Synthesis of Terminal Vanadium(V) Imido, Oxo, Sulfido, Selenido, and Tellurido Complexes by Imido Group or Chalcogen Atom Transfer to Trigonal Monopyramidal V[N3N] (N3N = [(Me3SiNCH2CH2)3N]3-)

Christopher C. Cummins, Richard R. Schrock, * **and William M. Davis**

Department of Chemistry, 6-331, Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139

Received October 3, 1993[@]

The crystalline trilithium salt Li3[N3N] (N3N = [(Me3SiNCH2CH2)3N]3-) reacts with VCl4(DME) (DME = 1,2-dimethoxyethane) to give [N3N]VCl in 45% yield. The structure of [N3N]VCl, as determined by X-ray crystallography, is a distorted trigonal bipyramid with three equatorial silylamido groups and axial chloride and amine donor ligands. Reduction of [N3N]VCl with Na/Hg in pentane provides trigonal monopyramidal V[N3N] in >90% yield. V[N3N] deoxygenates propylene oxide, *cis*- or *trans*-2-butene oxide, pyridine *N*-oxide, nitrous oxide, or dimethyl sulfoxide to produce [N3N]V≡O. Treatment of V[N3N] with either S8 or ethylene sulfide gives [N3N]V≡S, while gray selenium reacts with V[N3N] to give black crystalline [N3N]V≡Se. PMe3 abstracts selenium from [N3N]V≡Se, forming Me3P≡Se and regenerating V[N3N]. Elemental tellurium does not react with V[N3N], but when V[N3N] is treated with Me3P≡Te in toluene under vacuum, [N3N]V≡Te can be observed by NMR in solution. The chalcogenide complexes [N3N]V≡X (X = O, S, Se, Te) were characterized by ^{51}V NMR. Shifts ranged over 1600 ppm, with the more electronegative chalcogens producing greater upfield ^{51}V chemical shifts. V[N3N] reacts with trimethylsilyl azide to give [N3N]V≡NSiMe3. [N3N]V≡NSiMe3 also could be prepared by reducing [N3N]VN3 with Na/Hg, followed by treatment with Me3SiCl. V[N3N] reacts with C5H5NNC6F5 to give rust-red [N3N]V≡NC6F5 and with (trimethylsilyl)diazomethane to give [N3N]V≡N—N≡CH(SiMe3). [N3N]V≡N(p-CH3C6H4) was prepared by adding a solution of Li3[N3N] to Cl3V≡N(p-CH3C6H4) in ether. An NH group transfers from 2-methylaziridine to V[N3N], liberating propylene and forming yellow, crystalline [N3N]V≡NH. [N3N]V≡NH may be deprotonated and then silylated to give [N3N]V≡NSiMe3. The structure of [N3N]V≡NH was determined by X-ray crystallography. The imido hydrogen was located and refined; the V≡N—H unit is nearly linear (173(6)°), and the V–N$_{imido}$ bond length is 1.638(6) Å. The V–N$_{amine}$ bond length (2.241(6) Å) is comparable to that in [N3N]VCl (2.238(6) Å). The structure of [N3N]V≡NH is compared and contrasted with the structures of [N3N]VCl and V[N3N'] (N3N' = [(t-BuMe2SiNCH2CH2)3N]3-).

Introduction

Sterically-demanding silylamide ligands have been used for over two decades to stabilize low coordination numbers and unsaturated metal-containing fragments.[1–3] One of the most widely used ligands in this category, in part because of its ready availability, has been the bis(trimethylsilyl)amido ligand.[4] Our interest in high-oxidation-state chemistry[5–10] led us to explore the possibility of preparing relatively rigid and robust complexes that contain the readily-prepared trianionic trialkyl-silylated version of tris(2-aminoethyl)amine (tren). A [(R3-SiNCH2CH2)3N]3- ligand should enforce an approximately trigonal bipyramidal coordination geometry in which the three amido nitrogen atoms are bound in equatorial positions, the amine is bound in an axial position, and the three R3Si groups surround the other axial position (see Figure 1). Additionally, the size of the silyl substituent could be varied in order to alter the steric environment at the available axial coordination site. Since only
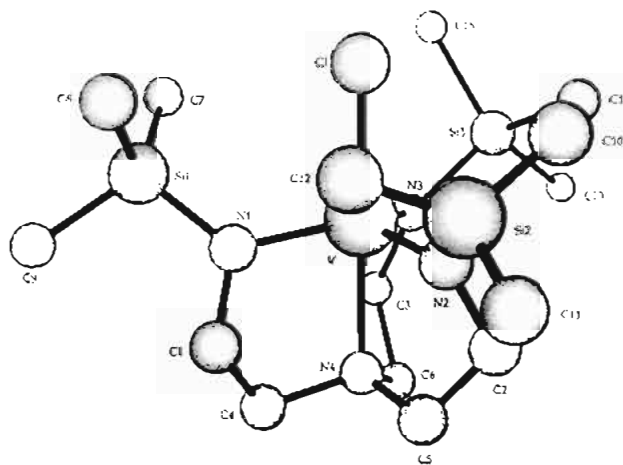

Figure 1. Structure of [N3N]VCl.

two MO's made up of the in-plane p orbitals on the sp²-hybridized equatorial nitrogen atoms can interact with metal-based orbitals in an approximate C_{3v} environment, the trianionic tetradentate ligand can be at *most* a 12-electron donor. The desired triply silylated tren derivative (Me3SiNHCH2CH2)3N was reported in 1989,[11] and silicon compounds containing it or related ligands (e.g., [(MeNCH2CH2)3N]3-) were prepared. Main group compounds containing ligands of this type are relatively common,[12] but transition metal complexes that contain a triamido amine

* Abstract published in *Advance ACS Abstracts*, February 15, 1994.
(1) Bradley, D. C. *Chem. Br.* **1975**, *11*, 393.
(2) Eller, P. G.; Bradley, D. C.; Hursthouse, M. B.; Meek, D. W. *Coord. Chem. Rev.* **1977**, *24*, 1.
(3) Power, P. P. *Comments Inorg. Chem.* **1989**, *8*, 177.
(4) Bradley, D. C.; Copperthwaite, R. G. *Inorg. Synth.* **1978**, *18*, 112.
(5) Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1.
(6) Fox, H. H.; Yap, K. B.; Robbins, J.; Cai, S.; Schrock, R. R. *Inorg. Chem.* **1992**, *31*, 2287.
(7) Schofield, M. H.; Kee, T. P.; Anhaus, J. T.; Schrock, R. R.; Johnson, K. H.; Davis, W. M. *Inorg. Chem.* **1991**, *30*, 3595.
(8) Williams, D. S.; Schrock, R. R. *Organometallics* **1993**, *12*, 1148.
(9) Glassman, T. E.; Vale, M. G.; Schrock, R. R.; Kol, M. *J. Am. Chem. Soc.* **1993**, *115*, 1760.
(10) Toreki, R.; Vaughan, G. A.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1993**, *115*, 127.

(11) Gudat, D.; Verkade, J. G. *Organometallics* **1989**, *8*, 2772.
(12) Verkade, J. G. *Acc. Chem. Res.* **1993**, *26*, 483.

ligand have been prepared only in the last 2 or 3 years.[13-21] A discovery that accelerated the development of the chemistry of silylated tren complexes in our laboratories was the synthesis of a solvent-free benzene-soluble trilithium salt of tris(2-((trimethylsilyl)amino)ethyl)amine (Li₃[N₃N]) by treating H₃[N₃N] with 3 equiv of *n*-butyllithium in pentane,[14] and the use of Li₃[N₃N] to make a variety of transition metal complexes from metal halides.[14,15] Some of the recent results that demonstrate the extent to which an apical coordination position can be "protected" by the three silyl substituents in a tetradentate [(RNCH₂CH₂)₃N]³⁻ ligand include the synthesis of a series of "trigonal monopyramidal complexes", M[N₃N′] (M = Ti, V, Cr, Mn, Fe; [N₃N′] = [(*t*-BuMe₂SiNCH₂CH₂)₃N]),[13] terminal phosphinidene complexes of the type [N₃N]Ta=PR (R = Ph, c-C₆H₁₁, *t*-Bu) that react with aldehydes to produce phosphaalkenes and [N₃N]Ta=O,[15] and [N₃N]Ta=X complexes in which X = Se or Te.[16] An Fe(IV) derivative, [N₃N′]FeCN, also has been prepared.[22] Recently *tridentate* triamido ligands (no donor atom is present) were synthesized that also form soluble trilithium salts[23,24] and that are beginning to be used to prepare transition metal derivatives.[25]

In this paper we report our studies of [N₃N] derivatives of vanadium, and in particular complexes prepared by atom or group transfer[26-28] to V[N₃N]. We anticipated that V[N₃N] would readily accept ligands that would form a pseudotriple bond to the metal, e.g., an O or NR group, given that vanadium(V) complexes of the types X₃V=O[29] and X₃V=NR[30] (X = halide, alkoxide) are well-known. The reaction type exemplified in this work, atom or group transfer to an *empty* coordination site, represents an unusual synthesis of terminal imido and chalcogenido species. We describe here a variety of vanadium complexes that contain the [N₃N] ligand, especially those of the type [N₃N]V=X (X = O, NR, S, Se, Te). We also report the X-ray structure of [N₃N]V=NH and compare it with the structures of trigonal monopyramidal V[N₃N′] and trigonal bipyramidal [N₃N]VCl. Portions of this work have appeared in preliminary reports.[13,14]

Results

Synthesis of [N₃N]VCl and V[N₃N] (N₃N = [(Me₃SiNCH₂CH₂)₃N]³⁻). Addition of *n*-butyllithium to H₃[N₃N] in pentane gives benzene-soluble Li₃[N₃N] in high yield. Addition of Li₃[N₃N] to VCl₄(DME) suspended in cold pentane produces blue-black [N₃N]VCl in 45% yield after 24 h. The crystal structure of [N₃N]VCl[14] showed it to be approximately a pseudo trigonal bipyramidal complex (Figure 1) in which the vanadium atom is displaced from the plane of the amido nitrogen atoms by 0.310 Å in the direction of the chloride ligand. Selected intramolecular distances and angles are listed in Tables 3 and 4
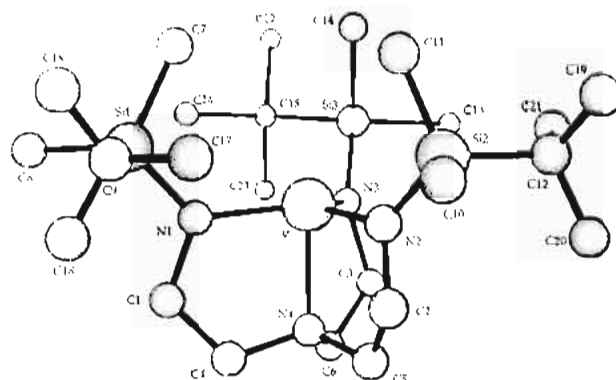
(13) Cummins, C. C.; Lee, J.; Schrock, R. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1501.
(14) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Organometallics* **1992**, *11*, 1452.
(15) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 756.
(16) Christou, V.; Arnold, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1450.
(17) Menge, W. M. P. B.; Verkade, J. G. *Inorg. Chem.* **1991**, *30*, 4628.
(18) Naiini, A. A.; Menge, W. M. P. B.; Verkade, J. G. *Inorg. Chem.* **1991**, *30*, 5009.
(19) Naiini, A. A.; Ringrose, S. L.; Su, Y.; Jacobson, R. A.; Verkade, J. G. *Inorg. Chem.* **1993**, *32*, 1290.
(20) Pinkas, J.; Gaul, B.; Verkade, J. G. *J. Am. Chem. Soc.* **1993**, *115*, 3925.
(21) Plass, W.; Verkade, J. G. *J. Am. Chem. Soc.* **1992**, *114*, 2275.
(22) Cummins, C. C.; Schrock, R. R. *Inorg. Chem.* **1994**, *33*, 395.
(23) Gade, L. H.; Mahr, N. *J. Chem. Soc., Dalton Trans.* **1993**, 489.
(24) Gade, L. H.; Becker, C.; Lauher, J. W. *Inorg. Chem.* **1993**, *32*, 2308.
(25) Friedrich, S.; Gade, L. H.; Edwards, A. J.; McPartlin, M. *Chem. Ber.* **1993**, *32*, 1797.
(26) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401.
(27) Holm, R. H. *Coord. Chem. Rev.* **1990**, *100*, 183.
(28) Harlan, E. W.; Holm, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 186.
(29) Preuss, F.; Noichl, H. *Z. Naturforsch.* **1987**, *42B*, 121.
(30) Devore, D. D.; Lichtenhan, J. D.; Takusagawa, F.; Maatta, E. A. *J. Am. Chem. Soc.* **1987**, *109*, 7408.

