Synthetic route to vanadium(III) dichalcogenidophosphinate complexes, V(S₂PPh₂)₃ and V(Se₂PPh₂)₃: A spectroscopic and structural comparative study with analogous complexes of chromium(III), Cr(E₂PPh₂)₃ (E = S, Se)

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Addition of the potassium dichalcogenidodiphenylphosphinate salts, KE_2PPh_2 (E=S, Se), to either the THF solvate of vanadium (III) chloride or unsolvated chromium(III) chloride results in rapid ligand substitution and the formation of a series of closely-related trivalent, neutral mononuclear complexes, $M(E_2PPh_2)_3$ (M=V, Cr; E=S, Se), isolated in modest to good yield. The metal dichalcogenidophosphinate complexes reported herein were characterized by IR, UV-vis, and ^1H NMR spectroscopies, and their solid-state molecular structures were determined by single-crystal X-ray crystallography. Importantly, the comparative analysis includes the structural and spectroscopic studies of two rare V(III) dithio- and diseleno-phosphinate VE_6 cores, as well as, two previously known CrE_6 analogues. In the solid-state the title complexes exhibit trigonal distortion from octahedral with torsion angles ranging from 43(2) to 50.3(6)° and structural parameters consistent with ligation of progressively 'softer' chalcogen-donors.

Introduction

Since the early 20th century the anions of thiophosphinic and selenophosphinic acids of the generic formula, HE_2PR_2 (E=S, Se; R=alkyl, aryl), have been well-studied in the literature.[1] Not only are these compounds highly modular where the alkyl and/ or aryl substituents can be modified by standard synthetic techniques, but they also ligate to a variety of Lewis acids.[1f,g,2] An array of coordination modes is observed with these platforms, including monodentate, isobidentate, anisobidentate, and bridging coordination patterns, affording metal-ligand complexes with diverse structures and geometries.[3] Previous studies have targeted such dichalcogenidophosphinate complexes for a number of purposes including improving olefin catalyst processes,[4] developing new single-source precursors for thin films and quantum dots,[5] and even promoting Ln(III)/ An(III) separations.[6]

Our group seeks to exploit the characteristics of the dichalcogenidophosphinate scaffold with the purpose of performing systematic analysis on a series of closely-related low-valent metal-ligand complexes with special attention to

elucidating trends and differences in geometry, reactivity, and the nature of the metal-chalcogen bond. We are particularly interested in better understanding vanadium-sulfur and -selenium bonding in neutral, monomeric V(III) VS_6 and VSe_6 systems, which surprisingly have not been well-explored via X-ray crystallography. Such structural studies should provide a framework for better understanding the vanadium-sulfur bond as it relates to certain biological and environmental systems, in particular, and the broader relevance of the vanadium-chalcogen bond more generally.[7] To date, only two neutral, mononuclear V(III) dithiophosphate complexes, namely $V(S_2P-(OEt)_2)_3$[8] and $V(S_2P(OPr^i)_2)_3$,[9] have been reported and structurally characterized by single-crystal X-Ray crystallography; no diseleno derivatives have been structurally characterized as of this publication (CSD search August 2020). If we expand our CSD search from dichalcogenidophosphinates to other neutral, mononuclear V(III) VS_6 cores, there are only two other relevant complexes reported, namely, $V(S_2CNEt_2)_3$[10] and $V(S_2CNCy)_3$.,[11] both of which are isolated from dithiocarbamate ligands. Expanding the CSD search to non-phosphinate VSe_6 cores, only three structures are reported. The first is a neutral V(III) species, namely, $V\{N(SePPh_2)_2\}_3$, which is derived from the imidodiphosphinoselenido scaffold; unfortunately this compound cannot be obtained pure and is consistently contaminated with a VO^{2+} species according to IR and UV-vis spectroscopies.[12] The second is the tridecaselenidodivanadate anion, $V_2Se_{13}^{2-}$ reported by Ibers and coworkers, where the μ-Se_5 unit which bridges the two adjacent V(III) atoms complicates systematic comparison with mononuclear V(III) species.[13] Finally, the third is the V(IV) diselenocatecholate dianion, $[V(C_6H_4Se_2)_3]^{2-}$, which for this paper is also not as useful for comparative purposes

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due to the charged nature of the complex and the +4 oxidation state.[14]

With the paucity of structurally characterized V(III) complexes employing the dichalcogenidophosphinate scaffold, we targeted syntheses of these systems by utilizing either the dithio- or diseleno-diphenylphosphinate anion, $^-E_2PPh_2$ (E=S, Se), a scaffold readily prepared in high yield by commercially available precursors. Previous reports have explored dichalcogenidodialkyl- or -diarylphosphinate derivatives with V(III)[15] but no single-crystal X-ray crystallographic data has been reported. The V(III) *tris*(dichalcogenidodiphenylphosphinate) complexes, $V(E_2PPh_2)_3$ (E=S, Se), reported herein were synthesized and isolated in modest yield, characterized by a suite of spectroscopies, and importantly, were structurally characterized by single-crystal X-ray crystallography. We also expand the understanding of these systems by reporting preliminary scoping experiments exploring their stability when exposed to ambient atmospheres (i.e. O_2 and water). Lastly, in order to facilitate a more insightful systematic bonding analysis and comparison, we also revisited previously reported analogous chemistry of another first-row trivalent transition metal. Herein we revisit the Cr(III) analogues, $Cr(E_2PPh_2)_3$ (E=S, Se),[16–18] providing more reliable synthetic procedures for their isolation, reporting solid-state molecular structures with higher resolution metrical data, and expanding on their solution-phase spectroscopic signatures.
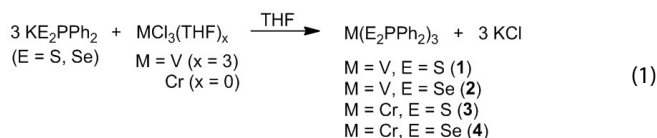
Results and Discussion

Synthesis, Isolation, and Characterization of V(III) and Cr(III) Dichalcogenidophosphinate Complexes

Adapting a reported procedure by Davies and coworkers,[19] addition of either elemental sulfur or selenium to a diphenylphosphide precursor allows for facile formation of the desired dichalcogenidodiphenylphosphinate anion, $^-E_2PPh_2$ (E=S, Se). It may be worth noting that insertion of tellurium is not readily achieved as the Te—P bond is not stabilized by the aromatic phenyl substituents, and hence this study is confined to S and Se donor dichalcogenidodiphenylphosphinate anions. Even in the most novice hands, the ligand preparation is reliable when performed under inert atmospheric conditions and conveniently employs commercially available precursors; the use of phosphinic acids or caustic materials used in other synthetic routes[15,20] is not needed for this procedure. Specifically, dropwise addition of a cold (−25 °C) 0.5 M THF solution of $KPPh_2$ to a cold toluene/THF mixture containing two equiv. of elemental chalcogen results in rapid oxidation of phosphorus to afford KE_2PPh_2 (E=S, Se). We found that great care should be taken not to add the phosphide solution too quickly, as the material isolated upon crystallization can become discolored (a tacky yellow-orange material rather than a crystalline white powder) and irretrievably contaminated; even after multiple recrystallizations, the material remains contaminated with one or more phosphorus-containing impurities according to ^{31}P NMR spectroscopy. Unfortunately, the intractable nature of the tacky,

yellow-orange material impeded our efforts to identity the unwanted side-products. However, slow addition of the potassium diphenylphosphide to the suspended chalcogen in a THF/toluene mixture, followed by stirring at ambient temperatures for <60 min and recrystallization from THF/hexanes, results in isolation of $K(E_2PPh_2)$ (E=S, Se) as a white crystalline powder in good yield (85–89%); their spectroscopic signals (see the SI) were consistent with previously reported literature values.[19,21]

