Preparation and Characterization of a Homoleptic Vanadium(III) Amide Complex and Its Transformation into Terminal Chalcogenide Derivatives $[(3,5\text{-}Me_2Ph)AdN]_3V{=}E$ (E = S, Se; Ad = Adamantyl)

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Reaction of $VCl_3(THF)_3$ with $(3,5\text{-}Me_2Ph)AdNLi{\cdot}Et_2O$ (Ad = adamantyl) yields the homoleptic vanadium complex $[(3,5\text{-}Me_2Ph)AdN]_3V$ (**1**), which reacts with chalcogens E (E = S, Se) to yield diamagnetic terminal chalcogenide derivatives $[(3,5\text{-}Me_2Ph)AdN]_3V{=}E$ [E = S (**3a**), Se (**3b**)] Crystal data for **1** and **3a** are as follows. **1**: $C_{54}H_{72}N_3V$, fw 814.09, triclinic $P\bar{1}$, $a = 10.441(1)$ Å, $b = 11.648(4)$ Å, $c = 19.321(2)$ Å, $\alpha = 83.69(2)°$, $\beta = 83.89(1)°$, $\gamma = 82.42(2)°$, $Z = 2$. **3a**: $C_{54}H_{72}N_3VS{\cdot}{}^1/_2Et_2O$, fw 883.25, monoclinic $C2/c$, $a = 43.400(9)$ Å, $b = 11.744(3)$ Å, $c = 20.705(4)$ Å, $\beta = 113.05(1)°$, $Z = 8$.

Introduction

One of the most attractive characteristics provided by anionic organic amides as ligands is the unlimited possibility of adjusting the steric hindrance around the metal center *via* the appropriate selection of the organic substituents. In particular, the utilization of sterically demanding amides has allowed the preparation of coordinatively unsaturated species able to perform several important transformations. This strategy was first successfully adopted by Wolczanski for the preparation of precursors of lanthanide nitrides,[1] and it was more recently used to perform the first example of well-documented transformation of dinitrogen into nitride,[2] NO cleavage,[3] and trapping of unstable and rare functionalities.[4]

Our interest in this field is mainly focused on low- and medium-valent early transition metals, where the amide ligands considerably enhance the reactivity of the metal center and allow a number of transformations spanning a broad range of reactivity (dinitrogen fixation,[5] dinitrogen cleavage,[6] formation of carbenes,[7] metallacycles[8] and nitrides,[9] hydrogen transfer,[10] deoxygenation and fragmentation of THF,[11] formation of unsupported M−M bonds,[12] reductive couplings[13]). In addition, the M−N bond of a vanadium amide may undergo hydrogenolysis[6] and hydrogen may be removed from the amide alkyl side chain,[5c,14] which of course are desirable performances in view of using transition metal amides as active intermediates in catalytic cycles.

We recently prepared a series of vanadium tris(amide) derivatives where the fourth coordination site around vanadium was invariably occupied by either a Lewis base or a bridging nitrogen molecule. This paper describes the preparation and preliminary studies into the chemical behavior of a rare example of a mononuclear and homoleptic V(III) amide.

Results and Discussion

Scheme 1 outlines the reaction of $VCl_3(THF)_3$ with 3 equiv of $(3,5\text{-}Me_2Ph)AdNLi.Et_2O$ (Ad = adamantyl) in THF, which gave several subsequent color changes from orange to red-violet, to olive green, and finally to brown-green. Dark greenish-brown crystals of the paramagnetic $[(3,5\text{-}Me_2Ph)AdN]_3V$ (**1**) were isolated in reasonable yield from ether solution. The formulation was initially inferred from elemental analysis results and from a magnetic moment measurement ($\mu_{eff} = 2.72\ \mu_B$) which was in agreement with the expected d^2 electronic configuration of the V(III) metal center. A characteristic eight-line EPR spectrum was obtained in solution of benzene ($g = 1.99$, $A = 50$ G).

