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Synthesis, Characterization, and Electrochemical Analyses of Vanadocene Phosph(on/in)ate Derivatives

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ABSTRACT: The synthesis and characterization of a series of new vanadocene-derived cyclic polyphosphate or diphenylphosphinate complexes, $[\text{PPN}]_2[\text{CpV}(\text{P}_4\text{O}_{12})]$ (**1**), $[\text{Cp}_2\text{VOP}(\text{O})\text{Ph}_2]$ (**2**), $[\text{CpV}(\mu^2\text{-O}_2\text{PPh}_2)_4\text{VCp}]$ (**3**), and $[\text{Cp}_2\text{V}(\mu^2\text{-O}_2\text{PPh}_2)_2\text{VCp}_2][\text{PF}_6]_2$ (**4**) is reported ($[\text{PPN}]^+$ = bis(triphenylphosphoranylidene)ammonium; Cp = η^5 -cyclopentadienyl). The complexes were synthesized from the methyl vanadocene (Cp_2VMe) precursor, through protonation of the Me or Cp linkages using the phosph(on/in)ate acid precursors, $[\text{PPN}]_2[\text{P}_4\text{O}_{12}\text{H}_2]$ (for **1**) or $\text{Ph}_2\text{P}(\text{O})\text{OH}$ (for **2** and **3**). Oxidation of **2** with $[\text{Fc}][\text{PF}_6]$ resulted in dimerization yielding the bimetallic **4** ($[\text{Fc}]^+$ = ferrocenium). Electrochemical analysis of this reaction revealed a possible ECE mechanism that includes prior and subsequent electron transfer to this dimerization. The electronic structure of the dimer **4** was probed by SQUID magnetometry and X-band EPR spectroscopy (100 K and 4 K). The dimer was found to contain two antiferromagnetically coupled V^{IV} centers, as well as a small portion of monomeric V^{IV} species, **2**⁺. In contrast to **2**, oxidation of **1** resulted in an EC mechanism, the product of which remains unknown. Preliminary reactions with compounds **1** and **2** bearing free P=O groups were performed using H-atom donors to test their ability to undergo H-atom transfer in the context of the proposed “reduction-coupled oxo activation” mechanism; however, no clear reaction pathway supporting this mechanism was yet observed.

Considerable interest lies in the structure and bonding of vanadium phosphate complexes due to their varied applications, such as in size-selective inorganic hosts, ion exchangers, and magnetic systems.¹⁻⁴ From the industrial perspective, DuPont’s “butox” process utilizes a surface vanadium phosphate oxide (VPO) catalyst for the oxidative conversion of butane to maleic anhydride (MA) on a 500 kt scale (Scheme 1a). The commodity chemical is used as a resin, a food additive, an agricultural chemical, as well as in pharmaceuticals.⁵ The conversion of butane to MA is considered one of the most complex in industry, involving the abstraction of 8 H-atoms and the insertion of 3 O-atoms, as part of an overall 14 e[−] process. As such, this process has been the subject of extensive mechanistic investigations over the decades,⁵⁻⁹ and continues to be the subject of considerable interest today.¹⁰⁻¹⁴ However, in spite of these extensive studies, no consensus mechanism yet exists as to the exact steps of this transformation.

Recent gas-phase studies by Schwarz and co-workers have described the ability of simple oxidized oxide clusters, such as $[\text{P}_4\text{O}_{10}]^{*+}$ or $[\text{V}_4\text{O}_{10}]^{*+}$, to abstract a H atom from methane or other simple hydrocarbons, through an H-atom transfer (HAT) process. It was further found that the *in*

situ-generated $[\text{P}_4\text{O}_{10}]^{*+}$ was more reactive than the metallic analog, $[\text{V}_4\text{O}_{10}]^{*+}$.¹⁵⁻¹⁶ The increased reactivity upon P-incorporation into the clusters was further demonstrated by comparison of the smaller oxide cations, $[\text{VPO}_4]^{*+}$ and $[\text{V}_2\text{O}_4]^{*+}$, wherein the former was more reactive towards HAT than the latter. These experimental conclusions were further supported by theoretical work by Goddard and co-workers who proposed that the terminal P=O linkages in VPO are responsible for C–H functionalization at butane (Scheme 1b-c). The mechanism, coined “reduction-coupled oxo activation” (ROA), occurs as a result of the strong basicity at the P=O bond coupled with the neighboring high-valent, oxidative V^{V} centers which undergoes reduction,^{10, 12} and is in many respects analogous to well-studied proton-coupled electron transfer (PCET) reactions common to both biological and artificial systems.¹⁷⁻²¹

