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Synthesis of [(HIPTNCH$_2$CH$_2$)$_3$N]V Compounds (HIPT = 3,5-(2,4,6-*i*-Pr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$) and an Evaluation of Vanadium for the Reduction of Dinitrogen to Ammonia

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Green [HIPTN$_3$N]V(THF) ([HIPTN$_3$N]$^{3-}$ = [(HIPTNCH$_2$CH$_2$)$_3$N]$^{3-}$, where HIPT = 3,5-(2,4,6-*i*-Pr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$) can be prepared in a 70–80% yield via the addition of H$_3$[HIPTN$_3$N] to VCl$_3$(THF)$_3$ in THF, followed by the addition of LiN(SiMe$_3$)$_2$. From [HIPTN$_3$N]V(THF), the following have been prepared: {[HIPTN$_3$N]VN$_2$}K, [HIPTN$_3$N]V(NH$_3$), [HIPTN$_3$N]V═NH, [HIPTN$_3$N]V═NSiMe$_3$, [HIPTN$_3$N]V═O, [HIPTN$_3$N]V═S, and [HIPTN$_3$N]V(CO). No ammonia is formed from dinitrogen using {[HIPTN$_3$N]VN$_2$}K, [HIPTN$_3$N]V═NH, or [HIPTN$_3$N]V(NH$_3$) as the initial species under conditions that were successful in the analogous [HIPTN$_3$N]Mo system. X-ray structural studies are reported for [HIPTN$_3$N]V(THF) and [HIPTN$_3$N]V(NH$_3$).

Introduction

We have been exploring early transition metal complexes that contain a triamidoamine ligand ([(RNCH$_2$CH$_2$)$_3$N]$^{3-}$).[1] In the last several years we have been interested primarily in Mo complexes that contain the [(HIPTNCH$_2$CH$_2$)$_3$N]$^{3-}$ ligand, where HIPT = 3,5-(2,4,6-i-Pr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$ = hexaisopropylterphenyl),[2] because various [(HIPTNCH$_2$CH$_2$)$_3$N]-Mo complexes have been found to serve as catalysts for the catalytic reduction of dinitrogen to ammonia at room temperature and pressure with protons and electrons.[3] The [(HIPTNCH$_2$CH$_2$)$_3$N]$^{3-}$ ligand ([HIPTN$_3$N]$^{3-}$) was designed to prevent the formation of relatively stable and unreactive μ-dinitrogen complexes, maximize steric protection of a monometallic metal coordination site, and provide increased solubility of complexes in nonpolar solvents relative to the triamidoamine complexes that contain unsubstituted terphenyl groups. Examples of Mo species that serve as catalysts and that are believed to lie on the catalytic pathway to ammonia include [HIPTN$_3$N]MoN$_2$, [HIPTN$_3$N]Mo−N═N−H, [HIPTN$_3$N]Mo≡N, and [HIPTN$_3$N]Mo(NH$_3$). We have shown that [HIPTN$_3$N]W analogues of many of the [HIPTN$_3$N]Mo species can be prepared, but none serves as a catalyst for the reduction of dinitrogen catalytically under conditions analogous to those employed for reduction with Mo catalysts.[4] Among the problems associated with the tungsten system is the apparent instability of [HIPTN$_3$N]W-(NH$_3$), the analogue of [HIPTN$_3$N]Mo(NH$_3$). [HIPTN$_3$N]Mo-(NH$_3$) is of central importance in the catalytic reduction of dinitrogen by [HIPTN$_3$N]Mo complexes since the step in which ammonia is replaced by dinitrogen "restarts" the catalytic cycle. We also have explored [HIPTN$_3$N]Cr species, which are not catalysts for the catalytic reduction of dinitrogen, primarily, it is believed, because dinitrogen does not bind to [HIPTN$_3$N]Cr.[5]

In addition to the relatively well-studied Mo−Fe nitrogenase,[6] V−Fe and Fe−Fe nitrogenases are known.[7] These variants are formed when molybdenum (V−Fe) or molyb-

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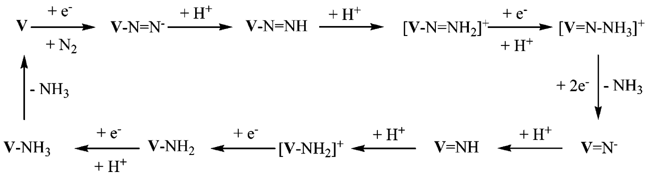
denum and vanadium (Fe−Fe) are not available. Unlike the Mo−Fe nitrogenase,[8] V−Fe and Fe−Fe nitrogenases have not been structurally characterized. The simplest proposal is that the V−Fe and Fe−Fe nitrogenases adopt the same core structure as the Mo−Fe nitrogenase with vanadium or iron atom in place of the molybdenum. Since the efficiency of the selective formation of ammonia from dinitrogen by these enzymes appears to follow the order Mo−Fe > V−Fe > Fe−Fe (from most to least efficient), we felt that a vanadium-catalyzed reduction of dinitrogen might be demonstrable. A number of vanadium dinitrogen complexes are known. The most common oxidation states of V in dinitrogen complexes are V(3+),[9] V(2+),[10] and V(−1).[11] Only in the V(−1) species, which have the formula $[L_4V(N_2)_2]^-$, where L is a phosphine or L_2 is a bisphosphine, is dinitrogen bound end-on with $\nu_{NN} = 1706-1833\ cm^{-1}$; all others are bimetallic species that contain a μ-N_2 ligand. The $[L_4V(N_2)_2]^-$ complexes are isoelectronic with the Chatt-type neutral Mo(0) and W(0) d^6 complexes with the same stoichiometry.[12] The V(3+) complexes are analogous to niobium and tantalum complexes that contain what has been described as a N_2^{4-} ligand[13] (i.e., the two V(3+) metals could reduce dinitrogen by up to four electrons). There may be a special stability associated with such "d^0" (M═N−N═M) species that contain a N_2^{4-} bridging ligand, perhaps even for V, which one would expect to be the least reducing of the d^2 metals in Group 5.

Scheme 1. Plausible Mechanism for the Reduction of Dinitrogen to Ammonia in the $[HIPTN_3N]V$ System



Vanadium complexes have been reported that contain the triamidoamine ligands $[MeN_3N]^{3-}$,[14] $[C_6F_5N_3N]^{3-}$,[15] $[Me_3SiN_3N]^{3-}$,[16] and $[t\text{-}BuMe_2SiN_3N]^{3-}$,[17] but none of the chemistry explored with these species focused on dinitrogen chemistry per se. For $[C_6F_5N_3N]V$, $[Me_3SiN_3N]V$, and $[t\text{-}BuMe_2SiN_3N]V$, no evidence for the coordination of dinitrogen, either end-on or bridging, was obtained. However, $[C_6F_5N_3N]V$, $[Me_3SiN_3N]V$, and $[t\text{-}BuMe_2SiN_3N]V$ complexes bind some σ donors (e.g., THF or acetonitrile), and several V(5+) species have been prepared that contain $[C_6F_5N_3N]^{3-}$ and $[Me_3SiN_3N]^{3-}$ ligands (e.g., V═NH, V═NSiMe$_3$, and V═O species). Failure to form an end-on V(3+) dinitrogen complex may not be surprising because the only known end-on V dinitrogen complexes contain V(−1) (vide supra), where back-bonding to a single dinitrogen is significant. It should be noted, however, that even these $[L_4V(N_2)_2]^-$ species lose dinitrogen in vacuo.[11] Cleavage of dinitrogen by a (presumably bimetallic) vanadium complex that contains the $[Me_3SiN(CH_2CH_2NSiMe_3)_2]^{2-}$ ligand has been reported to give a $V_2(\mu\text{-}N)_2$ species.[18]