The molecular connectivity of **1** was confirmed by an X-ray crystal structure determination. The molecule features a trigonal planar vanadium atom connected to three nitrogen atoms of three amide ligands (Figure 1). The coordination geometry around each of the three nitrogens is trigonal planar, suggesting a considerable extent of N−V π-donation. In agreement, the

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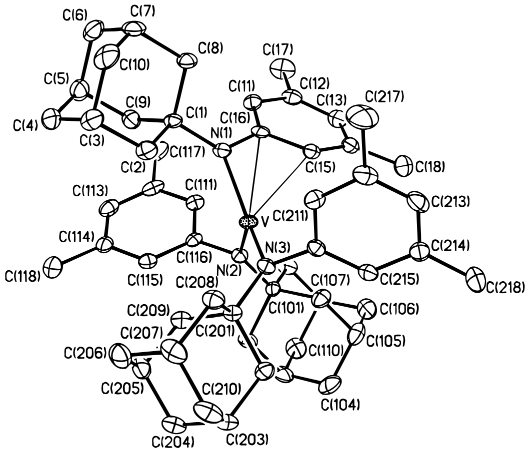
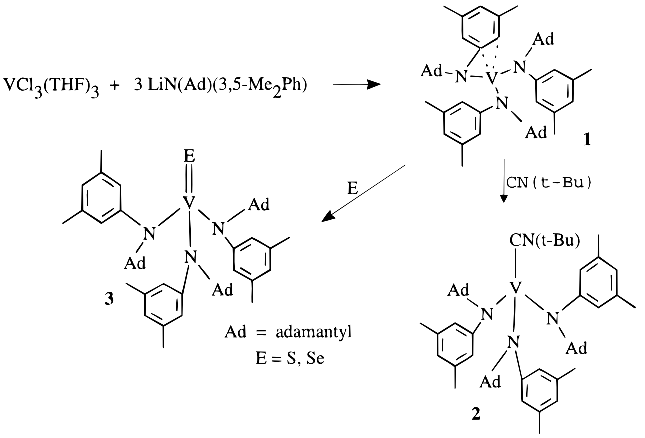


Figure 1. ORTEP plot of **1**. Thermal ellipsoids are drawn at the 50% probability level.

Scheme 1



V$-$N distances are noticeably short in spite of the considerable steric bulk. An aromatic ring of one of the three amide groups is significantly bent toward the vanadium atom, forming a bonding contact between vanadium and two ring carbon atoms, thus creating with the amido nitrogen a sort of η^3-allylic-like system.[15] Corresponding bond alterations have also been observed within the ring C$-$C and the $C_{ring}-N$ distances.

Since $(R_2N)_3V-N_2-V(NR_2)_3$ complexes are remarkably robust,[5b] the inactivity of **1** with elemental nitrogen or THF[5a-d] might be ascribed to the large steric bulk of the adamantyl group, which hinders accessibility to the vanadium atom. It is possible that the pyramidalization of the vanadium center, necessary for the fixation of N_2, is sterically demanding and might not be triggered by the nonpolar N_2 molecule. Conversely, reactions of **1** with *t*-BuNC, which is strongly polar, with a negative charge on the isocyanide carbon atom, readily gave the corresponding tetrahedral adduct $[(3,5\text{-}Me_2Ph)AdN]_3V[CN(t\text{-}Bu)]$ (**2**). This observation prompted us to explore the reactivity of **1** with oxidizing agents which, by increasing the steric hindrance around the metal center, should in principle lead to major molecular reorganization or to the trapping of rare and unstable functionalities. We have selected for this preliminary study the chalcogens (S, Se) due the large atomic dimensions and moderately strong oxidizing ability.

Addition of the elemental chalcogen E (E = S_8, Se) to a toluene solution of **1** gave an immediate dark reddish-violet mixture from which the corresponding derivatives $[(3,5\text{-}Me_2Ph)AdN]_3V{=}E$ [E = S (**3a**), Se (**3b**)] were isolated in crystalline form. The two complexes are diamagnetic, and combustion analysis data are in agreement with the formulation $[(3,5\text{-}Me_2Ph)AdN]_3V{=}E$ [E = S (**3a**), Se (**3b**)]. Both complexes reacted readily with acids to liberate the corresponding H_2E. The IR and ^1H and ^{13}C NMR spectra were almost identical for the two complexes, thus suggesting that the two compounds are isostructural. A very small upfield shift was observed for the ^1H NMR resonances of the selenide derivative. Despite repeated efforts using the widest possible range of frequencies associated with selenium, no resonance was observed in the ^{77}Se NMR spectrum. This is probably due to a strong coupling between the ^{77}Se and the quadrupolar ^{51}V nuclei.[16] Nevertheless, X-ray fluorescence experiments consistently confirmed the presence of this element in a 1:1 ratio with vanadium.