Scheme 1. a) Partial oxidation of butane to maleic anhydride using the VPO catalyst at high temperature. b) A partial representation of the surface VPO catalyst comprised of terminal V=O and P=O bonds at the surface. c) Proposed ROA mechanism for the C-H reaction at a P=O bond. The dashed box represents the target motif used for the synthesis of the complexes in this report.

While several heterogeneous and homogeneous VPO model complexes have been synthesized in order to elucidate the reaction mechanism,^{22–31} the vast majority of these contain vanadyl (V=O) linkages hindering the ability to distinguish V=O from terminal P=O bond reactivity (Scheme 1c).^{30, 32–35} In the cases where V=O is absent, bimetallic species bridged by -OPR₂O- linkers dominate, with very few having terminal P=O bonds present.³⁶ In order to probe possible new C-H bond functionalization pathways, such as the proposed ROA mechanism, new VPO model complexes are needed containing terminal P=O linkages bound to encapsulated V centers. Herein, we report the synthesis, characterization, and electrochemical analysis of a series of vanadocene-based molecular precursors encompassing the central V-O-P=O linkage (Schemes 1c (box) and 2). Preliminary reactivity studies with H-atom donors are also described.

RESULTS AND DISCUSSION

In order to target molecular V-O-P=O linkages, we employed the known,³⁷ coordinatively saturated, and basic methylvanadocene (Cp₂VMe) complex in conjunction with phosphorus acid derivatives, such as Cummins' reported cyclic phosphoric acid ([PPN]₂[P₄O₁₂H₂])³⁸ or the commercial diphenylphosphinic acid (Ph₂P(O)OH), resulting in acid/base formation of methane and, in some cases, CpH (Scheme 2).

Scheme 2: Synthesis of 1-4.

Addition of a dichloromethane (DCM) solution of [PPN]₂[P₄O₁₂H₂] to 1 eq. of Cp₂VMe in DCM resulted in an immediate color change from black to pale blue. Monitoring this reaction in a sealed J-Young NMR tube revealed the formation of CH₄ and CpH by ¹H NMR spectroscopy (Figure S1). Removal of the volatile byproducts and purification resulted in the isolation of the salt **1** as a pale blue powder in 60% yield (Scheme 2). The structure of **1** was confirmed by single crystal X-ray diffraction (XRD) studies (Figure 1). The solid-state structure of **1** revealed a piano-stool ligand arrangement around V with the phosphate oxo groups occupying the basal tetragonal plane and the Cp capping the apical end. Bond metrics in **1** are mostly unremarkable, with the exception of slightly shortened P=O double bonds (avg. 1.453(6) Å). To the best of our knowledge, **1** is only the second example of the tetrameta-phosphate ligand binding in a κ⁴ fashion to a metal center.³⁸ The diamagnetically corrected³⁹ magnetic moment (μ_{eff}: 2.82 μ_B) was determined using the Evans method⁴⁰ and is consistent with an expected spin-only value (μ_{eff}: 2.83 μ_B) for a high-spin, S = 1 V^{III} center. The effects of this paramagnetism are seen in the ³¹P and ¹H NMR spectra displaying expected diamagnetic resonances for the cations ([PPN]⁺), and paramagnetically silent resonances for the anion ([CpV(P₄O₁₂)]²⁻).

Figure 1: Solid state molecular structure of the anion of **1**. Hydrogen atoms, [PPN]⁺ cations, and co-crystallized solvent are omitted for clarity.