In the $[HIPTN_3N]^{3-}$ species, μ-dinitrogen complexes cannot form for steric reasons. A plausible mechanism for reduction of dinitrogen by $[HIPTN_3N]V$ species is shown in Scheme 1. It is interesting to note that $\{[HIPTN_3N]Mo\}^+$ (d^2), which is isoelectronic with $[HIPTN_3N]V$, only relatively weakly binds dinitrogen, as judged by the fact that $\nu_{NN} = 2255\ cm^{-1}$ and $^{15}N_2$ exchanges for N_2 over a period of minutes at room temperature.[3d] The likely lower V−N_2 bond strength in $[HIPTN_3N]V(N_2)$ versus the Mo−N_2 bond strength in $[HIPTN_3N]Mo(N_2)$ would appear to make $[HIPTN_3N]V(N_2)$ unlikely. However, $\{[HIPTN_3N]V\}^-$ is isoelectronic with $[HIPTN_3N]Mo$, which readily binds dinitrogen ($\nu_{NN} = 1990\ cm^{-1}$). Therefore $\{[HIPTN_3N]V(N_2)]^-$ may be viable from $[HIPTN_3N]V$ in the presence of the appropriate reducing agent, or $[HIPTN_3N]V$−N═NH may be formed from $[HIPTN_3N]V$ in the presence of the appropriate reducing agent and a proton source under dinitrogen. In this paper, we report the synthesis of $[HIPTN_3N]V$ compounds, including $\{[HIPTN_3N]V(N_2)]^-$, along with some preliminary studies concerned with the catalytic reduction of dinitrogen.

Results and Discussion

Synthesis and Structure of $[HIPTN_3N]V(THF)$. A violet solution is formed upon mixing of $H_3[HIPTN_3N]$ with $VCl_3(THF)_3$ in THF. The violet solution turns dark green upon addition of $LiN(SiMe_3)_2$. Green $[HIPTN_3N]V(THF)$ (**V**(THF) where **V** = $[HIPTN_3N]V$) can be isolated from this solution

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Table 1. Crystal Data and Structure Refinement for [HIPTN$_3$N]V(THF) and [HIPTN$_3$N]V(NH$_3$)[a]

	[HIPTN$_3$N]V(THF)	[HIPTN$_3$N]V(NH$_3$)
empirical formula	$C_{132}H_{199}N_4OV$	$C_{121}H_{178}N_5V$
fw	1908.89	1753.62
temp	100(2) K	193(2) K
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	Cc
unit cell dimensions		
a	17.7727(6) Å	16.1153(4) Å
b	18.3700(7) Å	39.7548(11) Å
c	21.2032(9) Å	18.0197(5) Å
α	113.9930(10)°	90°
β	99.8920(10)°	93.0540(10)°
γ	96.5660(10)°	90°
vol	6098.5(4) Å^3	11528.1(5) Å^3
Z	2	4
density (calcd)	1.040 Mg/m^3	1.010 Mg/m^3
abs coeff	0.130 mm^{-1}	0.132 mm^{-1}
F(000)	2100	3848
cryst size	0.20 × 0.20 × 0.08 mm^3	0.20 × 0.17 × 0.10 mm^3
θ range for data collection	1.40−28.28°	1.99−25.03°
index ranges	$-23 \leq h \leq 23$ $-24 \leq k \leq 24$ $-28 \leq l \leq 27$	$-18 \leq h \leq 19$ $-47 \leq k \leq 41$ $-21 \leq l \leq 13$
reflns collected	127 420	29 563
independent reflns	30 238 [$R_{int} = 0.0638$]	15 469 [$R_{int} = 0.0305$]
completeness to θ	99.9% (28.28°)	99.9% (25.03°)
max./min. transm	0.9897/0.9745	0.9869/0.9741
data/restraints/params	30 238/397/1243	15 469/3023/1536
GOF on F^2	1.043	1.015
final R indices [$I > 2\sigma(I)$]	R1 = 0.0696 wR2 = 0.1764	R1 = 0.0584 wR2 = 0.1452
R indices (all data)	R1 = 0.1069 wR2 = 0.2005	R1 = 0.0766 wR2 = 0.1585
largest diff. peak and hole	0.896 and −0.562 e Å^{-3}	0.317 and −0.268 e Å^{-3}

[a] In all cases, the wavelength was 0.71073 Å, the absorption correction was semiempirical from equivalents, and the refinement method was full-matrix least-squares on F^2.

and recrystallized from pentane at low temperature (ca. −35 °C) in good overall yield (70−80%). Freshly isolated **V**(THF) is a bright lime green, but the color darkens to an army green as the solvent of crystallization is lost. The lime green color returns upon dissolution in pentane or toluene. **V**(THF) is analogous to known [C$_6$F$_5$N$_3$N]V(THF).[15a] Blue [Me$_3$SiN$_3$N]V[16b] turns green upon the addition of substrates such as MeCN, but it apparently does not bind THF strongly enough to yield [Me$_3$SiN$_3$N]V(THF). **V**(THF) tends to crystallize as flakes, but a crystal suitable for single-crystal X-ray diffraction was finally obtained from a heptane solution at room temperature by slowly concentrating the solution stepwise over a period of days.

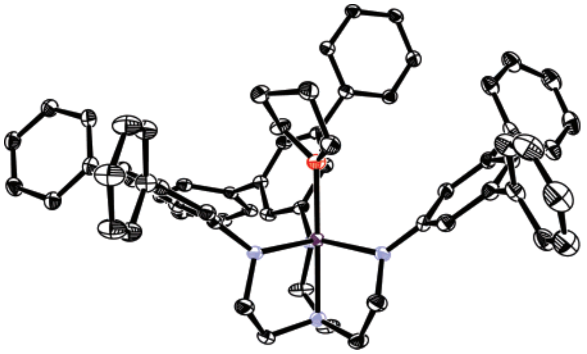


Figure 1. Thermal ellipsoid drawing of [HIPTN$_3$N]V(THF) (ellipsoids at 50% probability) with isopropyl groups and hydrogen atoms removed for clarity.

