Synthesis of Vanadium(III), -(IV), and -(V) Complexes That Contain the Pentafluorophenyl-Substituted Triamidoamine Ligand $[(C_6F_5NCH_2CH_2)_3N]^{3-}$

Kotohiro Nomura, Richard R. Schrock,* and W. M. Davis

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

Received November 9, 1995⊗

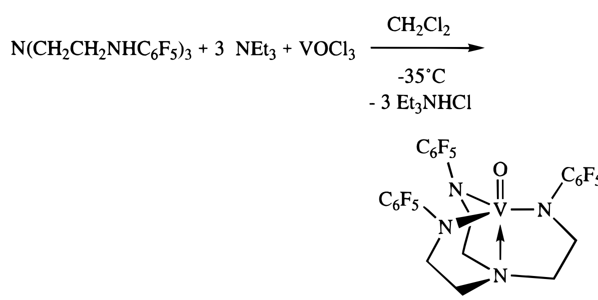
$[N_3N]V{=}O$ ($[N_3N]^{3-} = [(C_6F_5NCH_2CH_2)_3N]^{3-}$) was prepared from $VOCl_3$ and $H_3[N_3N]$ in the presence of Et_3N. Related arylimido complexes, $[N_3N]V{=}NAr$ (Ar = *p*-MeC_6H_4, *p*-$CF_3C_6H_4$, or *p*-FC_6H_4), were prepared in high yields from the known $V(NAr)Cl_3(THF)$ complexes in a similar manner or by treating $[N_3N]V{=}O$ with an aryl isocyanate in refluxing *m*-xylene. New imido complexes also were prepared by reacting an imido complex with an aryl isocyanate over a period of 2 days in refluxing mesitylene. The reaction between $VCl_3(THF)_3$ and $H_3[N_3N]$ in the presence of triethylamine gave $[HNEt_3]\{[N_3N]VCl\}$ (**3**) when the reaction was carried out in ether and $[N_3N]V(CH_3CN)$ (**4a**) when carried out in acetonitrile, while the reaction between $VCl_3(THF)_3$ and $H_3[N_3N]$ in the presence of triethylamine and *tert*-butyl isocyanide gave green $[N_3N]V(t\text{-}BuNC)$. $[N_3N]V(CH_3CN)$ reacts with propylene oxide to give $[N_3N]V{=}O$ and with diazoalkanes to give $[N_3N]V{=}NN{=}CHR$ (R = $SiMe_3$, $CO_2C_2H_5$). An X-ray structure determination of **4a** ($C_{26}H_{15}N_5F_{15}V$, a = 13.021(1) Å, b = 13.021(1) Å, c = 14.221(1) Å, $\gamma = 120°$, rhombohedral, *R*3 (h), $Z = 3$) shows it to be a pseudo-trigonal-bipyramidal species with acetonitrile coordinated in the apical position. An attempt to prepare the iodo analog of **3** by adding Me_3SiI in THF to it yielded green crystalline $[N_3N]V(THF)$ (**5**). An X-ray structure determination of **5** ($C_{28}H_{20}N_4F_{15}OV$, a = 15.390(7) Å, b = 12.189(6) Å, c = 16.468(7) Å, β = 109.96 (3)°, monoclinic, $P2_1/n$, $Z = 4$) shows it to be a pseudo trigonal bipyramid containing 1 equiv of THF in the axial position in a structure that otherwise is similar to that of **4a**. $[HNEt_3]\{[N_3N]VCl\}$ reacts with ferrocenium triflate to yield $[N_3N]VCl$, a species that can be reduced to **5** in THF by sodium amalgam.

Introduction

A variety of vanadium complexes that contain triamidoamine ligands of the type $[(RNCH_2CH_2)_3N]^{3-}$ (where R is a trialkylsilyl group) have been reported.[1−6] Initially we were surprised that the "trigonal monopyramidal" versions[3] do not bind dinitrogen for several reasons. First, a variety of vanadium dinitrogen complexes are known, some of which contain largely or exclusively amido ligands.[7−13] Second, the coordination site in $[(RNCH_2CH_2)_3N]V$ complexes contains two orthogonal π orbitals and a σ orbital pointing along the *z* axis, a circumstance that would seem to be optimal for binding dinitrogen in an "end-on" fashion. Third, we recently reported several triamidoamine complexes of molybdenum, including two that contain dinitrogen.[14] One of them was proposed to be paramagnetic $\{[(C_6F_5NCH_2CH_2)_3N]Mo\}_2(N_2)$, an analog of structurally characterized $\{[(t\text{-}BuMe_2SiNCH_2CH_2)_3N]Mo\}_2(N_2)$.[15] The other was proposed to be the sodium salt of the d^4 "Mo(II)" species $\{[(C_6F_5NCH_2CH_2)_3N]Mo(N_2)\}^-$, i.e., $[(C_6F_5NCH_2CH_2)_3N]Mo{-}N{=}N{-}Na$, judging from its reaction with *i*-Pr_3SiCl to give structurally characterized diamagnetic $[(C_6F_5NCH_2CH_2)_3N]Mo{-}N{=}N{-}Si(i\text{-}Pr)_3$. Therefore, we became interested in the possibility that trigonal-monopyramidal vanadium complexes that contain the $[(C_6F_5NCH_2CH_2)_3N]^{3-}$ ligand would be more likely to bind dinitrogen than those that contain an $[(R_3SiNCH_2CH_2)_3N]^{3-}$ ligand. In this paper we report the preparation of several types of vanadium complexes that contain the $[(C_6F_5NCH_2CH_2)_3N]^{3-}$ ligand.

Results

Vanadium(V) Oxo and Arylimido Complexes. The vanadium oxo complex $[N_3N]V{=}O$ (**1**; $[N_3N]^{3-} = [(C_6F_5NCH_2CH_2)_3N]^{3-}$) was prepared in ~50% yield as orange microcrystals by treating $VOCl_3$ with $H_3[N_3N]$ in cold dichloromethane in the presence of Et_3N (eq 1). This result is not



(1)

1

surprising in view of the prevalence of the oxo ligand in V(5+)

⊗ Abstract published in *Advance ACS Abstracts,* May 15, 1996.

(1) Plass, W.; Verkade, J. G. *J. Am. Chem. Soc.* **1992**, *114*, 2275.
(2) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Organometallics* **1992**, *11*, 1452.
(3) Cummins, C. C.; Lee, J.; Schrock, R. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1501.
(4) Plass, W.; Verkade, J. G. *Inorg. Chem.* **1993**, *32*, 3762.
(5) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Inorg. Chem.* **1994**, *33*, 1448.
(6) Hill, P. L.; Yap, G. A.; Rheingold, A. L.; Maatta, E. A. *J. Chem. Soc., Chem. Commun.* **1995**, 737.
(7) Woitha, C.; Rehder, D. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1438.
(8) Leigh, G. J.; Prietoalcon, R.; Sanders, J. R. *J. Chem. Soc., Chem. Commun.* **1991**, 921.
(9) Rehder, D.; Woitha, C.; Priebsch, W.; Gailus, H. *J. Chem. Soc., Chem. Commun.* **1992**, 364.
(10) Ferguson, R.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 396.
(11) Buijink, J.-K. F.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 2004.
(12) Berno, P.; Hao, S.; Minhas, R.; Gambarotta, S. *J. Am. Chem. Soc.* **1994**, *116*, 7417.
(13) Song, J.-I.; Berno, P.; Gambarotta, S. *J. Am. Chem. Soc.* **1994**, *116*, 6927.
(14) Kol, M.; Schrock, R. R.; Kempe, R.; Davis, W. M. *J. Am. Chem. Soc.* **1994**, *116*, 4382.
(15) Shih, K.-Y.; Schrock, R. R.; Kempe, R. *J. Am. Chem. Soc.* **1994**, *116*, 8804.