Figure 2. Structure of V[N₃N′].

and compared in a later section with corresponding distances and angles in [N₃N]V=NH and V[N₃N′] ([N₃N′] = [(*t*-BuMe₂SiNCH₂CH₂)₃N]).
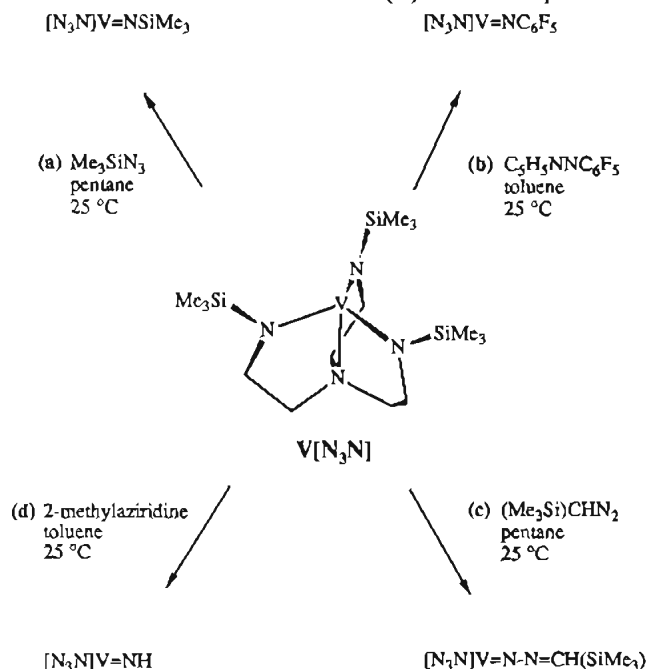
[N₃N]VCl is reduced smoothly by sodium amalgam in pentane on a scale of 5–10 g (eq 1). After removal of NaCl and mercury from the mixture, waxy blue V[N₃N] is obtained in >90% yield

(1)
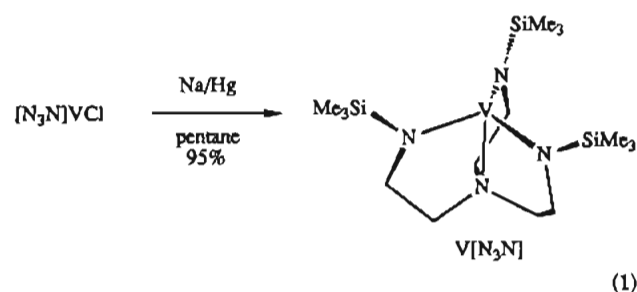
and >95% purity simply by removing the pentane *in vacuo*. Further purification is often not necessary, although V[N₃N] can be crystallized from pentane at −35 °C. Unfortunately, the fraction recovered is usually only ~50% because V[N₃N] is so soluble. V[N₃N] is difficult to separate from impurities, since it crystallizes readily only when it is already quite pure. Reactions between Li₃[N₃N] and sources of vanadium(III) such as VCl₃(THT)₂ (THT = tetrahydrothiophene) or VCl₃(THF)₃ did not prove to be suitable synthetic routes. Although V[N₃N] is formed, it can be separated by sublimation only in low yield and with accompanying decomposition. Therefore, although the yield of the reaction between VCl₄(DME) and Li₃[N₃N] to give [N₃N]VCl is only 45%, synthesis of V[N₃N] via reduction of [N₃N]VCl is still the best route at this time. V[N₃N] is paramagnetic, as is d² V[N₃N′][13] ([N₃N′] = [(*t*-BuMe₂SiNCH₂CH₂)₃N]). We presume that the structure of V[N₃N] is similar to that of V[N₃N′] (Figure 2), bond distances and angles of which are reported here (Tables 3 and 4) and compared with those of [N₃N]VCl and [N₃N]V=NH in a later section.

Weak donors such as ether or tetrahydrofuran have little or no tendency to coordinate to the empty coordination site in V[N₃N]; the complex is the same color (blue) in these solvents as it is in pentane. Tertiary amines and phosphines also do not exhibit any affinity for V[N₃N], possibly for steric reasons. Cylindrically symmetric σ donors such as acetonitrile and *tert*-butyl isocyanide, on the other hand, give lime-green adducts that crystallize easily from pentane at −35 °C. Other adducts that have been observed include lavender [N₃N]V(CH₂PMe₃), [N₃N]V(OPMe₃), and [N₃N]V(OSMe₂), which form upon adding Me₃P=CH₂, Me₃P=O, and Me₂S=O, respectively, to V[N₃N]. These adducts crystallize from pentane, but they could not be characterized by elemental analysis because the donor ligand is lost readily in vacuo. The adducts are paramagnetic, presumably d² complexes. The trimethylphosphine oxide adduct can be heated in a sealed tube in C₆D₆ at 80 °C for 16 h without

Scheme 1. Formation of Vanadium(V) Imido Complexes

$[N_3N]V=NSiMe_3$ $[N_3N]V=NC_6F_5$

(a) Me₃SiN₃
pentane
25 °C

(b) C₅H₅NNC₆F₅
toluene
25 °C

V[N₃N]

(d) 2-methylaziridine
toluene
25 °C

(c) (Me₃Si)CHN₂
pentane
25 °C

$[N_3N]V=NH$ $[N_3N]V=N-N=CH(SiMe_3)$

change, but the dimethyl sulfoxide adduct decomposes to dimethyl sulfide and $[N_3N]V=O$ (see later) upon heating in C_6D_6 at 60 °C in a sealed tube. This deoxygenation reaction could be monitored either by following the loss of paramagnetism in the sample by the Evans technique or by tracking the appearance of diamagnetic $[N_3N]V=O$ by proton NMR. Rate profiles obtained using either technique were similar, but the reaction did not follow pseudo-first-order kinetics, even when a vast excess of DMSO was employed. Other deoxygenation reactions that yield $[N_3N]V=O$ are discussed in a later section.

Vanadium(V) Imido Complexes, $[N_3N]V=NR$. Orange-red, crystalline $[N_3N]V=N(p-CH_3C_6H_4)$ was prepared by adding a solution of $Li_3[N_3N]$ to $Cl_3V=N(p-CH_3C_6H_4)$[30] in ether. Spectral data for $[N_3N]V=N(p-CH_3C_6H_4)$ are consistent with its being a 3-fold-symmetric, distorted trigonal bipyramidal complex analogous to $[N_3N]VCl$ (Figure 1).

Addition of trimethylsilyl azide to blue $V[N_3N]$ resulted in a color change to orange over a 48-h period; the silylimido complex $[N_3N]V=NSiMe_3$ was subsequently isolated (36%) as orange-yellow crystals (Scheme 1, path a). The imido-transfer reaction observed upon treating $V[N_3N]$ with pyridino(perfluorophenyl)-imine (Scheme 1, path b) is also sluggish, requiring several hours at 25 °C for completion. The (pentafluorophenyl)imido complex $[N_3N]V=NC_6F_5$ was isolated in 58% yield as rust-red crystals after a 24-h reaction time at 25 °C.
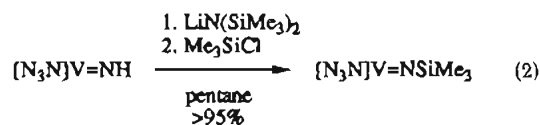
In contrast to the sluggish reactions a and b, in which dinitrogen or pyridine must be lost, brick-red $[N_3N]V=N-N=CH(SiMe_3)$ forms in seconds at room temperature upon adding (trimethylsilyl)diazomethane to $V[N_3N]$ (Scheme 1, path c). The diazoalkane ligand's CH group is characterized by resonances at 8.35 ppm in its ^1H NMR spectrum and 168.4 ppm in its ^{13}C NMR spectrum, consistent with the view that the carbon is sp²-hybridized and imine-like. $[N_3N]V=N-N=CH(SiMe_3)$ is stable in C_6D_6 at 110 °C for 6 h and upon exposure to a medium-pressure mercury

(31) Rocklage, S. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 3077.
(32) Rupprecht, G. A.; Messerle, L. W.; Fellmann, J. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 6236.
(33) Roland, E.; Walborsky, E. C.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 5795.
(34) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Raterman, A. L. *Inorg. Chem.* **1984**, *23*, 2303.
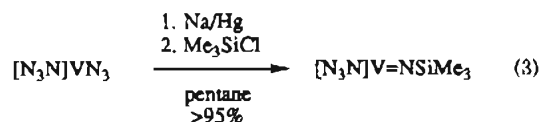(35) Hillhouse, G. L.; Haymore, B. L. *J. Am. Chem. Soc.* **1982**, *104*, 1537.
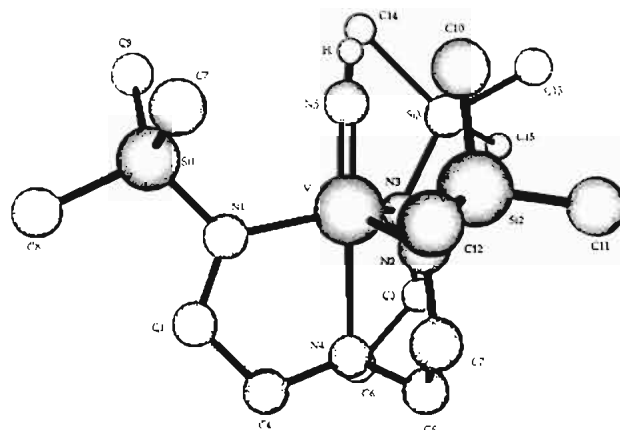
Figure 3. Structure of $[N_3N]V=NH$.

lamp (Hanovia, 2 days, Pyrex); there was no evidence for formation of $[N_3N]V=CH(SiMe_3)$. An attempt to convert $[N_3N]V=N-N=CH(SiMe_3)$ into a bimetallic μ-dinitrogen complex[31] employing $Ta(CH-t-Bu)Cl_3(THF)_2$[32] was unsuccessful; no reaction was observed at 25 °C after several hours. The reaction between a metal complex and a substituted diazomethane to produce a complex that contains a metal–nitrogen multiple bond is a reaction type that has been known for about 10 years.[33-35]

When $V[N_3N]$ is treated with 2-methylaziridine in ether or benzene (Scheme 1, path d), a color change to orange-amber is observed immediately. Proton NMR spectra reveal that the resonances attributed to paramagnetic $V[N_3N]$ are shifted (e.g., the SiMe₃ resonance appears at 4.46 ppm), but propylene resonances are not yet observed. These data are consistent with formation of a paramagnetic 2-methylaziridine adduct. Resonances assigned to diamagnetic $[N_3N]V=NH$ and propylene then appear over a period of hours at 25 °C. Although $[N_3N]V=NH$ seems to be formed quantitatively by ^1H NMR, it could be isolated as yellow crystals in only ~50% yield because of its high solubility in hydrocarbon solvents. A resonance ascribable to the imido proton was not found in the ^1H NMR spectrum of $[N_3N]V=NH$ at 25 °C, presumably because of coupling to ^{51}V ($I = ^7/_2$, 99.75%) and ^{14}N ($I = 1$, 99.63%), but a sharp peak of medium intensity that can be assigned to an NH stretch is observed at 3391 cm⁻¹ in the IR spectrum (pentane/KBr). The imido proton was located and successfully refined in an X-ray study (Figure 3) to be discussed later. Deprotonation of $[N_3N]V=NH$ with LiN-$(SiMe_3)_2$, followed by addition of an excess of Me_3SiCl, yielded $[N_3N]V=NSiMe_3$ (>95% purity by ^1H NMR; eq 2).

