Homoleptic Selenolates of Vanadium(II), -(III), and -(IV): Generation, Trapping, and Disproportionation of Tris[tris(trimethylsilyl)silylselenolate]vanadium

Christopher P. Gerlach and John Arnold*

Department of Chemistry, University of California, Berkeley, California 94720-1460

Received November 12, 1997

Homoleptic selenolates of V(II) and V(IV) are prepared by selenolysis of the amide ligands in [(Me$_3$Si)$_2$N]$_2$VSeSi-(SiMe$_3$)$_3$ with 2 equiv of HSeSi(SiMe$_3$)$_3$. The products were isolated by fractional crystallization from a mixture of hexanes/HMDSO (HMDSO = hexamethyldisiloxane), which first gave a V(II) selenolate of empirical composition V[SeSi(SiMe$_3$)$_3$]$_2$(HMDSO)$_{1/2}$, followed by the more soluble monomeric V(IV) species, V[SeSi-(SiMe$_3$)$_3$]$_4$. These compounds are proposed to be the disproportionates of a V(III) precursor (i.e. "V[SeSi-(SiMe$_3$)$_3$]$_3$"). Room-temperature EPR spectra of the tetraselenolate exhibited an 8-line pattern typical of V(IV) with g_{iso} = 1.92 and A_{iso} = 65 G. Addition of 2 equiv of DMPE (DMPE = 1,2-bis(dimethylphosphino)ethane) to the V(II) selenolate afforded *trans*-(DMPE)$_2$V[SeSi(SiMe$_3$)$_3$]$_2$ which has been characterized by X-ray crystallography. "V[SeSi(SiMe$_3$)$_3$]$_3$" can be generated in cold hexanes and trapped with Lewis bases to afford the 4-coordinate adducts V[SeSi(SiMe$_3$)$_3$]$_3$(L) (L = pyridine, 2,6-dimethylphenylisocyanide). For L = pyridine, addition of styrene oxide resulted in a 2-electron oxidation and formation of diamagnetic OV[SeSi(SiMe$_3$)$_3$]$_3$. Reaction of $^1/_2$ equiv of pyrazine with "V[SeSi(SiMe$_3$)$_3$]$_3$" gave the pyrazine-bridged dimer {V[SeSi(SiMe$_3$)$_3$]$_3$}$_2$-(μ-pyrazine) which was also crystallographically characterized.

Introduction

The recent burgeoning interest in the study transition metal selenolates and tellurolates[1] can be attributed to two main factors. The first is to determine the viability of using metal–EX(SiMe$_3$)$_3$ complexes (E = Se, Te; X = C, Si) as precursors to solid-state metal chalcogenides[2-10] where specific insights into the mechanisms[11-13] of these decomposition reactions may be useful in designing superior single-source precursors for technologically important materials; the second relates to the ability of derivatives incorporating large –EX(SiMe$_3$)$_3$ ligands to form stable, low-nuclearity complexes which may yield fundamental insights into the chemistry of compounds with single[1] and multiple[14] bonds between metals and the heavier chalcogens.

Toward the latter aim, we have synthesized compounds of the type M[ESi(SiMe$_3$)$_3$]$_4$, where M = Ti, Zr, Hf, and have described their structures and reactivities in detail.[6] The

diminished reactivity we observed for group 4 selenolates compared to tellurolates was ascribed primarily to steric effects where, due to the smaller size of the chalcogen in the former, the bulky tris(trimethylsilyl)silyl substituents are closer to the metal center, rendering it less prone to associative-type reactivity. To ease the steric constraint imposed by four –SeSi-(SiMe$_3$)$_3$ ligands, we sought to extend this chemistry to three-coordinate species, in particular to compounds of the type V[SeSi(SiMe$_3$)$_3$]$_3$. We report here that although "V[SeSi-(SiMe$_3$)$_3$]$_3$" can be generated in solution and trapped as various Lewis base adducts, at room temperature it decomposes to {V-[SeSi(SiMe$_3$)$_3$]$_2$}$_n$ and V[SeSi(SiMe$_3$)$_3$]$_4$. While our previously reported synthesis of V[TeSi(SiMe$_3$)$_3$]$_4$ is analogous to that described here for the selenium analogue (i.e. from V(III)),[15] evidence for disproportionation of V(III) in the tellurium case was circumstantial in that the fate of the low-valent vanadium species could not be determined. In the present case, isolation of both V(II) and V(IV) selenolates, as well as trapping the unstable "V[SeSi(SiMe$_3$)$_3$]$_3$", offers more convincing evidence that V(ER)$_3$ complexes decompose by disproportionation of the trivalent oxidation state. X-ray crystallography confirmed the product of reaction between "V[SeSi(SiMe$_3$)$_3$]" and pyrazine (pyrz) to be the dimer {V[SeSi(SiMe$_3$)$_3$]$_3$}$_2$(μ-pyrz). Finally, we note that group 5 selenolates are rare: other than our previous reports of [(Me$_3$Si)$_2$N]$_2$VSeR (R = Si(SiMe$_3$)$_3$, SiPh$_3$) and [(Me$_3$Si)$_2$N]$_2$V(E')(SeR) (E' = O, S, Se), only complexes of formula M(SeR)$_3$ (M = Nb, Ta; R = Ph, naphthyl) have been mentioned,[16] although nothing is known regarding their structures or reactivity.

(1) Arnold, J. In *Progress in Inorganic Chemistry*; Karlin, K. D., Ed.; Wiley: New York, 1995; Vol. 43, p 353.
(2) Cheon, J. W.; Arnold, J.; Yu, K. M.; Bourret, E. D. *Chem. Mater.* **1995**, *7*, 2273.
(3) Seligson, A. L.; Bonasia, P. J.; Arnold, J.; Yu, K. M.; Walker, J. M.; Bourret, E. D. *Proc. Mater. Res. Soc.* **1993**, *282*, 665.
(4) Seligson, A. L.; Arnold, J. *J. Am. Chem. Soc.* **1993**, *115*, 8214.
(5) Arnold, J.; Walker, J. M.; Yu, K.-M.; Bonasia, P. J.; Seligson, A. L.; Bourret, E. D. *J. Cryst. Growth* **1992**, *124*, 647.
(6) Gerlach, C. P.; Christou, V.; Arnold, J. *Inorg. Chem.* **1996**, *35*, 2758.
(7) Christou, V.; Arnold, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1450.
(8) Cheng, Y.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **1996**, *35*, 7339.
(9) Bochmann, M. *Chem. Vap. Deposition* **1996**, *2*, 85+.
(10) Brennan, J. G.; Siegrist, T.; Carroll, P. J.; Stuczynski, S. M.; Reynders, P.; Brus, L. E.; Steigerwald, M. L. *Chem. Mater.* **1990**, *2*, 403.
(11) Piers, W. E. *J. Chem. Soc., Chem. Commun.* **1994**, 309.
(12) Piers, W. E.; Parks, D. J.; MacGillivray, L. R.; Zaworotko, M. J. *Organometallics* **1994**, *13*, 4547.
(13) Gindelberger, D. E.; Arnold, J. *Organometallics* **1994**, *13*, 4462.
(14) Trnka, T.; Parkin, G. *Polyhedron* **1997**, *16*, 1031.

(15) Gerlach, C. P.; Wuller, S. W.; Arnold, J. *Chem. Commun.* **1996**, 2565.
(16) Andra, V. K. *Z. Anorg. Allg. Chem.* **1970**, *373*, 209.