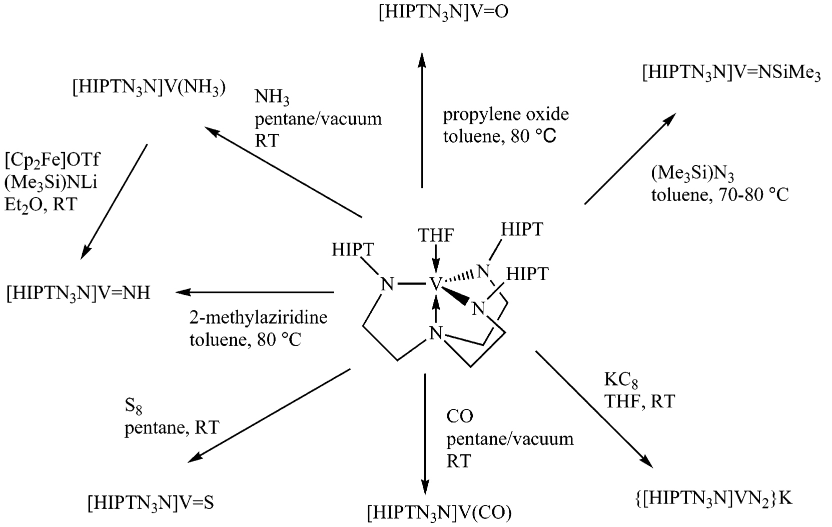
Table 2. Principle Bond Distances (Å) and Angles (deg) in [HIPTN$_3$N]V(THF) and [HIPTN$_3$N]V(NH$_3$)

	[HIPTN$_3$N]V(THF)	[HIPTN$_3$N]V(NH$_3$)
V−N(1)	1.9760(17)	1.9555(8)
V−N(2)	1.9675(18)	1.9576(7)
V−N(3)	1.9173(18)	1.9520(8)
V−N(4)	2.1627(18)	2.1486(7)
V−X$_{axial}$	2.1399(15)	2.1623(8)
N(1)−V−N(2)	123.82(8)	118.19(3)
N(1)−V−N(3)	114.39(8)	118.67(3)
N(2)−V−N(3)	115.95(8)	118.43(3)
N(1)−V−N(4)	81.06(7)	82.33(3)
N(1)−V−X	94.94(7)	97.57(3)
N(2)−V−N(4)	82.72(7)	82.90(3)
N(2)−V−X	105.76(7)	97.63(3)
N(3)−V−N(4)	82.00(7)	82.99(3)
N(3)−V−X	92.87(7)	96.57(3)
N(4)−V−X	171.42(6)	179.43(3)
X−V−N(1)−C	−20.4(2)	1.45(8)
X−V−N(2)−C	−10.5(2)	4.55(9)
X−V−N(3)−C	−15.3(2)	0.17(8)

An X-ray structural study of **V**(THF) (Tables 1 and 2 and Figure 1) reveals it to be analogous to several complexes of this general type and to have virtually the same structure as [C$_6$F$_5$N$_3$N]V(THF).[15a] For example, the five V-ligand bond lengths listed in Table 2 for **V**(THF) are similar to the corresponding values in [C$_6$F$_5$N$_3$N]V(THF) (1.968(3), 1.958(3), 1.946(3), 2.132(3), and 2.152(3) Å, respectively). In **V**(THF), the central ring of one of the HIPT groups is almost perpendicular (81.0°) to the plane that contains the amido nitrogen to which it is bound, while the other two are tilted ∼50° from vertical. The amido planes of the amido ligands are tipped between 10 and 20° from the vertical, according to the O−V−N−C$_{ipso}$ dihedral angles (Table 2). These dihedral angles are the largest of the two compounds reported here, simply, it is believed, because THF is sterically more demanding than ammonia. This finding is consistent with other structures in which the HIPT groups adopt a wide variety of orientations (in terms of rotation about the N−C$_{ipso}$ bond and "tipping" of the amido nitrogen plane from the vertical) in response to the steric demands of the ligand bound in the trigonal pocket. One of the most dramatic examples of the degree to which the ligand framework can accommodate a sterically demanding ligand in the apical pocket is the structure {[HIPTN$_3$N]Mo(2,6-dimethylpyridine)}$^+$,[3e] in which the 2,6-lutidine is bound "off-axis" to a significant degree (N$_{amine}$−Mo−N$_{lut}$ = 157°) in a "slot" created by two of the HIPT groups. Such asymmetry is not detectable in room-temperature NMR spectra since the HIPT groups are rotating and rearranging at a rate faster than the NMR time scale.

While **V**(THF) appears to be quite stable thermally at room temperature in an atmosphere of pure dinitrogen, it is extraordinarily sensitive to even traces of oxygen, with which it reacts irreversibly to give a purple compound. This oxygen sensitivity necessitates that the utmost precautions be taken to minimize the exposure of open samples even to an inert atmosphere in a glovebox over some period of time. **V**(THF) is not stable at high temperatures, however. At ∼60 °C, it starts to decompose to a black solid. The black solid is

Scheme 2. Reactions of [HIPTN$_3$N]V(THF)



soluble, even in Me_4Si, but so far has not been obtained in what we feel is a pure form. Therefore, **V**(THF) was always dried in vacuo at room temperature. All attempts to obtain a THF-free complex by heating the solid in vacuo led to decomposition. All reactions of **V**(THF) that are described beyond this point can be found in Scheme 2.

Synthesis of {[HIPTN$_3$N]VN$_2$}$^-$. The addition of potassium graphite or sodium naphthalenide to a solution of **V**(THF) in THF or DME under dinitrogen results in the immediate formation of a bright red solution that contains salts of the {[HIPTN$_3$N]VN$_2$}$^-$ anion. Potassium graphite is the preferred reductant since graphite is easily removed via filtration. The {[HIPTN$_3$N]VN$_2$}$^-$ anion is extremely reactive, readily attacking Teflon. The growth of single crystals of {[HIPTN$_3$N]VN$_2$}K suitable for X-ray study has proven to be difficult so far because of its ready oxidation. X-ray structures of related Mo[3] and W[4] species have been reported. {[HIPTN$_3$N]VN$_2$}$^-$ may be viewed either as a dinitrogen complex of V(2+) or as a deprotonated hydrazido complex of V(4+) (i.e., {[HIPTN$_3$N]V$-$N$=$N$_\beta^-$}) in which the negative charge is likely to be localized to a significant degree on N$_\beta$. Delocalization of electron density throughout the V$-$N$-$N system makes an assignment of the metal's oxidation state difficult. A {**V**N$_2$}$^-$ salt is not observed upon the addition of CrCp*$_2$ or CoCp*$_2$ to a THF solution of **V**(THF).

The IR spectra of THF or DME solutions of {[HIPTN$_3$N]VN$_2$}K reveal an absorption consistent with monomeric end-on dinitrogen ($\nu_{NN} = 1883$ cm^{-1} and $\nu_{^{15}N^{15}N} = 1821$ cm^{-1}). The value of 1883 cm^{-1} is slightly higher than the ν_{NN} values in the highly reducing V($-$1) species that have the formula [L$_4$V(N$_2$)$_2$]$^-$, where $\nu_{NN} = 1706-1833$ cm^{-1}.[11] To our knowledge, {[HIPTN$_3$N]VN$_2$}K is the only end-on-bound dinitrogen complex that is observable at room-temperature other than the [L$_4$V(N$_2$)$_2$]$^-$ species. Interestingly, the IR spectrum of {[HIPTN$_3$N]V^{15}N$_2$}K reveals that ~50% of the sample consists of {[HIPTN$_3$N]VN$_2$}K, after filtration and performance of the IR spectrum (~10 min) under a natural N$_2$ atmosphere (Figure 2). After 1 day, only {[HIPTN$_3$N]VN$_2$}K is present, further confirming the exchange of ^{15}N$_2$ with N$_2$. The mechanism of this exchange reaction is not known. In the isoelectronic [HIPTN$_3$N]MoN$_2$ species, the exchange of ^{15}N$_2$ with N$_2$ is first order in Mo and zero order in dinitrogen (at least at ~3 atm overpressure) with $t_{1/2} \approx 30$ h.[3d,f] This result is consistent with slow unimolecular loss of dinitrogen to yield the "naked" [HIPTN$_3$N]Mo species, followed by binding of free dinitrogen, to yield [HIPTN$_3$N]MoN$_2$. In contrast, the replacement of THF with dinitrogen in [HIPTN$_3$N]Mo(THF) is complete in seconds.[3d,f] The order of the reaction in which THF is replaced with dinitrogen has been proposed to be first order in dinitrogen. Therefore, the theory has arisen that replacement of a σ donor with a π acceptor (or vice versa) is fast relative to the replacement of a π acceptor with a π acceptor.[3f] In the latter circumstance, replacement must proceed via the relatively high-energy naked species, [HIPTN$_3$N]Mo.