S0020-1669(95)01433-9 CCC: $12.00 © 1996 American Chemical Society

chemistry and the synthesis of an analogous complex containing the $[(Me_3SiNCH_2CH_2)_3N]^{3-}$ ligand.[4,5] All data suggest that this 3-fold symmetric diamagnetic compound is a monomer in solution. Since the oxo ligand is almost certainly pseudo triply bound to the metal,[4] **1** can be viewed as an 18-electron complex. (Only two of the possible three nitrogen p orbitals that lie in the VN_3 "plane" can form a π bond to the metal.) The V═O stretch cannot be located with certainty in the IR spectrum because of the presence of strong CF absorptions in the same region. The ^{19}F NMR spectrum of **1** shows three sharp resonances for the ortho (−149.85, d, 6), meta (−164.86, t, 6), and para (−163.07, t, 3) fluorines in a region that we now regard as characteristic of diamagnetic species that contain this ligand. (Resonances for the free ligand are found at −160.54 (6), −164.61 (6), and −171.62 (3) ppm.[14]) Fluorine resonances in paramagnetic complexes containing the $[(C_6F_5NCH_2CH_2)_3N]^{3-}$ ligand (see below) are sometimes also found in this region of the ^{19}F NMR spectrum, but they are relatively broad and easily distinguished from those for diamagnetic species.

Arylimido complexes, $[N_3N]V{=}NAr$ (**2a**−**c**; Ar = *p*-MeC_6H_4, *p*-$CF_3C_6H_4$, *p*-FC_6H_4), could be prepared in high yields (∼80%) from the known $V(NAr)Cl_3(THF)$ complexes[16] in a similar manner (eq 2). Although $[N_3N]V{=}NPh$ (**2d**) could not be prepared and isolated in pure form in this manner, it could be prepared in high yield from **1** as shown in eq 3, a type of

$$V(NAr)Cl_3(THF) + H_3[N_3N] \xrightarrow[-3Et_3NHCl]{THF,\ 3Et_3N} \underset{\mathbf{2a-c}}{[N_3N]V{=}NAr} \quad (2)$$

$$Ar = p\text{-}MeC_6H_4\ (\mathbf{2a}),\ p\text{-}CF_3C_6H_4\ (\mathbf{2b}),\ p\text{-}FC_6H_4\ (\mathbf{2c})$$

$$[N_3N]V{=}O \xrightarrow[m\text{-xylene, reflux, } -CO_2]{PhNCO\ (excess)} \underset{\mathbf{2d}}{[N_3N]V{=}NPh} \quad (3)$$

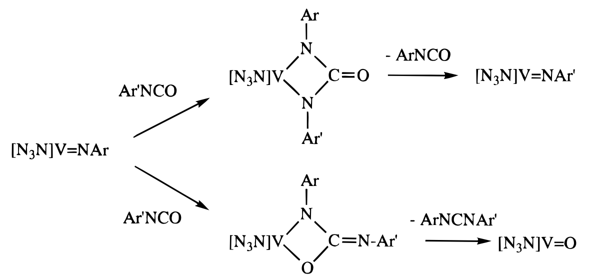
reaction that is often used for preparing imido complexes.[17] This reaction is slow; therefore, it must be carried out in refluxing *m*-xylene in the presence of an excess of aryl isocyanate. (There was essentially no reaction in refluxing toluene after 1 day in the presence of 1 equiv of PhNCO.) Other imido complexes (**2a**, **2c**, **2e** (Ar = *o*-FC_6H_4), **2f** (Ar = *o*-MeC_6H_4), and **2g** (Ar = 3,5-$Me_2C_6H_3$)) also could be prepared by some version of the reaction shown in eq 3. $[N_3N]V{=}N(aryl)$ complexes are extremely stable thermally. They show no sign of decomposition after being heated in refluxing *m*-xylene (138 °C) for several days. Attempts to prepare $[N_3N]V{=}NMe$ or $[N_3N]V{=}NH$ by treating **1** with excess $(Me_3Si)_2NMe$ or $(Me_3Si)_2NH$ were unsuccessful, even in refluxing *m*-xylene; **1** was simply recovered quantitatively.

The reaction shown in eq 3 produced a new organic product slowly (∼20 of 40 equiv consumed in 3 days) that by GC/MS showed a parent ion consistent with it being PhN═C═NPh. This type of catalytic reaction (2 (aryl)NCO yielding CO_2 and (aryl)N═C═N(aryl)) has been reported recently to be catalyzed by V(V) oxo and imido species.[18] This result encouraged us to try to prepare one imido complex by treating another with an aryl isocyanate. The reaction shown in eq 4 in fact proceeds

$$\mathbf{2a}\ \text{or}\ \mathbf{2d} \xrightarrow[\text{mesitylene, reflux, 2 days}]{p\text{-}FC_6H_4NCO\ (excess)} \underset{\mathbf{2c}}{[N_3N]V{=}N(p\text{-}FC_6H_4)} \quad (4)$$

(16) Devore, D. D.; Lichtenhan, J. D.; Takusagawa, F.; Maata, E. A. *J. Am. Chem. Soc.* **1987**, *109*, 7408.
(17) Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 2239.

smoothly in good yield (70% yield after 2 days) in refluxing mesitylene (162−164 °C). The two mechanisms for this reaction for which there is precedent in the literature are the "ureato mechanism" and the "metathesis mechanism" (eqs 5a and 5b, respectively). Isolated monomeric ureato complexes



(5a)
(5b)

are relatively new,[19−25] although bridging ureato complexes have been known for some time.[26] Addition of an aryl isocyanate to an oxo species gives an imido species via a similar VOCN metallacycle, presumably the intermediate in this analogous, well-known reaction. The "metathesis mechanism"[27−29] is less well-known, although the vanadium-catalyzed condensation of aryl isocyanates to *N,N′*-carbodiimides almost certainly involves formation of this type of metallacycle.[18] In view of this precedent, the demonstrated reaction between $[N_3N]V{=}O$ and arylisocyanates,[17] and the catalytic formation of PhN═C═NPh from PhNCO, we at present assume that the reaction proceeds slowly as shown in eq 5b followed by the subsequent *relatively* rapid reaction of $[N_3N]V{=}O$ with an aryl isocyanate.

Synthesis and Reactions of Vanadium(III) Complexes. A "monopyramidal" $[N_3N]V$ complex analogous to those prepared with silylated TREN ligands[3] was one of our primary goals. The most straightforward approach would seem to be the reaction between $VCl_3(THF)_3$ and $H_3[N_3N]$ in the presence of triethylamine. When this reaction was carried out in diethyl ether, a complex mixture resulted, according to ^{19}F NMR spectra. However, one of the components could be isolated in ∼50% yield as golden needles (eq 6) by multistep recrystalli-

$$VCl_3(THF)_3 + H_3[N_3N] \xrightarrow[-2Et_3NHCl]{3Et_3N/ether} \underset{\mathbf{3}}{[HNEt_3]^+\{[N_3N]VCl\}^-} \quad (6)$$

zation from mixtures of ether and dichloromethane. The proton NMR spectrum of **3** showed two broad resonances at 0.30 and 1.86 ppm that we ascribe to the ethyl group of the ammonium salt, while the ^{19}F NMR spectrum showed two broad resonances

(18) Birdwhistell, K. R.; Boucher, T.; Ensminger, M.; Harris, S.; Johnson, M.; Toporek, S. *Organometallics* **1993**, *12*, 1023.
(19) Michelman, R. I.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 5100.
(20) Hasselbring, R.; Roesky, H. W.; Noltemeyer, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 601.
(21) Herrmann, W. A.; Weichselbaumer, G.; Paciello, R. A.; Fischer, R. A.; Herdtweck, E.; Okuda, J.; Marz, D. W. *Organometallics* **1990**, *9*, 489.
(22) Legzdins, P.; Phillips, E. C.; Rettig, S. J.; Trotter, J.; Veltheer, J. E.; Yee, V. C. *Organometallics* **1992**, *11*, 3104.
(23) Lueng, W.-H.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1991**, 2791.
(24) Atagi, L. M.; Mayer, J. M. *Organometallics* **1994**, *13*, 4794.
(25) Coffey, T. A.; Forster, G. D.; Hogarth, G. *J. Chem. Soc., Dalton. Trans.* **1995**, 2337.
(26) Braunstein, P.; Nobel, D. *Chem. Rev.* **1989**, *89*, 1927.
(27) Green, M. L. H.; Hogarth, G.; Konidaris, P. C.; Mountford, P. *J. Chem. Soc., Dalton Trans.* **1990**, 3781.
(28) Hogarth, G.; Konidaris, P. C. *J. Organomet. Chem.* **1990**, *399*, 149.
(29) Forster, G. D.; Hogarth, G. *J. Chem. Soc., Dalton Trans.* **1993**, 2539.