$$[N_3N]V=NH \xrightarrow[\substack{\text{pentane} \\ >95\%}]{\substack{1.\ LiN(SiMe_3)_2 \\ 2.\ Me_3SiCl}} [N_3N]V=NSiMe_3 \quad (2)$$

Addition of excess sodium azide in tetrahydrofuran at 25 °C over 48 h to $[N_3N]VCl$ yielded black, crystalline $[N_3N]VN_3$. The proton NMR spectrum of this d^1 azidovanadium species contains characteristic shifted ligand resonances, and its IR spectrum shows a strong azide stretch at 2088 cm⁻¹. $[N_3N]$-$V=NH$ is occasionally an impurity in preparations of $[N_3N]$-VN_3. Sodium amalgam reduction of $[N_3N]VN_3$ in tetrahydrofuran at 25 °C produced a nondescript yellow-green solution, which, when treated after 24 h with excess Me_3SiCl, produced $[N_3N]V=NSiMe_3$ in >90% yield according to a proton NMR spectrum (eq 3). We speculate that the species formed upon

$$[N_3N]VN_3 \xrightarrow[\substack{\text{pentane} \\ >95\%}]{\substack{1.\ Na/Hg \\ 2.\ Me_3SiCl}} [N_3N]V=NSiMe_3 \quad (3)$$

Table 1. Crystallographic Data for [N₃N]V=NH[a]

formula	$C_{15}H_{40}N_5Si_3V$	fw	424.70
temp (°C)	20	cryst color	yellow
a (Å)	9.798(3)	space group	$P2_1/n$
b (Å)	16.82(2)	D_{calc} (g cm⁻³)	1.138
c (Å)	15.460(8)	μ (cm⁻¹)	5.37 (Mo Kα)
α (deg)	90	cryst size (mm)	0.20, 0.20, 0.30
β (deg)	103.38(3)	λ; $2\theta_{max}$ (deg)	Mo Kα; 55.0
γ (deg)	90	final R/R_w (%)	5.4/6.0
Z; V (Å³)	4; 2478(3)		

[a] N₃N = [(Me₂SiNCH₂CH₂)₃N³⁻]. Crystallographic data for V[N₃N′] (N₃N′ = [(t-BuMe₂SiNCH₂CH₂)₃N³⁻] and [N₃N]VCl can be found in refs 13 and 14, respectively.

Table 2. Fractional Coordinates for [N₃N]V=NH

	x	y	z	B_{eq} (Å²)
V	0.1719(1)	0.09643(8)	0.77090(8)	2.82(5)
N5	0.0442(7)	0.0737(5)	0.6857(5)	4.3(4)
H	−0.019(8)	0.068(5)	0.643(5)	5.1
N1	0.1499(6)	0.0120(4)	0.8506(4)	3.5(3)
N2	0.1154(6)	0.1998(4)	0.8012(4)	3.7(3)
N3	0.3257(6)	0.0927(4)	0.7131(4)	3.6(3)
N4	0.3512(6)	0.1232(4)	0.8863(4)	3.2(3)
Si1	−0.0322(3)	0.2555(2)	0.7555(2)	5.3(1)
Si3	0.2991(3)	0.0874(2)	0.5979(2)	4.7(1)
C1	0.258(1)	0.0013(6)	0.9308(6)	5.2(5)
C2	0.202(1)	0.2369(5)	0.8813(6)	5.3(5)
C3	0.4663(8)	0.1127(6)	0.7644(6)	5.0(5)
C4	0.327(1)	0.0782(6)	0.9619(6)	5.4(5)
C5	0.350(1)	0.2085(6)	0.8983(6)	6.0(5)
C6	0.4782(9)	0.0959(7)	0.8595(6)	6.3(5)
C7	−0.159(1)	−0.0065(6)	0.8039(8)	7.7(6)
C8	0.019(1)	−0.1221(6)	0.9247(9)	9.1(7)
C9	0.028(1)	−0.1210(7)	0.7345(8)	9.0(7)
C10	−0.153(1)	0.2128(8)	0.6573(8)	9.5(7)
C11	0.022(1)	0.3518(8)	0.718(1)	14(1)
C12	−0.136(1)	0.269(1)	0.8372(8)	15(1)
C13	0.188(1)	0.1692(7)	0.5410(6)	7.8(7)
C14	0.222(1)	−0.0097(6)	0.5525(7)	7.2(6)
C15	0.472(1)	0.0962(7)	0.5673(6)	7.5(6)

Table 3. Intramolecular Distances (Å) for Vanadium Triamido Amine Complexes[a]

	V[N₃N′]	[N₃N]VCl	[N₃N]V=NH
V–Cl		2.278(2)	
N5–H			0.79(7)
V–N5			1.638(6)
V–N1	1.926(3)	1.883(6)	1.925(6)
V–N2	1.936(3)	1.890(6)	1.916(7)
V–N3	1.928(3)	1.875(6)	1.922(6)
V–N4	2.083(3)	2.238(6)	2.241(6)
N1–Si1	1.717(3)	1.743(6)	1.727(6)
N1–C1	1.470(5)	1.474(9)	1.44(1)
C1–C4	1.413(6)	1.49(1)	1.49(1)
N4–C4	1.455(5)	1.49(1)	1.46(1)

[a] N₃N′ = [(t-BuMe₂SiNCH₂CH₂)₃N³⁻; N₃N = [(Me₃SiNCH₂CH₂)₃-N³⁻].

reduction of [N₃N]VN₃ is ([N₃N]VN₃)⁻ and that this route is equivalent to treating V[N₃N] with Me₃SiN₃ (route a in Scheme 1). The reaction shown in eq 3 is the third synthesis of [N₃N]V=NSiMe₃ that is reported here.

Comparison of the X-ray Structures of V[N₃N′], [N₃N]VCl, and [N₃N]V=NH. Crystallographic data and fractional coordinates for [N₃N]V=NH can be found in Tables 1 and 2, and bond lengths, bond angles, and selected dihedral angles for V[N₃N′], [N₃N]VCl, and [N₃N]V=NH are compared in Tables 3 and 4. (Crystallographic data for V[N₃N′][13] and [N₃N]VCl[14] can be found in preliminary publications, where fractional coordinates have also been deposited.) Drawings with atom-labeling schemes are given in Figures 1–3; the numbering scheme is consistent in order to facilitate direct comparison of distances and angles. Since the structures of V[N₃N′] and [N₃N]VCl

Table 4. Intramolecular and Dihedral Angles (deg) for Vanadium Triamido Amine Complexes

	V[N₃N′]	[N₃N]VCl	[N₃N]V=NH
Cl–V–N4		179.4(2)	
Cl–V–N1		100.0(2)	
Cl–V–N2		99.2(2)	
Cl–V–N3		99.2(2)	
V–N5–H			173(6)
N5–V–N4			177.8(3)
N5–V–N1			99.5(3)
N5–V–N2			101.4(3)
N5–V–N3			98.9(3)
N1–V–N2	119.2(1)	117.0(3)	115.6(3)
N2–V–N3	119.2(1)	114.6(3)	116.4(3)
N3–V–N1	119.6(1)	120.4(3)	119.3(3)
N4–V–N1	84.9(1)	80.2(2)	79.7(2)
N4–V–N2	85.3(1)	81.3(2)	80.8(2)
N4–V–N3	85.6(1)	80.2(2)	79.8(2)
V–N1–Si1	127.6(2)	126.1(3)	123.0(4)
Si1–N1–C1	120.2(2)	119.8(5)	118.6(5)
V–N1–C1	112.2(2)	113.6(5)	118.2(5)
V–N4–C4	107.2(2)	107.0(5)	106.9(5)
C4–N4–C5	112.0(4)	110.8(6)	113.8(7)
N1–C1–C4	113.2(3)	107.3(7)	111.0(7)
C1–C4–N4	115.2(4)	107.7(7)	109.8(7)
N4–V–N1–Si1	168.0	143.8	183.1
N4–V–N2–Si2	167.8	149.6	178.5
N4–V–N3–Si3	166.8	147.0	170.2

were not discussed in detail in preliminary accounts, they will be compared with the structure of [N₃N]V=NH here.

The coordination sphere of [N₃N]V=NH contains three equatorial amido donors (V–N_amido = 1.925(6), 1.916(7), 1.922-(6) Å), an axial imido (NH) ligand (V–N_imido = 1.638(6) Å), and an axial tertiary amine (V–N_amine = 2.241(6) Å). These bond lengths are within the range that one would expect for vanadium-nitrogen single, double, and dative bonds, respectively, as shown by selected data from the literature (1.83–1.91 Å (single), 1.59–1.73 Å (double), 2.12–2.32 Å (dative)).[2,30,36–40] The V–N_amido bond lengths are close to the sum of vanadium and nitrogen covalent radii (1.92 Å), consistent with relatively little V–N_eq π bonding. As mentioned in the Introduction, only two out of a possible three π bonds could form between the three amido nitrogen atoms and the metal; perhaps even those π bonds are not strong enough to shorten the vanadium–amido bond lengths to a significant degree in view of the steric pressure between the axial substituent and the three trimethylsilyl substituents and the relatively poor π-bonding abilities of a silylated amido ligand anyway.[1–3] The V–N_amido bond lengths are somewhat longer in [N₃N]V=NH than they are in [N₃N]VCl, in spite of the smaller covalent radius of V(V), perhaps because of the more electrophilic nature of the metal in [N₃N]VCl. The V–N_amine bond length in [N₃N]V=NH (2.241(6) Å) is comparable to that in [N₃N]VCl (2.238(6) Å). The V–N_imido bond length in [N₃N]V=NH (1.638-(6) Å) is consistent with its being a pseudotriple bond, the d_{xz} and d_{yz} orbitals (taking the C_3 axis to be z axis) presumably being employed to form the pseudotriple bond. The imido hydrogen atom was located and refined; the V–N–H angle is 173(6)°. The imido proton in [N₃N]V=NH is located within a pocket formed by the trimethylsilyl methyl groups. The imido hydrogen atom is 2.43 Å away from vanadium while the trimethylsilyl carbon atoms that line the pocket in which the NH ligand sits are 3.85 Å away from vanadium. The vanadium is displaced 0.33 Å from the equatorial plane toward the imido ligand, as reflected in the

(36) Edema, J. J. H.; Meetsma, A.; van Bolhuis, F.; Gambarotta, S. *Inorg. Chem.* **1991**, *30*, 2056.
(37) Greene, P. T.; Orioli, P. L. *J. Chem. Soc. A* **1969**, 1621.
(38) Solari, E.; DeAngelis, S.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1992**, *31*, 96.
(39) Ruiz, J.; Vivanco, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1991**, 762.
(40) Wills, R. A.; Edwards, P. G.; Short, R. L.; Hursthouse, M. B. *J. Chem. Soc., Chem. Commun.* **1988**, 115.