Next, we targeted systems with reduced V:P ratios using the Ph₂P(O)OH acid as our P source. Addition of an equimolar slurry of Ph₂P(O)OH in DCM to a cold (-40 °C) solution of Cp₂VMe resulted in methane generation and an immediate color change from black to blue. Following workup, the pure product (**2**) was isolated in good yield (63%) and its structure confirmed by single crystal XRD studies (Scheme 2 and Figure 2). The structure of **2** reveals a bent Cp₂V conformation with a V(1)-O(1)-P(1) bond angle of 145.21(1)°. The P(1)=O(2) bond length (1.500(2) Å) is consistent with a double bond,⁴¹ while the P(1)-O(1) bond (1.5560(19) Å) is contracted compared to typical P-O single bonds (~1.63 Å).⁴¹ The V(1)-O(1) bond length (2.043(2) Å) is similar to reported single bonds.²⁸ While most vanadium phosphates contain bridging phosphates, **2** is a rare example of a monomeric vanadium phosphate with a V:P ratio of 1:1.^{29, 36, 42–44} The magnetic moment of **2** was determined using the Evans method (μ_{eff}: 2.90 μ_B) and, similar to **1**, is

consistent with a high-spin V^{III} center.³⁹⁻⁴⁰ The paramagnetic nature of **2** resulted in absent 1H NMR signals for the Cp ring protons, and broadened resonances for the phenyl ring protons. Complex **2** was indefinitely stable when stored in the glovebox at $-40\text{ }^\circ\text{C}$, but is unstable in solution at room temperature as decomposition is observed after several days. The products of decomposition remain unclear.

Figure 2: Solid-state molecular structure of **2**. Hydrogen atoms are omitted for clarity.

We observed that the synthesis of **2** was sensitive to excess $\text{Ph}_2\text{P}(\text{O})\text{OH}$. Treatment of Cp_2VMe with 2 eq. of $\text{Ph}_2\text{P}(\text{O})\text{OH}$ resulted in an initial blue-colored solution (consistent with **2**), followed by a subsequent change to green. 1H NMR analysis of a sealed reaction mixture revealed the formation of both CH_4 and CpH over time (12 h). Single crystals suitable for XRD analysis were grown directly from the acetonitrile (MeCN) reaction mixture and confirmed the formation of the bimetallic caged structure, **3** (Scheme 2, Figure 3). The solid-state structure of **3** revealed a cage-like motif with each V bordered by a tetragonal phosphinate ligand field in the basal plane, and a Cp at the apical position, similar to **1** and to previous bridged V species.^{22, 43} In contrast to **2**, the P–O bonds in **3** are essentially equivalent ($\sim 1.50\text{--}1.51\text{ \AA}$), indicative of a delocalized π framework. While we assign each V to the +3

Figure 3: Solid-state molecular structure of **3**. Hydrogen atoms, phenyl groups (except *ipso*-C), and co-crystallized solvent are omitted for clarity.

oxidation state and likely be high spin like **1-2**, attempts to acquire solution-phase magnetic measurements using the Evans method were hampered due to the extremely poor solubility of **3**. Complex **3** could also be synthesized by addition of 1 eq. of $\text{Ph}_2\text{P}(\text{O})\text{OH}$ to **2** (Scheme 2).

In order to probe the redox properties of **1** and **2**, we studied their electrochemistry by cyclic voltammetry (CV).⁴⁵ The CV of **1** dissolved in DCM with 0.1 M $[\text{Bu}_4\text{N}][\text{PF}_6]$ as supporting electrolyte was analyzed at varying scan rates (Figure 4). While a quasi-reversible oxidation event is observed at fast scan rates, this event becomes irreversible at slow scan rates (Figure 4, inset). These data suggest that the *electron transfer* (oxidation) event results in a *chemical transformation*, as part of a proposed EC mechanism.⁴⁶ We attempted to chemically isolate the oxidized product using various oxidants, such as cerium ammonium nitrate, nitrosonium tetrafluoroborate, and tris(4-bromophenyl)ammoniumyl hexachloroantimonate; however, the isolation of a pure product has thus far been unsuccessful.