The *tris*(dithiodiphenylphosphinate) vanadium(III) complex, $V(S_2PPh_2)_3$ (**1**), was prepared by addition of 3 equiv. of KS_2PPh_2 to the THF solvate precursor, $VCl_3(THF)_3$, in THF (equ 1). The reaction can be conducted either at ambient temperature or the reaction mixture can be gently heated (~65 °C) which slightly increases the yield of the isolated product. Regardless of which temperature the reaction is conducted at, upon workup and crystallization from a THF solution of the complex layered with hexanes, **1** crystallizes as a burgundy (red-brown) material in modest yield. The material is fully soluble in THF and chlorinated solvents (i.e. CH_2Cl_2 and $CHCl_3$) without noticeable decomposition based on lack of color changes, previous literature reports,[15] and ^1H NMR spectroscopic studies (*vide infra*); **1** is only partially soluble in Et_2O and acetonitrile and is insoluble in hexanes and pentanes. The solid-state IR spectrum of **1** (KBr mull) is largely identical to the dithiophosphinate ligand used in its preparation, especially at frequencies above 900 cm^{-1}. However, several new features (640, 687, 706, and 846 cm^{-1}) are observed in **1** which are not present in the free ligand, KS_2PPh_2 (see the SI). The observed features of **1** are similar to previous reports[15] and are largely due to subtle changes in vibrational energies of the P—C and P—S modes upon complexation to V(III); the features are not likely attributable to V—S vibrations as these modes are expected to be observed in the far IR region. The electronic absorption spectrum of **1** (in THF) in the visible region exhibits a strong absorption band at 451 nm, consistent with the solution's observed color and assignable to a charge-transfer (CT) band.[8,15] A second less intense feature is observed at 587 nm assignable to the $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ transition and is consistent with an octahedral V(III) complex (in solution the complex does not indicate large deviations from octahedral symmetry although crystallographic determination suggest D_3 symmetry; see structural discussion below).[8,15] Other weakly absorbing $d \rightarrow d$ transitions (i.e. the low energy transition $^3T_{1g}(F) \rightarrow {}^3T_{2g}$ toward the nIR region and the rare two-electron high energy transition $^3T_{1g}(F) \rightarrow {}^3A_{2g}$)[8,15] were not observed, thereby inhibiting an approximate field splitting energy or Racah parameter calculations. In the UV region, a very broad feature spanning ~250 nm is observed, exhibiting a distinct shoulder at 258 nm and a more intense peak at 230 nm. Based on the UV spectrum of the dithiodiphenylphosphinate ligand in THF (see the SI), the observed features in the UV region for **1** are mostly likely attributable to various ligand-based transitions (e.g. $\pi \rightarrow \pi^*$ transitions from the aromatic phenyl substituents). Despite the paramagnetic nature of V(III), we also characterized **1** by ^1H NMR spectroscopy and followed its solution-phase stability over time both under inert atmosphere and when exposed to

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ambient atmosphere. The ^{1}H NMR spectrum of **1** in THF-d_8 exhibits three paramagnetically broadened resonances at 7.63, 8.70, and 9.02 ppm assignable to the *para*, *meta*, and *ortho* protons on the phenyl substituents, respectively; no ^{31}P NMR signal was observed for **1**. When oxygen and water is rigorously excluded, complex **1** is stable in THF for prolonged periods of time (at least 1 week) with no observable change in the solution's color or consistency. Following a solution of **1** in THF-d_8 by ^{1}H and ^{31}P NMR spectroscopies for up to a week, the observed resonances attributable to the phenyl substituents undergo no discernable change in profile or intensity (see the SI). The presence of free ligand (or any other phosphorus-containing organic) was also not observed in both the ^{1}H and ^{31}P spectra. In contrast, upon the solution being exposed to and aerated with ambient atmosphere (i.e. O_2 and water), a color change from amber to blue with the deposition of a flocculent material was observed after 24 h. The ^{1}H NMR spectrum indicates a coalescence from three peaks (as observed in **1**) to two ill-defined features ranging from 7.41 to 7.83 ppm; more notable is the appearance of a distinct peak at 69.04 ppm in the ^{31}P NMR spectrum (see the SI). This species is currently unidentified but is likely not the free dithiophosphinate anion, $^-S_2PPh_2$, based on preliminary experiments.

$$3\ KE_2PPh_2\ +\ MCl_3(THF)_x\ \xrightarrow{\text{THF}}\ M(E_2PPh_2)_3\ +\ 3\ KCl$$

(E = S, Se) M = V (x = 3) Cr (x = 0)

M = V, E = S (**1**)
M = V, E = Se (**2**)   (1)
M = Cr, E = S (**3**)
M = Cr, E = Se (**4**)

The V(III) diseleno complex, V(Se$_2$PPh$_2$)$_3$ (**2**), was prepared in a similar manner as **1**, crystallizing as a dark purple solid in modest yield (equ 1). The material has similar solubility properties as **1** and also like **1**, in the solid-state is quite stable when kept under anhydrous and anaerobic conditions. When exposed to air and water, noticeable decomposition is observed as the crystalline material begins to decompose and discolor rapidly; in solution (THF), this color change is delayed by several hours. The IR spectrum of **2** (KBr mull) is largely dominated by vibrational frequencies associated with the diselenodiphenyl-phosphinate ligands, where some features are shifted by only a few wavenumbers relative to the free ligand (see the SI). Consistent with the observed color for **2**, its visible spectrum (THF solution) exhibits a very broad feature with a λ_{max} of 544 nm assignable to a ligand-based transition (CT). Due to the broadness of this feature (spanning some 200 nm), it is likely several $d{\to}d$ transitions are obscured by the dominant band again impeding accurate determination of either the crystal field splitting energy or Racah parameter. The UV region of **2** largely resembles that of **1** in both its broadness and overall profile where again, relative to the UV spectrum of KSe$_2$PPh$_2$ in THF (see the SI), any observed transitions are likely attributable to the aromatic substituents of the phosphinate ligands. In THF-d_8 the ^{1}H NMR spectrum of **2** is very similar to **1**; the resonances assignable to the phenyl substituents on the diselenophosphinate anion, -Se$_2$PPh$_2$, split from two multiplets in the free ligand to three broad features in **2** observed at 7.15, 7.96, and

8.64 ppm, assignable to the ortho, meta, and para protons, respectively; as with **1** no ^{31}P NMR signal was observed. When a THF-d_8 solution of **2** is kept free of air and water, the complex appears thermally stable with no observable changes in color or composition and no significant changes in the ^{1}H NMR spectra are observed for up to four days (see the SI). When the solution is exposed to ambient atmosphere, a color change from purple to yellow is observed after 24 h. The resulting ^{1}H NMR spectrum (see the SI) is similar to **1** when under the same conditions and a new ^{31}P signal is observed at 39.31 ppm. This feature is attributable to an as of yet unidentified decomposition product, though we can say with some confidence this peak is not attributable to the diselenophosphinate anion ($^-Se_2PPh_2$ exhibits a ^{31}P NMR signal at ~22 ppm in THF-d_8, see the SI).[19] Further, as this decomposition species has a different ^{31}P NMR signal than that of the decomposition species formed from the exposure of **1** to air (observed at ~69 ppm), the formation of $^-O_2PPh_2$ in both experiments seems unlikely; however these particular studies are still ongoing.