Scheme 2. Formation of Vanadium(V) Chalcogenide Complexes
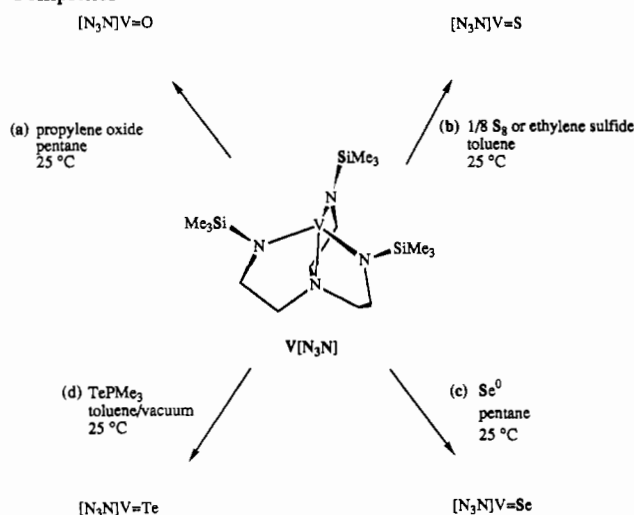
N_{amido}–V–N_{amine} angles 79.7(2), 80.8(2), and 79.8(2)°. In [N$_3$N]-VCl the vanadium lies 0.31 Å above the equatorial plane of amido nitrogens and the N_{amido}–V–N_{amine} angles are 80.2(2), 81.3(2), and 80.2(2)°. The apical ligand–V–N_{eq} angles in [N$_3$N]V=NH and [N$_3$N]VCl are all within 1° of 100°. The structure of [N$_3$N]V=NH is similar to that reported for [(MeNCH$_2$-CH$_2$)$_3$N]V=O,[21] in which a typical V–N_{amido} distance is 1.895-(3) Å and the V–N_{amine} distance is 2.321(6) Å.

The structure of V[N$_3$N'] differs significantly from the structures of [N$_3$N]V=NH and [N$_3$N]VCl. (We will assume that steric differences between the [N$_3$N'] and [N$_3$N] ligands are relatively inconsequential as far as the structure of the core is concerned.) In V[N$_3$N'] the metal is displaced from the equatorial plane by only 0.16 Å (versus 0.33 Å in [N$_3$N]V=NH and 0.31 Å in [N$_3$N]VCl). The short V–N_{amine} bond length observed in V[N$_3$N'] (2.083(3) Å) may be ascribed in part to the lower coordination number but, most likely, primarily to the absence of any *trans* donor. This result is particularly interesting in view of the fact that vanadium(III) (ionic radius 0.78 Å) is significantly larger than vanadium(IV) and –(V) (ionic radii 0.72 and 0.68 Å, respectively). The V–N_{eq} bond lengths in V[N$_3$N'] are comparable to what they are in [N$_3$N]V=NH, even though one might expect π bonding to be more significant in a situation in which V lies nearly in the plane of equatorial nitrogen atoms. Shortening of the V–N_{eq} bonds must be counteracted by the larger ionic radius of vanadium(III) (0.78 Å).

The chemistry of complexes containing the [N$_3$N] ligand type is expected to be dominated by the nature of the steric pocket surrounding the axial substituent (if any). The conformational differences associated with varying pocket angles can be identified with a key dihedral angle (last three entries in Table 4). This angle (e.g., N4–V–N1–Si1) is a measure of the "tilt" of the C/N_{eq}/Si plane with respect to the plane that contains the three equatorial nitrogens. A value of 180° for N4–V–N1–Si1 signifies that the silyl groups are "upright" and that the vanadium experiences a local approximately C_{3v} environment, with the amido pπ orbitals residing in the equatorial plane. A value of 180° for N4–V–N1–Si1 also suggests that the axial coordination position is shielded most effectively. The values for N4–V–N1–Si1 listed in Table 4 suggest that the trialkylsilyl groups are "upright" in [N$_3$N]V=NH, not quite upright in V[N$_3$N'], and tilted to a significant degree in [N$_3$N]VCl (N4–V–N1–Si1 angles are 143.8, 149.6, and 147.0°). At this time we can only speculate that the large "tilt angle" in [N$_3$N]VCl is a steric consequence of the presence of the relatively large chloride ligand.

Vanadium(V) Chalcogenide Complexes, [N$_3$N]V=E (E = O, S, Se, Te). Propylene oxide is the reagent of choice for synthesizing
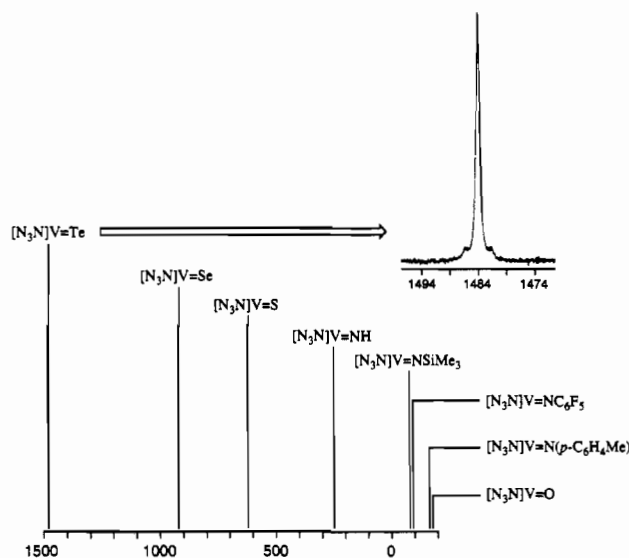
Figure 4. ^{51}V NMR shifts for [N$_3$N]V=X complexes. The signal for [N$_3$N]V=Te is shown as an inset. Spectra were obtained at 300 MHz and were referenced to external VOCl$_3$; a positive sign indicates a downfield shift. Axes are labeled in units of ppm.

[N$_3$N]V=O on a preparative scale from V[N$_3$N] (Scheme 2, path a); yellow [N$_3$N]V=O forms quantitatively over a period of $\sim$30 min at concentrations of ca. 0.05 M in vanadium. Other reagents that are smoothly deoxygenated by V[N$_3$N] include nitrous oxide, pyridine *N*-oxide, and dimethyl sulfoxide. Due to the exceedingly high solubility of [N$_3$N]V=O in pentane, it is recovered in only 44% yield after one crystallization from pentane at –35 °C. When the propylene oxide reaction is followed by NMR in C$_6$D$_6$, characteristic resonances for propylene and [N$_3$N]V=O are observed as those for paramagnetic V[N$_3$N] disappear. All NMR data (^{1}H, ^{13}C, ^{51}V) for [N$_3$N]V=O are in accord with its being a 3-fold-symmetric species on the NMR time scale, presumably with a structure very similar to those of [N$_3$N]V=NH (Figure 3) and [(MeNCH$_2$CH$_2$)$_3$N]V=O.[21] Coupling of the set of ligand methylene protons nearest the metal to ^{51}V is observed in the ^{1}H NMR spectrum of [N$_3$N]V=O, yielding a broad resonance for what would otherwise appear as a pseudotriplet. A sharp resonance at –173 ppm (upfield of neat VOCl$_3$ as an external reference) was observed in the ^{51}V NMR spectrum of [N$_3$N]V=O. As illustrated in Figure 4, the oxo complex exhibits the greatest upfield shift of any of the vanadium [N$_3$N] species discussed in this work. A strong oxo peak is observed at 996 cm^{-1} in the IR spectrum of [N$_3$N]V=O, as expected.
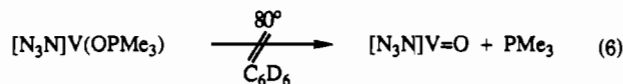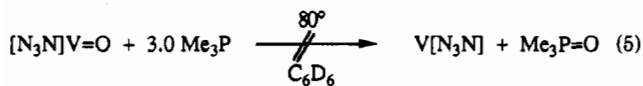
Deoxygenation of *cis*-2-butene oxide by V[N$_3$N] produced a mixture of *cis*- and *trans*-2-butene in a 1:6 ratio, as determined by ^{1}H NMR integration, while deoxygenation of *trans*-2-butene oxide yielded a 1:7 ratio of *cis*- to *trans*-2-butene. This result suggests that deoxygenation is not a concerted process, but probably involves a V(IV) alkoxide intermediate in which the carbon β to the oxygen is a radical center. (See discussion later.) A competition experiment in which V[N$_3$N] and V[N$_3$N'] were allowed to compete for a single equivalent of propylene oxide (eq 4) yielded [N$_3$N]V=O (>95%, ^{1}H NMR); no [N$_3$N']V=O was

$$V[N_3N] + V[N_3N'] \xrightarrow[\substack{C_6D_6 \\ - propylene}]{1.0\ propylene\ oxide} [N_3N]V=O + V[N_3N']$$

(4)
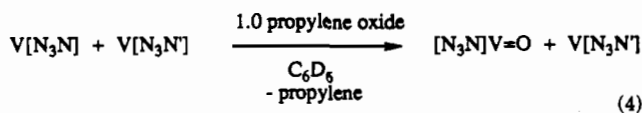
formed and no V[N$_3$N'] was consumed. In a separate experiment, V[N$_3$N'] *did* react with propylene oxide (3 equiv; 0.05 M in vanadium) slowly over a period of days to afford partial conversion to [N$_3$N']V=O (by ^{1}H NMR).

An attempt to deoxygenate $[N_3N]V=O$ with trimethylphosphine (3 equiv) at 80 °C in C_6D_6 was unsuccessful; no reaction was observed after 30 h (eq 5). We stated earlier that heating $[N_3N]V(OPMe_3)$ did not yield trimethylphosphine and $[N_3N]\cdot V=O$ (eq 6). We were surprised to find that the barriers to

$$[N_3N]V=O + 3.0 \ Me_3P \xrightarrow[C_6D_6]{80°} \ \ V[N_3N] + Me_3P=O \quad (5)$$

$$[N_3N]V(OPMe_3) \xrightarrow[C_6D_6]{80°} \ \ [N_3N]V=O + PMe_3 \quad (6)$$

interconversion of $V[N_3N]$ and $[N_3N]V=O$ in this manner are significant. It is interesting to speculate whether either reaction would be significantly faster if the low-spin configuration of $V[N_3N]$ were accessible.

Facile formation of $[N_3N]V=O$ upon treating $V[N_3N]$ with various sources of an oxygen atom suggested that other chalcogenide complexes might be readily accessible. This proved to be the case (Scheme 2, paths b–d). Crystalline, red $[N_3N]V=S$ was the sole product when $^1/_8$ equiv of S_8 was added to $V[N_3N]$ in toluene solution. NMR spectra (^1H, ^{13}C) for $[N_3N]V=S$ are similar to those for $[N_3N]V=O$; coupling of one set of the ligand's methylene protons to ^{51}V again was observed in the ^1H NMR spectrum. The sharp ^{51}V NMR resonance for $[N_3N]V=S$ was found 621 ppm downfield of the ^{51}V resonance in $VOCl_3$ (Figure 4). $[N_3N]V=S$ also can be prepared rapidly from $V[N_3N]$ in pentane solvent at 25 °C employing ethylene sulfide as the source of sulfur.

Elemental selenium reacts with $V[N_3N]$ in pentane (Scheme 2, path c), although the reaction requires approximately 48 h to go to completion. $[N_3N]V=Se$ typically was obtained in 65% crystallized yield. $[N_3N]V=Se$ forms virtually black crystals but is brown-red in solution. Proton and carbon NMR spectra are analogous to those observed for $[N_3N]V=O$ and $[N_3N]V=S$. The ^{51}V resonance for $[N_3N]V=Se$ is found downfield of that in $[N_3N]V=S$ (Figure 4) at +921 ppm ($\Delta\nu_{1/2} = 55$ Hz). Addition of trimethylphosphine to $[N_3N]V=Se$ yielded $V[N_3N]$ and $Me_3P=Se$ (eq 7). The reaction is slow at 25 °C ($t_{1/2} \sim 24$ h

$$[N_3N]V=Se + Me_3P \xrightarrow[C_6D_6]{25°, \sim24 \ h} \ V[N_3N] + Me_3P=Se \quad (7)$$
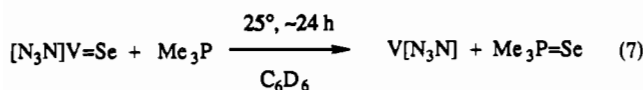
at 0.05 M in phosphorus and vanadium) but contrasts with the failure of the corresponding reactions involving $[N_3N]V=O$ and $V[N_3N]$ in either direction, as noted above.