Experimental Section

General. Standard inert atmosphere glovebox and Schlenk-line techniques were employed for all manipulations. All solvents were predried over 4 Å molecular sieves and in the case of benzene-d_6, hexanes, hexamethyldisiloxane (HMDSO), toluene, THF, and pyridine (pyr) were distilled from sodium. CH_2Cl_2 was distilled from CaH_2. CNXyl (Xyl = 2,6-dimethylphenyl) was purchased from Fluka and used as received. Pyrazine (pyrz) was recrystallized from hexanes, and styrene oxide was distilled prior to use. The compounds HSeSi-$(SiMe_3)_3$,[17] $[(Me_3Si)_2N]_2VSeSi(SiMe_3)_3$,[18] and 1,2-bis(dimethylphosphino)ethane (DMPE)[19] were prepared by the literature procedures. ^{1}H and $^{13}C\{^1H\}$ NMR spectra were recorded in C_6D_6 at 300 and 75 MHz. $^{51}V\{^1H\}$ NMR spectra were recorded in C_6D_6 at 78.94 MHz and externally referenced to neat $VOCl_3$ at 0 ppm. Melting points were determined under N_2 in sealed capillaries. Samples for IR spectroscopy were prepared as mineral oil mulls between KBr plates. Magnetic susceptibility measurements were made in solution by the method of Evans[20,21] or in the solid state using a Johnson-Mathey balance. The calculated magnetic moments were corrected for underlying diamagnetism. The EPR spectrum of V[SeSi(SiMe_3)_3]_4 (10^{-2} M, benzene) was measured at room temperature on an X-band spectrometer. C, H, and N analyses and EIMS measurements were done within the College of Chemistry, University of California, Berkeley. X-ray data were collected and the structures solved at the University of California at Berkeley, chemistry X-ray facility.

{V[SeSi(SiMe_3)_3]_2}_n. A hexanes solution (20 mL) of $HSeSi(SiMe_3)_3$ (725 mg, 2.21 mmol) was added to a magnetically stirred, cold (-40 °C) hexanes solution of $[(Me_3Si)_2N]_2VSeSi(SiMe_3)_3$ (773 mg, 1.11 mmol). The mixture immediately turned crimson on addition of the selenol. The mixture was gradually warmed to room temperature and stirred overnight, after which it was golden brown. After removal of the volatile materials under reduced pressure, the solid was extracted with ca. 40 mL of HMDSO and then 20 mL of hexanes to dissolve virtually all of the material. The combined filtrates were concentrated to ca. 20 mL and cooled to -25 °C for 48 h. Dark green crystals of "V[SeSi(SiMe_3)_3]_2" (300 mg) were isolated by filtration. The material tenaciously retained HMDSO (^{1}H NMR) even after extended exposure to vacuum. Quantitative hydrolysis experiments conducted in C_6D_6 in the presence of a standard (C_6Me_6) along with elemental analysis indicate the empirical formula: V[SeSi(SiMe_3)_3]_2(HMDSO)_{1/2}. Mp: 181−184 °C (dec). IR: 1307 w, 1244 s, 1160 w br, 1055 w br, 859 s sh, 837 vs, 721 m, 688 m, 624 m cm^{-1}. μ_{eff} = 3.95 μ_B (per V). Anal. Calcd for $C_{24}H_{72}OSe_2Si_{10}V$: C, 32.12; H, 8.09. Found: C, 31.84; H, 8.22.

V[SeSi(SiMe_3)_3]_4. Further concentration of the filtrate from the above reaction to ca. 5 mL followed by cooling to -25 °C for 24 h afforded dark red-brown crystals of V[SeSi(SiMe_3)_3]_4 (605 mg, 40% on V) that were isolated by filtration and dried under vacuum. The compound retained a small amount of HMDSO as evidenced by ^{1}H NMR spectroscopy. Mp: 224−227 °C (dec). ^{1}H NMR: δ 0.78 ($\Delta\nu_{1/2}$ ca. 80 Hz). IR: 1307 w, 1244 s, 1160 w br, 1055 w br, 859 s sh, 837 vs, 721 m, 688 m, 624 m cm^{-1}. μ_{eff} = 2.65 μ_B. EIMS: 1357 (M$^+$, correct isotope pattern). Anal. Calcd for $C_{36}H_{108}Se_4Si_{16}V$: C, 31.85; H, 8.02. Found: C, 32.26; H, 8.29.

V[SeSi(SiMe_3)_3]_3(pyr). A hexanes solution (20 mL) of HSeSi-$(SiMe_3)_3$ (376 mg, 1.15 mmol) was added to a magnetically stirred, cold (-45 °C) hexanes solution (20 mL) of $[(Me_3Si)_2N]_2VSeSi(SiMe_3)_3$ (401 mg, 0.574 mmol). Pyr (47 μL, 0.58 mmol) was added, and the red mixture was gradually warmed to room temperature and stirred a further 30 min. The volatile materials were removed under reduced pressure and the solid was extracted with HMDSO (2 × 30 mL). The combined filtrates were concentrated to ca. 5 mL and cooled to -25 °C for 24 h. Two crops of red-brown crystals were isolated by filtration

and dried under vacuum (400 mg, 63%). Mp: 121−123 °C (dec). ^{1}H NMR: δ 1.1 (s, $\Delta\nu_{1/2}$ ca. 120 Hz). IR: 1602 w, 1306 w, 1256 sh s, 1243 s, 1160 w, 1068 w, 1044 w, 1008 w, 860 sh s, 835 vs, 758 w, 743 w, 724 w, 690 m, 623 m cm^{-1}. μ_{eff} = 2.98 μ_B (solid). Anal. Calcd for $C_{32}H_{86}NSe_3Si_{12}V$: C, 34.63; H, 7.81; N, 1.26. Found: C, 32.17; H, 7.68; N, 1.16.

V[SeSi(SiMe_3)_3]_3(CNXyl). A cold (-30 °C) hexanes solution (25 mL) of $HSeSi(SiMe_3)_3$ (606 mg, 1.85 mmol) was added to a magnetically stirred, cold (-40 °C) hexanes solution (25 mL) of $[(Me_3Si)_2N]_2VSeSi(SiMe_3)_3$ (646 mg, 0.925 mmol) resulting in a crimson mixture. The solution was transferred to a flask containing CNXyl (121 mg, 0.922 mmol), and the reaction gradually warmed to room temperature. After stirring the orange-red mixture overnight, the volatile materials were removed under reduced pressure, and the residue dried for 1 h under vacuum. The solid was extracted with HMDSO (60 mL), the solution filtered, and the filtrate concentrated to ca. 20 mL. Slowly cooling the solution to -25 °C for 24 h afforded 662 mg (62%) of maroon crystals. Mp: 161−165 °C (dec). ^{1}H NMR (0.04 M): δ 1.4 ($\Delta\nu_{1/2}$ ca. 115 Hz). IR: 2126 (ν_{CN}) m, 1259 sh; 1242 s, 860 s sh, 837 vs, 723 m, 689 m, 624 m cm^{-1}. μ_{eff} = 2.97 μ_B (C_6D_6). Anal. Calcd for $C_{36}H_{90}NSe_3Si_{12}V$: C, 37.21; H, 7.81; N, 1.21. Found: C, 37.37; H, 7.98; N, 1.23.