While both the Cr(III) dithio- and diseleno-diphenylphosphinate complexes, Cr(S$_2$PPh$_2$)$_3$ (**3**) and Cr(Se$_2$PPh$_2$)$_3$ (**4**), have been previously reported,[16–18] we thought it was necessary to reproduce some of the data, especially the crystallographic data, in order to better facilitate direct structural and spectroscopic comparison to our V(III) derivatives. We also found previous reports for their preparation either employed less than desirable methods such as using hydrated Cr(III) precursors[16] or were not reproducible in our hands.[18] As such, we prepared **3** and **4** using similar procedures to **1** and **2**, respectively; importantly we found thermolysis at ~65 °C for at least ~48 h is critical for effective and efficient chelation of the $^-E_2PPh_2$ anion when using the anhydrous Cr(III) chloride salt. These modified procedures resulted in highly reproducible syntheses and dramatically increased reaction time and yield of the isolated product relative to performing the reactions at room temperature as previously reported.[18] Upon work up of the reaction mixture, **3** crystallizes as a blue-purple solid (dichroism is observed when in solution) while **4** crystallizes as a dark green solid; both are isolated consistently in moderate to good yield. These molecules have similar solubility properties as **1** and **2** and when kept under inert atmosphere they can be stored for prolonged periods both in the solid-state and in solution without observable decomposition. The solid-state IR spectra for **3** and **4** (KBr mulls) are similar to their V(III) counterparts, **1** and **2**, respectively, and match previous reports,[16,18] again indicating that the IR spectra for this class of compounds is largely dominated by ligand-based vibrational modes. The UV-vis spectra for **3** and **4** are generally consistent with previous reports of similar Cr(III) complexes (i.e. octahedral, d^3 centers; see structural discussion below) where several spin-allowed $d{\to}d$ transitions and CT bands are observed (see the SI).[12,16,18] Consistent with their color in a THF solution, we observe a strong absorption CT band at 368 nm for **3** and 434 nm for **4**. The $d{\to}d$ transitions, $^4A_{2g}{\to}^4T_{2g}$ and $^4A_{2g}{\to}^4T_{1g}(F)$, are rather weak as expected, while the $^4A_{2g}{\to}^4T_{1g}(P)$ transition is likely obscured by the CT band near or at the UV region which has been observed for other Cr(III) complexes.[23] As observed in the

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V(III) dichalcogenidophosphinate complexes **1** and **2**, the UV spectra for both **3** and **4** are dominated by various ligand-based bands that are broad and ill-defined. It should be noted that the D_3 symmetry observed in the solid-state molecular structures of **3** and **4** (*vide infra*) does not seem to result in significant splitting of the T states when in the solution-phase; in other words, the observed transitions in the UV-vis spectra are relatively broad and any deviation from octahedral or reduction in symmetry is likely negligible; we assume similar effects for complexes **1** and **2** as well. We also probed **3** and **4** by ^1H and ^{31}P NMR spectroscopies. In THF-d_8 **3** exhibits only two paramagnetically broadened features at 8.38 and 9.64 ppm, tentatively assignable to the *ortho* and *meta/para* protons, respectively; there was no observable ^{31}P NMR signal as expected. Qualitatively, complex **3** is very stable in solution, exhibiting no changes in color or formation of precipitates upon standing in solution for up to one week. In contrast to the V(III) derivatives described above, upon exposure of a solution of **3** in THF-d_8 to ambient atmosphere, there continues to be no noticeable change in color or consistency even after one week.

There is however, the presence of a new feature at 2.65 ppm in the ^1H NMR spectrum which appears after 24 h and continues to increase in intensity over time; interestingly there is no corresponding ^{31}P NMR signal observed in these solutions (see the SI). As observed with **3**, complex **4** is also quite stable in solution exhibiting two broad features at 8.06 and 9.67 ppm in its ^1H NMR spectrum in THF-d_8 (see the SI). When exposed to ambient atmosphere, **4** behaves the same as **3**; no changes to color or composition of the solution is observed. The presence of a new feature at 2.63 ppm, very similar to the one observed for **3**, is observed in the ^1H NMR spectrum with no accompanying features in the ^{31}P NMR spectrum.

Comparative Analysis of Solid-State Molecular Structures

The solid-state molecular structures and a summary of relevant structural parameters for the title complexes, **1–4**, can be found in Figures 1–3 and Tables 1 and 2 (full crystallographic details as CIF files can be found in the Associated Content). It is
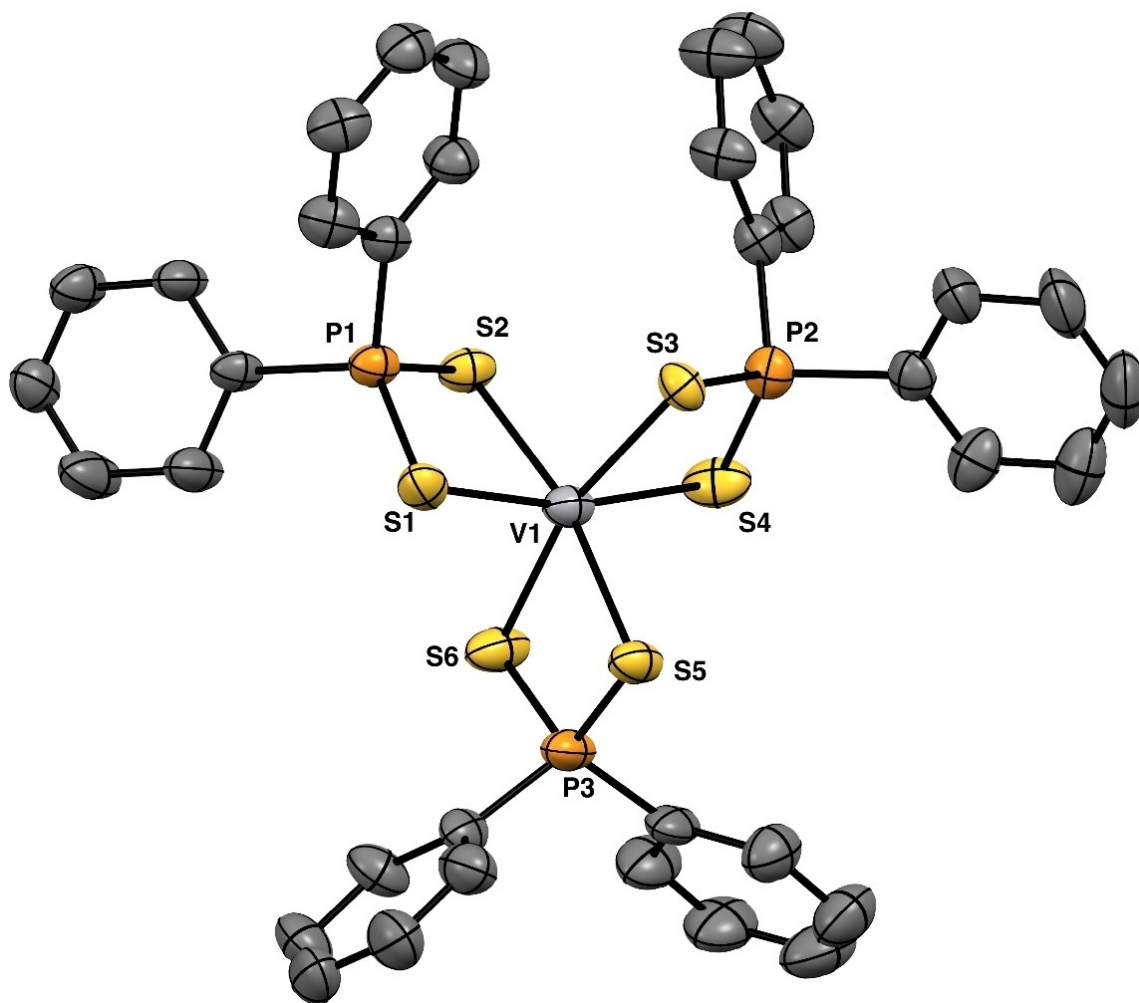

Figure 1. Solid-state molecular structure of **1** with 30% probability ellipsoids. Minor components of disorder and hydrogen atoms are omitted for clarity.

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Table 1. Selected bond distances (Å) and bond angles (°) for compounds **1**–**4**.

	1	2·THF·Et$_2$O	3	4
(M—E)$_{av.}$	2.463(21)	2.596(15)	2.432(13)	2.554(14)
(E—P)$_{av.}$	2.007(11)	2.169(6)	2.009(8)	2.164(6)
(E—M—E)$_{av.}$	81.9(5)	83.3(6)	82.9(3)	84.8(2)
(E—P—E)$_{av.}$	107.0(8)	105.3(5)	106.5(8)	105.4(6)
(M—E—P)$_{av.}$	85.2(3)	85(1)	84.9(3)	84.3(5)
av. twist angle	44.3(9)	43(2)	48.5(4)	50.3(6)

* The error in the averages reported are equal to the standard deviation in the experimental values.