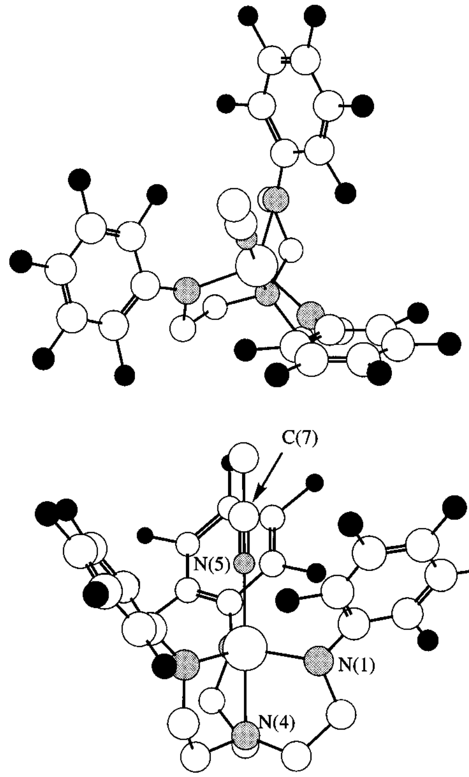


Figure 1. Two Chem 3D views of the structure of $[(C_6F_5NCH_2CH_2)_3N]V(CH_3C{\equiv}N)$ (**4a**).

at -141.9 ($\Delta_{1/2} = 508$ Hz) and -176.8 ppm ($\Delta_{1/2} = 170$ Hz) in a 2:1 ratio that we ascribe to meta and para fluorines on the aryl ring. We presume that resonances ascribable to the ortho fluorines in the ^{19}F NMR spectrum are too broad to be observed, as they are the closest to the high-spin d^2 center. An N−H stretch characteristic of $[HNEt_3]^+$ also can be observed in the IR spectrum.

When the reaction shown in eq 6 is carried out in the presence of acetonitrile, then $[N_3N]V(CH_3CN)$ (**4a**) could be isolated in good yield. **4a** was obtained as lime green microcrystals by multistep extractions with ether and recrystallized from CH_3CN layered with pentane at -30 °C. The ^{19}F NMR spectrum showed two broad resonances ascribable to meta (-146.3 ppm, $\Delta_{1/2} = 340$ Hz) and para (-175.7 ppm, $\Delta_{1/2} = 113$ Hz) fluorines in a ratio of 2:1; the ortho fluorine resonance again could not be observed. The analytical sample appeared to contain two molecules of acetonitrile, although the X-ray structure (see below) showed that only one is present and is coordinated to the metal. **4a** also could also be prepared by recrystallizing **3** from a mixture of acetonitrile and ether. What we presume to be analogous adducts that contain $Me_2CHCH_2C{\equiv}N$ (**4b**) or $CH_2{=}CHCN$ (**4c**) were prepared by similar methods. The reaction between **4a** and propylene oxide at -30 °C gave **1** in 91% yield, but **4a** failed to react with carbon monoxide, ethylene, acetylene, phenylacetylene, pyridine, or trimethylsilyl azide in toluene at 25 °C over periods of time varying from 2 to 10 days.

The X-ray structure of **4a** shows it to be a trigonal-bipyramidal species with acetonitrile coordinated in the apical position (Figure 1, Tables 1 and 2). The compound whose structure could be compared with **4a** is the d^1 species $[(Me_3SiNCH_2CH_2)_3N]VCl$;[2] selected distances and angles for this species are also listed in Table 1. There are several slight differences between the structures of **4a** and $[(Me_3SiNCH_2CH_2)_3N]VCl$. The L_{axial}−V−N(1) angle is larger and the V−N(4) distance is longer in $[(Me_3SiNCH_2CH_2)_3N]VCl$, but the V−N(1) distance is longer in **4a**. The V−N(1)−C_{ipso} angles, a measure of the size of the 3-fold cavity, are virtually the same for the two compounds. The V−N(5) distance in **4a** is about what would be expected for a donor nitrogen to vanadium bond.

An attempt to prepare the iodo analog of **3** by adding Me_3SiI in THF to it yielded green crystalline $[N_3N]V(THF)$ (**5**; eq 7). $[N_3N]V(THF)$ is an exceedingly sensitive compound that

$$[HNEt_3]\{[N_3N]VCl\} + Me_3SiI \xrightarrow[-Et_3NH^+I^-,\ -Me_3SiCl]{THF} \underset{\mathbf{5}}{[N_3N]V(THF)} \quad (7)$$

reacts instantly with acetonitrile to give **4a**, with propylene oxide to give $[N_3N]V{=}O$, or with ethyl diazoacetate to give $[N_3N]V{=}NN{=}CH(CO_2Et)$ (see below). An X-ray structure of **5** (Figure 2, Tables 1 and 2) shows it to contain 1 equiv of THF coordinated in the axial position with a rather long V−O(1) distance of 2.152 Å. The long V−O(1) distance accounts for the lability of the THF molecule and the consequent high sensitivity and reactivity of **5**. In contrast, nitrile ligands (as in **4a**) experience relatively little steric pressure to dissociate from the axial coordination position. The remainder of the structure of **5** is similar to the structure of **4a** and deserves little additional comment.

The reaction between $VCl_3(THF)_3$ and the parent ligand in the presence of *tert*-butyl isocyanide gave complex **6** (eq 8) as

$$VCl_3(THF)_3 + H_3[N_3N] \xrightarrow[-3Et_3NHCl]{ether/t\text{-}BuNC/3Et_3N} \underset{\mathbf{6}}{[N_3N]V(t\text{-}BuNC)} \quad (8)$$

green microcrystals. A proton NMR spectrum of **6** showed a broad resonance at 4.35 ppm ($\Delta_{1/2} = 190$ Hz) due to the *tert*-butyl group. Two broad resonances ascribable to the $[N_3N]$ ligand were observed in the ^{19}F NMR spectrum at -148.5 ppm ($\Delta_{1/2} = 280$ Hz) and -170.2 ppm ($\Delta_{1/2} = 60$ Hz) in a ratio of 2:1, while the IR spectrum showed a strong absorption band due to the isocyanide group at 2180 cm^{-1}. These data are all consistent with the formation of a high-spin d^2 vanadium(III) isocyanide complex with a structure analogous to that found for the nitrile and THF adducts.

Addition of excess (trimethylsilyl)diazomethane to **4a** gave the imido-like diazo complex $[N_3N]V{=}NN{=}CH(SiMe_3)$ (**7a**; eq 9) in high yield (82%) as brick red microcrystals. The

$$\underset{\mathbf{4a}}{[N_3N]V(CH_3CN)} + N_2CH(SiMe_3) \xrightarrow[-30\text{ to }25\text{ °C, 3 h}]{toluene} \underset{\mathbf{7a}}{[N_3N]V{=}NN{=}CH(SiMe_3)} \quad (9)$$

diazoalkane ligand's CH group is characterized by resonances at 7.18 ppm in its ^{1}H NMR spectrum and -170.2 ppm in its ^{13}C NMR spectrum, consistent with the view that the carbon is sp^2-hybridized and imine-like. Like related imido complexes mentioned earlier, **7a** is extremely stable thermally, no change being observed after 1 week in refluxing xylene. **7a** could be prepared from **3** in the same manner. An attempt to convert **7a** into $[N_3N]V{=}CH(SiMe_3)$ by heating it in the presence of CuCl or tris(hexafluoroacetylacetonato)copper failed; no reaction was observed. A similar complex, $[N_3N]V{=}NN{=}CH(CO_2C_2H_5)$ (**7b**), was also prepared in high yield (81%) as brick red microcrystals from **4a**. Compounds similar to **7a** and **7b** have

Table 1. Selected Distances (Å) and Angles (deg) in $[N_3N]V(CH_3C{\equiv}N)$ (**4a**), $[N_3N]V(C_4H_8O)$ (**5**), and $[(Me_3SiNCH_2CH_2)_3N]VCl$[a]

4a		5		$[(Me_3SiNCH_2CH_2)_3N]VCl$	
		Distances			
V−N(5)	2.081 (6)	V−O(1)	2.152 (3)	V−Cl	2.278 (2)
V−N(1,2,3)	1.941(3)[b]	V−N(1)	1.968(3)	V−N(1)	1.883(6)
V−N(4)	2.149(5)	V−N(2)	1.958(3)	V−N(4)	2.238(6)
N(5)−C(7)	1.150(8)	V−N(3)	1.946(3)		
		V−N(4)	2.132(3)		
		O(1)−C(1)	1.445(4)		
		Angles			
N(5)−V−N(1)	96.88(9)	O(1)−V−N(1)	92.34(11)	Cl−V−N(1)	100.0(2)
N(1)−V−N(4)	83.12(9)	N(1)−V−N(4)	82.33(12)	N(1)−V−N(4)	80.2(2)
V−N(1)−C(1)	128.2(2)	V−N(1)−C(11)	131.5(2)	V−N(1)−Si(1)	126.1(3)
N(5)−V−N(4)	180[b]	O(1)−V−N(4)	169.74(11)	Cl−V−N(4)	179.4(2)
V−N(1)−C(10)	112.7(2)	V−N(1)−C(17)	114.4(2)	V−N(1)−C(1)	113.6(5)
N(1)−V−N(2)	120[b]	N(1)−V−N(2)	119.79(13)	N(1)−V−N(2)	120.4(3)

[a] See reference 1. [b] Defined crystallographically.