{V[SeSi(SiMe_3)_3]_3}_2(μ-pyrz). A hexanes solution (20 mL) of $HSeSi(SiMe_3)_3$ (797 mg, 2.43 mmol) was added to a magnetically stirred, cold (-50 °C) hexanes solution (20 mL) of $[(Me_3Si)_2N]_2VSeSi(SiMe_3)_3$ (850 mg, 1.22 mmol). The red solution was transferred to a flask containing pyrz (49 mg, 0.61 mmol). The reaction mixture turned emerald green but quickly became deep green-brown. The solution was allowed to gradually warm to room temperature and was stirred for 24 h. The volatile materials were removed under reduced pressure, leaving a brown solid. Following extraction into 45 mL of hexanes, the solution was filtered and concentrated to ca. 20 mL. Cooling the mixture to -25 °C overnight afforded a first crop of 245 mg of dark green crystals. A second crop of 315 mg was obtained after further concentration and cooling of the filtrate (net yield 43%). The filtrate from the second crop may be stripped dry, and the solid washed with cold (-70 °C) HMDSO to afford additional product as a powder whose physical and spectroscopic data match that of crystalline material. Mp: 192−194 °C (dec). ^{1}H NMR (0.02 M): δ 0.63 ($\Delta\nu_{1/2}$ ca. 20 Hz). IR: 1307 w, 1255 m sh, 1243 s, 859 s, 835 vs, 744 w, 723 w, 689 m, 663 w, 623 m, 546 w br, 460 w, 451 w, 410 m cm^{-1}. μ_{eff} = 2.80 μ_B (C_6D_6, 1.98 μ_B per V). Anal. Calcd for $C_{29}H_{83}NSe_3Si_{12}V$: C, 32.53; H, 7.81; N, 1.31. Found: C, 32.78; H, 8.08; N, 1.30.

OV[SeSi(SiMe_3)_3]_3. PhCH(O)CH_2 (42 μL, 0.37 mmol) was added to a hexanes solution (20 mL) of V[SeSi(SiMe_3)_3]_3(pyr) (410 mg, 0.369 mmol), giving a green mixture. After stirring for 1 h, the volatile materials were removed under reduced pressure. The dark green solid was extracted with hexanes (20 mL), and the filtered solution concentrated to ca. 5 mL. Slow cooling to -25 °C for 24 h afforded 100 mg (27%) of dark green, blocky needles that were isolated by filtration and dried under vacuum. Mp: 151−155 °C (dec). ^{1}H NMR: δ 0.43 (s). $^{13}C\{^1H\}$ NMR: δ 1.69 (s). ^{51}V NMR: δ 1190 ($\Delta\nu_{1/2}$ ca. 45 Hz, J_{VSe} ca. 75 Hz). IR: 1308 w, 1257 m sh, 1244 s, 1169 w, 1154 w, 1010 m ($\nu_{V=O}$), 856 s sh, 837 vs, 734 sh, 722 m, 689 m, 622 m cm^{-1}. EIMS: 1046 (M$^+$, correct isotope pattern).[22] Anal. Calcd for $C_{27}H_{81}OSe_3Si_{12}V$: C, 30.98; H, 7.80. Found: C, 29.94; H, 7.76.

(DMPE)_2V[SeSi(SiMe_3)_3]_2. DMPE (120 μL, 0.719 mmol) was added to a hexanes solution (15 mL) of V[SeSi(SiMe_3)_3]_2(HMDSO)_{1/2} (236 mg, 0.300 mmol). The reaction mixture gradually became orange and some product precipitated from solution. After stirring overnight, the volatile materials were removed under reduced pressure. The orange solid was extracted with toluene (30 mL) and the solution filtered through a fine frit padded with Celite. Concentration of the clear orange filtrate to 15 mL followed by cooling to -25 °C afforded the product

(17) Bonasia, P. J.; Christou, V.; Arnold, J. *J. Am. Chem. Soc.* **1993**, *115*, 6777.
(18) Gerlach, C. P.; Arnold, J. *Inorg. Chem.* **1996**, *35*, 5770.
(19) Burt, R. J.; Chatt, J.; Hussain, W.; Leigh, G. J. *J. Organomet. Chem.* **1979**, *182*, 203.
(20) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.
(21) Schubert, E. M. *J. Chem. Educ.* **1992**, *69*, 62.

(22) Under the conditions of the experiment, the complex was not sufficiently volatile at temperatures below its decomposition point. At elevated temperatures, a signal for the molecular ion of $[(Me_3Si)_3SiSe]_3VOSiMe_3$ was observed with a 3-fold greater intensity than that of OV[SeSi(SiMe_3)_3]_3.

Table 1. Summary of X-ray Diffraction Data: R = Si(SiMe₃)₃

	[V(SeR)₃]₂(μ−pyrz)	(DMPE)₂V(SeR)₂
empirical formula	C₅₈H₁₆₆N₂Se₆Si₂₄V₂	C₃₀H₈₂P₄Se₂Si₈V
mol wt	2146.66	1000.42
source, color, habit	hexanes, green, tabular	toluene, red, acicular
cryst size (mm)	0.40 × 0.29 × 0.12	0.16 × 0.14 × 0.05
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
T (°C)	−116	−107
a (Å)	13.9401(1)	9.7299(2)
b (Å)	14.5095(2)	26.9356(2)
c (Å)	17.6691(2)	10.8239(2)
α (deg)	68.513(1)	90
β (deg)	72.638(1)	103.459(1)
γ (deg)	64.469(1)	90
vol (Å³)	2958.39(7)	2758.83(11)
Z	1	2
ρ_{calcd} (g cm⁻³)	1.20	1.20
μ (cm⁻¹)	22.75	18.08
diffractometer	Siemens, CCD/area detector	Siemens, CCD/area detector
radiation (λ)	Mo Kα (0.710 73 Å)	Mo Kα (0.710 73 Å)
scan mode	ω (0.3° scans)	ω (0.3° scans)
collcn range	hemisphere	hemisphere
total no. of reflcns	12487	10732
no. of unique reflcns	8321	4033
R_{int}	0.0307	0.0591
abs type	semiempirical, XPREP	semiempirical, XPREP
transm coeff	0.579−0.876	0.775−0.885
structure soln	direct methods, TEXSAN	direct methods, TEXSAN
no. of obs (n_o), I > 3σ(I)	6513	2192
no. of params refined (n_v)	415	377
final R,^{a} R_w^{b}	0.0322, 0.0410	0.0352, 0.0366
GOF^c	1.43	1.20

^{a} $R = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$. ^{b} $R_w = \{[\Sigma_w(|F_o| - |F_c|)^2]/\Sigma_w F_o^2\}^{1/2}$. ^{c} GOF $= [\Sigma_w(|F_o|^2 - |F_c|^2)^2/(n_o - n_v)]^{1/2}$.

as orange needles that were isolated by filtration and dried under vacuum (122 mg, 40%). Mp: 200−203 °C (dec). ¹H NMR (300 MHz): δ 2.27 ($\Delta\nu_{1/2}$ ca. 95 Hz). IR: 1294 w, 1277 w, 1252 w sh, 1236 m, 948 m, 927 m, 887 w, 861 m sh, 833 s, 735 m, 722 m, 706 m, 681 m, 645 w, 622 m cm⁻¹. Anal. Calcd for C₃₀H₈₆P₄Se₂Si₈V: C, 35.87; H, 8.63. Found: C, 35.42; H, 8.72.

X-ray Crystallography. A summary of crystal, collection, and refinement data is given in Table 1. A listing of selected refined atomic coordinates is given in Table 2.

{V[SeSi(SiMe₃)₃]₃}₂(μ-pyrz). Green crystals were grown from hexanes at −25 °C. A suitable crystal was mounted on a glass capillary under Paratone-N hydrocarbon oil. The crystal was transferred to a Siemens SMART diffractometer/CCD area detector[23] and cooled by a nitrogen-flow, low-temperature apparatus. A preliminary orientation matrix and unit cell parameters were determined by collecting sixty, 10-s frames, followed by spot integration and least-squares refinement. A hemisphere of data was collected using 0.3° ω scans at 10 s per frame. The raw data were integrated (*XY* spot spread = 1.60°; *Z* spot spread = 0.60°) and the unit cell parameters refined (7930 reflections with I > 10σ(I)) using SAINT.[24] The space group $P\bar{1}$ was indicated by the absence of any higher symmetry, and the intensity statistics were consistent with a centric space group. Preliminary data analysis and a semiempirical ellipsoidal absorption correction (T_{min} = 0.579; T_{max} = 0.876; merging R_{int} before/after correction: 0.0678/0.0286) were performed using XPREP.[25] Of the 124 87 reflections measured, 8321 were unique and 6513 had I > 3σ(I) and were used in the refinement.