Table 2. Selected X-ray crystallographic data for compounds **1**–**4**.

	1	2·THF·Et$_2$O	3	4
Empirical formula sum	C$_{36}$H$_{30}$P$_3$S$_6$V$_1$	C$_{152}$H$_{138}$O$_2$P$_{12}$Se$_{24}$V$_4$	C$_{36}$H$_{30}$P$_3$S$_6$Cr$_1$	C$_{36}$H$_{30}$P$_3$Se$_6$Cr$_1$
Crystal Habit, color	thin flat wedge, dark orange	chip, red	flattened rod, blue	skewed octahedral block, green
Crystal size (mm)	0.30×0.22×0.02	0.12×0.08×0.01	0.30×0.06×0.04	0.20×0.16×0.14
Crystal system	orthorhombic	monoclinic	orthorhombic	orthorhombic
Space group	Pbca	Pc	Pbca	Pbca
Volume (Å^3)	7570.1(3)	8150.2(11)	7497.8(4)	7783.6(2)
a (Å)	18.0658(4)	15.6298(12)	18.1304(5)	18.3514(3)
b (Å)	17.6888(5)	15.5077(12)	17.6257(5)	17.9240(3)
c (Å)	23.6891(5)	34.181(3)	23.4628(7)	23.6634(3)
α(°)	90	90	90	90
β(°)	90	100.344(4)	90	90
γ(°)	90	90	90	90
Z	8	2	8	8
Formula weight (g/mol)	798.81	4467.06	799.87	1081.27
Density (calculated) (Mg/m^3)	1.402	1.820	1.417	1.845
Absorption coefficient (mm^{-1})	0.746	9.495	0.793	10.195
Total reflections	70729	141,489	90691	102578
Independent reflections	8679	29,578	8600	7135
R$_{int}$	0.0514	0.0842	0.0611	0.0437
Final R indices [$I>2\sigma(I)$]	R$_1$=0.0458, wR$_2$=0.1009	R$_1$=0.0584, wR$_2$=0.1730	R$_1$=0.0420, wR$_2$=0.0933	R$_1$=0.0289, wR$_2$=0.0725
GOF	1.023	0.994	1.011	1.052

noteworthy to mention while complexes **3** and **4** have been previously structurally characterized,[17,18] the redetermination reported below resulted consistently higher precision in the metrical parameters. Specifically, typical standard uncertainties for the Cr-S and S-P bond distances in Pinkerton[17] are 0.003 Å and 0.004 Å while the corresponding values observed in **3** are 0.001 Å and 0.001 Å, respectively (i.e. a factor of about three times better). This is also observed in **4**; the standard uncertainties for the Cr-Se and Se-P bond distances in Artem'ev[18] are 0.003 Å and 0.006 Å while the corresponding values observed in **4** are much smaller at 0.0006 Å and 0.0009 Å, respectively (i.e. an order of magnitude more precise). In addition, the updated structural data for **3** and **4** is further improved with collection at lower temperatures (which was limited by onset of modulation), acquisition of much better data:parameter ratios (this is especially apparent for complex **3**) and overall improved refinement statistics in both structures (this is most clearly apparent in complex **4**). Lastly, disorder is clearly present in both compounds **3** and **4** but has been

modelled in the most recent data while previous reports have neglected such disorder in the earlier structures.

Though originally reported in the early 1970s,[15] *tris* (diphenyldithiophosphinate) vanadium(III) has remained structurally uncharacterized. With the purpose to further its characterization and to provide a framework for crystal-growing conditions to be expanded to the unknown diseleno derivative, we sought to determine the solid-state molecular structure of V(S$_2$PPh$_2$)$_3$ (**1**). We found in the solid-state that **1** crystallizes in the orthorhombic space group *Pbca* with one molecule in the asymmetric unit (Figure 1). It features a 6-coordinate V(III) center coordinated to three, monoanionic diphenyldithiophosphinate ligands. The complex deviates from an ideal octahedral geometry and is best described as a trigonally distorted octahedron with D_3 symmetry. This geometric distortion from octahedron is not uncommon in similar *tris*(bidentate) complexes which employ ligands with relatively small bite angles (e.g. dithiolate ligands).[17,24] Specifically, the deviation from octahedral symmetry can be derived from the average trigonal twist angle which for **1** was determined to be 44.3(9)°, well

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below the accepted angle (60°) for a nondistorted octahedron. The six V–S bond distances range from 2.4390(9) to 2.4906(12) Å, affording a difference of *ca.* 0.05 Å and indicate the ligands chelate in an isobidentate fashion. In addition, the P–S bond distances (1.9917(12) to 2.0163(11) Å) are also quite similar differing by only *ca.* 0.02 Å and further support the symmetrical chelation mode of the dithiophosphinate ligands. The three V–S–S–P chelate rings are planar with average S–V–S and S–P–S bond angles of 81.9(5)° and 107.0(8)°, respectively, while the V–S–P bond angles are statistically identical (consistent with symmetrical coordination) and range from 84.55(4)° to 85.51(4)°. These metrical parameters are consistent with those reported for other neutral V(III) homoleptic VS_6 phosphinates (e.g. $V(S_2P(OEt)_2)_3$[8], $V(S_2P(OPr^i)_2)_3$[9]) indicating the phenyl substituents on the phosphorus atom have little impact on structural trends observed within this series.[8–11]

In the solid-state, *tris*(diphenyldiselenophosphinate) vanadium(III), $V(Se_2PPh_2)_3$ (**2**), crystallizes in the monoclinic space group *Pc* with four independent molecules in the asymmetric

