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Oxidation Reactions of $[(Me_3Si)_2N]_2VX(THF)$ (X = Cl, Me, Ph) with CuCl, PhCH(O)CH_2, and Ph_2CN_2 and the Syntheses and Structures of the Vanadium(III) Anions $\{[(Me_3Si)_2N]_2VX_2\}^-$ (X = Cl, Me)

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One-electron oxidation of $[(Me_3Si)_2N]_2VX(THF)$ (X = Cl, Me, Ph) with CuCl afforded the V(IV), d^1 species $[(Me_3Si)_2N]_2VCl(X)$ in moderate yields after crystallization from acetonitrile. $[(Me_3Si)_2N]_2VCl_2$ has been characterized crystallographically. The methyl and phenyl derivatives were conveniently synthesized in one step from $[(Me_3Si)_2N]_2VCl(THF)$ by first reacting first with LiMe or $MgPh_2$, prior to treatment with CuCl. Reaction of $[(Me_3Si)_2N]_2VCl(THF)$ with dilithioacetylide in the presence of tetramethylethylenediamine (TMEDA) proceeded with redistribution of the Cl ligands, as the anionic V(III) compound $[Li(TMEDA)_2]\{[(Me_3Si)_2N]_2VCl_2\}$ was obtained in 44% yield as purple crystals. The analogous dimethyl anion $[Li(TMEDA)_2]\{[(Me_3Si)_2N]_2VMe_2\}$ was synthesized in 66% yield as deep-blue, highly air-sensitive crystals on treatment of $[(Me_3Si)_2N]_2VCl(THF)$ with 2 equiv of LiMe in the presence of TMEDA. X-ray crystallography showed that both salts crystallized as well-separated cations and anions. The reaction between styrene oxide and $[(Me_3Si)_2N]_2VMe(THF)$ proceeded stepwise, first yielding the μ-O intermediate $\{[(Me_3Si)_2N]_2VMe\}_2(\mu\text{-}O)$ and then the V(V) terminal oxo $[(Me_3Si)_2N]_2V(O)(Me)$. Styrene oxide also oxidized $[(Me_3Si)_2N]_2VPh(THF)$ to $[(Me_3Si)_2N]_2V(O)(Ph)$, however, in this case the putative μ-O intermediate could not be isolated as a stable material. Diphenyldiazomethane was reduced by two electrons to an alkylidenehydrazido(2^-) on displacing THF from $[(Me_3Si)_2N]_2VCl(THF)$ to form the V(V) complex $[(Me_3Si)_2N]_2V(Cl)(N_2CPh_2)$. A crystal structure showed the diazoalkane to be coordinated in a doubly-bent fashion.

Introduction

The ability of amido ligands to support and promote unusual chemistry at metal centers has been known for many years.[1] In this context, they complement the well-studied Cp-based systems, with the major difference being the greater reactivity of the former complexes due to their relatively higher unsaturation and lower coordination numbers for a given L_nM (L = NR_2 or Cp). Recent work probing the electronic effects of the substituents on the amide nitrogen has lead to a number of interesting results, such as fixation[2] and scission[3−5] of dinitrogen. Our focus here is on the more traditional bis(trimethylsilyl)amide ligand, developed extensively throughout the years by workers such as Bradley, Lappert, and Andersen, which is the prototypical bulky amide for stabilizing low-coordinate, electrophilic metal fragments.[6] Although it was recognized early on[7] that in some systems the use of $-N(SiMe_3)_2$ as an ancillary ligand could lead to intramolecular γ-hydrogen eliminaton across M−X bonds (X = Cl, H/D, Me, Et, CH_2SiMe_3),[8−11] we recently showed that the $\{[(Me_3Si)_2N]_2V\}^+$ fragment[12] can stabilize three-coordinate V(III) selenolate and tellurolate complexes[12] and $[(Me_3Si)_2N]_2VMe(THF)$,[13] a rare "Cp-free" vanadium−hydrocarbyl. In this paper, we report the one-electron oxidation of this latter V−Me complex, the analogous V−Ph complex, and the parent V(III) chloride complex to yield the bis(amide) V(IV) methyl−chloride, phenyl−chloride, and dichloride derivatives, respectively. This last species completes the homologous series of group 5 $[(Me_3Si)_2N]_2MCl_2$ compounds (M = V, Nb, Ta), as the niobium[14,15] and tantalum[16,17] analogs were recently reported by Hoffman. The syntheses and structures of related four-coordinate V(III) anions, i.e., $\{[(Me_3Si)_2N]_2VCl_2\}^-$ and $\{[(Me_3Si)_2N]_2VMe_2\}^-$, are also reported. We have also explored the two-electron oxidation chemistry of these species, which yields V(V) terminal oxo species $[(Me_3Si)_2N]_2NV(O)(R)$. In the case of the methyl derivative, the

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reaction proceeds stepwise through an isolable μ-O intermediate $\{[(Me_3Si)_2N]_2VMe\}_2(\mu\text{-O})$. The synthesis and structure of $[(Me_3Si)_2N]_2VCl(N_2CPh_2)$, formed in what may also be viewed as an oxidation reaction, is also presented. Lastly, given the well-established ease of interconversion between Cp_2V, Cp_2VX, and Cp_2VX_2 species,[18] illustrative comparisons will be made between the chemistry of $\{Cp_2V\}$ versus $\{[(Me_3Si)_2N]_2V\}$ systems.