(23) *SMART Area-Detector Software Package*; Siemens Industrial Automation, Inc.: Madison, WI, 1993.

(24) *SAINT: SAX Area-Detector Integration Program*, v. 4.024; Siemens Industrial Automation, Inc.: Madison, WI, 1994.

Table 2. Atomic Coordinates and Equivalent Isotropic Thermal Parameters for Selected Atoms of (DMPE)₂V[SeSi(SiMe₃)₃]₂ and {V[SeSi(SiMe₃)₃]₃}₂(μ-pyrz)

atom	x	y	z	B_{eq} (Å)
	(DMPE)₂V[SeSi(SiMe₃)₃]₂			
Se	0.19480(7)	0.06072(3)	0.12846(7)	3.40(3)
V	0	0	0	2.15(6)
P(1)	−0.1402(2)	0.06572(6)	−0.1415(2)	2.85(7)
P(2)	0.1380(2)	0.00340(6)	−0.1687(2)	2.76(7)
Si(1)	0.2363(2)	0.13430(6)	0.2335(2)	2.41(7)
Si(2)	0.4054(2)	0.11223(7)	0.4194(2)	2.94(8)
Si(3)	0.0690(2)	0.18291(7)	0.3076(2)	3.42(8)
Si(4)	0.3548(2)	0.18333(7)	0.1108(2)	3.22(8)
C(1)	0.5752(8)	0.0935(4)	0.3802(8)	4.6(4)
C(2)	0.3400(9)	0.0579(3)	0.4961(7)	4.3(4)
C(3)	0.450(1)	0.1640(3)	0.5384(8)	5.2(4)
C(4)	0.032(1)	0.1588(3)	0.4581(7)	4.5(4)
C(5)	0.150(1)	0.2458(3)	0.3445(9)	4.7(4)
C(6)	−0.1050(8)	0.1940(4)	0.1941(8)	5.3(4)
C(7)	0.474(1)	0.2309(3)	0.2089(9)	4.8(4)
C(8)	0.229(1)	0.2165(3)	−0.020(1)	5.6(5)
C(9)	0.471(1)	0.1424(3)	0.0381(9)	5.3(5)
C(10)	−0.119(1)	0.1305(4)	−0.095(1)	6.6(5)
C(11)	−0.3303(8)	0.0624(3)	−0.1982(8)	4.3(4)
C(12)	−0.0778(8)	0.0653(4)	−0.2883(7)	5.1(4)
C(13)	0.0831(8)	0.0608(3)	−0.2582(9)	5.2(4)
C(14)	0.3295(7)	0.0075(3)	−0.1340(7)	3.9(4)
C(15)	0.1026(9)	−0.0430(3)	−0.2941(8)	4.7(4)
	[(Me₃Si)₂N]₂VSeSi(SiMe₃)₃			
Se(1)	0.59134(3)	0.08904(3)	0.19337(2)	2.86(4)
Se(2)	0.36368(3)	−0.01102(3)	0.29573(3)	3.04(4)
Se(3)	0.31928(3)	0.25296(3)	0.33771(3)	2.82(4)
V(1)	0.44708(5)	0.09334(5)	0.30641(4)	2.15(5)
Si(1)	0.72559(9)	0.15455(8)	0.17097(7)	2.6(1)
Si(2)	0.6585(1)	0.31973(9)	0.19859(8)	3.1(1)
Si(3)	0.7742(1)	0.1789(1)	0.02723(7)	3.5(1)
Si(4)	0.8763(1)	0.0318(1)	0.23471(8)	3.4(1)
Si(5)	0.4675(1)	−0.18811(8)	0.30406(7)	2.8(1)
Si(6)	0.5318(1)	−0.1973(1)	0.16723(8)	5.2(1)
Si(7)	0.60681(9)	−0.27289(9)	0.38276(8)	3.1(1)
Si(8)	0.3300(1)	−0.2579(1)	0.36771(9)	4.4(1)
Si(9)	0.16778(8)	0.34087(8)	0.27600(7)	2.5(1)
Si(10)	0.1970(1)	0.3432(1)	0.13726(7)	3.4(1)
Si(11)	0.1206(1)	0.5118(1)	0.2880(1)	4.2(1)
Si(12)	0.03725(9)	0.2701(1)	0.36411(7)	3.1(1)
N(1)	0.4817(2)	0.0327(2)	0.4177(2)	2.3(3)
C(28)	0.4056(3)	0.0123(3)	0.4854(2)	2.6(4)
C(29)	0.4235(3)	−0.0186(3)	0.5636(2)	2.7(4)

Redundant reflections were averaged. The data were corrected for Lorentz−polarization, but no correction for crystal decay was applied. The structure was solved by direct methods using the TEXSAN package[26] on a Digital microvax workstation and refined using standard least squares and Fourier techniques. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included at idealized positions and included in F_c but not refined. Neutral atomic scattering factors were taken from Cromer and Waber,[27] and anomalous dispersion effects were included in F_c.[28] The final residuals for 415 variables refined against 6513 data for which I > 3σ(I) were R = 0.0322, R_w = 0.0410, and GOF = 1.434.

(DMPE)₂V[SeSi(SiMe₃)₃]₂. Red needles were grown from a concentrated toluene solution at −25 °C. A preliminary orientation matrix and unit cell parameters were determined as described above.

(25) *XPREP: Part of the SHELXTL Crystal Structure Determination Package*; Siemens Industrial Automation: Madison, WI, 1994.

(26) *TEXSAN: Crystal Structure Analysis Package*; Molecular Structure Corporation: The Woodlands, TX, 1992.

(27) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(28) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.
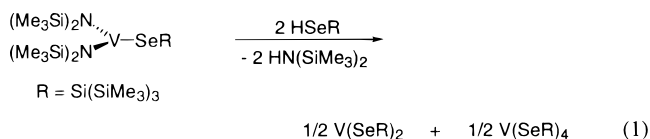
A hemisphere of data was collected using 0.3° ω scans at 20 s per frame. The raw data were integrated as above, and the unit cell parameters were refined (4516 reflections with $I > 10\sigma(I)$) using SAINT. The intensity statistics were consistent with a centric space group, and the space group $P2_1/n$ (No. 14, setting No. 3) was uniquely defined by the systematic absences. Preliminary data analysis and a semiempirical ellipsoidal absorption correction were performed using XPREP. Redundant reflections were averaged. No correction for crystal decay was applied. The structure was solved as above. All non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were located from the difference map and refined with isotropic thermal parameters. The final residuals for 377 variables refined against 2192 data for which $F^2 > 3\sigma(F^2)$ were $R = 0.0352$, $R_w = 0.0366$, and GOF = 1.20.

Results and Discussion

Homoleptic Selenolates of V(II) and V(IV). Our first attempts at preparing homoleptic vanadium selenolates involved salt metathesis reactions between $VX_3(THF)_3$ (X = Cl, Br) and 3 equiv of $(THF)_2LiSeSi(SiMe_3)_3$ under a variety of reaction conditions. Both reduction of the vanadium and incomplete reaction of the starting reagents hampered these reactions. In the most promising cases, the low yields, high solubility, and paramagnetism of the reaction products prevented adequate characterization.