The ^1H NMR spectra of both compounds show some unusual features. The methylene proton resonances of the adamantyl groups are observed as two separate resonances, each appearing as a doublet of doublets, while the methyne proton resonance is a slightly broad singlet. HQMC experiments correlate this resonance with a C$-$H line of the ^{13}C NMR spectrum. The broadness of the methylene line is probably due to a second-order effect, since the COSY spectrum clearly indicated that this singlet is coupled with both doublet of doublets. The methyl groups attached to phenyl rings are nonequivalent and display proton resonances with well-separated chemical shifts. In a parallel fashion, the aromatic ring protons resonate as three distinct singlets at 7.21, 6.67, and 4.58 ppm and at 7.11, 6.66, and 4.50 ppm for **3a** and **3b**, respectively. Correlation experiments clearly indicated that the three resonances correspond to the aromatic methyne in spite of the very unusual chemical shifts of one of them. Variable-temperature experiments show that the resonances at 7.21 and 4.58 ppm coalesce at 350 K, forming a broad feature centered at 5.9 ppm. This indicates that the two resonances arise from the two *ortho* protons, obviously experiencing remarkably different magnetic environments. The solid state crystal structure clearly shows that while one of these two protons points outside the molecule, the other points against the aromatic ring of another amide function. If we assume that, because of the large steric bulk, the solid state structure is preserved in solution, by pointing against the plane of an aromatic ring, one *ortho* proton is placed in the anisotropic magnetic field of the ring. This can cause a significant shielding, which may reasonably explain the unusual chemical shift of this proton. Correspondingly, the two methyl group resonances also significantly broaden without reaching coalescence within the temperature frame used for the experiment.

In the case of **3a**, the connectivity was elucidated by X-ray analysis. Although one badly disordered molecule of ether present in the unit cell prevented satisfactory convergence, the structure was of sufficient accuracy to determine the molecular connectivity. The structure features a monomeric complex with the vanadium center surrounded by three bulky amide groups and one terminal sulfide atom in a distorted tetrahedral geometry (Figure 2). The V$-$S distance is not particularly short [V1$-$S1 = 2.045(3) Å], given the high oxidation state of vanadium, and compares well with those of the few other terminal thiovanadyl species reported in the literature.[17]

The solid state structure is in agreement with the solution NMR features of the complex. In fact, the nonequivalent *ortho* hydrogen may well become equivalent at high temperature due to an increased rotation of the aromatic ring along the $C_{ring}-N$ bond. However, the very unusual chemical shift of one of the

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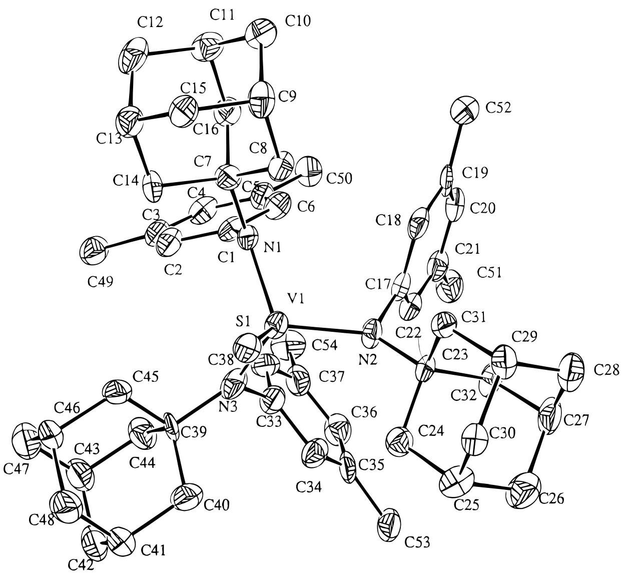

Figure 2. ORTEP plot of **3a**. Thermal ellipsoids are drawn at the 50% probability level.

protons is not clearly understood since the analogous proton−vanadium interatomic separations of all three adamantyl moieties are comparable and consistently too large for significant agostic interactions in the solid state. Investigations into trapping highly reactive functionalities utilizing **1** and into the thermal degradation chemistry of **3** are currently underway.