Figure 4: CVs of **1** (1.0 mM) in 0.1 M $[\text{Bu}_4\text{N}][\text{PF}_6]$ DCM solution at varying scan rates using a glassy carbon working electrode, platinum wire counter electrode, and referenced to the Fc/Fc^+ couple. Inset: CV at a 25 mV s^{-1} scan rate.

We next analyzed freshly recrystallized **2** by CV under similar conditions. While again an irreversible oxidation event is observed at slow scan rates, we were nonetheless able to chemically isolate the oxidized product. Addition of $[\text{Fc}][\text{PF}_6]$ to a chilled ($-78\text{ }^\circ\text{C}$) solution of **2** in DCM resulted in a rapid color change from bright blue (**2**) to green. Upon warming to r.t. and allowing to stand, a green powder precipitated from solution, was purified, and isolated yielding the dimeric salt (**4**) in high yield ($> 90\%$) (Scheme 2). The identity of the product was confirmed by single crystal XRD studies revealing the oxidation-induced dimerization of **2** to the bimetallic, **4** (Figure 5). Complex **4** adopts the known “retracted chair” conformation, similar to other organophosphorus-bridged dinuclear V^{IV} complexes.^{23, 28} Similar to **3**, the P–O bonds in **4** also become approximately equivalent ($\sim 1.50\text{--}1.51\text{ \AA}$), indicating a delocalized π framework. The V–O bond lengths ($2.0290(17)\text{--}$

Figure 6: a) CVs of **2** (1.0 mM) in 0.1 M [Bu₄N][PF₆] DCM solution at varying scan rates using a glassy carbon working electrode, platinum wire counter electrode, and referenced to the Fc/Fc⁺ couple. Inset: Randles-Ševčík plot for an *n* = 1 irreversible oxidation and theoretical peak current assuming a diffusion coefficient of: $1.74 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (i_p = peak current; v = scan rate) (see SI). b) Stacked CVs of **2** at 1 mM (black) and 10 mM (red) concentrations with designated scan rates. c) Proposed ECE mechanism for the oxidative dimerization of **2** to **4**.

Figure 5: Solid state molecular structure of the cation of **4**. Phenyl groups (except *ipso*-C), hydrogen atoms, and [PF₆][−] anions are omitted for clarity.

2.0368(17) Å) are essentially equivalent and similar in length to **2**. The V(1)–V(2) bond length is 5.3892(10) Å.

The mechanism of dimerization was further investigated by CV. Variable scan rates ranging from 10–400 mV s^{−1} were applied to probe the oxidation of **2** (Figure 6a). The slowest scan rate (10 mV s^{−1}) reveals the emergence of two irreversible oxidation events which coalesce to a single feature at faster scan rates (Figures 6a and 6b, black). An analysis of the first oxidation event using the Randles-Ševčík equation for an irreversible process is consistent with a single electron transfer process at low scan rates (Figure 6a, inset); however, at faster scan rates the experimental results deviate from the *n* = 1 theoretical model.^{46–47} Furthermore, probing the oxidation at a 400 mV s^{−1} scan rate from low (1 mM) to high (10 mM) concentrations reveals the reemergence of the second oxidation event (Figure 6b, red). Taken together, these data are consistent with a proposed electron transfer–chemical reaction–electron transfer (ECE) mechanism,^{48–50} wherein the initial 1 e[−] electrochemical oxidation of **2** to **2**⁺ results in its dimerization

with an equivalent of **2** forming an intermediate **2/2**⁺ dimer, which may then undergo a further 1 e[−] electrochemical oxidation to **4** (Figure 6c). The individual oxidation steps in this ECE mechanism are observable at either low scan rates or high concentrations (Figure 6b), either of which favor rapid dimerization ($\mathbf{2} + \mathbf{2}^+ \rightarrow \mathbf{2/2}^+$) relative to the scan rate timescale and result in the emergence of the second oxidation event ($\mathbf{2/2}^+ \rightarrow \mathbf{4}$). At fast scan rates (400 mV/s, 1000 mV/s (see SI)) and low concentrations, a quasi-reversible oxidation event occurs ($\mathbf{2} \rightleftharpoons \mathbf{2}^+$) wherein the dimerization step is outrun by the voltage scan rate.