Experimental Section

General Considerations. Standard inert atmosphere glovebox and Schlenk-line techniques were employed for all manipulations. All solvents were predried over 4 Å molecular sieves, and in the case of benzene, hexanes, diethyl ether, and tetrahydrofuran (THF), the solvents were distilled from purple sodium/benzophenone ketyl under N_2. Tetramethylethylenediamine (TMEDA) and hexamethyldisiloxane (HMDSO) were distilled from sodium, while acetonitrile was distilled from CaH_2. $[(Me_3Si)_2N]_2VX(THF)$ (X = Cl,[19] Me[13]), $MgPh_2$,[20] Ph_2CN_2,[21] and $(THF)_xLi_2C_2$[22] were prepared according to literature procedures. A diethyl ether solution of LiMe was purchased from Aldrich. Styrene oxide was distilled and degassed prior to use. CuCl was dried overnight under vacuum at 160 °C. Samples for IR spectroscopy were prepared as mineral oil mulls between KBr plates. Conductivity measurements were made in acetonitrile at ambient temperature. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a 300 MHz spectrometer at ambient temperature, using C_6D_6 as the solvent unless otherwise noted. ^{51}V NMR spectra were measured at 78.94 MHz and externally referenced to neat $VOCl_3$ at 0 ppm. Melting points were determined under N_2 in flame-sealed capillary tubes. Magnetic susceptibility measurements were made by the method of Evans[23,24] and are uncorrected. C, H, N and EIMS analyses were performed at the analytical facilities within the College of Chemistry, University of California, Berkeley. X-ray data were collected and the structures solved at the University of California at Berkeley chemistry X-ray facility (CHEXRAY, Dr. F. J. Hollander, supervisor).

$[(Me_3Si)_2N]_2VCl_2$. $[(Me_3Si)_2N]_2VCl(THF)$ (7.84 g, 16.4 mmol) and CuCl (1.62 g, 16.4 mmol) were mixed with THF (100 mL), giving a deep red solution and a precipitate of metallic Cu. After the mixture was stirred for 1 h, the volatile materials were removed under reduced pressure. The solid was extracted with hexanes (125 mL and 30 mL), and the filtrate was stripped dry under reduced pressure. The solid was then extracted with MeCN (125 mL and 50 mL), filtered, and then concentrated to ca. 100 mL and cooled to −25 °C. Red crystals (4.36 g, 60%) of the product were isolated in two crops by filtration. Mp: 95−105 °C (dec). ^1H NMR (0.10 M): δ 0.6 ($\Delta\nu_{1/2}$ ca. 135 Hz). IR: 1406 (m), 1266 (s sh), 1263 (s), 1155 (w), 1096 (w), 847 (s), 790 (s), 711 (s), 677 (s), 642 (s) cm^{-1}. $\mu_{eff} = 1.68\ \mu_B$ (C_6D_6). Anal. Calcd for $C_{12}H_{36}Cl_2N_2Si_4V$: C, 32.56; H, 8.20; N, 6.33. Found: C, 32.63; H, 8.33; N, 6.16.

$[(Me_3Si)_2N]_2V(Cl)(Me)$. Method A. $[(Me_3Si)_2N]_2VMe(THF)$ (1.02 g, 2.23 mmol) and CuCl (222 mg, 2.24 mmol) were mixed with THF (30 mL). The mixture turned green, and over about 10 s it became red with metallic Cu apparent. After the mixture was stirred for 10 min, the volatile materials were removed under reduced pressure. The red solid was extracted with hexanes (50 mL) and filtered. The filtrate was evaporated under reduced pressure to a red residue, which was extracted with MeCN (40 mL). The filtrate was concentrated to ca. 30 mL and cooled to −25 °C for 14 h. Red crystals of the product (735 mg, 78%) were isolated by filtration and dried under vacuum.

Method B. $[(Me_3Si)_2N]_2VCl(THF)$ (3.98 g, 8.30 mmol) was dissolved in THF (40 mL) and treated with LiMe (5.6 mL, 1.48 M in Et_2O). After the mixture was stirred for 1 h, it was added to CuCl (822 mg, 8.30 mmol), giving a deep red mixture along with metallic Cu. After the mixture was stirred for 6 h, the volatile materials were removed under reduced pressure. Extraction with MeCN (2 × 75 mL) and then Et_2O (30 mL) was followed by filtration and concentration of the combined filtrates. Cooling to −25 °C for 24 h yielded 2.15 g (61%) of brick-red product, which was isolated by filtration and dried under vacuum. Mp: 51−55 °C (dec). ^1H NMR (0.11 M): δ 1.1 ($\Delta\nu_{1/2}$ ca. 150 Hz). IR: 1404 (w), 1299 (w), 1261 (m sh), 1252 (s), 877 (vs), 856 (vs), 845 (vs), 791 (s), 765 (m), 715 (s), 676 (m), 656 (w), 646 (m), 618 (w), 575 (w), 542 (w), 508 (m), 440 (m) cm^{-1}. $\mu_{eff} = 1.69\ \mu_B$ (C_6D_6). EIMS: 421 (M^+, correct isotope pattern). Anal. Calcd for $C_{13}H_{39}ClN_2Si_4V$: C, 36.98; H, 9.31; N, 6.64. Found: C, 36.85; H, 9.27; N, 6.63.