Table 2. Summary of Crystallographic Data, Collection Parameters, and Refinement Parameters

	$[N_3N]V(CH_3C{\equiv}N)$ (**4a**)	$[N_3N]V(THF)$ (**5**)
empirical formula	$C_{26}H_{15}N_5F_{15}V$	$C_{28}H_{20}N_4F_{15}OV$
fw	733.36	764.42
a, Å	13.021(1)	15.390(7)
b, Å	13.021(1)	12.189(6)
c, Å	14.221(1)	16.468(7)
β, deg	90	109.96(3)
γ, deg	120	90
V, Å^3	2088.2(5)	2904(2)
space group	$R3$ (h)	$P2_1/n$
Z	3	4
ρ(calc), g/cm^3	1.749	1.749
collecn temp, °C	-86 ± 1	-86 ± 1
μ(Mo Kα), cm^{-1}	4.69	4.71
R^a	0.043	0.0625
$R_w{}^b$	0.040	0.1734
goodness of fit^c	1.48	1.010

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

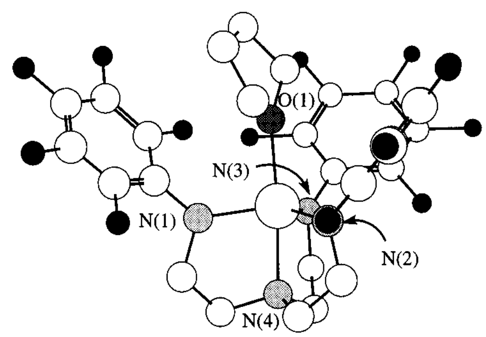


Figure 2. Chem 3D drawing of the structure of $[(C_6F_5NCH_2CH_2)_3N]V(THF)$ (**5**).

been isolated from reactions between (for example) $[(Me_3SiNCH_2CH_2)_3N]V$ and diazoalkanes such as $N_2CH(SiMe_3)$.[5]

Addition of ferrocenium triflate to **3** afforded $[N_3N]VCl$ (**8**) in high yield (95%) as black microcrystals (eq 10). Two broad

$$\underset{\mathbf{3}}{[HNEt_3]^+\{[N_3N]VCl\}^-} \xrightarrow[-30\ °C]{FcOTf,\ CH_2Cl_2} \underset{\mathbf{8}}{[N_3N]VCl} \quad (10)$$

$[N_3N]$ methylene proton resonances at −11.5 ppm ($\Delta_{1/2}$ = 300 Hz) and −68.5 ppm ($\Delta_{1/2}$ = 800 Hz)) were observed in the proton NMR spectrum of **8**, while *three* broad resonances at −146.50 ppm ($\Delta_{1/2}$ = 180 Hz), −152.74 ppm ($\Delta_{1/2}$ = 45 Hz), and −171.99 ppm ($\Delta_{1/2}$ = 80 Hz) in a ratio of 2:2:1 could be

Table 3. Observed Magnetic Moments for Several Vanadium(3+) and Vanadium(4+) Complexes

complex	μ_{obs},[a] μ_B	complex	μ_{obs},[a] μ_B
$[N_3N]V(t\text{-}BuNC)$	3.3	$[N_3N]V(CH_2{=}CHCN)$	3.6
$[N_3N]V(Me_2CHCH_2CN)$	3.4	$[N_3N]V(THF)$	3.7
$[HNEt_3]\{[N_3N]VCl\}$	3.4	$[N_3N]VCl$	1.9
$[N_3N]V(MeCN)$	3.5		

[a] Measured using the Evan's method with $Me_3SiOSiMe_3$ as an indicator.

observed in the ^{19}F NMR spectrum of **8**. We assign the fluorine resonances to ortho, meta, and para fluorines, respectively, in the pentafluorophenyl groups. The magnetic moment of **8** is consistent with it being a d^1 species, as shown in Table 3, in contrast to the magnetic moments observed for the closely analogous d^2 species discussed so far.

Reduction of **8** with sodium amalgam in tetrahydrofuran under dinitrogen over a period of 12 h at room temperature yielded green microcrystals of **5** (eq 11). We rationalize that **5** is formed

$$\underset{\mathbf{8}}{[N_3N]VCl} \xrightarrow[THF]{Na\ amalgam} \underset{\mathbf{5}}{[N_3N]V(THF)} \quad (11)$$

under these conditions rather than a sodium salt analogous to **3** because highly insoluble sodium chloride can be formed in this case. Recent results suggest that reduction of **8** with sodium amalgam in a noncoordinating solvent yields trigonal-monopyramidal $[N_3N]V$, even under dinitrogen.[30] These results await confirmation via an X-ray study.

Conclusions

The results reported here suggest that $[(C_6F_5NCH_2CH_2)_3N]^{3-}$ complexes of vanadium can be formed readily and that some of them, especially "18-electron" V(5+) complexes, are remarkably stable thermally. Attempts to prepare trigonal-monopyramidal V(3+) complexes yielded solvent or chloride adducts, presumably because the metal is more electrophilic in $[(C_6F_5NCH_2CH_2)_3N]^{3-}$ complexes than in $[(R_3SiNCH_2CH_2)_3N]^{3-}$ complexes and because dinitrogen cannot compete with σ donors in binding to d^2 vanadium centers in complexes of this type under the conditions employed so far. At this stage it is unknown whether dinitrogen will bind to vanadium, even if a "trigonal-monopyramidal" species that contains a vacant coordination position is prepared, although preliminary results[30] suggest that it may not.

(30) Rosenberger, C. Unpublished results.

Experimental Section

General Procedure. All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques, unless otherwise specified. All chemicals used were reagent grade and were purified by standard procedures. 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 N_2. Reagent grade diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl under nitrogen. Toluene, *m*-xylene, and mesitylene were distilled from sodium; CH_2Cl_2 and DMSO (dimethyl sulfoxide) were distilled from CaH_2. VCl_4(dme),[31] $VCl_3(THF)_3$,[31] V(N(aryl))Cl_3(THF),[16] and 2,2′,2″-tris((pentafluorophenyl)amino)triethylamine[14] were prepared by published methods. $VOCl_3$, VCl_3, VBr_3, VCl_4, aryl isocyanates, propylene oxide, and trimethylsilyl iodide were purchased from commercial sources and used as received. Acetonitrile, acrylonitrile, and isovaleronitrile were passed through a column of activated alumina in a drybox and stored over molecular sieves or distilled from CaH_2. All deuterated NMR solvents were passed through a column of activated alumina in a drybox and stored over molecular sieves.

NMR operating frequencies and reference standards for heteronuclei on the scale of ^{1}H (300 MHz, $SiMe_4$ at 0 ppm) are as follows: ^{13}C (75.5 MHz, $SiMe_4$ at 0 ppm), and ^{19}F (282.21 MHz, $CFCl_3$ at 0 ppm). Proton and carbon spectra were referenced using the partially deuterated solvent as an internal reference. Fluorine NMR spectra were referenced externally. Multiciplicities in fluorine spectra are quantified as "*J*", an apparent or pseudo coupling constant. Chemical shifts are in ppm, and coupling constants and line widths are in hertz. All spectra were acquired at ∼22 °C unless otherwise noted.