The electronic structure of **4** was probed by solid-state magnetic measurements (SQUID), as well as X-band EPR spectroscopy. The molar magnetic susceptibility as a function of temperature is given in Figure 7. The data reveals an initial broad maximum at 50 K attributed to internuclear antiferromagnetic coupling. A least-squares fit of the χ_M vs *T* data from 2–300 K using the dimeric exchange Hamiltonian, $\widehat{H}_{ex} = -2J_{12}S_1S_2$ ($S_1 = S_2 = \frac{1}{2}$) with a temperature independent paramagnetism (TIP) correction yields good agreement with the experimental data for the parameters: $J = -21.8 \text{ cm}^{-1}$, $g = 1.972$ (from EPR measurements), and TIP = $796.1 \times 10^{-6} \text{ emu}$ (Figure 7, blue trace). These values agree well with reported analogous antiferromagnetically coupled vanadium phosphate extended structures.^{3, 51–54} Below 8 K the magnetic susceptibility increases sharply rather than dropping to zero as modeled for the dimer. This is attributed to a small amount (~3% by mass) of monomeric V^{IV} (**2**⁺, $S = \frac{1}{2}$) centers exhibiting Curie-like behavior (Figure 7, red trace), as is often observed with bimetallic complexes.^{51–52, 54} Summation of the dimer and monomer models results in a satisfactory fit to the experimental data (Figure 7, black trace).

Figure 7: Molar magnetic susceptibility (χ_M) vs. temperature measurements for bulk crystalline **4** collected from 2–300 K with an applied 0.1 T field (gray circles). The final fit (black dashed) is a summation of a dimeric (**4**) contribution (blue trace), as well as a small (3%) monomeric (2^+) contribution (red trace).

Compound **4** was further analyzed by X-band EPR spectroscopy. While the r.t. spectrum of **4** in MeCN is silent, frozen solution spectra (100 K and 4 K) are readily observed (Figure 8). The 100 K spectrum (Figure 8a) reveals a single, mostly unstructured isotropic signal ($g = 1.972$) similar to reported exchange-coupled di-vanadium(IV) systems and is ascribed to the low-lying triplet excited state of the dimer,^{23, 54–55} wherein the zero-field splitting of the triplet is small in magnitude so that the appearance resembles that of an isotropic $S = 1/2$ species.^{56–57} In addition to this major absorption, some minor fine-structure is also observed and is the result of a small amount ($\sim 3\%$) of the monomeric 2^+ (which is $S = 1/2$) resulting in a superimposed 8-line pattern due to hyperfine coupling to the ^{51}V ($I = 7/2$, 100% abundance) center. In contrast, the 4 K spectrum reveals a much more intense contribution from the monomeric 2^+ resulting in a readily observable spectrum more typical of V^{IV} , including $[\text{Cp}_2\text{V}]^{2+}$ species,^{58–59} exhibiting resolved hyperfine coupling⁶⁰ (simulation parameters: $g = [2.02, 1.99, 1.945]$ ($g_{\text{avg}} = 1.985$), $A(^{51}\text{V}) = [80, 80, 350]$ MHz ($a_{\text{avg}} = 170$ MHz), W (Gaussian, hwhm) = 50 MHz).⁶¹ The breadth of this spectrum is ascribed to an underlying contribution from the spin triplet **4**, although this contribution is greatly reduced compared to the 100 K spectrum, consistent with the magnetic measurements above (Figure 7).

Figure 8: X-band EPR spectra of **4** in MeCN at: a) 100 K, and; b) 4 K. The experimental traces are in black and the simulations in red. The relative intensities between (a) and (b) are arbitrary. See manuscript and SI for simulation parameters.