Elemental tellurium did not react with $V[N_3N]$, even after 1 week at 25 °C. Tellurium that had been prepared by decomposition of $Me_3P=Te$ *in vacuo* also did not react with $V[N_3N]$. Given the fact that trimethylphosphine is capable of removing Se from $[N_3N]V=Se$, we were not surprised to find that $Me_3P=Te$ does not transfer its tellurium atom to $V[N_3N]$. However, when a vacuum is applied to a solution of $V[N_3N]$ and $Me_3P=Te$ in toluene, $[N_3N]V=Te$ is generated in variable yield according to ^1H NMR during the time required for removing solvent completely (Scheme 2, path d). $[N_3N]V=Te$ appears to be unstable; Te^0 mirrors appear frequently on the inner walls of NMR tubes containing $[N_3N]V=Te$. Proton and ^{13}C NMR spectra are completely consistent with the formulation of $[N_3N]V=Te$. Perhaps the most convincing evidence for formation of $[N_3N]V=Te$ is observation of a ^{51}V resonance at +1484 ppm (Figure 4) in the ^{51}V NMR spectrum accompanied by satellites attributable to $^{51}V/^{125}Te$ coupling ($J_{VTe} = 360$ Hz; natural abundance of $^{125}Te = 7.14\%$). The magnitude of the coupling to ^{125}Te suggests that the V–Te bond has a considerable amount of multiple-bond character. The synthesis of $[N_3N]\cdot$

Ta=Te was reported recently; a single-crystal X-ray study suggests that the tantalum–tellurium bond is approximately a double bond.[16]

Discussion

Four-coordinate complexes of vanadium(III) are not common. Representative examples are $[V(S\text{-}t\text{-}Bu)_4]^-$,[41] $[V(Mes)_4]^-$ (Mes = $2,4,6\text{-}Me_3C_6H_2$),[42,43] $V(silox)_3(THF)$ (silox = $t\text{-}Bu_3SiO^-$),[44] and $V(Mes)_3(THF)$.[39,43,45–47] Of the structurally-characterized examples, the structure of $V(Mes)_3(THF)$[43] most closely resembles that of $V[N_3N]$. In an early report, the complex was described as a pseudotetrahedron,[46] while it later was described as a trigonal pyramid.[45] We have described $V[N_3N']$ as a trigonal monopyramid,[13] i.e., a trigonal bipyramid that is missing one axial ligand. A similar geometry was recently proposed for $Al[N_3N]$.[20] We believe that the first structurally-characterized example of this general trigonal monopyramidal structural type was the 18e nickel-(0) species $Ni[(Ph_2PCH_2CH_2)_3N]$.[48] $V[N_3N]$ and $V(Mes)_3$-(THF) are related in a formal sense (by loss of a donor ligand) to the three-coordinate complexes $V[N(SiMe_3)_2]_3$[4,49] and $V[CH(SiMe_3)_2]_3$.[50] The d^2 tantalum complex $Ta(silox)_3(THF)$, which was recently proposed as an intermediate in the deoxygenative scission of carbon monoxide (in the presence of THF) by three-coordinate $Ta(silox)_3$,[51,52] is a third-row relative of $V[N_3N]$ and $V(Mes)_3(THF)$. Studies of $M(silox)_3(pyridine)$ (M = V, Ta) complexes have shown that pyridine is bound in the standard η^1 manner to vanadium, while it is bound to tantalum in an $\eta^2\text{-}N,C$ binding mode.[44] This difference was accounted for on the basis of molecular orbital studies, which indicated that a trigonal d^2 tantalum species has little affinity for a standard 1σ dative ligand but can bind substrates that behave as π acceptors, while vanadium in a similar coordination environment acts simply as a Lewis acid and binds dative 1σ ligands in the standard fashion.

Oxygen atom transfer to a transition metal has received increased attention in the past decade because of its relevance to reactions in biology.[26,27] The mild and stereospecific (including both retention *and* inversion) deoxygenation of epoxides is also a desirable organic reaction.[53–71] An epoxide or sulfoxide is a

(41) Heinrich, D. D.; Folting, K.; Huffman, J. C.; Reynolds, J. G.; Christou, G. *Inorg. Chem.* **1991**, *30*, 300.
(42) Seidel, W.; Kreisel, G. *Z. Chem.* **1976**, *16*, 115.
(43) Seidel, W.; Kreisel, G. *Z. Anorg. Allg. Chem.* **1977**, *435*, 146.
(44) Covert, K. J.; Neithamer, D. R.; Zonnevylle, M. C.; LaPointe, R. E.; Schaller, C. P.; Wolczanski, P. T. *Inorg. Chem.* **1991**, *30*, 2494.
(45) Vivanco, M.; Ruiz, J.; Floriani, C.; Chiesivilla, A.; Rizzoli, C. *Organometallics* **1993**, *12*, 1794.
(46) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1984**, 886.
(47) Ferguson, R.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 396.
(48) Mealli, C.; Sacconi, L. *J. Chem. Soc., Chem. Commun.* **1973**, 886.
(49) Alyea, E. C.; Bradley, D. C.; Copperthwaite, R. G. *J. Chem. Soc., Dalton Trans.* **1972**, 1580.
(50) Barker, G. K.; Lappert, M. F.; Howard, J. A. K. *J. Chem. Soc., Dalton Trans.* **1978**, 734.
(51) Neithamer, D. R.; LaPointe, R. E.; Wheeler, R. A.; Richeson, D. S.; Van Duyne, G. D.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1989**, *111*, 9056.
(52) LaPointe, R. E.; Wolczanski, P. T.; Mitchell, J. F. *J. Am. Chem. Soc.* **1986**, *108*, 6382.
(53) Whinnery, L. L.; Henling, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1991**, *113*, 7575.
(54) Afonso, C. A. M.; Motherwell, W. B.; Roberts, L. R. *Tetrahedron Lett.* **1992**, *33*, 3367.
(55) Kang, K. T.; Choi, Y. D.; Park, C. Y. *Bull. Chem. Soc. Korea* **1990**, *11*, 471.
(56) Kang, K. T.; Park, C. Y.; Kim, J. S. *Bull. Chem. Soc. Korea* **1992**, *13*, 48.
(57) Karaman, R.; Fry, J. L. *Tetrahedron Lett.* **1989**, *30*, 4931.
(58) King, R. R.; Greenhalgh, R. *Can. J. Chem.* **1985**, *63*, 1089.
(59) Martin, G. M.; Ganem, B. *Tetrahedron Lett.* **1984**, 251.
(60) Matsubara, S.; Kanemoto, S.; Okuda, Y.; Nonaka, T.; Nozaki, H.; Oshima, K. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1480.
(61) Matsukawa, M.; Inanaga, J.; Tabuchi, T.; Yamaguchi, M. *Chem. Lett.* **1987**, 2101.
(62) Mitchell, P. W. D. *Org. Prep. Proc. Int.* **1990**, *22*, 534.

common source of the oxygen atom in oxygen atom transfer studies. A metallaoxetane is the most commonly proposed intermediate in a reaction involving oxygen atom transfer from an epoxide to a transition metal,[70,72-76] in spite of the facts that few stable metallaoxetanes have been prepared and characterized[77-81] and that a metallaoxetane was shown *not* to be an intermediate in the reaction between epoxides and d^2 [(η^5-C$_5$-Me$_5$)$_2$Ta(CH$_3$)].[53,82] Although such reactions can be stereospecific,[39] low-valent β-diketonate complexes of vanadium and molybdenum were found to yield a mixture of *cis* and *trans* olefins upon treatment with epoxides.[83] When the reaction is not stereospecific, a mechanism involving a 1,4-biradical (metal and carbon based) more neatly explains the experimental findings. The reasons that radical chemistry is most likely involved in deoxygenation of epoxides by V[N$_3$N] could be related to the fact that V[N$_3$N] is a ground-state triplet (complexes such as [(η^5-C$_5$Me$_5$)$_2$Ta(CH$_3$)], Ta(silox)$_3$, and MoO(S$_2$CNEt$_2$)$_2$ possess singlet ground states) or that oxidation of V(III) to V(IV) is much faster than subsequent oxidation of V(IV) to V(V), especially under the steric limitations imposed by the [N$_3$N] ligand.

By analogy to deoxygenation of expoxides, transfer of an imido group from an aziridine to a transition metal center might be anticipated, although the typical list of candidates for imido group transfer usually does not include aziridines.[28] In fact, transfer of an NH group from 2-methylaziridine to V[N$_3$N] to give [N$_3$N]V=NH appears to be the first reported example of NH group transfer.[84] Only a handful of complexes containing the parent imido (NH) group are known; examples include [MoCl$_2$(NH)O(EtPh$_2$PO)$_2$],[85] [MoBr(NH)(Ph$_2$PCH$_2$-CH$_2$PPh$_2$)$_2$]Br,[86] [W(NH)Br(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$]Br,[87] TaCp*$_2$-(NH)(H),[88] MoCp*Me$_3$(NH),[89] and WCp*Me$_3$(NH).[9,90,91] Parent imido complexes are of interest as possible intermediates in

the fixation of dinitrogen by the Mo[92-95] or vanadium[96,97] nitrogenases. [N$_3$N]V=NH is the first parent (NH) imido complex for this element to our knowledge.

Interest in multiple bonds between transition metals and heavier main group elements has been gaining momentum during the past few years.[98] Examples of recent syntheses of terminal sulfido complexes include the reaction of [TaCp*$_2$(R)] with ethylene sulfide to give TaCp*$_2$(R)(S),[99] dehydrohalogenation of Cp*$_2$-Zr(SH)X to give [Cp*$_2$Zr(S)] as a reactive intermediate,[100,101] synthesis of species such as (tmtaa)Ti=S[102] (tmtaa = the dianion of 7,16-dihydro-6,8,15,17-tetramethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine) and *trans*-W(S)$_2$(PMe$_3$)$_4$ employing H$_2$S as the source of sulfur,[103] and synthesis of (*t*-BuO)$_3$V=S from V(O-*t*-Bu)$_4$ and elemental sulfur.[29] A set of niobium chalcogenide complexes of the type NbCp*(N-2,6-*i*-Pr$_2$C$_6$H$_3$)(X)(PMe$_3$) (X = S, Se, Te) have been prepared by treating NbCp*(N-2,6-*i*-Pr$_2$C$_6$H$_3$)(PMe$_3$)$_2$ in toluene with the appropriate elemental chalcogen.[104] Presumably PMe$_3$ is responsible for catalyzing the chalcogenide transfer via Me$_3$P=X (X = S, Se, Te) in the niobium systems, as was found to be the case in the synthesis of *trans*-W(Te)$_2$(PMe$_3$)$_4$.[105] (Phosphine tellurides[106,107] are also now well-known reagents for preparing transition metal tellurides.[108,109]) A route to terminal tellurides of zirconium and hafnium involving elimination of Te(Si[SiMe$_3$]$_3$)$_2$ was recently reported.[110] A feature of the vanadium complexes reported here that distinguishes them from perhaps all other reported transition metal chalcogenide complexes is that the chalcogenide-free species, V[N$_3$N], is stable; therefore the kinetics and thermodynamics of X transfer could be explored in much more detail than we have reported here. The stability of the heavy chalcogenide complexes, [N$_3$N]V=X (X = S, Se, Te), might be ascribed to steric factors, since there are other examples of unusual complexes whose existence could be ascribed to steric protection by triamido amine ligands.[14,15] We have already noted that the tantalum analogs, [N$_3$N]Ta=X (X = Se or Te), were also reported recently.[16]

The ^{51}V NMR spectra of the [N$_3$N]V=X complexes (Figure 4) deserve some comment. Maatta found that the vanadium in vanadium(V) tolylimido complexes[30] is increasingly shielded as the electronegativity of the ligands other than the imido ligand is increased. A similar effect, the so-called "inverse halogen dependence", was noted by other authors for oxovanadium trihalides[111] and for vanadium chalcogenides in the solid state.[112] The steadily increasing downfield shifts in the ^{51}V NMR spectra