unit (Figure 2), along with one noncoordinating molecule of THF and Et_2O (derived from the crystallization solvent conditions). Regarding structural parameters, all four molecules are statistically equivalent to one another and isostructural to **1**. Accordingly, relevant bond distances and bond angles were averaged across all four molecules for the purpose of structural analysis and comparison (Table 1). Analogous to **1**, the selenium atoms bind to the V(III) center in a symmetrical manner, with V–Se bond distances ranging from 2.573(3) to 2.635(3) Å. As expected the larger chalcogen atom affords an average V–Se bond distance (2.596(15) Å) that is elongated relative to the average V–S bond distance in **1** (2.463(21) Å). The isobidentate nature of the diselenophosphinate ligand is also evident by the P–Se bond distances which range from 2.161(4) to 2.180(4) Å across all four molecules in the unit cell ($\Delta = 0.02$ Å). The distortion from octahedral is reflected in the average twist angle for the four individual molecules in the unit cell which range from 41(2)° to 44(1)°; crystal packing effects may be influencing the smaller torsion angle observed in **2**·THF·Et_2O
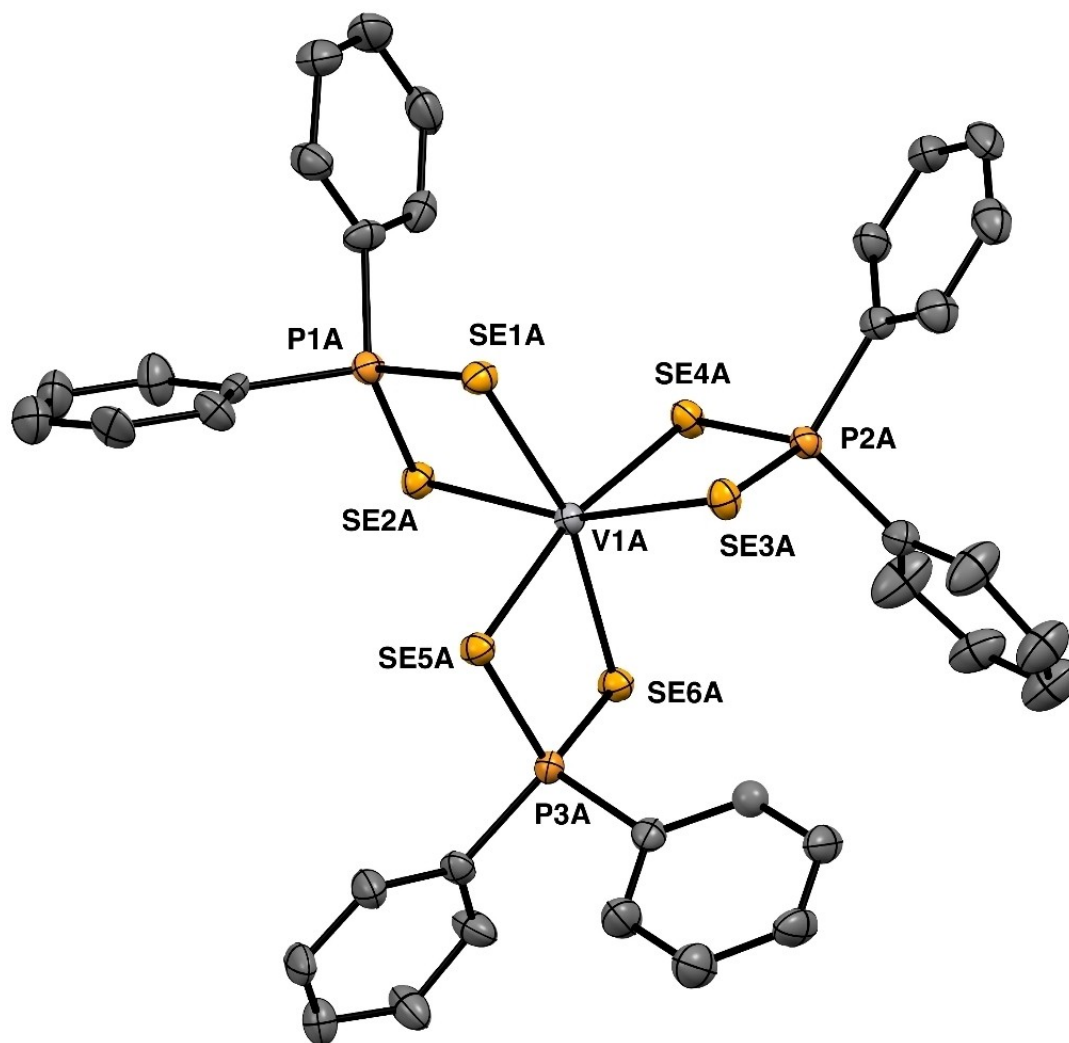

Figure 2. Solid-state molecular structure of **2**·THF·Et_2O with 30% probability ellipsoids. Only one molecule from the asymmetric unit is shown. Hydrogen atoms and solvent molecules are also omitted for clarity.

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relative to **1**. Similar to **1**, the V–Se–Se–P chelate rings in **2**·THF·Et$_2$O are planar with average Se–V–Se and Se–P–Se bond angles of 83.3(6)° and 105.3(5)°, respectively. The V–Se–P bond angles have a larger range (82.87(13)° to 87.09(13)°) relative to **1** but remain consistent with symmetrical coordination. The structural parameters in **2** are consistent with the only other structurally characterized monomeric V(III) VSe$_6$ core reported in the CSD as of this publication, namely, V{N-(SePPh$_2$)$_2$}$_3$.[12] While the structural data on VSe$_6$ cores is a limited, it appears coordination of three bidentate diselenido ligands (despite the differences between imidodiphosphinoselenido and diselenophosphinate platforms) about a V(III) center results in several structural consistencies including the observed distortion from octahedral and V–Se bond distances.

When crystals of Cr(S$_2$PPh$_2$)$_3$ (**3**) were grown from a THF solution layered with hexanes, two distinct morphologies of crystal growth were observed: flattened rods and regular blocks. When the blocks were analyzed by X-ray crystallography, a partial data set was collected and quickly established that like **2**·THF·Et$_2$O, four independent molecules of Cr(S$_2$PPh$_2$)$_3$ were present in the asymmetric unit; these block crystals crystallized in the same the orthorhombic space group as **1** however, namely, *Pbca*. When the rods were analyzed by X-ray crystallography, a full data set was collected which indicated only one molecule of Cr(S$_2$PPh$_2$)$_3$ was present in the asymmetric unit (Figure 3(a)). The rods also crystallized in the orthorhombic space group *Pcba* and are isostructural to **1**, featuring a 6-coordinate Cr(III) center coordinated to three, monoanionic diphenyldithiophosphinate ligands. To facilitate a more appropriate structural comparison to **1** and to account for any structural differences influenced by crystal packing effects, the following structural analysis will be in reference to the full data set collected on the rods with a single molecule in the asymmetric unit. Similar to **1** and **2**·THF·Et$_2$O, **3** is also a

distorted octahedron with D_3 symmetry as demonstrated by an average torsion angle of 48.5(4)°. The dithiophosphinate ligand again chelates in an isobidentate fashion exhibiting Cr–S bond distances ranging from 2.4170(8) to 2.4541(10) Å, which are statistically equivalent to both the V–S bond distances observed in **1** and the CrS$_6$ structures previously reported.[17] Other indications of the symmetric chelation mode of the phosphinate ligand are the P–S bond distances that differ by only *ca.* 0.02 Å and the statistically equivalent P–S–Cr bond angles ranging from 84.95(4)° to 85.26(4)°. The three Cr–S–S–P chelate rings remain planar as well, with average S–Cr–S and S–P–S bond angles of 82.(3)° and 106.5(8)°.

Similar to previous work,[18] *tris*(diselenodiphenylphosphinate) chrominum(III), Cr(Se$_2$PPh$_2$)$_3$ (**4**), crystallizes as green blocks in the same orthorhombic space group *Pbca* as **1** and **3**, with only one molecule present in the asymmetric unit (Figure 3(b)). Complex **4** is isostructural to the other three dichalcogenidophosphinate complexes presented thus far sharing effectively identical structural parameters, including chelation mode, planarity of the phenyl substituents, and the tetrahedral nature of the P atoms. Complex **4** also exhibits the same trigonal distortion (the average twist angle is 50.3(6)°) commonly observed in these dichalcogenido phosphinate systems. Due to the larger chalcogen atom the average M–Se bond distance (2.554(14) Å) is slightly elongated relative to **3** (2.432(13) Å) but is statistically identical to **2**·THF·Et$_2$O (2.596(15) Å) and previous reports of similar complexes.[12,13,18] In effort to make some broad observations on the general structural trends for this series, it seems traversing the first-row transition metals from V(III) to Cr(III) with these dichalcogenidophosphinate ligands results in little significant difference in the observed structural parameters when comparing the VS$_6$ core to the CrS$_6$ core (or the VSe$_6$ core versus the CrSe$_6$ core) and any observed differences when descending the chalcogen group
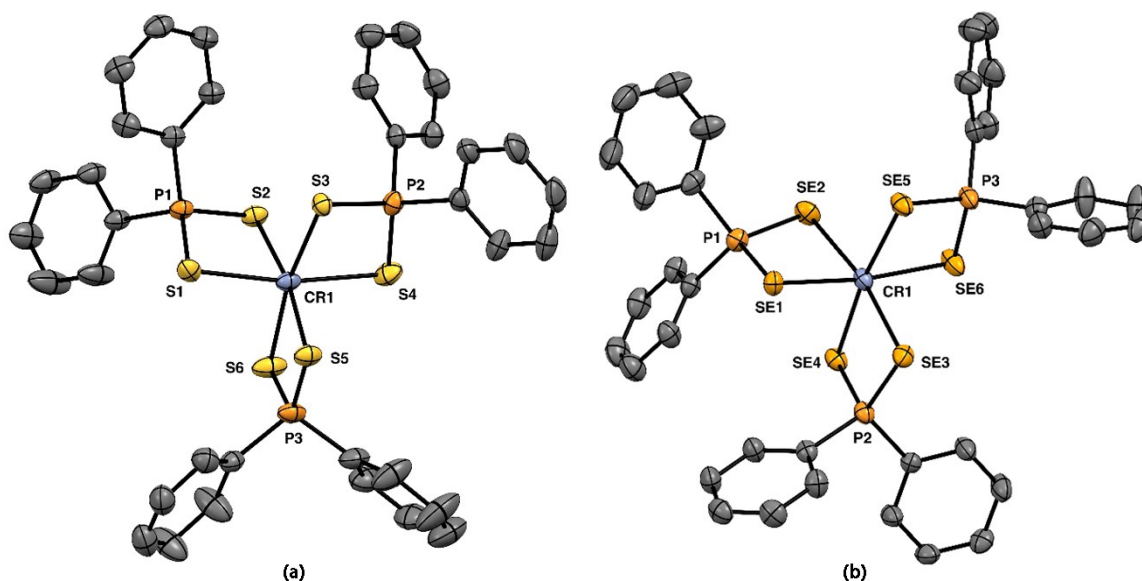

Figure 3. Solid-state molecular structures of (a) **3** and (b) **4** with 30% probability ellipsoids. Minor components of disorder and hydrogen atoms omitted for clarity.