With the new compounds in hand, we have initiated preliminary studies to probe possible ROA reactions at the $\text{P}=\text{O}$ multiple bonds.^{10, 12} Both **1** and **2**, containing unbound $\text{P}=\text{O}$ bonds, were exposed to various H-atom donors (HADs), such as 1,4-cyclohexadiene (CHD), 9,10-dihydroanthracene (DHA), or 1-hydroxy-2,2,6,6-tetramethyl-piperidine (TEMPO-H). Deuterated DCM or MeCN solutions of **1** with varying equivalents of CHD, DHA, and TEMPO-H (0.5–10 eq.) at both r.t. and elevated temperatures (80 °C) revealed no reactions as observed by ^1H NMR spectroscopy. Similarly, the reaction of **2** with CHD or DHA under analogous, varying conditions also revealed no reactions with the HADs. Only the production of CpH was observed; however, this is also observed upon heating **2** in the absence of HADs and is, thus, attributed to thermal decomposition of **2** (*vide supra*). Lastly, **2** reacts with TEMPO-H, but preliminary data suggests an O-atom transfer mechanism, generating a vanadyl ($\text{V}=\text{O}$) bond, rather than a ROA mechanism.

CONCLUSIONS

In this report, we have outlined the synthesis and characterization of a series of new vanadocene-derived cyclic polyphosphate or diphenylphosphinate complexes (**1–4**), as well as the electrochemical behaviors of **1** and **2**. Complex **1** was found to undergo an irreversible EC mechanism upon oxidation, the product of which remains unknown. In contrast, the electrochemical data on **2** is consistent with a proposed stepwise ECE mechanism, forming the dimeric product **4**. The electronic structure of **4** was also probed using SQUID magnetometry and EPR spectroscopy and was found to contain antiferromagnetically coupled V^{IV} centers with a low-lying accessible triplet state, as well as a small contribution from monomeric 2^+ . Further studies into the reactivity of these compounds in the context of possible ROA-initiated C–H activation continues to be a focus of study in our laboratory.

EXPERIMENTAL SECTION

General Considerations: All manipulations were performed under an atmosphere of dry, oxygen-free N_2 by means of standard Schlenk or glovebox techniques (MBRAUN UNILab Pro SP Eco equipped with a -40 °C freezer). Pentane, tetrahydrofuran, diethyl ether, hexanes, and DCM (Aldrich) were dried using an MBRAUN-Solvent

Purification System and stored over activated 4 Å molecular sieves for two days prior to use. Acetonitrile (Aldrich) was dried over CaH₂ for 2 days then distilled over 4 Å molecular sieves. Deuterated solvents were purchased from Cambridge Isotope Labs, then degassed and stored over 4 Å molecular sieves for at least 2 days prior to use. Celite was dried by heating above 250 °C under dynamic vacuum for at least 48 h prior to use. Diphenylphosphinic acid and [Fc][PF₆] were purchased from Aldrich and used without further purification. Vanadocene⁶² (purified by sublimation), Cp₂VMe,³⁷ and [PPN]₂[P₄O₁₂H₂]³⁸ were prepared according to literature procedures. Elemental analyses (C, H, N) were recorded at the University of California, Berkeley using a Perkin Elmer 2400 Series II combustion analyzer.

Spectroscopic Analysis: NMR spectra were obtained on an Agilent Technologies 400 MHz spectrometer, and referenced to residual solvent or externally (³¹P: 85% H₃PO₄, ¹⁹F: CFC₃). Chemical shifts (δ) are recorded in ppm and the coupling constants are in Hz. Perpendicular-mode X-band EPR spectra were collected on a Bruker EMX EPR spectrometer equipped with an Oxford ESR 900 liquid helium cryostat. EPR simulations used the program QPOWA by Belford and co-workers, as modified by J. Telser.⁶³ UV-Vis spectroscopy was performed using a Shimadzu UV-2401PC spectrophotometer with quartz cuvettes equipped with a J-young air-tight adaptor.