These disappointing results contrasted with our earlier finding that V(III) selenolates and tellurolates are readily prepared using $[(Me_3Si)_2N]_2VBr$ (THF) as the vanadium starting material, where salt metathesis reactions involving the bromide ligand lead to clean substitution with a variety of selenolate and tellurolate anions. For example, $[(Me_3Si)_2N]_2VSeSi(SiMe_3)_3$ was isolated in ca. 80% yield by reaction of $[(Me_3Si)_2N]_2VBr$-(THF) with $(THF)_2LiSeSi(SiMe_3)_3$.[18] Suspecting that the two $-N(SiMe_3)_2$ ligands should be susceptible to protonation, we attempted to prepare homoleptic selenolates by reaction with the selenol $HSeSi(SiMe_3)_3$.

Treatment of a red-brown hexanes solution of $[(Me_3Si)_2N]_2VSeSi(SiMe_3)_3$ with 2 equiv of $HSeSi(SiMe_3)_3$ at low temperature immediately gave a crimson solution. On warming the mixture to room temperature, the color gradually settled to golden brown. Two products were isolated by fractional crystallization from a mixture of hexanes and HMDSO (eq 1).

$$\begin{array}{c}(Me_3Si)_2N_{\diagdown} \\ (Me_3Si)_2N^{\diagup}V-SeR\end{array} \quad \xrightarrow[- 2\ HN(SiMe_3)_2]{2\ HSeR}$$

$$R = Si(SiMe_3)_3$$

$$\qquad\qquad 1/2\ V(SeR)_2 \quad + \quad 1/2\ V(SeR)_4 \qquad (1)$$

A dark green compound we formulate as $\{V[SeSi(SiMe_3)_3]_2(HMDSO)_{1/2}\}_n$ (35% yield based on V) was the less soluble of the two products. Even after extended exposure to vacuum, the amount of HMDSO remained fairly constant from sample-to-sample, and thus it is possible that the solvent is an integral part of the crystal lattice. The empirical formula deduced by elemental analysis was confirmed by hydrolysis experiments[29] which gave a stoichiometry of selenolate ligands and $^1/_2$ HMDSO per vanadium. The complex dissolved readily in aromatic solvents, affording deep green solutions that were indefinitely stable under an $N_2(g)$ or Ar(g) atmosphere but were

highly air and moisture sensitive. Other than a signal for the HMDSO, the ^1H NMR spectrum in C_6D_6 was completely featureless and a magnetic susceptibility measurement in the same solvent yielded a magnetic moment of 3.95 μ_B. Given the spin-only value of 3.87 μ_B for high spin, d^3 V(II), the magnetic moment is consistent with a +2 oxidation state for the vanadium. The IR and NMR data gave no evidence of any functional groups other than the selenolate ligands. Attempts to observe $\{V[SeSi(SiMe_3)_3]_2\}_n$ species in the gas phase using EI mass spectroscopy experiments were not successful, as the compound was not sufficiently volatile prior to its decomposition point. The compound may be a dimer in the solid state, analogous in structure to $\{Zn[TeSi(SiMe_3)_3]_2\}_2$,[30] $\{Cd[SeC-(SiMe_3)_3]_2\}_2$,[31] or $\{Sn[TeSi(SiMe_3)_3]_2\}_2$;[4] however, all of these are significantly more volatile.

After isolation of the V(II) selenolate, further concentration and cooling of the filtrate lead to crystallization of a second product, the homoleptic V(IV) selenolate $V[SeSi(SiMe_3)_3]_4$. Dark crystals were isolated in typical yields of ca. 40% yield based on vanadium (eq 1). Compounds of the class $V(OR)_4$ include $V(OSiPh_3)_4$,[32] as well as alkoxides of tertiary and some secondary alcohols.[33,34] $V(SBu^t)_4$[32,35] is the only well-characterized example of a homoleptic V(IV) thiolate; $V[SeSi(SiMe_3)_3]_4$ and the tellurium analog[15] are the first examples of heavier chalcogenolates of this type.

A broad signal (δ 0.8, $\Delta\nu_{1/2}$ ca. 80 Hz) due to the 12 $-SiMe_3$ groups of $V[SeSi(SiMe_3)_3]_4$ was observed in the ^1H NMR spectrum of the paramagnetic (d^1) complex. The IR spectrum of the material was virtually identical to that of $\{V[SeSi-(SiMe_3)_3]_2\}_n$. Although elemental analysis was consistent with the proposed formulation, a rather high magnetic moment of 2.65 μ_B leads us to not exclude the possibility that some additional V(II) selenolate may crystallize with the V(IV) product. Given that the tellurium analogue crystallizes as well-separated $V[TeSi(SiMe_3)_3]_4$ monomers,[15] the selenium complex is no doubt isostructural both in the solid state and in solution. A strong peak for the molecular ion ($m/z = 1357$) was observed in the EI mass spectrum. The complex had a somewhat higher decomposition point than the V(II) selenolate, and at 224−227 °C, it is about 30 °C lower than those observed for the series $M[SeSi(SiMe_3)_3]_4$ (M = Ti, Zr, Hf).[6] In contrast to the ease of ligand hydrolysis in $V[TeSi(SiMe_3)_3]_4$, the tetraselenolate reacts only very slowly in wet benzene to give $HSeSi(SiMe_3)_3$. $V[SeSi(SiMe_3)_3]_4$ is also very thermally stable in solution, as C_7D_8 samples stored at 115 °C for 24 h showed no sign of decomposition. Although the metal center is electron deficient, with four bulky selenolate ligands the vanadium is effectively coordinatively saturated and does not react with Lewis bases such as pyridine.

The X-band EPR spectrum of $V[SeSi(SiMe_3)_3]_4$ was recorded in benzene at room temperature. An 8-line pattern, resulting from coupling of the unpaired electron with ^{51}V ($I = ^7/_2$) is characteristic for the d^1 electronic configuration of V(IV), yielded $g_{iso} = 1.92$ and $A_{iso} = 65$ G. Christou et al. have pointed out that the increase in g_{iso} and decrease in A_{iso} on going from

(29) Quantitative hydrolysis experiments were conducted in C_6D_6 with C_6-Me_6 as an internal standard. The reaction of $\{V[SeSi(SiMe_3)_3]_2$-$(HMDSO)_{1/2}\}_n$ with ca. 10 equiv of H_2O (degassed) immediately yielded a clear, colorless solution with a small amount of brown precipitate. Selenol $(HSeSi(SiMe_3)_3)$ was the only product detected by ^1H NMR spectroscopy.

(30) Bonasia, P. P.; Arnold, J. *Inorg. Chem.* **1992**, *31*, 2508.
(31) Bonasia, P. J. Ph.D. Thesis, University of California at Berkeley, December 1993.
(32) Preuss, F.; Noichl, H. *Z. Naturforsch* **1987**, *42B*, 121.
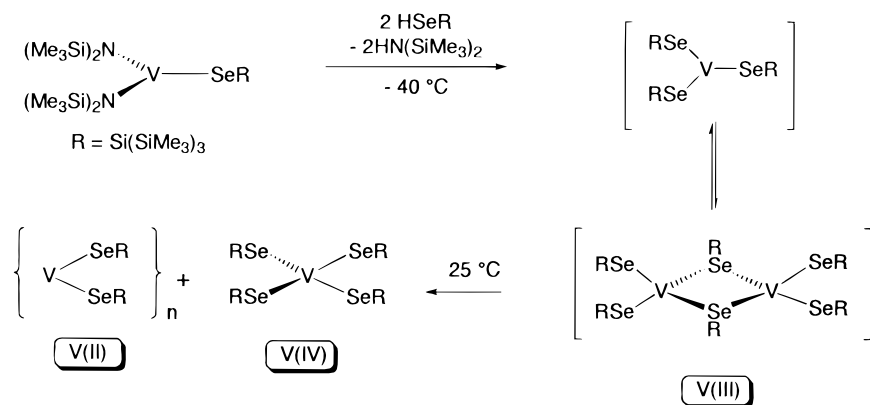(33) $V(OCH_2Bu^t)_4$ is apparently an exception as it is reported to be monomeric in solution; see: Bradley, D. C.; Mehta, M. L. *Can. J. Chem.* **1962**, *40*, 1183.
(34) Bochmann, M.; Wilkinson, G.; Young, G. B.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1980**, 901.
(35) Heinrich, D. D.; Folting, K.; Huffman, J. C.; Reynolds, J. G.; Christou, G. *Inorg. Chem.* **1991**, *30*, 300.