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(i.e. comparing VS_6 to VSe_6) is largely attributed the expected trends of the larger ('softer') chalcogen donor-atom. A more comprehensive series of transition metal-chalcogen complexes is greatly desired and current efforts in our group towards this end are currently ongoing.

Summary and Conclusions

Addition of either KS_2PPh_2 or KSe_2PPh_2 to the THF solvate of vanadium(III) chloride ($VCl_3(THF)_3$) in THF results in facile substitution of the chloride ligands to afford the neutral *tris*(dichalcogenidophosphinate) complexes, $V(E_2PPh_2)_3$ (E=S, Se), isolated in modest yield. When employing the unsolvated chromium(III) chloride salt ($CrCl_3$) gentle heating of the reaction mixture affords similar chemistry and the isolation of analogous complexes, namely, $Cr(E_2PPh_2)_3$ (E=S, Se), in moderate to good yield. The resulting compounds are isolated cleanly and are thermally stable in both the solid-state and solution-phase when kept in anaerobic and anhydrous conditions. All the reported complexes were characterized by UV-vis, IR, and ^1H NMR spectroscopies and exhibit well-defined spectroscopic signatures. Interestingly, upon exposure to ambient atmosphere, new, as of yet, unidentifiable oxidation products are observed indicated by both rapid changes in color and solution composition, and also by multi-nuclear NMR spectroscopy (e.g. new ^{31}P signals are observed).

The title complexes were also structurally characterized by single-crystal X-ray crystallography, which includes the rare neutral mononuclear dithio- and diseleno-phosphinate vanadium(III) complexes. Structural data for the entire series indicates trigonally distorted ME_6 cores (M=V, Cr; E=S, Se) exhibiting twist angles ranging from 43(2) to 50.3(6)° consistent with ligation patterns of similar complexes. There is little significant structural difference within the series beyond the expected trends of soft-donor chalcogen chelation and all reported complexes are consistent with the structural data previously reported for similar molecules. Future efforts include probing the M−E vibrational mode of the ME_6 core, conducting systematic solution-phase studies to elucidate the solvent influences on electronic absorption spectra, and performing a complete analysis on the nature of the oxidation products formed upon exposure of the title complexes to air and water, including determining the presence of any potential diamagnetic vanadyl compounds.

Experimental

General. All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions via an atmosphere of nitrogen using either a glove box or Schlenk line (i.e. vacuum gas manifold). Diethyl ether (Et_2O), hexanes, tetrahydrofuran (THF), and toluene were purchased in anhydrous grade from Sigma-Aldrich and stored over activated 3 Å molecular sieves for at least 48 h before use. THF-d_8 and MeCN-d_3 were purchased from either Sigma-Aldrich or Cambridge Isotopes, respectively, and dried over activated 3 Å molecular sieves for at least 48 h before use.

$VCl_3(THF)_3$[22] was prepared by literature procedures. All other reagents were purchased from commercial suppliers and used as received.

NMR spectra were recorded on a JEOL Eclipse 300 MHz FT NMR spectrometer. ^1H NMR spectra were referenced to external $SiMe_4$ using the residual protio solvent peaks as internal standards. $^{31}P\{^1H\}$ NMR spectra were referenced to external 85% H_3PO_4. IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer. UV-vis spectra were recorded on a Cary 100 Bio UV-vis spectrophotometer. Elemental analyses for compounds **1–4** were performed by the Midwest Microlab, LLC. (Indianapolis IN).

X-Ray Crystallography. All crystals studied became modulated at low temperature (~90 K), but the modulation gradually diminished at higher temperatures. Thus, X-ray diffraction data were collected at 250(2) K (**1** & **2**), 240(2) K (**3**), and 200 K (**4**) using either a Bruker-Nonius X8 Proteum diffractometer with graded-multilayer focussed CuK(alpha) X-rays (**4**) or a Bruker D8 Venture kappa-axis diffractometer using MoK(alpha) X-rays (**1** and **3**) or CuK(alpha) X-rays (**2**). Raw data were integrated, scaled, merged, and corrected for Lorentz-polarization effects using either APEX2[25] (**4**) or APEX3[26] (**1–3**). Corrections for absorption were applied using SADABS[27] or TWINABS.[28] The structures were solved by dual-space methods (SHELXT[29]) and refined against $F2$ by weighted full-matrix least-squares (SHELXL[30]). Hydrogen atoms were found in difference maps, but subsequently placed at calculated positions and refined using riding models. Non-hydrogen atoms were refined with anisotropic displacement parameters. Atomic scattering factors were taken from the International Tables for Crystallography.[31]

Synthesis of KS_2PPh_2. A 20-mL vial was loaded with a dark red solution of 0.5 M $KPPh_2$ solution in THF (1.5679 g, 0.88322 mmol). A second 20-mL vial was loaded with elemental sulfur (0.0573 g, 1.79 mmol) and suspended in a 2:1 mixture of THF and toluene. Both vials were cooled to −25 °C for ~10 min in the glove box freezer. Once cooled, the $KPPh_2$ solution (~1 mL) was added slowly and dropwise to the sulfur suspension (~2 mL) with vigorous stirring (great care should be taken to not add the phosphide too fast). The mother vial containing the phosphide was rinsed with an additional 1 mL of THF and added to the reaction vessel. A color change to pale yellow appeared initially, turning finally to a bright orange color which persisted for the rest of the addition (~2 min in total). The reaction was allowed to stir at ambient temperature until all of the sulfur was observed to be dissolved (< 20 min); no further color changes were observed. The reaction mixture was then filtered through a Celite column (0.5 cm×2 cm) supported on glass wool to afford a homogenous orange filtrate. The resulting filtrate (~4 mL) was subsequently layered with hexanes (~15 mL) and stored at −25 °C for ~48 h. Colorless crystals were isolated by decanting off the yellow-colored supernatant, washing with cold hexanes (~1 mL×3), and drying *in vacuo* for ~10 min. The ^1H and ^{31}P NMR spectra of the white microcrystalline material was consistent with previous reports and used as KS_2PPh_2 in subsequent reactions. Yield: 0.2254 g, 89%. ^1H NMR (25 °C, 300 MHz, MeCN-d_3): δ 7.27–7.29 (m, 6H, *meta-* & *para-*Ph), 8.03–8.10 ppm (m, 4H, *ortho-*Ph). $^{31}P\{^1H\}$ NMR (25 °C, 122 MHz, MeCN-d_3): δ 61.10 ppm. IR (KBr pellet, cm^{-1}): 3056(m), 3051(m), 2974(w), 2872(w), 1967(w), 1900(w), 1825(w), 1173(w), 1618(w sh), 1611(m), 1584(w), 1570(w), 1478(w sh), 1473(m), 1435(s), 1306(m), 1278(w), 1179(w sh), 1175(m), 1156(w), 1097(s), 1068(m), 1031(w sh), 1027(m), 999(m), 975(w), 923(w), 746(s), 744(s), 702(s), 693(s sh), 655(s), 614(s), 563(s), 486(s). UV-vis (THF solution, 0.060 mM, nm): 274 (ε = 2660 $L·mol^{-1}·cm^{-1}$), 229 (λ_{max}, ε = 9910 $L·mol^{-1}·cm^{-1}$). As expected, no discernable features in the visible region were observed, even at high concentrations (~0.10 mM).

