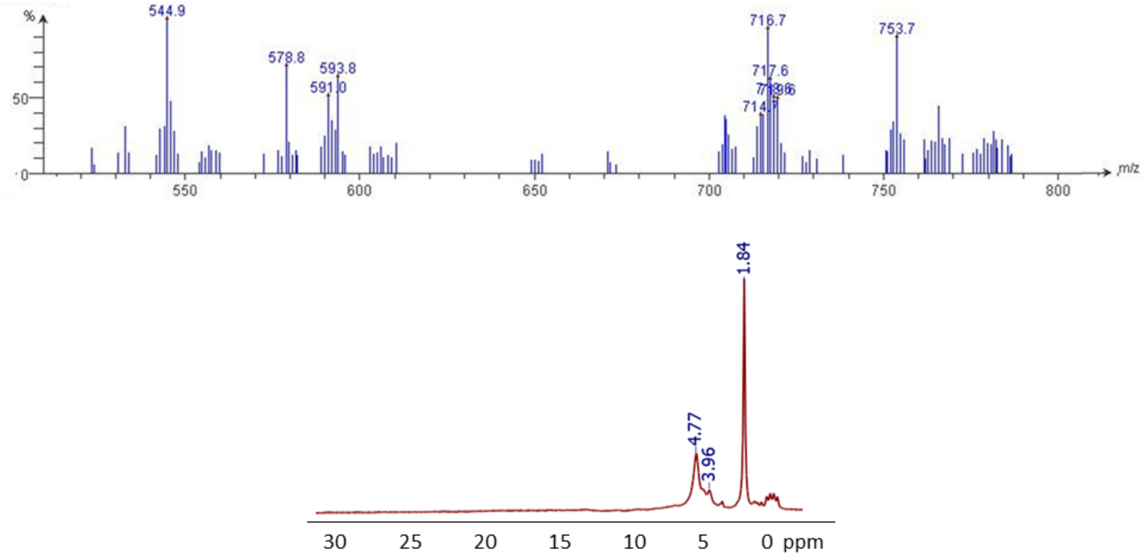


Figure S3. ESI-MS (negative mode) and 1H NMR (CD_3CN) of synthetic efforts to access **3-V_5TiCl**