IR spectra were recorded on a Perkin-Elmer FT-IR 1600 spectrometer as Nujol mulls between KBr plates in an airtight cell; all absorptions are in cm^{-1}. Microanalyses (C, H, N) were performed on a Perkin-Elmer PE2400 microanalyzer. Magnetic moments were measured by ^{1}H NMR (Evans method[32]) using $Me_3SiOSiMe_3$ as the indicator.

Preparations. $[N_3N]V{=}O$ (1). A cold (−30 °C) dichloromethane solution (18 mL) of 2,2′,2″-tris((pentafluorophenyl)amino)triethylamine ($H_3[N_3N]$; 3.57 g, 5.57 mmol) and triethylamine (1.90 g, 18.8 mmol) was added dropwise over a period of 1 h in several portions to a dichloromethane solution (50 mL) containing $VOCl_3$ (960 mg, 5.54 mmol) at −30 °C. The solution was warmed slowly to room temperature and was stirred for more than 10 h. The solvents were removed in vacuo, and the resulting orange-brown solid was extracted with toluene (∼40 mL) and ether (∼20 mL) and then with a mixture of ether and dme (150 mL). Solvents were removed from the ether/dme solution in vacuo to give an analytically pure orange precipitate (1.46 g). The solvents were removed from the orange-brown toluene and ether extracts in vacuo. A minimum amount of dme was added to the residue from the toluene extract and then ether to give a total volume of ∼20 mL. Orange microcrystals were filtered from the chilled (−30 °C) solution, washed quickly with a small amount of cold pentane, and dried in vacuo; yield 270 mg. The residue from the ether extract produced another 340 mg for a total yield of 2.07 g (53%). **1** is soluble in tetrahydrofuran, dichloromethane, dimethoxyethane, ether, and toluene and slightly in pentane: ^{1}H NMR ($CDCl_3$) δ 3.94 (t, 6, $J \approx$ 5.5), 3.24 (t, 6, $J \approx 5.5$); ^{1}H NMR (C_6D_6) δ 3.29 (t, 6, $J \approx 5.5$), 2.12 (t, 6, $J \approx 5.5$); ^{19}F NMR ($CDCl_3$) δ −149.85 (d, 6, "*J*" = 17), −163.07 (t, 3, "*J*" = 23), −164.86 (t, 6, "*J*" = 20); ^{19}F NMR (C_6D_6) δ −150.36 (d, 6), −162.00 (t, 3), −164.78 (t, 6). Anal. Calcd for $C_{24}H_{12}F_{15}N_4OV$: C, 40.69; H, 1.71; N, 7.91. Found: C, 40.60; H, 2.02; N, 7.69.

$[N_3N]V{=}N(p\text{-}MeC_6H_4)$ (2a). (i) From V(N-*p*-tol)Cl_3(THF). A THF solution (8 mL) of $H_3[N_3N]$ (1.0 g, 1.55 mmol) and triethylamine (580 mg, 5.73 mmol) was added dropwise to a THF solution (10 mL) containing V(N-*p*-tol)Cl_3(THF) (519 mg, 1.55 mmol) at −30 °C. The reaction mixture was then warmed slowly to room temperature and was stirred for 5 h. The reaction mixture was filtered through Celite, and the Celite was washed with toluene and ether until the filtrates were colorless. The filtrates were combined, and the solvents were removed in vacuo. The resulting solid was extracted with toluene (∼18 mL). The red-yellow extract was concentrated to 10−15 mL in vacuo and chilled to −30 °C overnight. The solution was decanted away from the yellow needles, and the needles were washed quickly with cold pentane and dried in vacuo (first crop 746 mg; second crop 220 mg; third crop 25 mg); total yield 991 mg (80%). The sample for elemental analysis was prepared by recrystallization from a mixture of toluene and ether.

(ii) From $[N_3N]V{=}O$. The preparation was carried out in a 100 mL Schlenk tube. Compound **1** (250 mg, 0.35 mmol), *p*-tolyl isocyanate (2.0 g), and toluene (20 mL) were placed in a Schlenk tube, and the solution was refluxed for 3 days under an atmosphere of dinitrogen. The reaction solution was cooled and filtered through Celite. The filtrate was concentrated to 2 mL. Ether (10 mL) was added to the residue, and the solution was chilled to −30 °C. The yellow microcrystals were collected, washed quickly with cold pentane, and dried in vacuo; yield 80 mg. The solution was concentrated to 2 mL, and pentane (10 mL) was added to give a second crop (80 mg). A third crop was obtained from a mixture of toluene and pentane; total yield 71%: ^{1}H NMR ($CDCl_3$) δ 6.62 (d, 2, J = 8.9), 5.76 (d, 2, J = 8.3), 3.92 (t, 6, $J \approx 5.5$), 3.31 (t, 6, $J \approx 5.5$), 2.16 (s, 3, Me); ^{1}H NMR (C_6D_6) δ 6.24 (d, 2, J = 9.0), 6.03 (d, 2, J = 8.4), 3.42 (t, 6, $J \approx 5.5$), 2.34 (t, 6, $J \approx 5.5$), 1.66 (s, 3, Me); ^{19}F NMR ($CDCl_3$) δ −150.26 (br s, 6), −165.88 (br s, 9); ^{19}F NMR (C_6D_6) δ −150.22 (br s, 6), −165.55 (br s, 9). Anal. Calcd for $C_{31}H_{19}F_{15}N_5V$: C, 46.69; H, 2.40; N, 8.78. Found: C, 46.56; H, 2.57; N, 8.66.

$[N_3N]V{=}N(p\text{-}CF_3C_6H_4)$ (2b). 2b was prepared in the same manner as **2a**, except that V(N-*p*-$CF_3C_6H_4$)Cl_3(THF) (603 mg, 1.55 mmol) was used in place of V(N-*p*-MeC_6H_4)Cl_3(THF), and the reaction mixture was stirred for 6 h. The brown-yellow extract was concentrated to 12 mL and chilled to −30 °C overnight. Orange-yellow needles of **2b** were collected, washed quickly with cold pentane, and dried in vacuo; yield 490 mg. Further crops contained impurities which are difficult to separate from **2b**: ^{1}H NMR ($CDCl_3$) δ 7.12 (d, 2, J = 8.9), 5.94 (d, 2, J = 8.2), 3.96 (t, 6, $J \approx 5.5$), 3.36 (t, 6, $J \approx 5.5$); ^{1}H NMR (C_6D_6) 6.65 (d, 2, J = 8.4), 6.05 (d, 2, J = 8.3), 3.37 (t, 6, $J \approx 5.5$), 2.31 (t, 6, $J \approx 5.5$); ^{19}F NMR ($CDCl_3$) δ −63.26 (s, 3, CF_3), −150.06 (br m, 6), −164.50 (t, 3, "*J*" = 24), −165.28 (t, 6, "*J*" = 19); ^{19}F NMR (C_6D_6) δ −62.63 (s, 3, CF_3), −150.26 (d, 6), −164.24 (t, 3, "*J*" = 23), −165.01 (t, 6, "*J*" = 19). Anal. Calcd for $C_{31}H_{16}F_{18}N_5V$: C, 43.73; H, 1.89; N, 8.23. Found: C, 43.42; H, 2.06; N, 8.22.

$[N_3N]V{=}N(p\text{-}FC_6H_4)$ (2c). (i) From V(N-*p*-FC_6H_4)Cl_3(THF). 2c was prepared in the same manner as **2b** except V(N-*p*-FC_6H_4)Cl_3(THF) (525 mg, 1.55 mmol) was used in place of V(N-*p*-MeC_6H_4)Cl_3(THF); total yield 980 mg (79%). The sample for elemental analysis was prepared by recrystallization from a mixture of ether and pentane.