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Synthesis of KSe$_2$PPh$_2$. A 20-mL vial was loaded with a dark red solution of 0.5 M KPPh$_2$ solution in THF (3.6044 g, 2.0304 mmol). A second 20-mL vial was loaded with elemental selenium (0.3327 g, 4.214 mmol) and suspended in a 2:1 mixture of THF and toluene. Both vials were cooled to −25 °C for ~10 min in the glove box freezer. Once cooled, the KPPh$_2$ solution (~4 mL) was added slowly and dropwise to the selenium suspension (~2 mL) with vigorous stirring (great care should be taken to not add the phosphide too fast). The mother vial containing the phosphide was rinsed with an additional 1 mL of THF and added to the reaction vessel. A color change to pale yellow appeared initially, turning finally to a bright yellow color which persisted for the rest of the addition (~4 min). The reaction was allowed to stir at ambient temperature until all of the selenium was observed to be dissolved (<60 min); no further color changes were observed. The reaction mixture was then filtered through a Celite column (0.5 cm×2 cm) supported on glass wool to give a homogenous yellow filtrate. The resulting filtrate (~7 mL) was concentrated in vacuo to ~4 mL, layered with hexanes (~15 mL), and stored at −25 °C for ~48 h. Colorless crystals were isolated by decanting off the pale yellow supernatant, washing with cold hexanes (~1 mL×3), and drying in vacuo for ~10 min. The ^{1}H and ^{31}P NMR spectra of the white microcrystalline material was consistent with previous reports and used as KSe$_2$PPh$_2$ in subsequent reactions. Yield: 0.6584 g, 85%. ^{1}H NMR (25 °C, 300 MHz, MeCN-d_3): δ 7.26–7.29 (m, 6H, *meta-* & *para* -Ph), 8.06–8.12 ppm (m, 4H, *ortho*-Ph). ^{31}P{^{1}H} NMR (25 °C, 122 MHz, MeCN-d_3): δ 22.91 ppm. ^{1}H NMR (25 °C, 300 MHz, THF-d_8): δ 7.15–7.18 (m, 6H, *meta-* & *para* -Ph), 8.16–8.23 ppm (m, 4H, *ortho*-Ph). ^{31}P{^{1}H} NMR (25 °C, 122 MHz, THF-d_8): δ 22.76 ppm. IR (KBr pellet, cm^{-1}): 3058(w sh), 3047(m), 2973(w), 2869(w), 1628(m), 1477(s), 1434(s), 1333(w), 1306(m), 1179(m), 1156(w), 1089(s), 1068(w sh), 1049(w sh), 1026(m), 998(m), 923(w), 751(s sh), 744(s), 691(s), 619(m), 539(s), 518(s), 474(s). UV-vis (THF solution, 0.064 mM, nm): 300 (broad shoulder, ε = 2,850 L·mol^{-1}·cm^{-1}), 260 (broad shoulder, ε = 5,300 L·mol^{-1}·cm^{-1}), 230 (λ_{max}, ε = 11,000 L·mol^{-1}·cm^{-1}). As expected, no discernable features in the visible region were observed, even at high concentrations (~0.10 mM).

V(S$_2$PPh$_2$)$_3$ (1). To a stirring, red solution of VCl$_3$(THF)$_3$ (32.5 mg, 0.0870 mmol) in THF (2 mL) was added, dropwise, a colorless solution of KS$_2$PPh$_2$ (73.0 mg, 0.253 mmol) in THF (2 mL). An immediate color change to burgundy (or a deep red-brown color) concomitant with the deposition of an insoluble precipitate (presumably KCl) was observed. The reaction mixture was transferred and sealed in a 100-mL schlenk flask and removed from the glovebox under inert atmosphere. The reaction mixture was then heated at ~65 °C for ~48 h under nitrogen; no further color change was observed but more insoluble precipitate was observed to form as the reaction proceeded. The reaction flask was transferred back into the glove box and the solution filtered through a Celite column (0.5 cm×2 cm) supported on glass wool to give a burgundy homogenous filtrate. The filtrate (~5 mL) was placed in the freezer at −25 °C as is for ~48 h. This resulted in the deposition of a very small amount of pink-colored powder. Based on the powder's IR spectrum, it appears to be mostly complex **1** contaminated with small amounts of VCl$_3$(THF)$_3$ and/or other unwanted, unidentified side-products. The supernatant was decanted and filtered again through a Celite column (0.5 cm×2 cm) supported on glass wool. The resulting filtrate (~5 mL) was concentrated in vacuo to ~3 mL, layered with hexanes (~15 mL), and stored at −25 °C for ~48 h. Burgundy crystals were isolated by decanting the pale yellow supernatant, washing with cold hexanes (~1 mL×3), and drying in vacuo for ~10 min. Yield: 0.0376 g, 56%. Anal. Calcd. for C$_{36}$H$_{30}$P$_3$S$_6$V$_1$: C, 54.12; H, 3.78. Found: C, 53.76; H, 4.01. ^{1}H NMR (25 °C, 300 MHz, THF-d_8): δ 7.63 (s, 6H, *para* -Ph), 8.70 ppm (s, 12H, *meta*-Ph), 9.02 ppm (s, 12H, *ortho*-Ph). IR (KBr pellet, cm^{-1}): 3143(w), 3062(m sh), 3052(m), 2866(w), 2680(w), 2610(w), 2579(w), 2322(w),

2198(w), 2125(w), 1978(m), 1959(m), 1906(m), 1889(m), 1809(m), 1763(w), 1667(m), 1583(m), 1574(m), 1483(m), 1475(w sh), 1436(s), 1383(w), 1335(w), 1325(w), 1307(m), 1278(m), 1185(s), 1159(s), 1099 (s), 1068(m), 1026(s), 998(s), 970(w), 920(m), 846(m), 801(w), 745(s), 706(s), 687(s), 640(s), 611(m), 567(s), 485(s). UV (THF solution, 1.2× 10^{-5} M, nm): 230 (ε = 51,700 L·mol^{-1}·cm^{-1}), 258 (sh, ε = 37,600 L·mol^{-1}·cm^{-1}). Visible (THF solution, 1.1×10^{-4} M, nm): 451 (ε = 3760 L·mol^{-1}·cm^{-1}), 587 (ε = 127 L·mol^{-1}·cm^{-1}). Performing the reaction at room temperature for 48 h results in isolation of **1** in a slightly lower yield (51%). The color, solubility, and IR spectrum of the material prepared at room temperature is consistent with the material prepared at ~65 °C.