In {[HIPTN$_3$N]MoN$_2$}MgX(THF)$_n$ species (X = Br or Cl and n is variable), the ν_{NN} values in the IR spectra depend strongly upon the solvent and the origin of the {[HIPTN$_3$N]MoN$_2$}MgX(THF)$_n$ sample, as a consequence of different degrees of solvation of the magnesium ion versus the interaction of magnesium with some part of the network of aryl rings.[3b] The highest values of ν_{NN} are observed in [Bu$_4$N]{[HIPTN$_3$N]MoN$_2$} ($\nu_{NN} = 1855$ cm^{-1} in benzene and 1859 cm^{-1} in THF), in which there is essentially no interaction of the counterion with the β nitrogen in the diazenido ligand.[3b] In the IR spectrum of {[HIPTN$_3$N]VN$_2$}K in C$_6$D$_6$, no single strong stretch is observed. The N$_2$ stretches in {[HIPTN$_3$N]VN$_2$}K in C$_6$D$_6$ are expected to be weak on the basis of studies of the analogous molybdenum compounds and may be obscured by ligand resonances. A sample of {[HIPTN$_3$N]VN$_2$}K in THF to which 18-Crown-6 had been added (1 equiv) shows $\nu_{NN} = 1884$ cm^{-1}, while in C$_6$D$_6$, ν_{NN} is observable at 1881 cm^{-1}. Both results are consistent with essentially complete solvation of the potassium ion by 18-Crown-6 or THF (in THF solvent). Therefore we can conclude that ν_{NN} in the free {[HIPTN$_3$N]VN$_2$}$^-$ ion is approximately 30 cm^{-1} higher than in the free {[HIPTN$_3$N]MoN$_2$}$^-$ ion. This finding is consistent with the expected

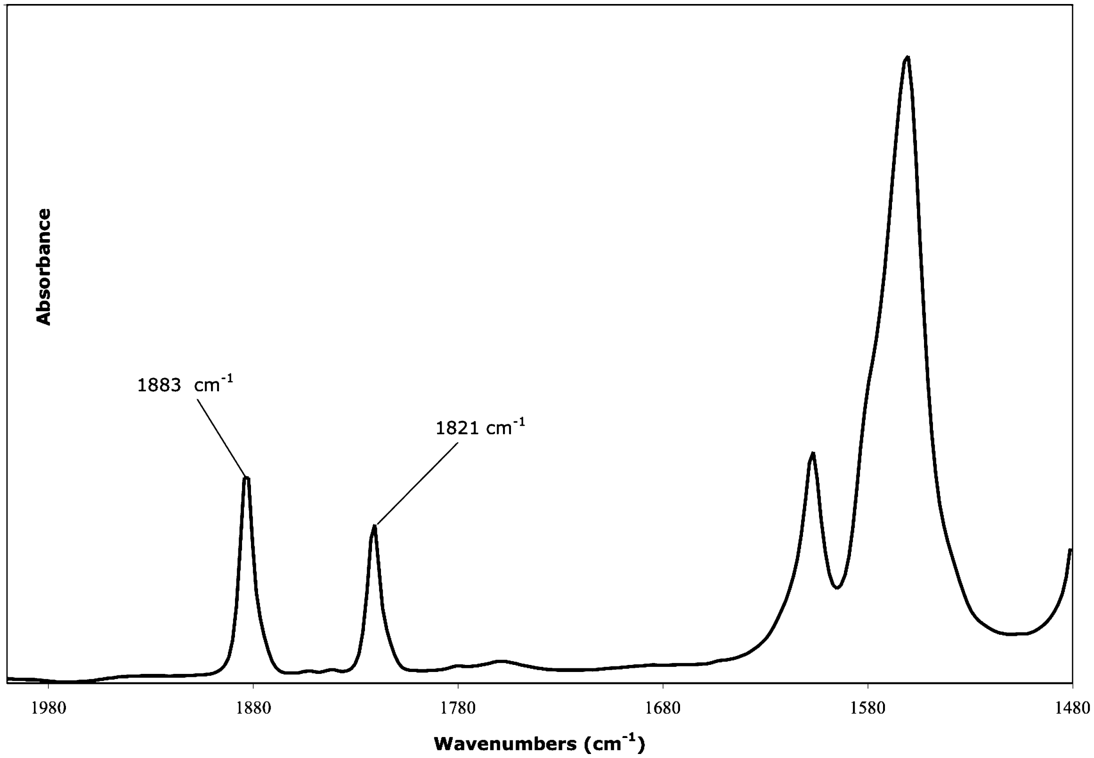


Figure 2. Solution IR spectrum of {[HIPTN$_3$N]V^{15}N$_2$}K in THF (subtracted) under dinitrogen showing a mixture that contains {[HIPTN$_3$N]V^{14}N$_2$}K as a consequence of ready exchange.

stronger π back-donation of electron density into dinitrogen from "Mo(2+)" versus "V(2+)".

Attempts to protonate the {[HIPTN$_3$N]VN$_2$}$^-$ ion with [2,6-lutidinium]BAr′$_4$ or H(Et$_2$O)$_2$BAr′$_4$ (Ar′ = 3,5-(CF$_3$)$_2$C$_6$H$_3$) under a variety of conditions have, so far, led only to solutions that contain multiple products from which no pure product could be isolated.

Synthesis of [HIPTN$_3$N]V(NH$_3$). Exposure of a degassed solution of [HIPTN$_3$N]V(THF) in pentane to NH$_3$ results in the immediate lightening of the solution's green color. [HIPTN$_3$N]V(NH$_3$) can be isolated from this solution and recrystallized from pentane, although it is much more soluble than [HIPTN$_3$N]V(THF); it is best crystallized from hexamethyldisiloxane. [HIPTN$_3$N]V(NH$_3$) is also more temperature sensitive than [HIPTN$_3$N]V(THF): it is not stable at room temperature over several months, as evidenced by the formation of a black solid which can be washed away with tetramethylsilane.

An X-ray study of [HIPTN$_3$N]V(NH$_3$) reveals it to have the expected structure (Tables 1 and 2 and Figure 3), which is similar to that of [HIPTN$_3$N]V(THF). It should be noted that the V−X distances in [HIPTN$_3$N]V(THF) (2.1399(15) Å) and [HIPTN$_3$N]V(NH$_3$) (2.1623(8) Å) are essentially the same, as are other corresponding distances and angles in the two species (Table 2). In [HIPTN$_3$N]V(NH$_3$), the X−V−N−C dihedral angles (where X is the atom bound to V in the apical pocket) are no larger than 5°, compared to up to 20° in [HIPTN$_3$N]V(THF). The steric demands of the ammonia ligand in the apical pocket are simply not as great as the steric demands of the THF ligand.

An attempt to convert [HIPTN$_3$N]V(NH$_3$) into {[HIPTN$_3$N]VN$_2$}$^-$ through the addition of 1 equiv of potassium graphite in heptane under dinitrogen led to formation of an unidentified black material. No electrochemical studies on [HIPTN$_3$N]V(NH$_3$) or {[HIPTN$_3$N]VN$_2$}$^-$ have yet been carried out.