Magnetic Measurements: Solution magnetic moment determinations were performed by the Evans method using fluorobenzene as residual solvent and were repeated in triplicate. Solid-state magnetic data was collected using a Quantum Design MPMS SQUID magnetometer in the RSO mode. The sample was prepared in the glovebox using eicosene to suspend the sample in an air-free environment. Variable temperature measurements were collected upon warming from 2–300 K at 0.1 T. The magnetic susceptibility data was corrected for diamagnetism of the sample, estimated using Pascal's constants.³⁹ The data was modeled using the julX modeling software.

Electrochemical Analyses: Cyclic voltammetry was performed on a CH Instruments 630E electrochemical analysis potentiostat, equipped with a 3 mm diameter glassy carbon working electrode, a Ag wire pseudo-reference electrode, and a Pt wire counter electrode with [Bu₄N][PF₆] (0.1 M) supporting electrolyte solution in DCM. The glassy carbon working electrode was cleaned prior to each experiment by polishing with 1, 0.3, 0.05 mm alumina (CH Instruments) in descending order, followed by sonication in distilled water. Background scans were conducted for each reported scan rate in a solution containing only electrolyte, and was then subtracted from each experiment. All voltammograms were performed on freshly recrystallized products, repeated in duplicate, and referenced to the Fc/Fc⁺ redox couple. All individual voltammograms can be found in the supporting information.

XRD Analyses: Intensity data was collected on a Bruker KAPPA APEX II diffractometer equipped with an APEX II CCD detector using a TRIUMPH monochromator with a Mo Kα X-ray source (α = 0.71073 Å). The single crystals were mounted on a cryoloop with Paratone-N oil, and all

data were collected at 100(2) K using an Oxford nitrogen gas cryostream system. A hemisphere of data was collected using ω scans with 0.5° frame widths. Data collection and cell parameter determination were conducted using the APEX2 program. Integration of the data frames and final cell parameter refinement were performed using SAINT software. Absorption correction of the data was carried out using SADABS. Structure determination was done using direct or Patterson methods and difference Fourier techniques. All hydrogen atom positions were idealized and rode on the atom of attachment. Structure solution, refinement, and creation of publication materials was performed using Olex2.

Synthesis of [PPN]₂[CpV(P₄O₁₂)] (1): In the glovebox, a 20 mL scintillation vial equipped with a magnetic stirbar was charged with Cp₂VMe (0.020 g, 0.102 mmol) and dissolved in DCM (5 mL). A separate solution of [PPN]₂[P₄O₁₂H₂] (0.142 g, 0.102 mmol) was dissolved in DCM (5 mL) and added dropwise at r.t. Immediately after addition the solution turned from black to a pale blue color. The solution was allowed to stir for 6 hours then filtered over a pad of celite through a fine porosity Buchner funnel. The filtrate was dried *in vacuo* to yield a blue residue. The residue was triturated with hexanes and dried *in vacuo* to yield a fluffy light blue powder (0.091 g, 0.060 mmol, 59.7 %). Blue plate-shaped single crystals suitable for X-ray diffraction were grown by slow diffusion of pentane into a concentrated solution of **1** in DCM. ¹H NMR (400 MHz, CD₂Cl₂): δ 7.48 (bs, 12H, *p*-C₆H₅), 7.66 (bs, 48H, *o,m*-C₆H₅). ³¹P{¹H} NMR (161.9 MHz, CD₂Cl₂): δ 21.11 (s, 4P, 2[PPN]⁺). Anal. Calc. for C₇₇H₆₅N₂O₁₂P₈V: C, 61.28; H, 4.34; N, 1.86. Found: C, 61.15; H, 4.26; N, 1.98. UV-Vis. λ (nm): 245 (max), 262, 407, 578. μ_{eff} (Evans): 2.82 μ_B.