Scheme 1

$V(OBu^t)_4$ to $V(SBu^t)_4$ is a natural consequence of the more covalent V–S bonds.[35] These trends in the EPR data do not continue for $V[SeSi(SiMe_3)_3]_4$; however, because the substituent on the chalcogen differs both sterically and electronically, it is difficult to draw any meaningful conclusions at this point.

It is likely that the above V(II) and V(IV) selenolates arise via disproportionation of the V(III) intermediate depicted in Scheme 1. Since $[(Me_3Si)_2N]_2VSeSi(SiMe_3)_3$ possesses both an electrophilic metal center and a vacant coordination site, it is reasonable that 2 equiv of $HSeSi(SiMe_3)_3$ react rapidly to liberate 2 equiv of $HN(SiMe_3)_2$ and give "$V[SeSi(SiMe_3)_3]_3$". The crimson color that was observed on mixing the reactants appeared to be persistent as long as the reaction mixture was kept cold (ca. −40 °C). Only on warming the mixture to room temperature did it gradually turn the golden-brown of the final product mixture, suggesting that the disproportionation step is rate limiting. At this point, any suppositions regarding the structure of "$V[SeSi(SiMe_3)_3]_3$" in solution are purely speculative. However, since 3-coordinate vanadium species are relatively rare[36] and, except for the cases of $V[CH(SiMe_3)_2]_3$[37,38] and $V(PC_6H_{11})_3$,[39] all involve amide ligands, we believe that any monomer–dimer equilibrium of "$V[SeSi(SiMe_3)_3]_3$" is displaced largely on the side of a dimeric species. Since the reaction is carried out in nonpolar, hexanes solvent, the dimeric structure in Scheme 1 would facilitate an inner sphere electron transfer between the vanadium centers followed by an irreversible scission of the dimer into the V(II) and V(IV) products. Although chalcogenolate chemistry of low valent vanadium is not extensively developed, precedent for the dimer in Scheme 1 is found in the solid-state structure of $[V(OAr)_2(\mu\text{-}OAr)]_2$-(THF) (Ar = 2,6-$Me_2C_6H_3$).[40] It is noteworthy that the putative intermediate $V(SBu^t)_3(bpy)$ (bpy = 2,2′-bipyridine) is unstable with respect to ligand distribution and exists as a salt with the structure $[V(SBu^t)_2(bpy)_2][V(SBu^t)_4]$.[35]

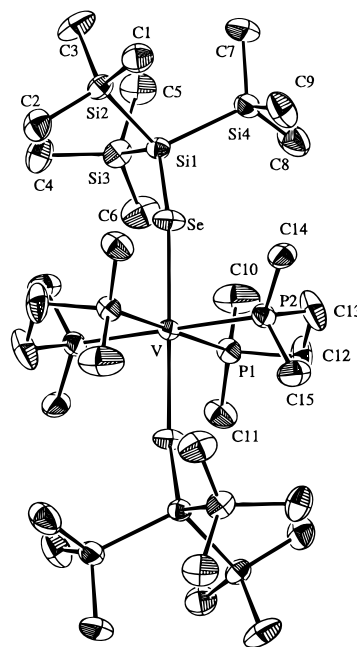The V(II) selenolate was successfully derivatized as shown in eq 2. Addition of 2 equiv of DMPE to green solutions of
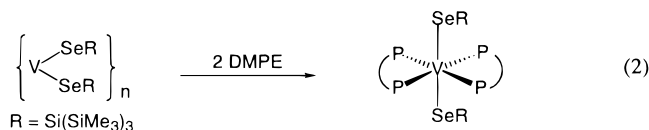
$\{V[SeSi(SiMe_3)_3]_2\}_n$ gradually gave an orange solution from

Figure 1. ORTEP drawing (50% ellipsoids) of $(DMPE)_2V[SeSi(SiMe_3)_3]_2$.

which *trans*-$(DMPE)_2V[SeSi(SiMe_3)_3]_2$ was isolated as orange needles from toluene in 40% yield. The ¹H NMR spectrum of the paramagnetic complex showed only a broad signal at δ 2.3 ($\Delta\nu_{1/2}$ ca. 95 Hz). No other products were detected when the reaction was monitored by NMR spectroscopy.

X-ray crystallography confirmed a trans orientation of the bulky –$SeSi(SiMe_3)_3$ ligands in the solid state. An ORTEP drawing of the structure is shown in Figure 1, and a listing of bonds and angles is given in Table 3. The molecule crystallized in the space group $P2_1/n$ with the vanadium atom resting on a center of inversion. The V–P distances and P–V–P angles are normal for *trans*-$(DMPE)_2VX_2$ compounds.[41–44] At 2.6408(6) Å, the V–Se interaction is on the long side, but not unexpectedly so, considering the low formal oxidation state of the metal. As observed for related species with *trans*-$L_4M[ESi(SiMe_3)_3]_2$

(36) Cummins, C. C. *Progress in Inorganic Chemistry*; Karlin, K. D., Ed.; Wiley: New York, 1998; Vol. 47, p 685.
(37) Barker, G. K.; Lappert, M. F. *J. Organomet. Chem.* **1974**, *76*, C45.
(38) Barker, G. K.; Lappert, M. F.; Howard, J. A. K. *J. Chem. Soc., Dalton Trans.* **1978**, 734.
(39) Issleib, K.; Wenschuh, E. *Chem. Ber.* **1964**, *97*, 715.

(40) Gambarotta, S.; van Bolhuis, F.; Chiang, M. Y. *Inorg. Chem.* **1987**, *26*, 4301.
(41) Sussmilch, F.; Olbrich, F.; Gailus, H.; Rodewald, D.; Rehder, D. *J. Organomet. Chem.* **1994**, *472*, 119.
(42) Morris, R. J.; Wilson, S. R.; Girolami, G. S. *J. Organomet. Chem.* **1994**, *480*, 1.
(43) Jensen, J. A.; Girolami, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 4450.
(44) Girolami, G. S.; Wilkinson, G.; Galas, A. M. R.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1985**, 1339.