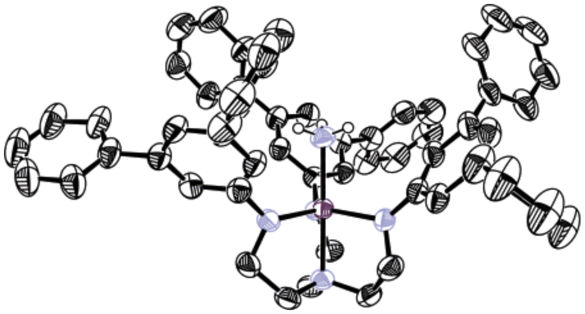


Figure 3. Thermal ellipsoid drawing of [HIPTN$_3$N]V(NH$_3$) (ellipsoids at 50% probability) with isopropyl groups and non-ammonia hydrogen atoms removed for clarity.

Synthesis of [HIPTN$_3$N]V=X Species. The addition of 2-methylaziridine to a toluene solution of **V**(THF) at room temperature produces a red solution that remains red over a period of 12 h. NMR studies suggest that the species that is present at this stage is paramagnetic. There is no noticeable color change upon heating this solution at 80 °C over a period of 12 h, but diamagnetic [HIPTN$_3$N]V=NH can be isolated from this solution and recrystallized readily from pentane as large blocks. The ^{1}H NMR spectrum of [HIPTN$_3$N]V=NH contains sharp resonances, while the ^{51}V NMR spectrum contains a broad resonance at −334 ppm (2365 Hz wide athalf-height). No detectable coupling of ^{51}V to ^{15}N could be observed in the ^{51}V NMR spectrum of **V**=^{15}NH. The magnitude of the coupling of ^{51}V to ^{15}N is likely to be on

Table 3. ^{51}V NMR Shifts (C_6D_6, ppm) of analogous $[Me_3SiN_3N]V$ and $[HIPTN_3N]V$ Complexes

	$[Me_3SiN_3N]^{3-}$	$[HIPTN_3N]^{3-}$
V═S	621	756
V═NH	252	−334
V═N($SiMe_3$)	∼ −80	−276
V═O	−173	−115

the order of 100−200 Hz,[19] which is much too small to observe in such a broad peak. No resonance could be found for the imido hydrogen in the proton NMR spectrum, a circumstance that also was encountered for $[Me_3SiN_3N]V{=}NH$.[16b] Vanadium NMR shifts in $[HIPTN_3N]V{=}X$ and $[Me_3SiN_3N]V{=}X$ species are listed in Table 3.

It is interesting to note that $[HIPTN_3N]V{=}NH$ also can be prepared via the addition of 2 equiv of $LiN(SiMe_3)_2$ to **V**(NH_3), followed by 2 equiv of $[FeCp_2]OTf$. We propose that this reaction consists of alternating oxidations followed by deprotonations (i.e, $\mathbf{V}(NH_3) \rightarrow \mathbf{V}(NH_3)^+ \rightarrow \mathbf{V}(NH_2) \rightarrow \mathbf{V}(NH_2)^+ \rightarrow \mathbf{V}{=}NH$). The conversion of **V**(NH_3) into **V**═NH is quite facile, occurring even without the addition of $LiN(SiMe_3)_2$. The addition of even 1 equiv of $[FeCp_2]OTf$ to **V**(NH_3) results in the formation of **V**═NH as the only identifiable product. This reaction was employed to synthesize $\mathbf{V}{=}^{15}NH$ and thereby identify the N−H stretch in its infrared spectrum: in C_6D_6, $\nu_{^{15}NH} = 3351$ cm^{-1} compared to $\nu_{^{14}NH} = 3360$ cm^{-1}. Like $[Me_3SiN_3N]V{=}NH$, **V**═NH is not especially susceptible to oxidation and thus is relatively stable in air. In comparison to **V**═NH, it should be noted that d^1 $[HIPTN_3N]Mo{=}NH$ is unstable, losing dihydrogen to yield $[HIPTN_3N]Mo{\equiv}N$, which is relatively stable toward air. The mechanism of dihydrogen formation is not known.

Treatment of **V**(THF) with Me_3SiN_3 yields orange **V**═$NSiMe_3$ in a variable yield depending on the length of time that the reaction mixture is heated. The reaction must be heated, but heating for too long produces low yields; the optimum conditions for maximum yield were not determined. The ^{1}H NMR spectrum of **V**═$NSiMe_3$ is typical of a diamagnetic complex with sharp proton resonances and a broad ^{51}V NMR resonance at −276.31 ppm (1326 Hz wide at half-height). The Me_3Si resonance (0.12 ppm) is shifted upfield slightly from where it is in $[Me_3SiN_3N]V{=}NSiMe_3$ (0.55 ppm).[16b]

The addition of S_8 to a stirred solution of **V**(THF) yields dark green **V**═S, which displays a sharp ^{1}H NMR spectrum and a sharp ^{51}V NMR resonance at 756 ppm (30 Hz wide at half-height). Even after multiple recrystallizations, a small (∼2−3% by integration) ^{51}V resonance can be observed for an unidentified vanadium complex. The same phenomenon is observed in **V**═O (vide infra), although the unidentified species in **V**═O samples is not the same as that in **V**═S samples. $[Me_3SiN_3N]V{=}S$ was prepared also simply by the addition of sulfur to $[Me_3SiN_3N]V$.[16b]

The addition of propylene oxide to a solution of **V**(THF) led to formation of a purple solution. Heating is required to generate diamagnetic purple **V**═O, which can be isolated as a microcrystalline powder and can be recrystallized from pentane. Its vanadium NMR spectrum shows a resonance at −116 ppm (785 Hz wide at half-height); a small impurity is present with a vanadium resonance at −69 ppm, even in spectra of multiply recrystallized material. An attempt to synthesize **V**═O from $Cl_3V{=}O$, as in the synthesis of $[C_6F_5N_3N]V{=}O$,[15a] yielded multiple products according to the ^{51}V NMR spectra, and was abandoned in favor of the propylene oxide route.

Other Reactions. Attempts to deprotonate **V**═NH with $LiN(SiMe_3)_2$ or LiNH-*i*-Pr produced no reaction, while the use of Li-*n*-Bu led to unidentified decomposition products. In contrast, it has been reported that the reaction between $[Me_3SiN_3N]V{=}NH$ and $LiN(SiMe_3)_2$, followed by addition of Me_3SiCl, generates $[Me_3SiN_3N]V{=}NSiMe_3$; although $[Me_3SiN_3N]V{=}NLi$ was not isolated and characterized, it presumably is formed as an intermediate.[16b] Attempts to remove the TMS group from **V**═$NSiMe_3$ using LiNH-*i*-Pr, a method employed[20] for the synthesis of $[(Ph_2N)_3VN]Na(THF)_3$,[9c] yielded no reaction at room temperature and decomposition upon heating. A similar result was observed with *n*-Bu_4NF. Attempts to generate $\{\mathbf{V}(N)\}^-$ in reactions between **V**(THF) and NaN_3 or *n*-Bu_4NN_3 so far have failed. Anionic vanadium nitride complexes in the literature[9c,21] have been isolated that are supported by three monoamido ligands.