(ii) From $[N_3N]V{=}O$. The preparation was performed in a 50 mL Schlenk tube. A mixture of **1** (50 mg, 0.071 mmol) and *p*-fluorophenyl isocyanate (1.0 g) in *m*-xylene (5.0 g) was added into a Schlenk tube, and the solution was refluxed for 3 days under an atmosphere of nitrogen. The reaction mixture was cooled and filtered through Celite. The solvents were removed from the filtrate in vacuo. Toluene (0.5 mL), ether (5 mL), and pentane (5 mL) were added to the residue, and the mixture was then chilled to −30 °C. The yellow microcrystals were collected, washed quickly with cold pentane, and dried in vacuo (32 mg). The second crop was isolated from the chilled mixture of ether and pentane (10 mg); total yield 74%: ^{1}H NMR ($CDCl_3$) δ 6.53 (t, 2, J = 8.6), 5.86 (dd, 2, J = 8.7, 5.2), 3.94 (t, 6, $J \approx 5.5$), 3.33 (t, 6, $J \approx 5.5$); ^{1}H NMR (C_6D_6) δ 6.01 (br s, 2), 5.98 (d, 2, J = 2.5), 3.38 (t, 6, $J \approx 5.5$), 2.31 (t, 6, $J \approx 5.5$); ^{19}F NMR (C_6D_6) δ −108.82 (t or m, 1), −150.22 (d, 6, "*J*" = 17), −164.88 (t, 3, "*J*" = 22), −165.29 (t, 6, "*J*" = 20). Anal. Calcd for $C_{30}H_{16}F_{16}N_5V$: C, 44.96; H, 2.01; N, 8.74. Found: C, 44.75; H, 2.33; N, 8.49.

$[N_3N]V{=}NPh$ (2d). A mixture of **1** (752 mg, 1.06 mmol) and phenyl isocyanate (1.0 g) in *m*-xylene (5.0 g) was added to a 200 mL Schlenk tube, and the solution was refluxed for 5 days under an atmosphere of nitrogen. After the reaction, the solution was cooled and filtered through Celite. The filtrate was concentrated to 20 mL in vacuo, pentane (10−15 mL) was added, and the reaction mixture was chilled to −30 °C. The yellow microcrystals were collected, washed quickly with cold pentane, and dried in vacuo; yield 342 mg. The yield was increased to 82% by using a mixture of toluene/ether, toluene/ether/dme, or toluene/pentane: ^{1}H NMR (C_6D_6) δ 6.43 (t, 2, J = 7.5),

(31) Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 135.
(32) Evans, D. F. *Chem. Commun.* **1959**, 2003.

6.32 (t, 1, J = 7.4), 6.15 (d, 2, J = 7.7), 3.41 (t, 6, $J \approx 5.5$), 2.37 (t, 6, $J \approx 5.5$); ^{19}F NMR (C_6D_6) δ −150.22 (d, 6, "J" = 16), −165.22 (t, 3, "J" = 22), −165.50 (t, 6, "J" = 18).

[N$_3$N]V═N(*o*-FC$_6$H$_4$) (2e). The preparation was the same as that for **2c**, except that *o*-fluorophenyl isocyanate (1.0 g) was used in place of *p*-fluorophenyl isocyanate. The solvents were removed from the extract in vacuo, and the residue was washed quickly with cold pentane. The resulting yellow precipitate is pure enough for general use. Yellow microcrystals were obtained from chilled ether (3−5 mL), washed quickly with cold pentane, and dried in vacuo; yield 51 (91%): ^{1}H NMR ($CDCl_3$) δ 6.73−6.80 (m, 1), 6.53−6.61 (m, 2), 5.96 (t, 1, J = 7.9), 3.94 (t, 6, $J \approx 5.5$), 3.36 (t, 6, $J \approx 5.5$); ^{1}H NMR (C_6D_6) δ 6.24 (t, 1, J = 7.7), 5.97−6.12 (m, 3), 3.40 (t, 6, $J \approx 5.5$), 2.37 (t, 6, $J \approx 5.5$); ^{19}F NMR δ −122.34 (s, 1), −150.53 (br s, or d, 6), −165.54 (t, 3, "J" = 23), −166.28 (t, 6, "J" = 20); ^{19}F NMR (C_6D_6) δ −122.00 (s, 1), −150.11 (d, 6, "J" = 15), −164.96 (t, 3, "J" = 23), −165.71 (t, 6, "J" = 21).

[N$_3$N]V═N(*o*-MeC$_6$H$_4$) (2f). The preparation of **2f** was the same as that for **2c** except that *o*-tolyl isocyanate (1.0 g) was used in place of *p*-fluorophenyl isocyanate. The solvents were partially removed from the extract on a rotavaporator, and the yellow microcrystals were collected, washed quickly with cold pentane, and dried in vacuo; yield 40 mg (71%): ^{1}H NMR ($CDCl_3$) δ 6.55−6.70 (m, 3), 5.81 (d, 1, J = 7.5), 3.92 (t, 6, J = 5.6), 3.35 (t, 6, J = 5.7), 1.40 (s, 3); ^{1}H NMR (C_6D_6) δ 6.24−6.60 (m, 3), 6.12 (d, 1, J = 6.6), 3.40 (t, 6, J = 5.7), 2.40 (t, 6, J = 5.4), 1.39 (s, 3); ^{19}F NMR ($CDCl_3$) δ −150.00 (br d, 6), −165.22 (t, 3, "J" = 23), −165.97 (t, 6, "J" = 20); ^{19}F NMR (C_6D_6) δ −149.76 (br s d, 6), −164.81 (t, 3, "J" = 24), −165.55 (br t, 6).

[N$_3$N]V═N(3,5-Me$_2$C$_6$H$_3$) (2g). **2g** was prepared in the same manner as **2c** using 3,5-dimethylphenyl isocyanate (1.0 g). The filtrate was concentrated, ether and pentane were added, and the solution was chilled to −30 °C for at least 2 days. The yellow microcrystals were washed quickly with cold pentane and dried in vacuo; yield 27 mg (47%): ^{1}H NMR ($CDCl_3$) δ 6.48 (br s, 1), 5.42 (br s, 2), 3.93 (t, 6, $J \approx 5.5$), 3.31 (t, 6, $J \approx 5.5$), 1.93 (s, 6); ^{1}H NMR (C_6D_6) δ 6.13 (br s, 1), 5.78 (br s, 2), 3.42 (t, 6, $J \approx 5.5$), 2.33 (t, 6, $J \approx 5.5$), 1.77 (s, 6); ^{19}F NMR ($CDCl_3$) δ −150.46 (br s, 6), −166.47 (br s, 9); ^{19}F NMR (C_6D_6) δ −150.04 (br s or d, 6), −165.81 (br s, 9).

Procedure for Reactions between [N$_3$N]V═NAr and Various Aryl Isocyanates. All reactions were carried out in a 50 mL Schlenk tube. A mixture of [N$_3$N]V═NAr (50 mg, Ar = *p*-MeC$_6$H$_4$, Ph) and *p*-fluorophenyl isocyanate (1.0 g) in mesitylene (5.0 g) was added to a Schlenk tube, and the solution was refluxed for 2 days under an atmosphere of nitrogen. The reaction mixture was cooled and filtered through Celite. The crude reaction product was examined by ^{1}H and ^{19}F NMR in order to determine the extent of reaction. Isolated yields of **2c** from **2a** or **2d** were ∼70%.

[HNEt$_3$]$^+${[N$_3$N]VCl}$^-$ (3). A solution of H$_3$[N$_3$N] (2.00 g, 3.10 mmol) and triethylamine (1.10 g, 10.9 mmol) in 18 mL of ether was added gradually over a period of 1 h to a solution of $VCl_3(THF)_3$ (1.16 g, 3.10 mmol) in 50 mL of ether at −30 °C. The reaction mixture was warmed slowly to room temperature and was stirred for 1 day. The mixture was then filtered through Celite, and the filtrate was concentrated to ∼35 mL and chilled to −30 °C for several days. Red-purple microcrystals were collected, washed quickly with cold pentane, and dried in vacuo; yield 1.66 g. These were dissolved in a minimum amount of dichloromethane, and the solution was chilled to −30 °C for several days. The solution was decanted away from the golden needles, which were washed quickly with chilled ether and dried in vacuo; yield 1.20 g (1.45 mmol, 47%). The product at this stage was analytically pure. Samples from two different runs were both analyzed satisfactorily: ^{1}H NMR (C_6D_6) δ 1.86 (br s, 2, $\Delta_{1/2}$ = 160), 0.30 (br s, 3, $\Delta_{1/2}$ = 114); ^{19}F NMR (C_6D_6) δ −141.9 (br s, 6, $\Delta_{1/2}$ = 508), −176.8 (br s, 3, $\Delta_{1/2}$ = 170); IR (Nujol) 2771.8, 2720.7, 2690.0, 2614.4, 2484.1 cm^{-1} (HNEt$_3$$^+$). Anal. Calcd for $C_{30}H_{28}ClF_{15}N_5V$: C, 43.41; H, 3.40; N, 8.44. Found: C, 43.56, 43.27; H, 3.57, 3.47; N, 8.27, 8.29.