$1\ TiCl_3(thf)_3 + 5\ VO(OCH_3)_3 \xrightarrow[\text{MeCN}]{}$

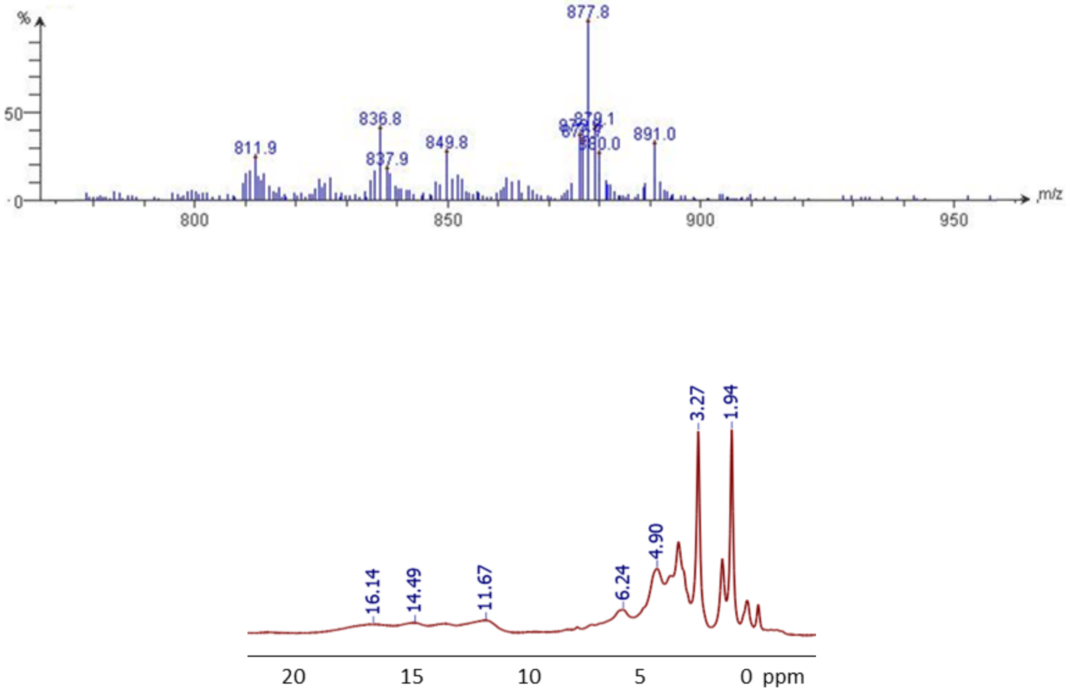


Figure S4. ESI-MS (negative mode) and 1H NMR (CD_3CN) of synthetic efforts to access **3-V_5TiCl** in toluene with $[NBu_4][BH_4]$

$1\ TiCl_3(thf)_3 + 5\ VO(OCH_3)_3 + 1\ [NBu_4][BH_4] \xrightarrow[\text{toluene}]{}$

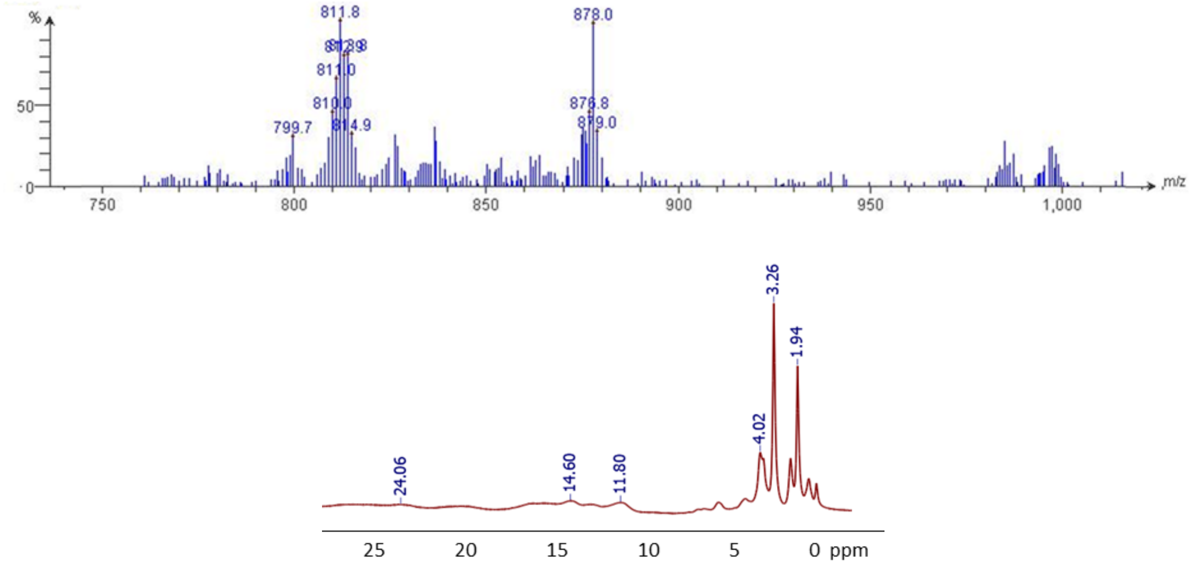


Figure S5. ESI-MS (negative mode) and 1H NMR (CD_3CN) of synthetic efforts to access **3-V_5TiCl** in MeCN with $[NBu_4][BH_4]$

$1\ TiCl_3(thf)_3 + 5\ VO(OCH_3)_3 + 1\ [NBu_4][BH_4] \xrightarrow[\text{MeCN}]{}$