Synthesis of [Cp₂VOP(O)Ph₂] (2): In the glovebox, a 100 mL roundbottom flask equipped with a magnetic stirbar was charged with Cp₂VMe (0.550 g, 2.81 mmol) and dissolved in DCM (20 mL). The black solution was cooled to -40 °C by placing it in the freezer. A separate slurry of Ph₂P(O)OH (0.510 g, 2.30 mmol) was prepared in DCM (10 mL) and added cold dropwise. The mixture was allowed to warm to r.t. over 1 h, then filtered over a pad of celite through a fine porosity Buchner funnel. The bright blue filtrate was dried *in vacuo*. The resulting blue residue was triturated with hexanes (25 mL) to yield a bright blue powder and recrystallized out of dichloromethane (5 mL) layered with pentane (5 mL) at -40 °C (0.576 g, 1.45 mmol, 62.9%). Blue plate-shaped single crystals suitable for XRD studies were grown by slow diffusion of pentane into a concentrated solution of **2** in DCM. ¹H NMR (400 MHz, CD₂Cl₂): δ 7.46 (bs, C₆H₅), 7.68 (bs, C₆H₅), 9.63 (bs, C₆H₅). Anal. Calc. for C₂₂H₂₀O₂PV: C, 66.34; H, 5.06. Found: C, 66.12; H, 4.87. UV-Vis λ (nm): 338 (max), 604, 752. μ_{eff} (Evans): 2.90 μ_B.

Synthesis of [CpV(μ²-O₂PPh₂)₄VcP] (3): In the glovebox, a 20 mL scintillation vial equipped with a magnetic stirbar was charged with Cp₂VMe (0.040 g, 0.20 mmol) and dissolved in MeCN (5 mL). A separate slurry of Ph₂P(O)OH (0.089 g, 0.41 mmol) was prepared in MeCN (5 mL) and added dropwise. The solution immediately turned bright

blue followed by gradual precipitation of a green solid after stirring for 12 hours. The precipitate was filtered using a fine porosity Buchner funnel, washed with MeCN (10 mL) and dried *in vacuo*. (0.069 g, 0.063 mmol, 30.7%). Green octahedral-shaped single crystals were grown directly from the reaction mixture in MeCN. ¹H NMR (400 MHz, CD₂Cl₂): δ 6.57 (bs, C₆H₅), 7.34 (bs, C₆H₅). Anal. Calc. for C₅₈H₅₀O₈P₄V₂: C, 63.28; H, 4.58. Found: C, 60.05; H, 4.39. Multiple attempts at obtaining satisfactory elemental analysis consistently resulted in reduced carbon percentages which we attribute to incomplete combustion as a result of vanadium carbide formation.⁶⁴ UV-Vis λ (nm): 328 (max), 458, 645.

Synthesis of [Cp₂V(μ-O₂PPh₂)₂VCp₂][PF₆]₂ (4): In the glovebox, a 50 mL roundbottom flask equipped with a magnetic stirbar was charged with **2** (0.040 g, 0.10 mmol) in DCM (10 mL). The solution was cooled to -78 °C using a dry ice/acetone cooled cold well inside the glovebox. A separate solution of [Fc][PF₆] (0.036 g, 0.11 mmol) in DCM (5 mL) was added dropwise. The solution was allowed to warm to r.t. for 1 hour while stirring and a green solid precipitated from solution. The mixture was filtered over a pad of celite and the green solid was washed with ether (10 mL) followed by benzene (10 mL). The green solid was eluted with MeCN (5 mL) and dried *in vacuo* (0.050 g, 0.092 mmol, 92.1%). Green plate-shaped single crystals were grown by slow diffusion of ether into a saturated MeCN solution of **4**. ³¹P{¹H} NMR (161.9 MHz, CD₂Cl₂): δ -144.62 (sep, 2P, 2[PF₆]⁻). ¹⁹F{¹H} NMR (376 MHz, CD₂Cl₂): δ -72.46 (d, 12F, 2[PF₆]⁻). Anal. Calc. for C₄₄H₄₀F₁₂O₄P₄V₂: C, 48.64; H, 3.71. Found: C, 48.39; H, 3.58. UV-Vis. λ (nm): 280 (max), 355. μ_{eff} (Evans): 1.95 μ_B.

ASSOCIATED CONTENT

Supporting Information. NMR, EPR, CVs and crystallographic CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interests.

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