[N$_3$N]V(CH$_3$CN) (4a). (i) From VCl$_3$(THF)$_3$. An ether solution (30 mL) of H$_3$[N$_3$N] (10.35 g, 16.1 mmol) and triethylamine (6.00 g, 59.4 mmol) was added gradually over 1 h to a solution of $VCl_3(THF)_3$ (1.74 g, 4.66 mmol) in 40 mL of ether at −30 °C. Acetonitrile (10 mL) was then added to the solution, and the reaction mixture was warmed slowly to room temperature. After 1 day the reaction mixture was filtered through Celite and solvent was removed from the filtrate in vacuo. The resulting lime green solid was extracted with cold ether, and the ether was removed from the extract in vacuo. The residue was dissolved in minimal acetonitrile, and this solution was covered with pentane and chilled to −30 °C. The solution was decanted away from the lime green microcrystals, which were washed quickly with cold pentane and dried in vacuo; total yield 7.03 g (57%). The compounds usually are pure enough for general use without recrystallization. The sample for the X-ray study was recrystallized from acetonitrile layered with pentane. The purification procedure was repeated if white microcrystals were found mixed with the lime green crystals.

(ii) From [HNEt$_3$]$^+${[N$_3$N]VCl}$^-$ (3). Golden needles of **3** (1.00 g) were partially dissolved in ether (30 mL), and to this mixture was added an excess amount of acetonitrile (5 mL). The reaction mixture was stirred for at least 3 h at room temperature, and the solvent was removed from the reaction mixture in vacuo. The resulting lime green solid was extracted with cold ether. The ether was removed from the extract in vacuo, and the residue was dissolved in minimal acetonitrile. The acetonitrile was then layered with pentane and chilled to −30 °C. The solvent was decanted away from the lime green microcrystals, which were washed quickly with cold pentane and dried in vacuo; total from two crops 610 mg (65%): ^{1}H NMR (C_6D_6) δ 0.60 (br s, CH$_3$CN, $\Delta_{1/2}$ = 42); ^{19}F NMR (C_6D_6) δ −146.3 (br s, $\Delta_{1/2}$ = 340), −175.7 (br s, $\Delta_{1/2}$ = 113); IR (Nujol) 2281.6 cm^{-1} (C≡N). Anal. Calcd for $C_{28}H_{18}F_{15}N_6V$: C, 43.42; H, 2.34; N, 10.85. Found: C, 43.06; H, 2.46; N, 10.37. According to this elemental analysis, this sample contains two molecules of acetonitrile, although in the sample used for the X-ray study one acetonitrile was found, and it was coordinated to the vanadium.

Reaction of 4a with Propylene Oxide. Propylene oxide (30 mg) was added dropwise to a solution of **4a** (49 mg, 0.067 mmol) in 5 mL of toluene at −30 °C. The reaction mixture was warmed slowly to room temperature and was stirred for 3 h. The reaction solution was filtered, and the solvents were removed from the filtrates in vacuo to give an orange precipitate (41 mg). Proton and ^{19}F NMR showed the precipitate to be almost pure [N$_3$N]V═O containing a trace of H$_3$[N$_3$N]; yield 91%.

[N$_3$N]V(Me$_2$CHCH$_2$CN) (4b). Preparation of **4b** was similar to that for **4a**, using isovaleronitrile instead of acetonitrile; yield 3.40 g (55%) of **4b** from 2.96 g (7.92 mmol) of $VCl_3(THF)_3$ and 5.11 g (7.93 mmol) of H$_3$[N$_3$N]: ^{19}F NMR (C_6D_6) δ −145.5 (br s, 6, $\Delta_{1/2}$ = 400), −176.0 (br s, 3, $\Delta_{1/2}$ = 120); IR (Nujol) 2267.1 cm^{-1} (C≡N). Anal. Calcd for $C_{29}H_{21}F_{15}N_5V$: C, 44.91; H, 2.73; N, 9.03. Found: C, 44.58; H, 2.76; N, 9.05.

[N$_3$N]V(CH$_2$═CHCN) (4c). A solution of H$_3$[N$_3$N] (1.01 g, 1.57 mmol) and triethylamine (600 mg, 5.94 mmol) in 5 mL of ether was added gradually over a period of 1 h to an ether solution (10 mL) containing $VCl_3(THF)_3$ (585 mg, 1.57 mmol) at −30 °C. Acrylonitrile (1.0 g) was then added to the solution, and the reaction mixture was warmed slowly to room temperature and was stirred for 1 day. The reaction mixture was filtered through Celite, and solvents were removed from the filtrate in vacuo. The green residue was extracted with ether, and the extract was concentrated to ∼10 mL in vacuo and placed in a freezer (−30 °C). The green microcrystals were washed quickly with cold pentane and dried in vacuo. Analytically pure green microcrystals of **4c** were collected in one crop; yield 360 mg (31%): ^{19}F NMR (C_6D_6) δ −146.3 (br s, 6, $\Delta_{1/2}$ = 350), −174.6 (br s, 3, $\Delta_{1/2}$ = 125); IR (Nujol) 2235.7 (C≡N), 1934.9, 1600 cm^{-1}. Anal. Calcd for $C_{27}H_{15}F_{15}N_5V$: C, 43.51; H, 2.03; N, 9.40. Found: C, 43.82; H, 1.83; N, 9.46.

[N$_3$N]V(THF) (5). (i) From [HNEt$_3$]$^+${[N$_3$N]VCl}$^-$. Trimethylsilyl iodide (92 mg, 1.05 equiv) was added dropwise over 5 min to a stirred solution of **3** (364 mg, 0.439 mmol) in 10 mL of THF at room temperature. After 3 h the solvents were removed in vacuo and the residue was extracted with cold ether containing a few percent of dichloromethane. The extract was cooled to −30 °C to give green microcrystals, which were washed quickly with cold pentane and dried in vacuo. The compounds were recrystallized from tetrahydrofuran covered with pentane at −30 °C; yield 31% (105 mg): ^{19}F NMR (C_6D_6) δ −114.3 (br s, 6, $\Delta_{1/2}$ = 260), −175.6 (br s, 3, $\Delta_{1/2}$ = 120). Anal. Calcd for $C_{28}H_{20}F_{15}N_4OV$: C, 44.00; H, 2.64; N, 7.33. Found: C, 44.13; H, 2.84; N, 7.34.

(ii) From $[N_3N]VCl$. Sodium amalgam (4.02 g, Na/Hg = 0.554/104.55 g) was added dropwise to a solution of $[N_3N]VCl$ (664 mg, 0.912 mmol; see below) in 15 mL of tetrahydrofuran at room temperature. The reaction mixture was stirred for 12 h and filtered through Celite. The filtrate was evaporated in vacuo, and the residue was extracted with cold ether. THF (2 mL) was added, and the solution was then concentrated to ~2 mL and covered with pentane (10 mL). Analytically pure green microcrystals of **5** (380 mg) were collected upon chilling the solution to −30 °C. A second crop (165 mg) was obtained by further similar manipulations; total yield 545 mg (78%). The sample for X-ray crystallography was prepared by recrystallization from chilled (−30 °C) tetrahydrofuran solution covered with pentane.

Reaction of 5 with Propylene Oxide. Propylene oxide (12 mg, 0.21 mmol) was added dropwise to a stirred solution of **5** (54 mg, 0.071 mmol) in ether at −30 °C. The color changed from yellow-green to orange. The reaction mixture was stirred for 10 min and then filtered. The solvents were removed from the filtrate in vacuo to give 51 mg of **1** (quantitative), according to proton and fluorine NMR.

Reaction of 5 with Acetonitrile. Acetonitrile (15 mg) was added to a stirred solution of **5** (45 mg, 0.059 mmol) in ether at −30 °C. The color changed from yellow-green to lime green immediately. The reaction mixture was stirred for 10 min and then filtered. The solvents were removed from the filtrate in vacuo to give 45 mg of **4a**, according to proton and fluorine NMR. The only other observable product was a trace of free ligand.

Reaction of 5 with Ethyl Diazoacetate. Ethyl diazoacetate (10 mg, 0.088 mmol) was added dropwise to a stirred solution of **5** (50 mg, 0.065 mmol) in ether at −30 °C. The color changed from yellow-green to red immediately. The reaction mixture was stirred for 10 min and then filtered. The solvents were removed from the filtrate in vacuo to give 52 mg of **7b** (quantitative), according to proton and fluorine NMR.