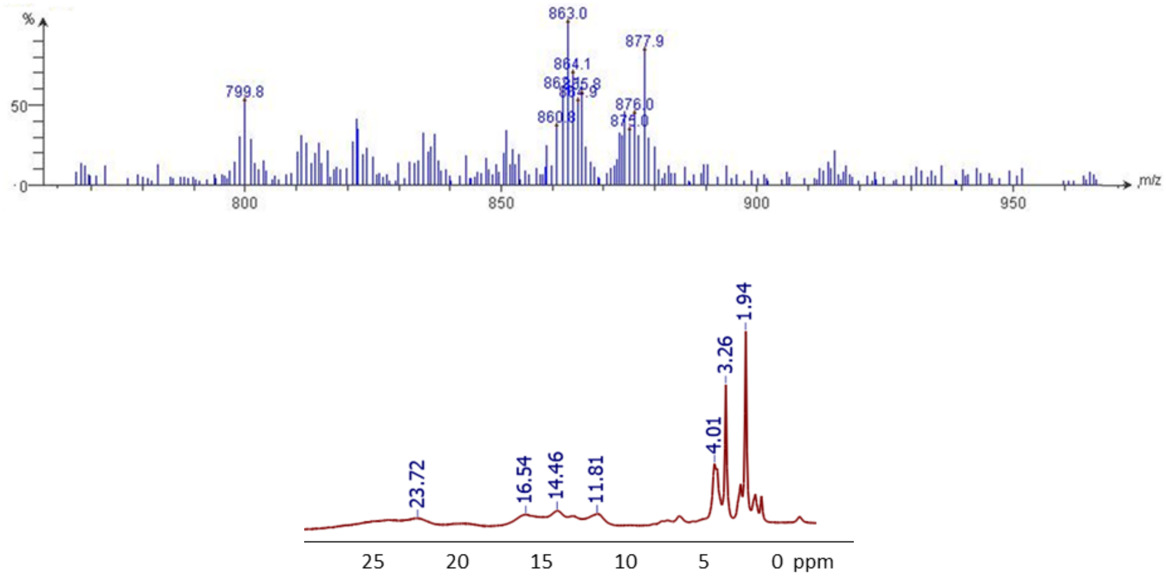


Figure S6. ESI-MS (negative mode) of **4-V_5TiOCH_3**

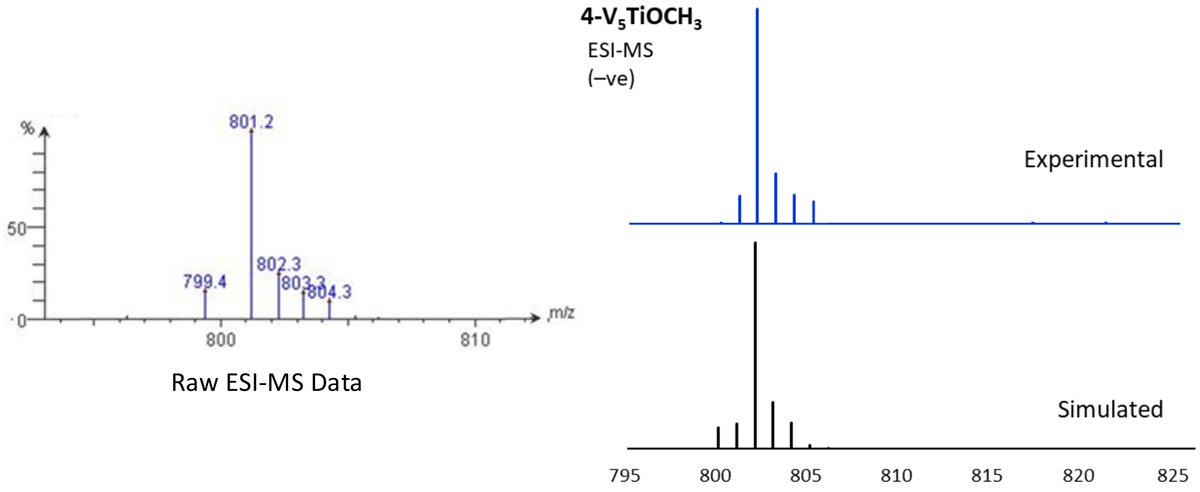


Figure S7. ^{1}H NMR of **4-V_5TiOCH_3** vs. **1-V_6O_7** in $CDCl_3$