(63) Ogawa, A.; Sonoda, N.; Miyake, J.; Murai, S. *Tetrahedron Lett.* **1985**, *26*, 669.
(64) Rajanbabu, T. V.; Nugent, W. A.; Beattie, M. S. *J. Am. Chem. Soc.* **1990**, *112*, 6408.
(65) Shields, C. J.; Schuster, G. B. *Tetrahedron Lett.* **1987**, *28*, 853.
(66) Singh, V.; Deota, P. *J. Chem. Res.* **1989**, 390.
(67) Tamao, K.; Nakajo, E.; Ito, Y. *J. Org. Chem.* **1988**, *53*, 414.
(68) Umbreit, M. A.; Sharpless, K. B. *Org. Synth.* **1981**, *60*, 29.
(69) Wong, H. N. C.; Fok, C. C. M.; Wong, T. *Heterocycles* **1987**, *26*, 1345.
(70) Yadav, J. S.; Shekharam, T.; Gadgil, V. R. *J. Chem. Soc., Chem. Commun.* **1990**, 843.
(71) Yamashita, M.; Sugiura, M.; Oshikawa, T.; Tsunekawa, K.; Inokawa, S. *Synthesis* **1985**, 65.
(72) Jørgensen, K. A.; Schiøtt, B. *Chem. Rev.* **1990**, *90*, 1483.
(73) Backvall, J. E.; Bokman, F.; Blomberg, M. R. A. *J. Am. Chem. Soc.* **1992**, *114*, 534.
(74) Berry, M.; Davies, S. G.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1978**, 99.
(75) Collman, J. P.; Kodadek, T.; Brauman, J. I. *J. Am. Chem. Soc.* **1986**, *108*, 2588.
(76) Moloy, K. G. *Inorg. Chem.* **1988**, *27*, 677.
(77) Bazan, G. C.; Schrock, R. R.; O'Regan, M. B. *Organometallics* **1991**, *10*, 1062.
(78) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *Organometallics* **1991**, *10*, 3344.
(79) Ho, S. C.; Hentges, S.; Grubbs, R. H. *Organometallics* **1988**, *7*, 780.
(80) Day, V. W.; Klemperer, W. G.; Lockledge, S. P. a. M., D. J. *J. Am. Chem. Soc.* **1990**, *112*, 2031.
(81) Zlota, A. A.; Frolow, F.; Milstein, D. *J. Am. Chem. Soc.* **1990**, *112*, 6411.
(82) Schiøtt, B.; Jørgensen, K. A. *Organometallics* **1992**, *11*, 4213.
(83) Hayasi, Y.; Schwartz, J. *Inorg. Chem.* **1981**, *20*, 3473.
(84) An unpublished example of transfer of an NH group in an aziridine to tantalum has been brought to our attention by J. Bonnano and P. Wolczanski. We thank them for communicating their results to us.
(85) Chatt, J.; Choukroun, R.; Dilworth, J. R.; Hyde, J.; Vella, P.; Zubieta, J. *Transition Met. Chem. (London)* **1979**, *4*, 59.
(86) Dilworth, J. R.; Dahlstrom, P. L.; Hyde, J. R.; Zubieta, J. *Inorg. Chim. Acta* **1983**, *71*, 21.
(87) Dilworth, J. R.; Henderson, R.; Dahlstrom, P.; Hutchinson, J.; Zubieta, J. *Cryst. Struct. Commun.* **1982**, *11*, 1135.
(88) Parkin, G.; Vanasselt, A.; Leahy, D. J.; Whinnery, L.; Hua, N. G.; Quan, R. W.; Henling, L. M.; Schaefer, W. P.; Santarsiero, B. D.; Bercaw, J. E. *Inorg. Chem.* **1992**, *31*, 82.
(89) Glassman, T. E.; Vale, M. G.; Schrock, R. R. *Organometallics* **1991**, *10*, 4046.

(90) Glassman, T. E.; Vale, M. G.; Schrock, R. R. *Organometallics* **1991**, *10*, 4046.
(91) Schrock, R. R.; Glassman, T. E.; Vale, M. G. *J. Am. Chem. Soc.* **1991**, *113*, 725.
(92) Shilov, A. E. *Pure Appl. Chem.* **1992**, *64*, 1409.
(93) Richards, R. L. *Chem. Br.* **1988**, *24*, 133.
(94) Henderson, R. A.; Leigh, G. J.; Pickett, C. J. *Adv. Inorg. Chem. Radiochem.* **1983**, *27*, 197.
(95) Burgess, B. K. *Chem. Rev.* **1990**, *90*, 1377.
(96) Rehder, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 148.
(97) Woitha, C.; Rehder, D. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1438.
(98) Siemeling, U. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 67.
(99) Nelson, J. E.; Parkin, G.; Bercaw, J. E. *Organometallics* **1992**, *11*, 2181.
(100) Carney, M. J.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 6426.
(101) Carney, M. J.; Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1992**, *11*, 761.
(102) Housmekerides, C. E.; Ramage, D. L.; Kretz, C. M.; Shontz, J. T.; Pilato, R. S.; Geoffroy, G. L.; Rheingold, A. L.; Haggerty, B. S. *Inorg. Chem.* **1992**, *31*, 4453.
(103) Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1991**, *113*, 5904.
(104) Siemeling, U.; Gibson, V. C. *J. Chem. Soc., Chem. Commun.* **1992**, 1670.
(105) Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1991**, *113*, 9421.
(106) Jones, C. H. W.; Sharma, R. D. *Organometallics* **1987**, *6*, 1419.
(107) Kuhn, N.; Henkel, G.; Schumann, H.; Fröhlich, R. *Z. Naturforsch.* **1990**, *45B*, 1010.
(108) Steigerwald, M. L.; Sprinkle, C. R. *Organometallics* **1988**, *7*, 245.
(109) Steigerwald, M. L.; Rice, C. E. *J. am. Chem. Soc.* **1988**, *110*, 4228.
(110) Christou, V.; Arnold, J. *J. Am. Chem. Soc.* **1992**, *114*, 6240.
(111) Priebsch, W.; Rehder, D. *Inorg. Chem.* **1985**, *24*, 3058.
(112) Becker, K. D.; Berlage, U. *J. Magn. Reson.* **1983**, *54*, 272.

that we observe upon replacing O with S, S with Se, and Se with Te (Figure 4) are fully consistent with previous findings and of course with assignment of the [N₃N]V=X (X = O, S, Se, Te) complexes as terminal chalcogenide complexes.

One of our goals of chemistry involving complexes that contain triamido amine ligands is to assess as far as possible the requirements for activation of dinitrogen. We have seen no evidence so far that dinitrogen interacts with high-spin V[N₃N]. Perhaps this is not surprising in view of the fact that V[N₃N] will not form stable adducts even with simple σ-donor ligands. On the other hand, we have found that reduction of Mo[(C₆F₅NCH₂-CH₂)₃N](OTf) by sodium amalgam under dinitrogen gives [(C₆F₅NCH₂CH₂)₃N]Mo(N₂)NaLₓ (L = ether or THF) or {[(C₆F₅NCH₂CH₂)₃N]Mo}₂(μ-N₂) and that these two species can be interconverted in a redox process; "Mo[(C₆F₅NCH₂-CH₂)₃N₂]⁻" has not been observed.[113] We suspect that activation of some substrates by some M[(RNCH₂CH₂)₃N] complexes may be relatively complex in detail. We hope to address a variety of questions in the future through studies of heavier transition metal analogs (Nb, Ta, Mo, W) of complexes of the type M[(RNCH₂-CH₂)₃N] and to examine what we believe are two important factors in determining reactions of M[(RNCH₂CH₂)₃N] complexes, the spin state and whether the axial amine donor remains bound to the metal at all times.

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by using standard Schlenk techniques, unless otherwise specified. Pentane was washed with sulfuric/nitric acid (95:5 v/v), sodium bicarbonate, and then water, stored over calcium chloride, and then distilled from sodium benzophenone ketyl under nitrogen. Reagent grade diethyl ether, tetrahydrofuran, toluene, and benzene were distilled from sodium benzophenone ketyl under nitrogen. C₆D₆ and DMSO-d₆ were subjected to three freeze–pump–thaw cycles and stored over activated 4-Å molecular sieves in the drybox. Tris(2-aminoethyl)amine (Strem) was distilled from CaH₂. Technical grade 2-methylaziridine was fractionally distilled and subsequently vacuum-transferred from CaH₂. (Trimethylsilyl)diazomethane in hexane and trimethylsilyl azide were purchased from Aldrich and used as received. *cis-* and *trans-*2-butene oxide were degassed and stored over activated 4-Å molecular sieves in the drybox. Nitrous oxide (Matheson) was used as received. Pyridine *N*-oxide was sublimed at 25 °C onto a 0 °C probe under dynamic vacuum. V[N₃N'] was prepared as reported in the literature.[13]

NMR spectra were recorded at either 250 or 300 MHz at 25 °C unless otherwise noted. ¹H and ¹³C data are listed in parts per million downfield from tetramethylsilane and were referenced using the residual protonated solvent resonance. ⁵¹V and ¹⁹F NMR data are listed in parts per million downfield from neat external VOCl₃ and CF₃Cl, respectively. Coupling constants and peak widths at half-height ($\Delta\nu_{1/2}$) are given in hertz. Obvious multiplicities and routine coupling constants usually are not listed. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400 CHN analyzer.

Preparation of Compounds. Li₃[N₃N]. A 1-L Schlenk flask was charged with tris(2-aminoethyl)amine (17.549 g, 120 mmol) and tetrahydrofuran (350 mL) and chilled to –78 °C under argon. *n*-Butyllithium (3.2 equiv, 240 mL, 1.6 M in hexane) was added via cannula. After 20 min the reaction mixture was allowed to warm slowly to 25 °C and was stirred for 5 h at room temperature. The reaction mixture was then cooled to –78 °C, and trimethylsilyl chloride was added (4 equiv, 480 mmol, 52.15 g). The reaction mixture was again allowed to warm slowly to 25 °C and was stirred for 12 h. Tetrahydrofuran was removed *in vacuo*, and the residue was extracted with pentane (500 mL total). The extract was filtered through Celite. The pentane extract was transferred to a 1 L Schlenk flask and chilled to –78 °C under argon. *n*-Butyllithium (3.2 equiv, 240 mL, 1.6 M in hexane) was added via cannula, and the reaction mixture was warmed slowly to 25 °C and stirred for 5 h. The total volume was reduced to ~175 mL *in vacuo*, and the resulting slurry was chilled to –35 °C for 12 h. The white, microcrystalline product was collected by filtration, washed quickly with cold pentane (20 mL, –35 °C), and dried in vacuo; yield 42.85 g (112.6 mmol, 94%): ¹H NMR

(113) Kol, M.; Schrock, R. R.; Kempe, R. *J. Am. Chem. Soc.*, in press.

(THF-d₈) δ 3.065 (t, 6, CH₂), 2.390 (t, 6, CH₂), –0.072 (s, 27, SiMe₃); ¹³C NMR (THF-d₈) δ 56.58 (t, $^1J_{CH}$ = 130, CH₂), 45.18 (t, $^1J_{CH}$ = 126, CH₂), 2.29 (q, $^1J_{CH}$ = 115, SiMe₃).