$[N_3N]V(t\text{-}BuNC)$ (6). An ether solution (8 mL) of $H_3[N_3N]$ (2.00 g, 3.10 mmol) and triethylamine (1.15 g, 11.39 mmol) was added dropwise over 1 h to an ether solution (10 mL) containing $VCl_3(THF)_3$ (1.16 g, 3.10 mmol) at −30 °C. *tert*-Butyl isocyanide (1.0 g) was then added, and the reaction mixture was warmed slowly to room temperature and was stirred for 1 day. The reaction mixture was filtered through Celite, and solvents were removed from the filtrate in vacuo. The resulting green solid was extracted with ether. The extract was concentrated to ~15 mL and placed in the freezer (−30 °C). The solvent was decanted away from the green microcrystals, which were washed quickly with cold pentane and dried in vacuo. Analytically pure **6** was obtained in two crops; yield 750 mg (31%): ^{1}H NMR (C_6D_6) δ 4.35 (br s, $\Delta_{1/2}$ = 190, CMe_3); ^{19}F NMR (C_6D_6) δ −148.5 (br s, $\Delta_{1/2}$ = 280), −170.2 (br s, $\Delta_{1/2}$ = 60); IR (Nujol) 2180.5 cm^{-1} (N≡C). Anal. Calcd for $C_{29}H_{21}F_{15}N_5V$: C, 44.91; H, 2.73; N, 9.03. Found: C, 45.29; H, 3.16; N, 9.00.

$[N_3N]V{=}NN{=}CH(SiMe_3)$ (7a). (Trimethylsilyl)diazomethane (1.0 g, 2 M solution in hexane) was added dropwise over 5 min to **4a** (500 mg, 0.65 mmol) in 10 mL of toluene at −30 °C. The reaction mixture was warmed slowly to room temperature and was stirred for 3 h. The solution was concentrated to ~3 mL and then poured into a stirred pentane solution (~15 mL), which was then placed in the freezer at −30 °C for 1 h. The red precipitate was filtered off, and the solvents were removed from the filtrate in vacuo to afford **7a.** The red solids were dissolved in a minimum amount of toluene. The toluene solution was covered with pentane, and the mixture was placed in the freezer (−30 °C). Analytically pure red microcrystals of **7a** were isolated, washed quickly with cold pentane, and dried in vacuo; yield 427 mg (82%): ^{1}H NMR (C_6D_6) δ 7.18 (s, 1, N=C*H*), 3.42 (t, 6, $J \approx 5.5$), 2.37 (t, 6, $J \approx 5.5$), 0.20 (s, 9, CHSi(C*H*$_3$)$_3$); ^{13}C NMR (C_6D_6) δ 176.70 (N=CH), 143.43, 140.24, 140.11, 138.95, 138.77, 138.65, 136.89, 136.63, 135.74, 135.59 (C_6F_5), 57.21, 54.01 (CH_2); ^{19}F NMR (C_6D_6) δ −150.46 (d, 6, "J" = 21), −165.75 (t, 6, "J" = 26), −166.19 (t, 6, "J" = 19). Anal. Calcd for $C_{28}H_{22}F_{15}N_6SiV$: C, 41.70; H, 2.75; N, 10.42. Found: C, 41.80; H, 2.61; N, 10.37.

$[N_3N]V{=}NN{=}CH(CO_2C_2H_5)$ (7b). **7b** was prepared in the same manner as that for **7a** using ethyl diazoacetate (500 mg) and 630 mg (0.81 mmol) of **4a**. Analytically pure red microcrystals of **7b** were obtained; yield 710 mg (81%): ^{1}H NMR (C_6D_6) δ 6.92 (s, 1, N=C*H*), 3.64 (q, 2, J = 7.1, C*H*$_2$CH$_3$), 3.38 (t, 6, $J \approx 5.5$), 2.39 (t, 6, $J \approx 5.5$), 0.69 (t, 3, J = 7.5, CH$_2$C*H*$_3$); ^{19}F NMR (C_6D_6) δ −150.61 (d, 6, "J" = 37), −163.74 (t, 6, "J" = 24), −164.81 (t, 6, "J" = 29); IR (Nujol) 1731.5 (C=O). Anal. Calcd for $C_{28}H_{18}F_{15}N_6O_2V$: C, 41.70; H, 2.25; N, 10.42. Found: C, 41.89; H, 2.21; N, 10.24.

$[N_3N]VCl$ (8). Ferrocenyl trifluoromethanesulfonate (833 mg, 2.49 mmol) was added to a solution of **3** (1.80 g, 2.17 mmol) in dichloromethane (50 mL) at −30 °C. The reaction mixture was warmed slowly to room temperature and stirred for ~20 h. The solution was filtered through Celite, and the solvents were evaporated from the filtrate in vacuo. The residue was dissolved in toluene (50 mL) and the solution placed in the freezer (−30 °C) overnight. The black microcrystals were isolated and dissolved in a minimum amount of dichloromethane. The solution was chilled to −30 °C to give black microcrystals of **8**, which were washed with chilled toluene and dried in vacuo; yield 1.50 g (95%). The analytical sample was prepared by recrystallization from dichloromethane: ^{1}H NMR (C_6D_6) δ −11.5 (br s, $\Delta_{1/2}$ = 300), −68.5 (br s, $\Delta_{1/2}$ = 800); ^{19}F NMR (C_6D_6) δ −146.50 (br s, 6, $\Delta_{1/2}$ = 180), −152.74 (br s, 6, $\Delta_{1/2}$ = 45), −171.99 (br s, 3, $\Delta_{1/2}$ = 80). Anal. Calcd for $C_{24}H_{12}ClF_{15}N_4V$: C, 39.61; H, 1.66; N, 7.70. Found: C, 39.69; H, 1.72; N, 7.76.

Brief Description of the Structure of $[(C_6F_5NCH_2CH_2)_3N]V(CH_3CN)$. The crystal was mounted on a glass fiber and transferred to an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 79 Å). Cell constants and an orientation matrix for data collection obtained from 25 carefully centered reflections in the range $14 < 2\theta < 22.00°$ corresponded to a rhombohedral (hexagonal axes) cell. On the basis of the systematic absences (*hkl*, $-h + k + l \neq 3n$), packing considerations, a statistical analysis of intensity distributions, and the successful solution and refinement of the structure, the space group was determined to be *R*3 (h) (No. 146). The data were collected using the $\omega{-}2\theta$ scan technique to a maximum 2θ value of 54.9°.

Of the 3345 reflections which were collected, 2145 were unique (R_{int} = 0.073); equivalent reflections were merged. The structure was solved by a combination of the Patterson method and direct methods. Non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 1775 observed reflections ($I > 3.00\sigma(I)$) and 142 variable parameters and converged (the largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of R = 0.043 and R_w = 0.040.[3]

Brief Description of the Structure of $[(C_6F_5NCH_2CH_2)_3N]V(THF)$. The crystal was mounted under Paratone N and transferred to a Siemens Smart/CCD three-circle (χ fixed at 54.78°) diffractometer equipped with a cold stream of N_2 gas. An initial unit cell was determined by harvesting reflections $I > 20\sigma(I)$ from 45 frames of 0.30 ω-scan data with monochromated Mo Kα radiation (λ = 0.710 73 Å). Crystal quality was checked by computing 3.0° rocking curves, from which the ω width at half-height was found to be 0.23°. The data were collected using 0.30 ω scans. The data that were collected (10 147 total reflections, 4198 unique, R_{int} = 0.044) were corrected for Lorentz and polarization effects but not for absorption. The structure was solved (SHELXTL 5.0) by direct methods and standard difference Fourier techniques.

Acknowledgment. We thank the National Institutes of Health (Grant No. GM 31978) and Sumitomo Chemical Co. Ltd. for support. We also thank the National Science Foundation for funds to help purchase a Siemens SMART/CCD diffractometer and Steve Reid for experiments confirming the catalytic production of PhN=C=NPh from PhNCO using $[N_3N]V{=}O$ as a catalyst.

Supporting Information Available: For both **4a** and **5**, text giving descriptions of the structures, ORTEP drawings, and tables of final positional parameters, final thermal parameters, and bond distances and angles for non-hydrogen atoms (13 pages). Ordering information is given on any current masthead page.

IC951433J