Experimental Section

All operations were performed under inert atmosphere by using standard Schlenk techniques. $VCl_3(THF)_3$ was prepared according to standard procedures. *t*-BuNC, S_8, 1-bromoadamantane (AdBr), and 3,5-Me_2PhNH_2 (Aldrich) were used as received. Solvents were dried with the appropriate drying agents and distilled prior to use. Infrared spectra were recorded on a Mattson 9000 FTIR instrument from Nujol mulls prepared in a drybox. Samples for magnetic susceptibility measurements were weighed inside a drybox equipped with an analytical balance and sealed into calibrated tubes. Magnetic measurements were carried out with a Gouy balance (Johnson Matthey) at room temperature. The magnetic moment was calculated by standard methods,[18] and corrections for underlying diamagnetism were applied to data.[19] Elemental analyses were carried out with a Perkin-Elmer 2400 CHN analyzer. Ratios between heavy atoms were determined by X-ray fluorescence by using a Philips 2400 instrument.

Preparation of 3,5-Me_2PhN(Ad)H (Ad = Adamantyl). In a modification of a published procedure,[20] AdBr (15.5 g, 72 mmol) was heated for 4 h at 165 °C in the presence of a stoichiometric amount of 3,5-Me_2PhNH_2 (8.7 g, 72 mmol). The resulting pale yellow solid was ground and washed with three portions of ether, yielding a white solid. The solid was treated with an aqueous solution of NaOH (10%) until the pH was basic. The mixture was extracted with several portions of CH_2Cl_2, and the organic phase was washed with water and dried over $MgSO_4$. After filtration, the solvent was removed *in vacuo*, yielding 3,5-Me_2PhN(Ad)H (16.0 g, 63 mmol, 87%) as a colorless microcrystalline solid. The purity was sufficient for the subsequent lithiation, and no further purification by recrystallization was necessary. Anal. Calcd (found) for $C_{18}H_{25}N$: C, 84.63 (84.96); H, 9.87 (10.10); N, 5.48 (5.35). IR (Nujol): ν 3288 (m), 1598 (s), 1356 (m), 1302 (m), 1167 (m), 1118 (s), 1091 (s), 846 (s), 830 (s), 803 (m), 711 (w), 640 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 20 °C, 200 MHz): δ 6.44 (m, 3H, C−$H_{aromatic}$), 2.9 (br, 1H, N−H), 2.22 (s, 6H, Me−Ph), 2.08 (br s, 3H, $CH_{adamantyl}$), 1.85 (br s, 6H, $CH_{2_{adamantyl}}$), 1.66 (br s, 6H, $CH_{2_{adamantyl}}$).