The exposure of a degassed pentane solution of **V**(THF) to an atmosphere of CO produces a red-gold solution which we assume contains **V**(CO) on the basis of a ν_{CO} stretch at 2076 cm^{-1} in the IR spectrum and a literature precedent for formation of a variety of early metal triamidoamine CO complexes.[1,2] When ^{13}CO is employed, $\nu_{^{13}CO}$ can be observed at 2030 cm^{-1}, and $\nu_{^{13}C^{18}O}$ can be found at 1980 cm^{-1}. Clearly, V(III) is capable of binding carbon monoxide, as expected, but not dinitrogen.

Evaluation of Activity for Dinitrogen Reduction. We have isolated three species that one might suspect could be intermediates in a catalytic reduction of dinitrogen (Scheme 1), namely, $\{\mathbf{V}N_2\}^-$, **V**═NH, and **V**(NH_3). We also have been able to readily convert **V**(NH_3) to **V**═NH, which by microscopic reversibility implies that conversion of **V**═NH to **V**(NH_3) is possible. Therefore, we were interested in the possibility that vanadium species might serve as catalysts for the reduction of dinitrogen by protons and electrons under conditions that have been successful for analogous molybdenum catalysts[2] using $CrCp^*_2$ as the reducing agent and 2,6-lutidinium BAr'_4 as the acid source. Reactions were carried out in the manner described for $[HIPTN_3N]Mo$ complexes and variations thereof using **V**(THF), $\{\mathbf{V}N_2\}^-$, and **V**═NH as the initial species. No ammonia was generated when **V**(THF) was employed, while $\{\mathbf{V}N_2\}^-$ and **V**═NH yielded 0.20 and 0.78 equiv, respectively. We presume that no ammonia is formed from dinitrogen in the atmosphere (i.e., under these conditions vanadium is not a catalyst for dinitrogen reduction).

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Conclusions

We have been able to prepare a variety of [HIPTN$_3$N]V (**V**) species, including three ({**V**N$_2$}K, **V**═NH, and **V**(NH$_3$)) that are relevant to a hypothetical reduction of dinitrogen. While the chemistry of **V** complexes is largely tractable and well-behaved, no ammonia was formed from dinitrogen using **V**(THF), {**V**N$_2$}$^-$, or **V**═NH as the initial species under conditions that were successful in the analogous Mo system. Although there are hints as to what some of the problems might be, more quantitative studies are needed to provide support. Certainly one of the concerns is the fact that the trianionic triamidoamine ligand demands that all charges of intermediates be one less than what they are in the analogous Mo system. Perhaps the most serious problem is that the nitride intermediate must be an anion. However, there are clearly other hurdles in a hypothetical dinitrogen reduction scheme, among them the decomposition of **V**(NH$_3$) upon reduction, at least with potassium graphite as the reducing agent. In future studies, we hope to further probe the [HIPTN$_3$N]V system to see if conditions can be found that will allow turnover.

Experimental Section

General. All experiments involving air- and moisture-sensitive complexes or reactions were performed under nitrogen in a Vacuum Atmospheres drybox or using standard Schlenk techniques with glassware stored in an oven at ∼190 °C for at least 12 h prior to use. Pentane was washed with HNO$_3$/H$_2$SO$_4$ (5:95 by volume), sodium bicarbonate, and water, dried over CaCl$_2$, and then sparged with nitrogen and passed through an alumina column followed by storage over Na/benzophenone and vacuum transfer prior to use. Dry and deoxygenated benzene was purchased from Aldrich and passed through Q5 and alumina columns. Heptane, benzene-*d*$_6$, and toluene-*d*$_8$ were dried over Na/benzophenone then degassed (freeze−pump−thaw) and vacuum transferred prior to use. THF, diethyl ether, and toluene were predried by passage through an alumina column followed by storage over Na/benzophenone. They were degassed (freeze−pump−thaw) and vacuum transferred prior to use. All solvents were stored over 4 Å molecular sieves in a drybox after transfer.

VCl$_3$ (Strem), CO (Aldrich, passed through dry ice/acetone), ^{13}CO (Matheson, passed through dry ice/acetone), NH$_3$ (BOC, condensed onto Na sand), ^{15}NH$_3$ (Cambridge Isotope Labs, condensed onto Na sand), ^{15}N$_2$ (Cambridge Isotope Labs), LiN(TMS)$_2$ (Aldrich, sublimed), 2-methylaziridine (Aldrich, vacuum transferred and stored at ca. −40 °C), (TMS)N$_3$ (Acros Organics), propylene oxide (Aldrich), 18-Crown-6 (Aldrich, dried in vacuo), and 15-Crown-5 (Acros Organics, degassed and stored over 4 Å molecular sieves) were purchased as used as received or purified as indicated.

H$_3$[HIPTN$_3$N],[3] VCl$_3$(THF)$_3$,[22] [FeCp$_2$]OTf,[23] and *n*-Bu$_4$NN$_3$[24] were synthesized via literature procedures. Potassium graphite was synthesized by stirring a 1:8 mixture of potassium/graphite under partial vacuum for 2 h using a glass stirbar at ∼200 °C.

^{1}H NMR spectra were obtained on a Varian Mercury (300 MHz) or Inova (500 MHz) spectrometer and were referenced to the residual protio-solvent peak. ^{51}V NMR spectra were obtained on a Varian Inova (131.5 MHz) spectrometer outfitted with an inverse probe and externally referenced to a commercial sample of VOCl$_3$ ($\delta(^{51}\mathrm{V}) = 0$ ppm). Infrared spectra were obtained on a Nicolet Avatar 360 FT-IR spectrometer using a demountable liquid cell (0.2 mm Teflon or lead spacer with KBr plates). UV−vis spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer equipped with a Hewlett-Packard 89090A Peltier temperature-control accessory with the solvent contribution manually subtracted using a standard background. Magnetic measurements (Evans method[25,26]) employed the shift of the toluene methyl group. The sample was dissolved in a 4:1 (by volume) mixture of C$_6$D$_6$/toluene, and a concentric sealed capillary filled with toluene was added; multiple determinations are listed as separate results. Elemental analyses were performed by H. Kolbe Microanalytics Laboratory, Mülheim an der Ruhr, Germany.

X-ray diffraction data were collected using a Siemens Platform three-circle diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), performing φ and ω scans. Data for the **V**(THF) structure was collected at 100 K on a Bruker-AXS Smart Apex CCD detector; all other structural data were collected at 193 K using a Bruker Smart 1000 CCD detector. The structures were solved by direct methods using SHELXS[27] and refined against F^2 on all data by full-matrix least squares with SHELXL-97.[28] All non-hydrogen atoms were refined anisotropically. Unless otherwise indicated in the discussion, all hydrogen atoms were included into the model at their geometrically calculated positions and refined using a riding model. Thermal ellipsoid drawings were generated using ORTEP-3.[29]

The refinement of the **V**(NH$_3$) structure did not converge well and required damping. As a result, the calculated standard uncertainties are underrated. In addition, the HIPT^{3-} ligand is heavily disordered. Some of those disorders could be refined with the help of similarity restraints on the 1−2 and 1−3 distances and displacement parameters, as well as rigid bond restraints for anisotropic displacement parameters. The ammonia hydrogens could be found in a Fourier difference map and refined semi-freely with the help of distance restraints