[N₃N]VCl. A 500-mL flask containing 250 mL of pentane at –35 °C was charged with VCl₄(1,2-dimethoxyethane) (6.507 g, 23.00 mmol), followed by Li₃[N₃N] (8.755 g, 23.00 mmol). The reaction mixture was allowed to warm slowly to 25 °C and was stirred for 24 h. Lithium chloride was then removed by filtration through Celite, and the pentane was removed from the filtrate *in vacuo*. Pentane (~60 mL) was added to the residue, and the slurry was transferred to a 100-mL flask, which was then stored at –35 °C for 24 h. The blue-black crystalline product was collected by filtration, washed quickly with cold pentane (10 mL, –35 °C), and dried in vacuo; yield 4.580 g (10.27 mmol, 45%): ¹H NMR (C₆D₆) δ 1.73 (s, 27, $\Delta\nu_{1/2}$ = 31, SiMe₃), –15.09 (s, 6, $\Delta\nu_{1/2}$ = 130, CH₂), –46.13 (s, 6, $\Delta\nu_{1/2}$ = 310, CH₂). Anal. Calcd for C₁₅H₃₉ClN₄Si₃V: C, 40.38; H, 8.81; N, 12.56. Found: C, 40.42; H, 8.99; N, 12.48.

[N₃N]VN₃. Sodium azide (4.1 mmol, 267 mg) was added to a stirred solution of [N₃N]VCl (730 mg, 1.636 mmol) in 10 mL of THF. The reaction mixture was stirred at 25 °C for 27 h before the THF was removed under vacuum. The residue was extracted with ether, the extract was filtered, and the ether was removed from the filtrate in vacuo. This procedure afforded a dry black solid (663 mg, 1.464 mmol, 90%). The black solid was dissolved in a minimum of pentane, the solution was filtered, and the filtrate was chilled to –35 °C overnight to afford a crop of black plates (209 mg). The black plates dissolve in C₆D₆ to give a green solution. ¹H NMR (C₆D₆): δ 1.19 (s, 27, $\Delta\nu_{1/2}$ = 31, SiMe₃), –10.64 (s, 6, $\Delta\nu_{1/2}$ = 144, CH₂), –49.82 (s, 6, $\Delta\nu_{1/2}$ = 318, CH₂). IR (pentane solution, KBr cells, background subtracted): 2088 cm⁻¹ (vs, ν_{azide}).

V[N₃N]. A solution of [N₃N]VCl (2.02 g, 4.53 mmol) in 30 mL of pentane was treated with freshly-prepared sodium amalgam (200 mg Na, 8.7 mmol; 39.8 g of Hg), and the mixture was stirred vigorously for 18 h at 25 °C. The aquamarine solution was decanted from the NaCl/Na/Hg mixture and filtered through Celite. The solvent was removed from the filtrate *in vacuo*, leaving V[N₃N] as a waxy blue solid (1.70 g, 4.13 mmol, 91%; >95% pure by ¹H NMR). It is possible to purify V[N₃N] by recrystallization from extremely concentrated pentane solutions at –35 °C (47% recovery): ¹H NMR (C₆D₆) δ 5.43 (s, 27, $\Delta\nu_{1/2}$ = 300, SiMe₃), –15.40 (s, 6, $\Delta\nu_{1/2}$ = 920, CH₂), –91.00 (s, 6, $\Delta\nu_{1/2}$ = 1700, CH₂). Anal. Calcd for C₁₅H₃₉N₄Si₃V: C, 43.87; H, 9.57; N, 13.64. Found: C, 44.00; H, 9.58; N, 13.91.

Adducts of V[N₃N]. A solution of V[N₃N] (462 mg, 1.125 mmol) in 7 mL of pentane was treated with CH₃CN (60 mg, 1.350 mmol), giving a lime-green color. The solution was chilled overnight at –35 °C to give green crystals (386 mg in two crops, 849 μmol, 75%): ¹H NMR (C₆D₆) δ 2.86 (s, 27, $\Delta\nu_{1/2}$ = 187, SiMe₃), –18.30 (s, 6, $\Delta\nu_{1/2}$ = 1300, CH₂), –82.30 (s, 6, $\Delta\nu_{1/2}$ = 2500, CH₂). Even short periods of time under vacuum cause the green crystals to turn to an oil, and elemental analyses were not reproducible from run to run, presumably due to loss of the labile ligand under vacuum.

Lavender, crystalline [N₃N]V(OPMe₃) was prepared similarly, but it was also subject to loss of trimethylphosphine oxide in vacuo. ¹H NMR (C₆D₆): δ 4.05 (s, 27, $\Delta\nu_{1/2}$ = 280, SiMe₃), 2.22 (s, 9, $\Delta\nu_{1/2}$ = 187, PMe₃), –23.80 (s, 6, $\Delta\nu_{1/2}$ = 1600, CH₂), –45.80 (s, 6, $\Delta\nu_{1/2}$ = 2800, CH₂).

Adducts that contain DMSO or *t*-BuNC as ligands could also be prepared but were also unstable with respect to loss of the ligand in vacuo.

[N₃N]V=O. A solution of V[N₃N] (1.00 g, 2.44 mmol) in 30 mL of pentane was treated with propylene oxide (340 μL, 4.87 mmol). After 3 h at 25 °C, the solvent was removed *in vacuo* from the mixture, giving [N₃N]V=O quantitatively as a waxy yellow solid (>95% pure by ¹H NMR). Subsequent crystallization from a minimum amount of pentane gave 460 mg (1.08 mmol, 44%) of this highly soluble species: ¹H NMR (C₆D₆) δ 3.290 (broad, 6, CH₂), 2.320 (t, 6, CH₂), 0.468 (s, 27, SiMe₃); ¹³C NMR (C₆D₆) δ 54.06 (t, $^1J_{CH}$ = 134, CH₂), 53.18 (t, $^1J_{CH}$ = 134, CH₂), 2.49 (q, $^1J_{CH}$ = 118, SiMe₃); ⁵¹V NMR (C₆D₆) δ –173 ($\Delta\nu_{1/2}$ = 46). Anal. Calcd for C₁₅H₃₉N₄OSi₃V: C, 42.22; H, 9.21; N, 13.13. Found: C, 42.14; H, 8.81; N, 12.87. IR (pentane solution, KBr cells, background subtracted): 996 cm⁻¹ (s, $\nu_{V=O}$).

Attempted Deoxygenation of [N₃N]V=O with PMe₃. A solution of [N₃N]V=O (41 mg, 96 μmol) and PMe₃ (3 equiv, 22 mg, 288 μmol) in 600 μL of C₆D₆ was transferred to a 5-mm NMR tube sealed to a vacuum adapter. The solution was frozen, the headspace was evacuated, and the tube was sealed with a torch. Examination by ¹H NMR after 20 min at 25 °C showed no initial reaction. The tube was then immersed

in a bath at 80 °C for 30 h. No color change was observed, and examination by ^{1}H NMR showed only unreacted [N$_3$N]V=O and PMe$_3$.

Attempted Thermolysis of [N$_3$N]V(OPMe$_3$). A solution containing [N$_3$N]V(OPMe$_3$) was prepared by adding Me$_3$P=O (2 equiv, 16.6 mg, 180 μmol) to V[N$_3$N] (37 mg, 90 μmol) in 600 μL of C$_6$D$_6$ in a 5-mm NMR tube sealed to a vacuum adapter. The solution was frozen, the headspace was evacuated, and the tube was sealed with a torch. Examination by ^{1}H NMR showed a broad resonance at 1.54 ppm due to the averaging of signals for free and bound PMe$_3$, along with the broad resonance at 4.07 ppm attributed to the SiMe$_3$ groups of [N$_3$N]V(OPMe$_3$). The tube was immersed in a bath at 80 °C for 16 h. No color change was observed, and examination by ^{1}H NMR revealed no change in the spectrum.

Reaction of V[N$_3$N] with *cis*- and *trans*-2-Butene Oxide. A sample of V[N$_3$N] (34 mg, 83 μmol) was stirred at 25 °C in C$_6$D$_6$, and a solution of *cis*-2-butene oxide (3 equiv, 250 μmol) in C$_6$D$_6$ was added. The total volume of C$_6$D$_6$ was 600 μL. An initial color change to green was observed, and the solution had become yellow-gold after 1 h. The solution was transferred to an NMR tube and examined by ^{1}H NMR at 300 MHz. The spectrum was very clean, and only resonances for [N$_3$N]V=O, *cis*-2-butene, *trans*-2-butene, and the excess *cis*-2-butene oxide were observed. Resonances for *cis*-2-butene, *trans*-2-butene, and the excess *cis*-2-butene oxide were assigned by comparison with spectra of authentic samples. The *trans:cis* ratios for the butenes were observed to be 5.9:1 and 6.4:1 by careful integration of the olefinic and aliphatic resonances, respectively. The deoxygenation of *trans*-2-butene oxide proceeded in a similar fashion, with *trans:cis* ratios of 6.7:1 and 7.0:1 observed for the olefinic and aliphatic butene resonances, respectively.

Reaction of V[N$_3$N] with N$_2$O. A pentane solution of V[N$_3$N] (930 mg, 2.266 mmol) was chilled to –78 °C and placed under vacuum to remove dissolved gases. N$_2$O (1 atm) was then admitted. While the solution was still cold, a rapid color change to amber-gold was observed. The reaction mixture warmed to 25 °C and was stirred 12 h. Removal of the volatiles under reduced pressure left a yellow solid, identified by ^{1}H NMR as [N$_3$N]V=O of >95% purity.

Reaction of V[N$_3$N] with Pyridine N-Oxide. When a solution of V[N$_3$N] (70 mg, 170 μmol) in 1 mL of toluene was added to a rapidly-stirred solution of pyridine N-oxide (33 mg, 340 mmol) in 1 mL of toluene, a color change from blue to yellow-orange took place over the course of 60–70 s.

[N$_3$N]V=S. A solution of V[N$_3$N] (920 mg, 2.242 mmol) in 50 mL of pentane was treated with sulfur (108 mg, 3.363 mmol, recrystallized from toluene prior to use). The mixture changed to deep orange solution in 1–2 min, and after 1 h the reaction was judged complete (^{1}H NMR of an aliquot). Excess sulfur was filtered off, and the filtrate was chilled to –35 °C to give crystalline [N$_3$N]V=S (801 mg, 1.809 mmol, 81%): ^{1}H NMR (C$_6$D$_6$) δ 3.370 (broad, 6, CH$_2$), 2.050 (t, 6, CH$_2$), 0.535 (s, 27, SiMe$_3$); ^{13}C NMR (C$_6$D$_6$) δ 57.67 (t, $^1J_{CH}$ = 136, CH$_2$), 55.63 (t, $^1J_{CH}$ = 135, CH$_2$), 3.46 (q, $^1J_{CH}$ = 118, SiMe$_3$); ^{51}V NMR (C$_6$D$_6$) δ 621 ($\Delta\nu_{1/2}$ = 41). Anal. Calcd for C$_{15}$H$_{39}$N$_4$SSi$_3$V: C, 40.69; H, 8.88; N, 12.65. Found: C, 41.10; H, 9.02; N, 12.50.

[N$_3$N]V=Se. A solution of V[N$_3$N] (1.86 g, 4.53 mmol) in 50 mL of pentane was treated with gray selenium (1.86 g, 23.56 mmol), and the mixture was stirred for 72 h at 25 °C. The dark orange-brown reaction mixture was filtered through Celite, and the solvent was removed from the filtrate *in vacuo*. The crude product was recrystallized from pentane (20 mL) at –35 °C to give 1.44 g of [N$_3$N]V=Se as black crystals (2.94 mmol, 65%): ^{1}H NMR (C$_6$D$_6$) δ 3.452 (broad, 6, CH$_2$), 1.925 (t, 6, CH$_2$), 0.561 (s, 27, SiMe$_3$); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 58.52 (CH$_2$), 55.18 (CH$_2$), 3.58 (SiMe$_3$); ^{51}V NMR (C$_6$D$_6$) δ 921 ($\Delta\nu_{1/2}$ = 55). Satisfactory analytical data for [N$_3$N]V=Se could not be obtained, perhaps due to some decomposition of the sensitive complex prior to analysis.