Preparation of 3,5-Me_2PhN(Ad)Li·Et_2O. A solution of 3,5-Me_2PhN(Ad)H (12.9 g, 50 mmol) in ether (250 mL) cooled at −80 °C was treated with a solution of MeLi in ether (36 mL, 1.4 M, 50 mmol). The mixture was allowed to warm slowly to room temperature while a white solid precipitated. After 1 h of stirring at room temperature, the solution was concentrated *in vacuo* and allowed to stand at room temperature. The resulting white precipitate was filtered off under nitrogen (13.3 g, 39 mmol, 78%) and sealed in ampules. The extreme air sensitivity prevented us from obtaining reproducible results in combustion analyses. IR (Nujol): ν 1573 (s), 1350 (w), 1324 (s), 1297 (s), 1179 (s), 1091 (s), 1064 (s), 979 (m), 899 (w), 845 (m), 801 (s), 726 (m), 706 (w), 674 (m) cm^{-1}, ^1H NMR (THF-d_8, 20 °C, 500 MHz): δ 5.79 (s, 2H, C−$H_{aromatic}$), 5.37 (s, 1H, $CH_{aromatic}$), 3.38 (q, 4H, $CH_{2_{ether}}$), 1.95 (br s, 6H, Me−Ph), 2.00 (br s, 3H, $CH_{adamantyl}$), 1.89 (br s, 6H, $CH_{2_{adamantyl}}$), 1.66 (br t, 6H, $CH_{2_{adamantyl}}$), 1.11 (t, 6H, $CH_{3_{ether}}$). ^{13}C NMR (THF-d_8, 20 °C, 125.7 MHz): δ 160.69 (quaternary, aromatic), 135.55 (quaternary, aromatic), 114.69 (C−H, aromatic), 108.12 (C−H, aromatic), 66.28 (CH_2, ether), 52.66 (quaternary, adamantyl), 44.95 (CH_2, adamantyl), 38.67 (CH_2, adamantyl), 31.75 (C−H, adamantyl), 22.48 (CH_3, aromatic), 15.65 (CH_3, ether). ^7Li NMR (THF-d_8, 20 °C, 194 MHz): δ 0.87.

Preparation of [3,5-Me_2PhN(Ad)]$_3$V (1). A suspension of Ad(3,5-Me_2Ph)NLi·Et_2O (4.3 g, 12.7 mmol) in toluene (100 mL) at 20 °C was reacted with $VCl_3(THF)_3$ (1.6 g, 4.3 mmol). After several color changes, the solution finally turned brownish-red. The reaction mixture was heated to about 70 °C for 1 h and subsequently stirred at 20 °C for additional 10 h. The resulting dark greenish brown solution was evaporated to dryness, the residual solid redissolved in ether (120 mL), and the solution quickly filtered. The filtrate was stored at room temperature for a few hours until incipient crystallization and subsequently at −30 °C to increase the yield. Dark green crystals of **1** separated (1.7 g, 2.0 mmol, 48%). Anal. Calcd (found) for $C_{54}H_{72}N_3V$: C, 79.67 (79.73); H, 8.91 (9.03); N, 5.16 (4.92). IR (Nujol): ν 1583 (s), 1352 (m), 1327 (w), 1297 (s), 1197 (m), 1181 (w), 1156 (m), 1110 (s), 1087 (s), 1029 (m), 992 (s), 950 (s), 924 (s), 845 (s), 823 (s), 804 (m), 689 (s) cm^{-1}. $\mu_{eff} = 2.72\ \mu_B$.

Preparation of [3,5-Me_2PhN(Ad)]$_3$V[CN(*t*-Bu)]·Et_2O (2). A solution of **1** (1.44 g, 1.8 mmol) in toluene (65 mL) was treated with neat *t*-BuNC (0.15 g, 1.8 mmol) at room temperature. The color slowly changed to dark brown-purple and finally to violet. After about 10 h of stirring, the solution was evaporated *in vacuo* to dryness. The residual solid was redissolved in ether (80 mL) and the solution filtered, concentrated, and allowed to stand at −30 °C overnight, upon which violet microcrystals of **2** separated (1.12 g, 66%). Anal. Calcd (found) for $C_{63}H_{91}N_4OV$: C, 77.88 (77.45); H, 9.46 (9.32); N, 5.77 (6.00). IR (Nujol): ν 1583 (s), 1350 (m), 1302 (m), 1288 (s), 1207 (w), 1184 (w), 1150 (m), 1106 (m), 1081 (s), 1025 (w), 987 (w), 949 (m), 922 (s), 846 (m), 709 (m), 689 (s) cm^{-1}. $\mu_{eff} = 2.78\ \mu_B$.