[HIPTN$_3$N]V(THF). VCl$_3$(THF)$_3$ (1.17 g, 3.14 mmol) and H$_3$[HIPTN$_3$N] (5.00 g, 3.15 mmol) were added to a 100 mL flask equipped with a 0−8 Teflon valve via a solid addition funnel, followed by THF (∼50 mL). The flask was sealed, and the resulting purple adduct was allowed to stir for 1 h. (TMS)$_2$NLi (1.53 g, 9.16 mmol) was then added, resulting in a dark green solution within minutes. After the reaction mixture was stirred for 1 h, the THF was removed in vacuo to minimum pressure (∼5−10 mTorr) at room temperature. The resulting solid was taken up in pentane, and the solution was filtered through Celite to remove LiCl. The filtrate was concentrated, and the product was obtained as a lime green solid through crystallization at approximately −35 °C. This solid was again dried at room temperature in vacuo to minimum pressure to yield the lime green product (4.6 g, 86%). The substitution of (TMS)$_2$NK for (TMS)$_2$NLi gave the same product (2.4 g, 45%). UV−vis ($\lambda_{\max}$ (nm), ϵ (M^{-1} cm^{-1}); heptane): 260 (sh), 6.6×10^4; 306, 1.9×10^4; 350 (sh), 1.1×10^4; 404 (sh), 5.8

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$\times$ 10^3. μ_{eff}: 2.51, 2.54, 2.55 μ_B. Anal. Calcd for $C_{118}H_{167}N_4VO$: C, 79.95; H, 7.85; N, 2.28; Cl, 0.00. Found: C, 80.11; H, 7.92; N, 2.25; Cl, 0.00.

{[HIPTN$_3$N]VN$_2$}K. [HIPTN$_3$N]V(THF) (300 mg, 0.176 mmol) and KC_8 (37.5 mg, 0.277 mmol) were added to a 20 mL scintillation vial along with a glass-coated stir-bar and 5−10 mL of solvent (typically THF, but also DME, ether, benzene, or toluene). Ethereal solvents were used, and the solution turned red within minutes (overnight in the case of toluene or benzene) and was filtered through glass wool in a pipet to remove the graphite and excess KC_8. The solvent was removed in vacuo to yield red solid. IR (THF, cm^{-1}): 1883 (ν_{NN}).

{[HIPTN$_3$N]V^{15}N$_2$}K. [HIPTN$_3$N]V(THF) (52.0 mg, 30 μmol) and KC_8 (9.4 mg, 70 μmol) were added to a J. Young tube. THF (∼1.6−2 mL) was then added to a second J. Young tube. Both J. Young tubes were connected to a transfer bridge. The tube containing the solid was evacuated, while the tube containing solvent was degassed using 5 freeze−pump−thaw cycles. The THF was then vacuum transferred onto the solid but was kept frozen in liquid nitrogen. This tube was attached to a gas transfer bridge and filled with ∼13 equiv of $^{15}N_2$. The tube was subsequently placed in a dry ice/acetone bath with occasional shaking. Once the sample was fully thawed, it was allowed to warm to room temperature, and the solution was filtered through glass wool in a pipet. The resultant red solution was used directly for IR measurements. IR (THF, cm^{-1}). 1821 (ν_{NN}).

{[HIPTN$_3$N]VN$_2$}K(18-Crown-6). [HIPTN$_3$N]V(THF) (300 mg, 0.176 mmol), KC_8 (38.1 mg, 0.282 mmol), and 18-Crown-6 (49.8 mg, 0.188 mmol) were added to a 20 mL scintillation vial, followed by a glass stirbar and DME (∼4 mL). The solution turned red immediately and was allowed to stir for 30 min. Graphite was removed by filtration through glass wool in a pipet, followed by removal of the solvent in vacuo. The sample was triturated with pentane and collected on a glass frit to yield **3** quantitatively. IR (C_6D_6, cm^{-1}): 1881 (ν_{NN}). IR (THF, cm^{-1}): 1884 (ν_{NN}). Anal. Calcd for $C_{126}H_{183}N_6VO_6K$: C, 76.90; H, 9.37; N, 4.27. Found: C, 77.08; H, 9.28; N, 4.22.

[HIPTN$_3$N]V(NH$_3$). [HIPTN$_3$N]V(THF) (1.00 g, 0.59 mmol) in a 100 mL solvent bomb-type flask equipped with a Teflon valve was dissolved in pentane and exposed to ∼1 atm of NH_3. The color immediately changed to a lighter shade of green, and removal of the volatiles in vacuo yielded a green solid quantitatively. Crystallization of the crude product from a supersaturated pentane solution at approximately −35 °C yielded green flakes (661 mg, 68%). UV−vis (λ_{max} (nm), ϵ (M^{-1} cm^{-1}); heptane): 214, 1.43 $\times$ 10^5; 280, 1.55 $\times$ 10^4; 316, 1.91 $\times$ 10^4; 352, 1.70 $\times$ 10^4. IR (C_6D_6, cm^{-1}): 3358 (ν_{NH}). μ_{eff}: 2.22, 2.23, 2.24 μ_B (two different samples). Anal. Calcd for $C_{114}H_{162}N_5V$: C, 82.81; H, 9.88; N, 4.24. Found: C, 82.69; H, 9.76; N, 4.21.

[HIPTN$_3$N]V(^{15}NH$_3$). [HIPTN$_3$N]V(THF) (500 mg, 0.29 mmol) in a 50 mL solvent bomb-type flask equipped with a Teflon valve was dissolved in pentane and exposed to ∼1 atm of $^{15}NH_3$. The color immediately changed to green, and the volatiles were removed in vacuo. Crystallization of the crude product from a supersaturated hexamethyldisiloxane solution at approximately −35 °C yielded green flakes (402 mg, 83%). IR (C_6D_6, cm^{-1}): 3349 (ν_{NH}).

[HIPTN$_3$N]V═NH. [HIPTN$_3$N]V(THF) (500 mg, 0.29 mmol) was dissolved in ∼20 mL of toluene in a 50 mL solvent bomb-type flask equipped with a Teflon valve. 2-Methylaziridine (41.4 μL, 0.59 mmol) was added, and the reaction mixture was left to stir at room temperature for ∼12 h. The resulting red solution was then heated at 80 °C for 12 h. The volatiles were removed in vacuo, and the resulting solid was crystallized from a supersaturated pentane solution at approximately −35 °C to give large dark red blocks (427 mg, 88%). ^{1}H NMR (C_6D_6): δ 7.54 (br s, 6H), 7.19 (s, 12H), 6.45 (s, 3H), 3.72 (br t, 6H), 3.09 (sept, J_{HH} = 6.8 Hz, 12H), 2.92 (sept, J_{HH} = 6.8 Hz, 6H), 2.15 (br t, 6H), 1.36 (d, J_{HH} = 6.9 Hz, 36H), 1.22 (d, J_{HH} = 6.8 Hz, 36H), 1.07 (d, J_{HH} = 6.6 Hz, 36H). ^{51}V NMR (C_6D_6): δ −334 (br s). UV−vis (λ_{max} (nm), ϵ (M^{-1} cm^{-1}); heptane): 266, 3.2 $\times$ 10^4; 376, 1.98 $\times$ 10^4; 466, 2.18 $\times$ 10^4. IR (C_6D_6, cm^{-1}): 3360 (ν_{NH}). Anal. Calcd for $C_{114}H_{160}N_5V$: C, 82.91; H, 9.77; N, 4.24. Found: C, 82.74; H, 9.85; N, 4.18.