Table 3. Selected Bond Distances and Angles for (DMPE)₂V[SeSi(SiMe₃)₃]₂ and {V[SeSi(SiMe₃)₃]₃}₂(μ-pyrz)

(DMPE)₂V[SeSi(SiMe₃)₃]₂		{V[SeSi(SiMe₃)₃]₃}₂(μ−pyrz)	
Bond Distances (Å)			
V−Se	2.6408(6)	V−Se(2)	2.3532(7)
Se−Si(1)	2.274(2)	V−Se(3)	2.3744(7)
V−P(1)	2.523(2)	V−N(1)	1.951(3)
V−P(2)	2.507(2)	Se(1)−Si(1)	2.319(1)
Si(1)−Si(2)	2.360(2)	Se(2)−Si(5)	2.316(1)
Si(1)−Si(3)	2.370(3)	Se(3)−Si(9)	2.304(1)
Si(1)−Si(4)	2.355(3)	Si−Si$_{av}$	2.352(6)
V−Se(1)	2.3713(7)		
Bond Angles (deg)			
V−Se−Si	145.62(5)	Se(1)−V−Se(3)	123.28(3)
Se−V−P(1)	96.06(4)	Se(1)−V−N(1)	118.19(9)
Se−V−P(1)*	83.94(4)	Se(2)−V−N(1)	105.34(9)
Se−V−P(2)	85.42(4)	Se(2)−V−Se(3)	112.03(3)
Se−V−P(2)*	94.58(4)	Se(3)−V−N(1)	91.59(9)
P(1)−V−P(2)	80.69(5)	V−Se(1)−Si(1)	125.96(3)
P(1)−V−P(2)*	99.31(5)	V−Se(2)−Si(5)	117.14(4)
Se(1)−V−Se(2)	105.13(3)	V−Se(3)−Si(9)	118.26(3)

geometries,[45,46] the V−Se−Si angle of 145.62(5)° is on the high end of the range observed for complexes of this ligand.
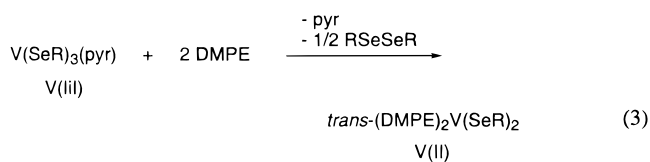
Reactivity of "V[SeSi(SiMe₃)₃]₃" and Derivatives. Although some VX₃ fragments have been observed to "trap" dinitrogen (e.g. [(BuᵗCH₂)₃V]₂(μ-N₂);[47] [(R₂N)₃V]₂(μ-N₂) (R = Prⁱ, C₆H₁₁)[48]), the reaction in eq 1 proceeded the same under a dinitrogen or argon atmosphere. However, the addition of better donors such as pyr and CNXyl to cold solutions of "VSeSi(SiMe₃)₃" led to the 4-coordinate complexes shown in Scheme 2.

The pyr adduct V[SeSi(SiMe₃)₃]₃(pyr) was extremely soluble in hydrocarbon and ethereal solvents but could be crystallized from HMDSO as red-brown crystals in ca. 60% yield. An absorption at 1602 cm⁻¹ in the IR spectrum indicates pyr is bound in the conventional η^1-mode as observed for V(OSiBuᵗ₃)₃-(pyr),[49] in contrast to the η^2-NC-pyr binding mode observed in the heavier congeners Nb(OSiBuᵗ₃)₃(pyr)[50] and Ta(OSiBuᵗ₃)₃-(pyr).[49] V[SeSi(SiMe₃)₃]₃(pyr) is paramagnetic, and the solid-state magnetic moment of 2.98 μ_B is consistent with a high spin d^2 electronic configuration. The ¹H NMR spectrum in C₆D₆ showed only a broad signal at δ 1.1 ($\Delta\nu_{1/2}$ ca. 120 Hz) for the −SiMe₃ groups.

Preparation of V[SeSi(SiMe₃)₃]₃(CNXyl) was analogous to that of the pyr adduct (Scheme 2), and the product was isolated cleanly as maroon crystals in ca. 60% yield. The ν_{CN} at 2126 cm⁻¹ is blue-shifted 11 cm⁻¹ relative to the free ligand, indicating a minor amount of back-donation from vanadium d orbitals ($d_{xz}{}^1 d_{yz}{}^1$) to CN π^* orbitals (electron deficient (e.g. d^0) CNR complexes typically have their ν_{CN} shifted approximately 30−50 cm⁻¹ higher in energy than that of the free ligand[51−53]).

Introduction of 2 equiv of DMPE into a C₆D₆ solution of

(45) Gindelberger, D. E.; Arnold, J. *Inorg. Chem.* **1994**, *33*, 6293.

(46) Gindelberger, D. E.; Arnold, J. *Inorg. Chem.* **1993**, *32*, 5813.

(47) Buijink, J.-K. F.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 2004.

(48) Song, J.-I.; Berno, P.; Gambarotta, S. *J. Am. Chem. Soc.* **1994**, *116*, 6927.

(49) Covert, K. J.; Neithamer, D. R.; Zonnevylle, M. C.; LaPointe, R. E.; Schaller, C. P.; Wolczanski, P. T. *Inorg. Chem.* **1991**, *30*, 2494.

(50) Kleckley, T. S.; Bennett, J. L.; Wolczanski, P. T.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **1997**, *119*, 247.

(51) Stults, S. D.; Andersen, R. A.; Zalkin, A. *Organometallics* **1990**, *9*, 115.

(52) Evans, W. J.; Drummond, D. K. *Organometallics* **1988**, *7*, 797.

(53) Moloy, K. G.; Fagan, P. J.; Manriquez, J. M.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 56.

V[SeSi(SiMe₃)₃]₃(pyr) resulted in an immediate color change to green, followed by a gradual transition over 1 h to a clear orange solution. Analysis by ¹H NMR spectroscopy showed only pyr, Se₂[Si(SiMe₃)₃)]₂, and a signal for (DMPE)₂V[SeSi-(SiMe₃)₃]₂ (see above), suggesting the net transformation in eq 3. Since lower oxidation states of vanadium are kinetically

$$\text{V(SeR)}_3\text{(pyr)} \quad + \quad 2\text{ DMPE} \xrightarrow[\;-\;1/2\text{ RSeSeR}\;]{-\text{ pyr}} \quad trans\text{-(DMPE)}_2\text{V(SeR)}_2 \qquad (3)$$

accessible and stable, reductive elimination of diselenide apparently provides a lower energy reaction pathway than extrusion of Se[Si(SiMe₃)₃]₂, the latter being pathway operative in Group 4 complexes of −ESi(SiMe₃)₃ ligands where reduction is much less favorable.[6]