Preparation of [3,5-Me_2PhN(Ad)]$_3$V═E·0.5Et_2O [E = S (3a), Se (3b)]. A greenish-brown solution of **1** (1.47 g, 1.8 mmol) in toluene (80 mL) was treated with chalcogen (0.3 mmol). The color changed to the burgundy red, immediately in the case of sulfur and more slowly in the case of selenium. After overnight stirring at room temperature, the mixture was filtered and the solvent evaporated *in vacuo*. The solid residue was redissolved in ether to yield burgundy red crystals of **3**, which were collected by filtration. A second crop of crystalline material was obtained upon allowing the mother liquor to stand in the freezer at −30 °C.

3a. Yield: 1.16 g, 1.4 mmol, 76%. Anal. Calcd (found) for $C_{54}H_{72}N_3VS\cdot{}^1/_2Et_2O$: C 76.15 (76.98); H, 8.79 (8.47); N, 4.76 (5.35). IR (Nujol): ν 1599 (m), 1585 (m), 1352 (w), 1342 (w), 1299 (s), 1185

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Table 1. Crystal Data and Structure Analysis Results

	1	**3a**
formula	$C_{54}H_{72}N_3V$	$C_{54}H_{72}N_3VS\cdot{}^1/_2Et_2O$
fw	814.09	883.25
space group	triclinic, $P\bar{1}$	monoclinic, $C2/c$
a (Å)	10.441(1)	43.400(9)
b (Å)	11.648(4)	11.744(3)
c (Å)	19.321(2)	20.705(4)
α (deg)	83.69(2)	
β (deg)	83.89(1)	113.05(1)
γ (deg)	82.42(2)	
V (Å^3)	2306.15(7)	9733(4)
Z	2	8
$\lambda_{K\alpha}$ (Å)	0.710 73	1.540 56
T (K)	233	111
D_{calcd} (g cm^{-3})	1.173	1.208
μ_{calcd} (cm^{-1})	2.54	24.1
F_{000}	880	3815
R,[a] R_w,[b] GOF	0.0468, 0.0998, 0.96	0.082, 0.103, 2.35

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg)

Compound **1**

V−N1	1.945(3)	V−C16	2.399(4)
V−N2	1.905(3)	V−C15	2.425(4)
V−N3	1.900(3)		
N1−V−N2	122.0(1)	N3−C216−C211	119.8(3)
N1−V−N3	118.1(1)	V−N1−C1	141.0(2)
N2−V−N3	117.6(1)	V−N2−C101	130.9(3)
V−N1−C16	90.6(2)	V−N3−C201	129.1(2)
N1−C16−C15	114.4(3)	C1−N1−C16	125.2(3)
V−N2−C116	110.7(2)	C101−N2−C116	118.2(3)
N2−C116−C111	121.2(4)	C201−N3−C216	116.1(3)
V−N3−C216	114.0(2)		

Compound **3a**

V1−S1	2.045(3)	V1−N2	1.893(6)
V1−N1	1.897(6)	V1−N3	1.885(7)
S1−V1−N1	108.7(2)	N2−V1−N3	111.3(3)
S1−V1−N2	107.0(2)	C1−N1−C7	113.5(6)
S1−V1−N3	109.3(2)	V1−N1−C1	115.6(5)
N1−V1−N2	111.7(3)	V1−N1−C7	130.0(5)
N1−V1−N3	108.7(3)		

(w), 1145 (m), 1103 (m), 1051 (s), 1025 (m), 945 (m), 925 (s), 889 (m), 850 (w), 817 (m), 728 (m), 706 (s), 691 (s) cm^{-1}. ^{1}H NMR (toluene-d_8, 20 °C, 500 MHz): δ 7.21 (s, 3H, CH$_{aromatic}$), 6.67 (s, 3H, CH$_{aromatic}$), 4.58 (s, 3H, CH$_{aromatic}$), 3.24 (q, 2H, ether), 2.56−2.25 (dd, 18H, CH$_{2_{adamantyl}}$), 2.21 (s, 9H, CH$_3$), 2.20 (s, 9H, CH$_{adamantyl}$), 2.04 (s, 9H, CH$_3$), 1.73−1.62 (dd, 18H, adamantyl), 1.12 (t, 3H, ether). ^{13}C NMR (toluene-d_8, 20 °C, 125.7 MHz): δ 154.1, 136.6, 135.9 (C$_{quaternary}$, aromatic), 128.9, 127.7, 127.1 (CH, aromatic), 65.5 (C$_{quaternary}$, adamantyl), 46.1, 36.9 (CH$_2$, adamantyl), 31.4 (CH, adamantyl), 21.9, 21.3 (CH$_3$, aromatic). ^{51}V NMR (toluene-d_8, 20 °C, 131.4 MHz): δ 676.2.