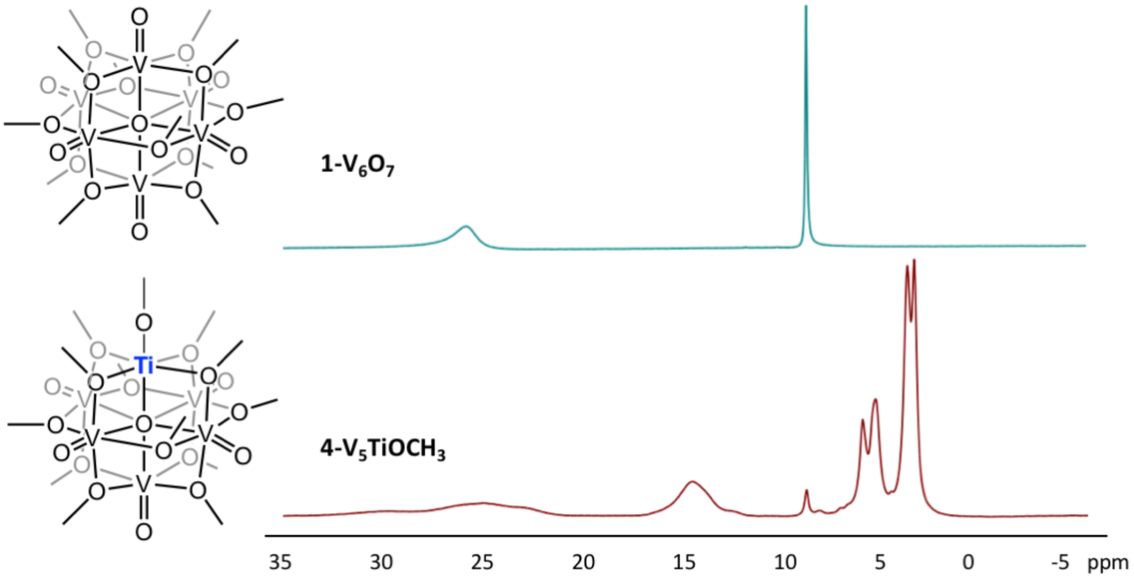


Figure S8. Full cyclic voltammogram of 1 mM **4-V_5TiOCH_3** in acetonitrile with 0.1 M $TBAPF_6$ supporting electrolyte.

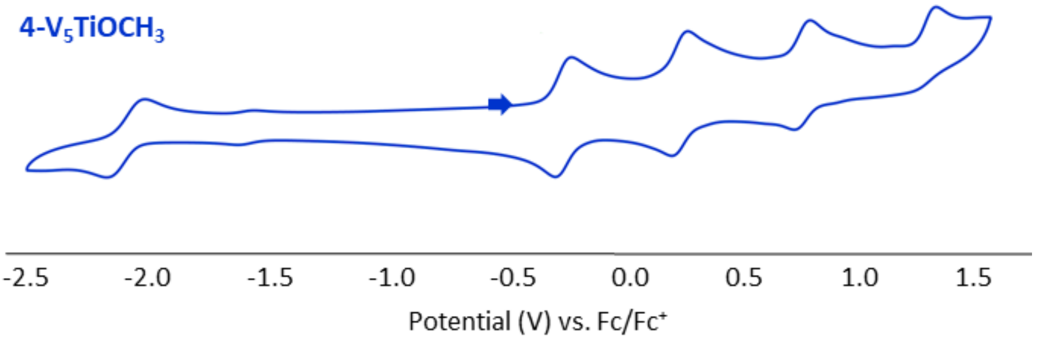
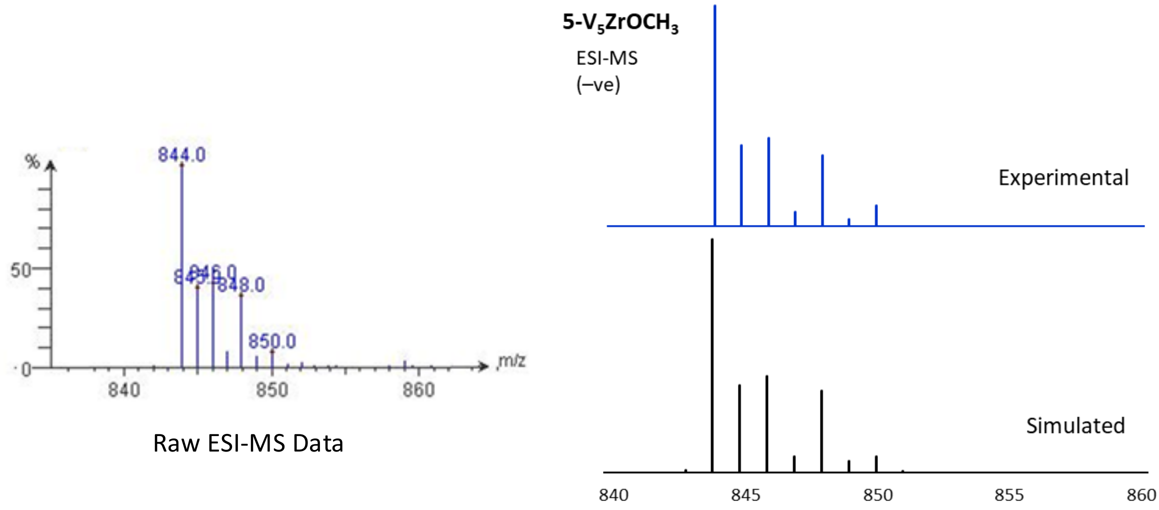