Generation of [N$_3$N]V=Te. Tellurium (140 mg, 1.1 mmol) was slurried in toluene (2 mL), and PMe$_3$ (378 μL, 278 mg, 3.7 mmol) was added. The solution became pale yellow, and most of the tellurium dissolved over 20 min. After 2 h, the solution was filtered, and the filtrate was added to a stirred toluene solution of V[N$_3$N] (250 mg, 0.61 mmol). No color change was observed. After 12 h at 25 °C, the system was placed under vacuum in order to remove solvent, eliciting a rapid color change to deep purple. After complete removal of the volatiles, a black crystalline residue remained. The residue was extracted into C$_6$D$_6$, and the solution was filtered into an NMR tube for analysis. Resonances for V[N$_3$N], Me$_3$P=Te, and [N$_3$N]V=Te were observed; integration of the signals showed that these species were present in approximately a 1.8:1.0:1.1 ratio. No other resonances were observed. The spectral data for [N$_3$N]V=Te are as follows: ^{1}H NMR (C$_6$D$_6$) δ 3.598 (broad, 6, CH$_2$),

1.627 (t, 6, CH$_2$), 0.659 (s, 27, SiMe$_3$); ^{13}{^{1}H} NMR (C$_6$D$_6$) δ 59.55 (t, CH$_2$), 53.65 (t, CH$_2$), 4.47 (q, SiMe$_3$); ^{51}V NMR (C$_6$D$_6$) δ 1484 ($\Delta\nu_{1/2}$ = 93, $^1J_{TeV}$ = 360).

Reaction of [N$_3$N]V=Se with PMe$_3$. A sample of [N$_3$N]V=Se (44 mg, 90 μmol) dissolved in C$_6$D$_6$ was treated with PMe$_3$ (2 equiv, 19 μL). No color change was observed initially, and the reaction mixture was allowed to sand at 25 °C for 72 h. Inspection of the reaction mixture by ^{1}H NMR showed a characteristic resonance for V[N$_3$N] at 5.4 ppm, along with a doublet for Me$_3$P=Se at 1.24 ppm (J_{PH} = 13.2 Hz) and a broad resonance for PMe$_3$ at 0.79 ppm. The spectrum was otherwise clean, and no [N$_3$N]V=Se remained.

[N$_3$N]V=NH. Addition of 2-methylaziridine (338 mg, 5.91 mmol) to a blue solution of V[N$_3$N] (1.21 g, 2.96 mmol) in 8 mL of ether produced an immediate color change to amber-orange. The solvent was removed *in vacuo* after 25 h at 25 °C, leaving a solid brown residue. The residue was dissolved in a minimum volume of pentane (~5 mL), the solution was filtered to remove any red-brown solid, and the filtrate was chilled to –35 °C overnight. Golden plates were collected by filtration and dried *in vacuo* (545 mg in two crops, 1.28 mmol, 43%): ^{1}H NMR (C$_6$D$_6$) δ 3.400 (t, 6, CH$_2$), 2.428 (t, 6, CH$_2$), 0.361 (s, 27, SiMe$_3$); ^{13}C NMR (C$_6$D$_6$) δ 54.37 (t, $^1J_{CH}$ = 134, CH$_2$), 53.17 (t, $^1J_{CH}$ = 134, CH$_2$), 3.86 (q, $^1J_{CH}$ = 118, SiMe$_3$); ^{51}V NMR (C$_6$D$_6$) δ 252.4 ($\Delta\nu_{1/2}$ = 360). Anal. Calcd for C$_{15}$H$_{40}$N$_5$Si$_3$V: C, 42.32; H, 9.47; N, 16.45. Found: C, 42.77; H, 8.80; N, 16.35. IR (pentane solution, KBr cells, background subtracted): 3391 cm^{-1} (m, ν_{NH}).

[N$_3$N]V=N—N=CHSiMe$_3$. A solution of V[N$_3$N] (616 mg, 1.50 mmol) in 20 mL of pentane was treated with Me$_3$SiCH(N$_2$) (1.80 mmol, 2.0 M in hexane). The color of the mixture changed to brick red. After 10 minutes the solvents were removed in vacuo and the red solid was recrysallized from pentane at –35 °C (248 mg, 472 μmol, 31%): ^{1}H NMR (C$_6$D$_6$) δ 8.350 (s, 1, N=CH), 3.474 (t, 6, CH$_2$), 2.529 (t, 6, CH$_2$), 0.401 (s, 27, SiMe$_3$), 0.253 (s, 9, CHSiMe$_3$); ^{13}C{^{1}H} NMR (d_8-toluene) δ 168.43 (N=CH), 56.09 (CH$_2$), 53.43 (CH$_2$), 3.76 (NSiMe$_3$), –2.15 (CSiMe$_3$). Anal. Calcd for C$_{19}$H$_{49}$N$_6$Si$_4$V: C, 43.47; H, 9.41; N, 16.01. Found: C, 43.10; H, 9.19; N, 15.64.

[N$_3$N]V=NSiMe$_3$. A solution of V[N$_3$N] (264 mg, 643 mmol) in 10 mL of pentane was treated with trimethylsilyl azide (67 mg, 582 μmol). The color of the reaction mixture changed to orange over a period of 48 h. The homogeneous reaction mixture was concentrated and cooled to –35 °C to yield a crop of orange crystals (115 mg, 230 mmol, 36%): ^{1}H NMR (C$_6$D$_6$) δ 3.255 (broad, 6, CH$_2$), 2.370 (t, 6, CH$_2$), 0.554 (s, 9, NSiMe$_3$), 0.326 (s, 27, SiMe$_3$); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 59.10 (CH$_2$), 54.11 (CH$_2$), 4.80 (NSiMe$_3$), 2.79 (SiMe$_3$). Anal. Calcd for C$_{18}$H$_{48}$N$_5$Si$_3$V: C, 43.42; H, 9.72; N, 14.07. Found: C, 43.51; H, 9.71; N, 14.03.

Conversion of [N$_3$N]V=NH to [N$_3$N]V=NSiMe$_3$. A solution of LiN(SiMe$_3$)$_2$ (18 mg, 108 μmol) in 2 mL of pentane was added via pipet to a solution of [N$_3$N]V=NH (46 mg, 108 μmol) in 3 mL of pentane. Crystals began to form in less than a minute. After 20 min, the supernatant was decanted from the sparkling, pale yellow crystals. The crystals (presumably [N$_3$N]V=NLi) were dried under vacuum: ^{1}H NMR (C$_6$D$_6$) δ 3.175 (t, 6, CH$_2$), 2.249 (t, 6, CH$_2$), 0.488 (s, 27, SiMe$_3$). A portion (ca. 20 mg) of the crystals was slurried in 2 mL of ether, and 1 mL THF was added. ClSiMe$_3$ (excess) was then added, and the color of the cloudy reaction mixture went from pale yellow to yellow gold. After 2 min, the solvent was removed under reduced pressure, the residue was extracted with 3 mL of pentane, the extract was filtered, and the pentane was removed under reduced pressure to reveal a crystalline yellow solid. Examination by ^{1}H NMR (C$_6$D$_6$) showed that [N$_3$N]V=NSiMe$_3$ had formed quantitatively.

Conversion of [N$_3$N]VN$_3$ to [N$_3$N]V=NSiMe$_3$. A solution of [N$_3$N]VN$_3$ (58 mg, 130 μmol) in 2.5 mL of THF was stirred and treated with Na/Hg (260 μmol Na; 0.5% amalgam). The color changed from green-black to olive-amber over 24 h. An aliquot was treated with ClSiMe$_3$ (5 drops), and the volatiles were removed from the green mixture after 1 min. After drying under vacuum, the solid appeared red-brown. Examination by ^{1}H NMR (C$_6$D$_6$) showed mainly (>90%) [N$_3$N]V=NSiMe$_3$.

[N$_3$N]V=NC$_6$F$_5$. A solution of V[N$_3$N] (495 mg, 1.21 mmol) in toluene (5 mL) was treated with C$_6$F$_5$NNC$_5$H$_5$ (314 mg, 1.21 mmol). The resulting green reaction mixture was stirred for 24 h at 25 °C. The toluene was removed *in vacuo*, and the rust red crystals were dissolved in pentane (4 mL). The pentane solution was filtered, and the filtrate was chilled to –35 °C to give a crop of crystals, which were collected by filtration and dried *in vacuo* (414 mg, 700 μmol, 58%): ^{1}H NMR (C$_6$D$_6$) δ 3.346 (t, 6, CH$_2$), 2.386 (t, 6, CH$_2$), 0.209 (s, 27, SiMe$_3$); ^{13}C NMR

(C_6D_6) δ 144.30 (d, $^1J_{CH}$ = 248, CF), 137.84 (d, $^1J_{CF}$ = 251, CF), 58.80 (t, $^1J_{CH}$ = 136, CH$_2$), 54.20 (t, $^1J_{CH}$ = 135, CH$_2$), 2.56 (q, $^1J_{CH}$ = 118, SiMe$_3$); ^{51}V NMR (C_6D_6) δ –95 ($\Delta\nu_{1/2}$ = 253); ^{19}F NMR (C_6D_6) δ –143.2 (d, ortho CF), –162.2 (t, meta or para CF), –165.3 (t, meta or para CF). Anal. Calcd for $C_{21}H_{39}F_5N_5Si_3V$: C, 42.62; H, 6.64; N, 11.83. Found: C, 42.74; H, 6.64; N, 11.68.

[N$_3$N]V=N(*p*-CH$_3$C$_6$H$_4$). A solution of Li$_3$[N$_3$N] (2.28 g, 5.98 mmol) in ether (15 mL) at –35 °C was treated with solid Cl$_3$V=N(*p*-CH$_3$C$_6$H$_4$)[30] (1.57 g, 5.98 mmol). The reaction mixture was warmed slowly to 25 °C and stirred for 24 h. LiCl was removed by filtration through Celite, and the solvent was removed from the filtrate *in vacuo*. The crude residue was dissolved in a minimum of pentane, and the solution was chilled to –35 °C for 24 h. The orange-red crystalline product was isolated by filtration on a frit, quickly washed with cold pentane (5 mL), and dried in vacuo (1.50 g, 2.91 mmol, 49%): ^{1}H NMR (C_6D_6) δ 7.636 (d, 2, Ar H), 6.942 (d, 2, Ar H), 3.388 (t, 6, CH$_2$), 2.433 (t, 6, CH$_2$), 2.068 (s, 3, Ar*Me*), 0.347 (s, 27, SiMe$_3$); ^{13}C{^{1}H} NMR (C_6D_6) δ 58.63 (CH$_2$), 53.10 (CH$_2$), 21.09 (Ar*Me*), 3.46 (SiMe$_3$); ^{51}V NMR (C_6D_6) δ –159 ($\Delta\nu_{1/2}$ = 414). Anal. Calcd for $C_{22}H_{46}N_5Si_3V$: C, 51.23; H, 8.99; N, 13.58. Found: C, 51.04; H, 8.36; N, 13.45.

X-ray Study of [N$_3$N]V=NH. Crystal data for [N$_3$N]V=NH are presented in Table 1. Data were collected at room temperature (20 °C) on a Rigaku AFC6S diffractometer in a capillary tube. A total of 6210 reflections were measured, of which 5873 were unique. The raw data were corrected for Lorentz and polarization factors, but no absorption correction was applied. The structure was solved by direct methods (SHELXS) and refined using the TEXSAN crystallographic package. The molecule was refined using anisotropic models for all non-hydrogen atoms; hydrogen atoms were placed in calculated positions with fixed thermal parameters, the only exception to this treatment being the imido H atom, which was located on a difference Fourier map and refined isotropically. Final atomic positions and equivalent isotropic thermal parameters are listed in Table 2. Anisotropic thermal parameters can be found in the supplementary material.

Supplementary Material Available: A labeled ORTEP drawing and listings of final positional and thermal parameters for [N$_3$N]V=NH (5 pages). Ordering information is given on any current masthead page. Data for the structures of [N$_3$N]VCl[14] and V[N$_3$N'][13] have been deposited in the form of supplementary material elsewhere.