3b. Yield: 1.13 g, 1.3 mmol, 70%. Anal. Calcd (found) for $C_{54}H_{72}N_3VSe\cdot{}^1/_2Et_2O$: C, 72.31 (72.87); H, 8.34 (8.16); N, 4.52 (4.31). IR (Nujol): ν 1599 (m), 1584 (m), 1351 (w), 1341 (w), 1298 (s), 1285 (m), 1262 (w), 1184 (w), 1145 (w), 1102 (m), 1047 (s), 1025 (m), 942 (m), 923 (s), 888 (m), 850 (w), 804 (w), 728 (m), 706 (s), 690 (s) cm^{-1}. ^{1}H NMR (toluene-d_8, 20 °C, 500 MHz): δ 7.11 (s, 3H, CH$_{aromatic}$), 6.66 (s, 3H, CH$_{aromatic}$), 4.50 (s, 3H, CH$_{aromatic}$), 3.25 (q, 2H, ether), 2.58−2.25 (dd, 18H, CH$_{2_{adamantyl}}$), 2.23 (s, 9H, CH$_3$), 2.16 (s, 9H, CH$_{adamantyl}$), 2.06 (s, 9H, CH$_3$), 1.73−1.61 (dd, 18H, CH$_{2_{adamantyl}}$), 1.12 (t, 3H, ether). ^{13}C NMR toluene-d_8, 20 °C, 125.7 MHz): δ 153.5, 136.5, 135.9 (C$_{quaternary}$, aromatic), 129.3, 128.1, 127.0 (CH, aromatic), 64.8 (C$_{quaternary}$, adamantyl), 46.5, 36.9 (CH$_2$, adamantyl), 31.4 (CH, adamantyl), 21.9, 21.3 (CH$_3$, aromatic). ^{51}V NMR (toluene-d_8, 20 °C, 131.4 MHz): δ 1001.2.

X-ray Crystallography. Data were collected at 233 and 111 K for **1** and **3a**, respectively. Air-sensitive crystals were mounted on glass fibers inside a drybox and transferred under the liquid-nitrogen stream of the cooling system of the X-ray diffractometer. The $\omega-2\theta$ (**1**) and $\theta-2\theta$ (**3a**) scan techniques were used. Cell constants and orientation matrices were obtained from the least-squares refinement of 25 and 24 centered reflections for **1** and **3a**, respectively. The intensities of three standard reflections, measured after every 150 reflections, showed no statistically significant decay over the duration of the data collections. Data were corrected for Lorentz and polarization effects and for absorption (ψ scan). The structures were solved by direct methods, resulting in location of all the non-hydrogen atoms. Their positions were refined anisotropically. Hydrogen atom positions were calculated but not refined. In the case of complex **3a**, a disordered molecule of ether was found in the lattice. Failure to successfully model the disorder prevented the convergence of the agreement factors to acceptable values. Nevertheless, the structure was sufficient to demonstrate the chemical connectivity. Refinements were carried out by using full-matrix least-squares techniques on F, minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o{}^2/\sigma^2(F_o{}^2)$ and F_o and F_c are the observed and calculated structure factors. Atomic scattering factors and anomalous dispersion terms were taken from the usual sources.[21] Details on the data collections and structure refinement are listed in Table 1. The final atomic coordinates are given as Supporting Information. Selected bond distances and angles are given in Table 2. All the calculations were performed on UNIX Silicon Graphics workstations by using the SHELXL and the NRCVAX structure solution and refinement packages.

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Supporting Information Available: Tables of crystal data and details of structure solution and refinement, atomic coordinates and isotropic thermal parameters, anisotropic thermal parameters, bond distances, and bond angles for **1** and **3a** (22 pages). Ordering information is given on any current masthead page.

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(21) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974.