Treatment of a hexanes solution of V[SeSi(SiMe₃)₃]₃(pyr) with 1 equiv of styrene oxide immediately resulted in a green solution from which the diamagnetic V(V) oxo was isolated in ca. 30% yield as green needles (eq 4). Reactions monitored
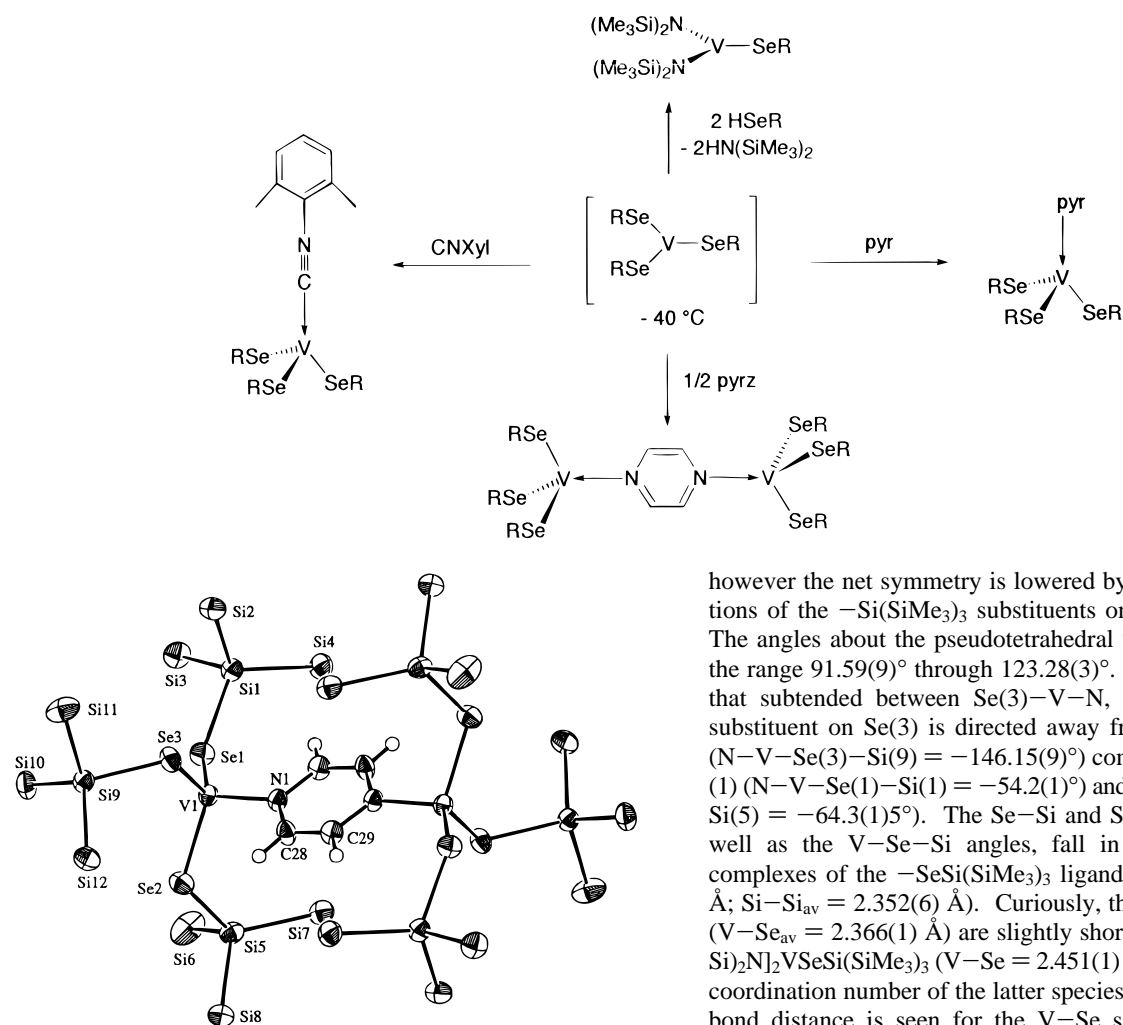

$$ (4) $$

R = Si(SiMe₃)₃
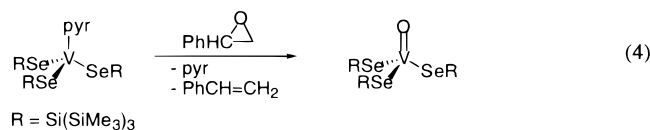
by NMR spectroscopy suggested a clean conversion to product, and thus it appears that recovery of the material by crystallization was hindered only by its extremely high solubility. An absorption at 1010 cm⁻¹ in the IR spectrum is indicative of the terminal V=O stretch. In contrast to eq 4, reaction of a hexanes solutions of "V[SeSi(SiMe₃)₃]₃" with styrene oxide gave purple mixtures from which a pure product could not be isolated. Although a resonance could not be detected in the ⁷⁷Se NMR spectrum (presumably due to quadrupolar broadening from ⁵¹V) the higher symmetry about the vanadium (C_{3v}) compared to other V(V) selenolates we have studied resulted in a relatively sharp signal in the ⁵¹V NMR spectrum at δ 1190 ($\Delta\nu_{1/2}$ ca. 45 Hz). Compared with a signal at δ 245 ($\Delta\nu_{1/2}$ ca. 275 Hz) for [(Me₃Si)₂N]₂V(O)[SeSi(SiMe₃)₃], it evident that replacing amide ligands with selenolate ligands results in deshielding the vanadium center and is consistent with greater pπ−dπ donation from −NR₂ relative to −SeR ligands. For example, the triamidoamine vanadium -oxo ([(Me₃SiNCH₂CH₂)₃N]V=O) has a considerably upfield signal at δ −173 ($\Delta\nu_{1/2}$ = 46 Hz) in its ⁵¹V NMR spectrum.[54]

Adding a cold hexanes solution of "V[SeSi(SiMe₃)₃]₃" to a flask containing ¹/₂ equiv of pyrazine (pyrz) turned the mixture first emerald green and then quickly to a darker brown-green. Workup of the reaction mixture gave dimeric {V[SeSi-(SiMe₃)₃]₃}₂(μ-pyrz) in 43% yield as a dark green, crystalline solid (Scheme 2). After crystallization of the product, the remaining solvent was stripped off to afford additional material as a clean powder, again suggesting that the high solubility of the complex inhibits recovery by crystallization. Quantitative hydrolysis experiments confirmed a stoichiometry of 6 −SeSi-(SiMe₃)₃ ligands per 1 pyrz, and X-ray crystallography (see below) confirmed the structure to consist of a pyrz unit trapped between two V[SeSi(SiMe₃)₃]₃ fragments. The complex is paramagnetic and has a solution state magnetic moment of 2.80

(54) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Inorg. Chem.* **1994**, *33*, 1448.

Scheme 2

Figure 2. ORTEP drawing (50% ellipsoids) of V(SeR)₃]₂(μ-pyrz) (R = Si(SiMe₃)₃)₂.

μ_B per dimer (1.98 μ_B per V). As a result, the ¹H NMR spectrum consisted of a broad resonance at δ 0.63 (Δ$\nu_{1/2}$ ca. 20 Hz), presumably for the −SiMe₃ groups, and no resonances were observed for the coordinated pyrz.

An ORTEP drawing of {V[SeSi(SiMe₃)₃]₃}₂(μ-pyrz) is shown in Figure 2 and selected metrical data is collected in Table 3. The molecule crystallized in the space group $P\bar{1}$, with a center of inversion lying in the middle of the bridging pyrz ring; thus the asymmetric unit consists of one-half of the molecule, with the entire dimeric unit making up the unit cell ($Z = 1$). The local symmetry about the vanadium is approximately C_{3v},

however the net symmetry is lowered by the different orientations of the −Si(SiMe₃)₃ substituents on the selenium atoms. The angles about the pseudotetrahedral vanadium center span the range 91.59(9)° through 123.28(3)°. The smallest angle is that subtended between Se(3)−V−N, since the bulky silyl substituent on Se(3) is directed away from the pyrazine ring (N−V−Se(3)−Si(9) = −146.15(9)°) compared to those on Se-(1) (N−V−Se(1)−Si(1) = −54.2(1)°) and Se(2) (N−V−Se(2)−Si(5) = −64.3(1)5°). The Se−Si and Si−Si bond lengths, as well as the V−Se−Si angles, fall in the usual range for complexes of the −SeSi(SiMe₃)₃ ligand (Se−Si$_{av}$ = 2.313(2) Å; Si−Si$_{av}$ = 2.352(6) Å). Curiously, the V−Se bond lengths (V−Se$_{av}$ = 2.366(1) Å) are slightly shorter than that in [(Me₃-Si)₂N]₂VSeSi(SiMe₃)₃ (V−Se = 2.451(1) Å),[18] despite the lower coordination number of the latter species. A more comparable bond distance is seen for the V−Se single bond in [(Me₃-Si)₂N]₂V(Se)[SeSi(SiMe₃)₃] (V−Se = 2.3620(8) Å). The pyrz ligand is coordinated with a normal V−N dative bond length of 1.951(3) Å and the plane of the ring, as judged from the C(28)/C(29)−N−V−Se torsion angles, is most closely aligned along the V−Se(1) bond (C(29)*−N−V−Se(1) = 21.5(3)°).