Figure S9. ESI-MS (negative mode) of **5-V_5ZrOCH_3**



Raw ESI-MS Data

Figure S10. ESI-MS (negative mode) of **6-V$_5$HfOCH$_3$**

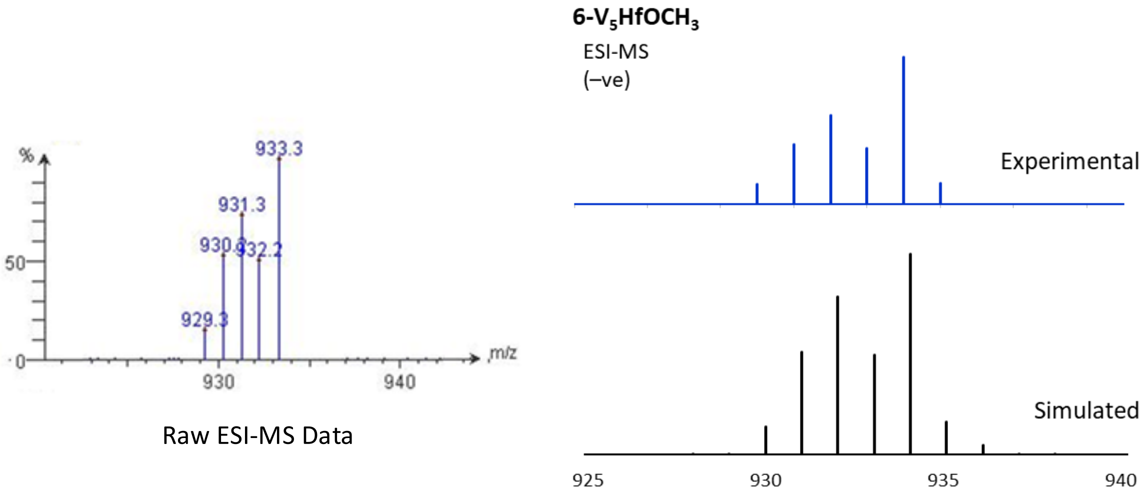


Figure S11. ^{1}H NMR of **4-V$_5$TiOCH$_3$**, **5-V$_5$ZrOCH$_3$**, and **6-V$_5$HfOCH$_3$** in CDCl$_3$.