V(Se$_2$PPh$_2$)$_3$ (2). To a stirring, red solution of VCl$_3$(THF)$_3$ (57.5 mg, 0.154 mmol) in THF (2 mL) was added, dropwise, a very pale yellow solution of KSe$_2$PPh$_2$ (183.4 mg, 0.4799 mmol) in THF (2 mL). An immediate color change to a very dark purple (or a deep purple color) concomitant with the deposition of an insoluble precipitate (presumably KCl) was observed. The reaction mixture allowed to stir at room temperature for ~48 h. No further color change was observed. The solution was then filtered through a Celite column (0.5 cm×2 cm) supported on glass wool to give a dark purple homogenous filtrate. The filtrate (~5 mL) was placed in the freezer at −25 °C as is for ~48 h. This resulted in the deposition of a very small amount of orange-colored powder. Based on the powder's IR spectrum, it seems to be mostly complex **2** contaminated with small amounts of VCl$_3$(THF)$_3$ and/or other unwanted, unidentified side-products. The supernatant was decanted and filtered again through a Celite column (0.5 cm×2 cm) supported on glass wool. The resulting filtrate (~5 mL) was concentrated in vacuo to ~3 mL, layered with hexanes (~15 mL), and stored at −25 °C for ~48 h. Dark purple crystals were isolated by decanting the pale purple supernatant, washing with cold hexanes (~1 mL×3), and drying in vacuo for ~10 min. Yield: 0.0940 g, 57%. Anal. Calcd. for C$_{36}$H$_{30}$P$_3$Se$_6$V$_1$: C, 40.03; H, 2.80. Found: C, 40.06; H, 2.91. ^{1}H NMR (25 °C, 300 MHz, THF-d_8): δ 7.15 (s, 6H, *para* -Ph), 7.96 ppm (s, 12H, *meta*-Ph), 8.64 ppm (s, 12H, *ortho*-Ph). IR (KBr pellet, cm^{-1}): 3061(w sh), 3049(m), 2966(w), 2858(w), 1629(w), 1479(m), 1435(s), 1330(m), 1306(m), 1182(m), 1158(w), 1093(s), 1067(m), 1047(w sh), 1026(m), 998(m), 917(w), 742(s), 704(w sh), 699(s), 688(s), 617(w), 536(s), 518 (s), 469(s). UV (THF solution, 1.0×10^{-5} M, nm): 232 (ε = 82,600 L·mol^{-1}·cm^{-1}), 281 (broad sh, ε = 36,200 L·mol^{-1}·cm^{-1}). Visible (THF solution, 1.0×10^{-4} M, nm): 544 (ε = 4060 L·mol^{-1}·cm^{-1}).

Cr(S$_2$PPh$_2$)$_3$ (3). A 100-mL Schlenk flask was loaded with purple crystalline CrCl$_3$ (37.8 mg, 0.239 mmol) and suspended in THF (2 mL) with a stir bar. To this flask was added, dropwise, a very pale yellow solution of KS$_2$PPh$_2$ (203.7 mg, 0.7063 mmol) in THF (2 mL) with stirring. No immediate color change was observed upon the addition. The Schlenk flask was then removed from the glovebox under inert atmosphere and the reaction mixture heated to ~65 °C for ~48 h under nitrogen. Over the course of the reaction, a color change to dark purple-blue was observed concomitant with the deposition of an insoluble precipitate (presumably KCl). Following heating for ~48 h, the reaction flask was transferred back into the glove box and the solution filtered through a Celite column (0.5 cm×2 cm) supported on glass wool to give a dichroic purple-blue homogenous filtrate. The resulting filtrate (~5 mL) was layered with hexanes (~13 mL), and stored at −25 °C for ~48 h. Crystals of two distinct morphologies were observed: blue blocks and purple rods. XRD studies indicate the crystals are the same complex where the blue blocks have four molecules of complex **3** in the asymmetric unit cell while the purple rods have only one molecule in the asymmetric unit cell. For yield and characterization studies, the blue-purple crystals were isolated by decanting the nearly colorless supernatant, washing with cold hexanes (~1 mL×3), and

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drying in vacuo for ~10 min Yield: 0.1339 g, 70%. Anal. Calcd. for $C_{36}H_{30}P_3S_6Cr_1$: C, 54.05; H, 3.78. Found: C, 53.98; H, 3.85. ^1H NMR (25 °C, 300 MHz, THF-d_8): δ 8.38 (s, 12H, *ortho*-Ph), 9.64 ppm (s, 18H, *meta-* and *para*-Ph). IR (KBr pellet, cm^{-1}): 3144(w), 3063(m sh), 3051 (m), 2867(w), 2680(w), 2609(w), 2579(w), 2321(w), 2198(w), 2125(w), 1975(m), 1958(m), 1908(m), 1889(m), 1810(m), 1766(w), 1667(m), 1586(m), 1573(m), 1482(m), 1476(w sh), 1435(s), 1385(w), 1333(w), 1325(w), 1307(m), 1279(w), 1161(w), 1185(s), 1159(s), 1100(s), 1068 (s), 1027(s), 998(s), 971(w), 923(m), 854(m), 804(w), 744(s), 708(s), 688(s), 637(s), 610(m), 566(s), 488(s). UV (THF solution, 1.0×10^{-5} M, nm): 217 (ε = 77,300 L·mol^{-1}·cm^{-1}), 260 (broad sh, ε = 35,000 L·mol^{-1}·cm^{-1}), 296 (ε = 30,000 L·mol^{-1}·cm^{-1}). Visible (THF solution, 1.0×10^{-4} M, nm): 368 (ε = 7710 L·mol^{-1}·cm^{-1}), 553 (ε = 530 L·mol^{-1}·cm^{-1}).

Cr(Se$_2$PPh$_2$)$_3$ (4). A 100-mL Schlenk flask was loaded with purple crystalline CrCl$_3$ (44.8 mg, 0.283 mmol) and suspended in THF (2 mL) with a stir bar. To this flask was added, dropwise, a very pale yellow solution of KSe$_2$PPh$_2$ (320.7 mg, 0.8391 mmol) in THF (3 mL) with stirring. No immediate color change was observed upon the addition. The Schlenk flask was then removed from the glovebox under inert atmosphere and the reaction mixture heated to ~65 °C for ~48 h under nitrogen. Over the course of the reaction, a color change to dark green was observed concomitant with the deposition of an insoluble precipitate (presumably KCl). Following heating for ~48 h, the reaction flask was transferred back into the glove box and the solution filtered through a Celite column (0.5 cm × 2 cm) supported on glass wool to give a dark green homogenous filtrate. The resulting filtrate (~5 mL) was layered with hexanes (~13 mL), and stored at −25 °C for ~48 h. Dark green crystals were isolated by decanting the pale green-yellow supernatant, washing with cold hexanes (~1 mL × 3), and drying in vacuo for ~10 min. Yield: 0.1934 g, 64%. Anal. Calcd. for $C_{36}H_{30}P_3Se_6Cr_1$: C, 39.99; H, 2.80. Found: C, 39.84; H, 2.81. ^1H NMR (25 °C, 300 MHz, THF-d_8): δ 8.06 (s, 12H, *ortho*-Ph), 9.67 ppm (s, 18H, *meta-* and *para*-Ph). IR (KBr pellet, cm^{-1}): 3059(w sh), 3048(m), 2970(w), 2858(w), 1576(w), 1572(w), 1479(m), 1435(s), 1330(m), 1306(m), 1181(m), 1158(w), 1093(s), 1067(m), 1047(w sh), 1026(m), 997(m), 969(w), 919 (w), 845(w), 742(s), 709(w sh), 699(s), 687(s), 617(w), 533(m), 517(s), 470(s). UV (THF solution, 1.0×10^{-5} M, nm): 225 (ε = 97,400 L·mol^{-1}·cm^{-1}), 280 (broad sh, ε = 33,000 L·mol^{-1}·cm^{-1}), 325 (broad sh, ε = 27,000 L·mol^{-1}·cm^{-1}). Visible (THF solution, 1.0×10^{-4} M, nm): 434 (ε = 7800 L·mol^{-1}·cm^{-1}), 593 (ε = 274 L·mol^{-1}·cm^{-1}).

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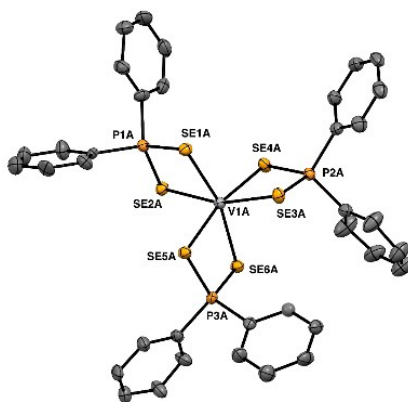
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1 – 12

Synthetic route to vanadium(III) dichalcogenidophosphinate complexes, V(S$_2$PPh$_2$)$_3$ and V-(Se$_2$PPh$_2$)$_3$: A spectroscopic and structural comparative study with analogous complexes of chromium (III), Cr(E$_2$PPh$_2$)$_3$ (E = S, Se)