[HIPTN$_3$N]V^{15}NH. [HIPTN$_3$N]V(^{15}NH$_3$) (50 mg, 30 μmol) and $(TMS)_2NLi$ (10 mg, 60 μmol) were dissolved in diethyl ether in a 20 mL scintillation vial. [FeCp$_2$]OTf (20 mg, 60 μmol) was added to the stirred solution to give a red solution immediately. The volatiles were removed in vacuo. Pentane was added to the resulting residue, and the solution was filtered through Celite. The solvent was removed in vacuo at ∼70 °C. IR (C_6D_6, cm^{-1}): 3351 (ν_{NH}).

[HIPTN$_3$N]V═N(TMS). [HIPTN$_3$N]V(THF) (300 mg, 0.18 mmol) was added to a 50 mL solvent bomb-type flask with a Teflon valve and dissolved in ∼10 mL of toluene. (TMS)N$_3$ (47 μL, 0.35 mmol) was added, followed by another 1−2 mL of toluene to wash the valve stem of the flask. The reaction mixture was stirred at 70−80 °C for 12 h to give a red solution. The volatiles were removed in vacuo to give an orange powder that could be recrystallized from pentane to yield the product (30 mg, 10%). ^{1}H NMR (C_6D_6): δ 7.19 (s, 12H), 7.11 (d, J_{HH} = 1.2 Hz, 6H), 6.78 (br t, 3H), 3.79 (br t, 6H), 3.18 (sept, J_{HH} = 6.7 Hz, 12H), 2.91 (sept, J_{HH} = 6.8 Hz, 6H), 2.39 (br t, 6H), 1.36 (d, J_{HH} = 6.6 Hz, 36H), 1.20 (d, J_{HH} = 6.9 Hz, 72H), −0.12 (s, 9H). ^{51}V NMR (C_6D_6): δ −276 (br s). UV−vis (λ_{max} (nm), ϵ (M^{-1} cm^{-1}); heptane): 262 (sh), 3 $\times$ 10^4; 304, 1.3 $\times$ 10^4; 368, 1.0 $\times$ 10^4; 456, 1.2 $\times$ 10^4. Anal. Calcd for $C_{117}H_{168}N_5SiV$: C, 81.52; H, 9.83; N, 4.06. Found: C, 81.61; H, 9.88; N, 4.05.

[HIPTN$_3$N]V═S. [HIPTN$_3$N]V(THF) (1.00 g, 0.59 mmol) was added to a 100 mL solvent bomb-type flask and dissolved in pentane. While the solution was stirred, S_8 (19 mg, 74 μmol) was added. Within minutes, the solution turned dark green. The stirring was continued for 12 h, but no further color change was observed. The reaction mixture was filtered through Celite and concentrated in vacuo. Crystallization of the crude product from pentane at −35 °C yielded a microcrystalline green product (751 mg, 77%). ^{1}H NMR (C_6D_6): δ 7.42 (br s, 6H), 7.21 (s, 12H), 6.48 (t, J_{HH} = 1.3 Hz, 3H), 3.73 (br t, 6H), 3.10 (sept, J_{HH} = 6.8 Hz, 12H), 2.92 (sept, J_{HH} = 6.9 Hz, 6H), 1.70 (t, J_{HH} = 5.0 Hz, 6H), 1.35 (d, J_{HH} = 6.9 Hz, 36H), 1.24 (d, J_{HH} = 6.9 Hz, 36H), 1.11 (br d, J_{HH} = 6.3 Hz, 36H). ^{51}V NMR (C_6D_6): δ 755.93 (s). UV−vis (λ_{max} (nm), ϵ (M^{-1} cm^{-1}); heptane): 260, 4.0 $\times$ 10^4; 296, 1.2 $\times$ 10^4; 354, 1.2 $\times$ 10^4; 414, 1.5 $\times$ 10^4; 606, 8.0 $\times$ 10^4. Anal. Calcd for $C_{114}H_{159}N_4SV$: C, 82.06; H, 9.61; N, 3.36; S, 1.92. Found: C, 82.15; H, 9.48; N, 3.31; S, 1.97.

[HIPTN$_3$N]V═O. [HIPTN$_3$N]V(THF) (300 mg, 0.18 mmol) was added to a 25 mL solvent bomb-type flask with a Teflon valve, to which was added ∼15 mL of toluene. While the solution was stirring, propylene oxide (25 μL, 0.34 mmol) was added, resulting in an immediate color change to black-violet. The reaction mixture was heated at ∼80 °C for 16 h, and the solvent was removed on a vacuum line. The solid residue was dissolved in pentane, and the solution was filtered through Celite. Crystallization from a supersaturated pentane solution at approximately −40 °C yielded [HIPTN$_3$N]V═O as a purple powder (198 mg, 68%). ^{1}H NMR (C_6D_6): δ 7.78 (br s, 6H), 7.20 (s, 12H), 6.51 (s, 3H), 3.69 (br s, 6H), 3.08 (sept, J_{HH} = 6.7 Hz, 12H), 2.93 (sept, J_{HH} = 6.9 Hz, 6H), 1.98 (br s, 6H), 1.36 (d, J_{HH} = 6.9 Hz, 36H), 1.21 (d, J_{HH} =

6.8 Hz, 36H), 1.07 (br s, 36H). ^{51}V NMR (C_6D_6): δ −115 (s). UV−vis (λ_{max} (nm), ϵ (M^{-1} cm^{-1}); heptane): 264 (sh), 2.4×10^4; 288 (sh), 1.7×10^4; 412, 1.6×10^4; 542, 1.5×10^4. Anal. Calcd for $C_{114}H_{159}N_4OV$: C, 82.85; H, 9.70; N, 3.39. Found: C, 82.75; H, 9.63; N, 3.35.

Observation of [HIPTN$_3$N]V(CO). A sample of [HIPTN$_3$N]V(THF) (50 mg, 29 μmol) was added to a 25 mL solvent bomb-type flask with a Teflon valve and was dissolved in ∼6−7 mL of pentane. The resulting green solution was degassed once (freeze−pump−thaw) and exposed to 1 atm of CO. In ∼5 min, the solution turned red-gold and was allowed to stir for another 30 min. The volatiles were then removed in vacuo, and the resulting residue was taken up in ∼1 mL of heptane and used for IR analysis directly. IR (heptane, cm^{-1}): 2076 (ν_{CO}).

Observation of [HIPTN$_3$N]V(^{13}CO). A sample of [HIPTN$_3$N]V(THF) (50 mg, 29 μmol) was added to a 25 mL solvent bomb-type flask with a Teflon valve and was dissolved in ∼6−7 mL of pentane. The resulting green solution was degassed once (freeze−pump−thaw) and exposed to 1 atm of CO. In ∼5 min, the solution turned red-gold and was allowed to stir for another 30 min. The volatiles were then removed in vacuo, and the resulting residue was taken up in ∼1 mL of heptane and used for IR analysis directly. IR (heptane, cm^{-1}): 2030 (ν_{CO}, ^{13}CO), 1980 (ν_{CO}, $^{13}C^{18}O$).

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Supporting Information Available: Fully labeled thermal ellipsoid drawing, crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, and anisotropic displacement parameters for [HIPTN$_3$N]V(THF) (05099) and [HIPTN$_3$N]V(NH_3) (03316). This material is available free of charge via the Internet at http://pubs.acs.org. Details concerning the structures also can be found on http://www.reciprocalnet.org.

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