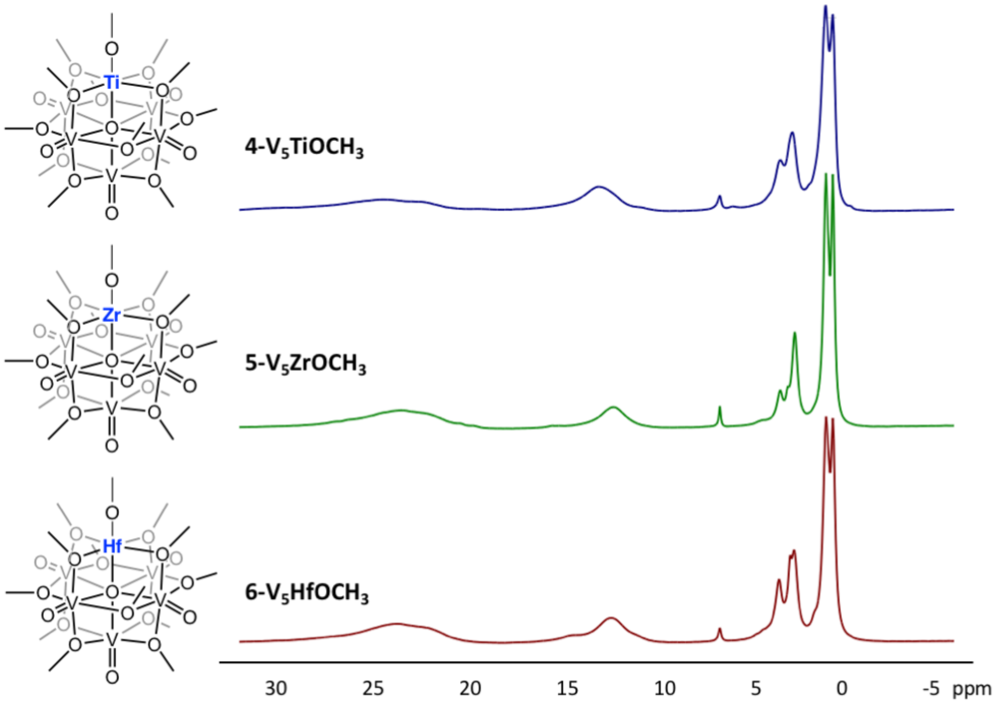
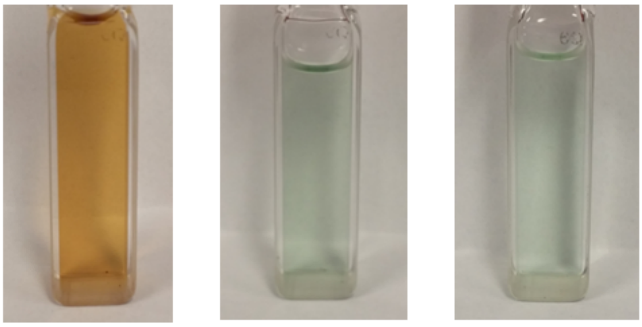
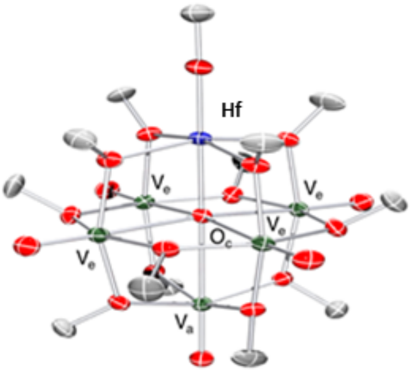


Figure S12. Solutions of complexes **4-V_5TiOCH_3**, **5-V_5ZrOCH_3**, and **6-V_5HfOCH_3** to demonstrate the color differences between 3d and 4d/5d heterometal functionalized POV-alkoxide clusters.



4-V_5TiOCH_3 **5-V_5ZrOCH_3** **5-V_5HfOCH_3**

Figure S13. Molecular structure of **6-V_5HfOCH_3** shown with 50% probability ellipsoids. Hydrogen atoms and tetrabutylammonium counter ion has been removed for clarity.



$[V_5O_6(OCH_3)_{12}HfOCH_3]$ (**6-V_5HfOCH_3**)

Table S2. Parameters of **6-V_5HfOCH_3** and **1-V_6O_7**.[2]

Bond	6-V_5HfOCH_3	1-V_6O_7
Hf-O	1.925(6) Å	--
Hf-O-C	177.8(3)°	--
Hf-O_b (avg)	2.090 Å	--
Hf-O_c	2.147(5) Å	--
V_a-O_c	2.503(6) Å	--
V_e-O_c (avg)	2.363 Å	2.305 Å
V-O_t (avg)	1.604 Å	1.601 Å

References:

1. C. Daniel and H. Hartl, *Journal of the American Chemical Society*, 2009, **131**, 5101-5114.
2. C. Daniel and H. Hartl, *Journal of the American Chemical Society*, 2005, **127**, 13978-13987.
3. F. Li, S. H. Carpenter, R. F. Higgins, M. G. Hitt, W. W. Brennessel, M. G. Ferrier, S. K. Cary, J. S. Lezama-Pacheco, J. T. Wright, B. W. Stein, M. P. Shores, M. L. Neidig, S. A. Kozimor and E. M. Matson, *Inorganic Chemistry*, 2017, **56**, 7065-7080.
4. G. M. Sheldrick, *SHELXT-2014/5*. University of Gotingen: Gotingen, Germany, 2014.
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