$[(Me_3Si)_2N]_2V(Cl)(Ph)$. $[(Me_3Si)_2N]_2VCl(THF)$ (1.03 g, 2.15 mmol) and $MgPh_2$ (192 mg, 1.08 mmol) were mixed with THF (30 mL), giving a deep blue solution. After 1.5 h, the mixture was added to CuCl (213 mg, 2.15 mmol), giving a dark orange-red mixture. After the mixture was stirred overnight, the volatile materials were removed under reduced pressure. The residue was extracted with hexanes (50 mL), and the filtrate was stripped dry under reduced pressure, leaving an oily residue that was redissolved in 20 mL of MeCN. Concentration, followed by cooling to −25 °C, afforded 440 mg (42%) of brick-red crystals, which were isolated by filtration and dried under vacuum. Mp: 82−86 °C (dec). ^1H NMR (0.08 M): δ 1.1 ($\Delta\nu_{1/2}$ ca. 325 Hz). IR: 1301 (w), 1265 (m sh), 1252 (s), 1053 (w), 993 (w), 879 (s), 850 (vs), 790 (s), 767 (m), 710 (s), 693 (m), 676 (m), 658 (w), 646 (m), 589 (w), 453 (w), 439 (m), 426 (m), 405 (m) cm^{-1}. $\mu_{eff} = 1.69\ \mu_B$ (C_6D_6). Anal. Calcd for $C_{18}H_{41}ClN_2Si_4V$: C, 44.64; H, 8.53; N, 5.78. Found: C, 44.27; H. 8.64; N, 5.81.

$[Li(TMEDA)_2]\{[(Me_3Si)_2N]_2VCl_2\}$. $[(Me_3Si)_2N]_2VCl(THF)$ (1.53 g, 3.20 mmol) and $Li_2C_2\cdot 0.17(THF)$ (165 mg, 3.29 mmol) were mixed with Et_2O (30 mL). The blue-green mixture gradually darkened to black, and after 15 min TMEDA (1.5 mL, 9.9 mmol) was added. After 24 h, the volatile materials were removed under reduced pressure. The black solid was extracted with Et_2O (25 mL), and the solution was filtered from some pyrophoric black solid. Concentration of the filtrate to ca. 10 mL followed by slow-cooling to −25 °C for 24 h afforded 965 mg (44% on V) of purple needles, which were isolated by filtration and dried under vacuum. Hydrocarbon solutions of the salt have a blue appearance. Large, purple, tabular crystals may be grown by slowly recrystallizing the material from diethyl ether. Mp: 97−99 °C (dec). ^1H NMR (CD_3CN, 300 MHz): δ 2.8 (SiMe_3, $\Delta\nu_{1/2}$ ca. 200 Hz), 2.32 (s, 8H, TMEDA-CH_2), 2.17 (s, 24H, TMEDA-CH_3). IR: 1359 (m), 1292 (m), 1242 (s), 1186 (w), 1163 (m), 1132 (m), 1101 (w), 1070 (w), 1036 (m), 1017 (m), 948 (s), 924 (vs), 886 (s), 852 (s), 837 (s), 783 (s), 762 (m), 722 (w), 692 (m), 669 (m), 635 (m), 615 (w) cm^{-1}. $\mu_{eff} = 2.64\ \mu_B$ (C_6D_6). Λ_M (MeCN, 1.29×10^{-3} M): 92 S cm^2 mol^{-1}. Anal. Calcd for $C_{24}H_{68}Cl_2LiN_6Si_4V$: C, 42.27; H, 10.05; N, 12.32. Found: C, 42.36; H, 10.05; N, 12.29.

$[Li(TMEDA)_2]\{[(Me_3Si)_2N]_2VMe_2\}$. A Et_2O solution of LiMe (4.0 mL, 5.9 mmol) was added to 20 mL of Et_2O. TMEDA (0.90 mL, 6.0 mmol) was then added, followed by a Et_2O solution (20 mL) of $[(Me_3Si)_2N]_2VCl(THF)$ (1.42 g, 2.96 mmol). The mixture turned deep blue and was stirred for 2 h before the volatile materials were removed under reduced pressure leaving a blue solid. Extraction with Et_2O (25 mL), followed by concentration and cooling of the filtrate to −25 °C for 24 h, afforded 1.26 g (66% on V) of blue crystals. Mp: 146−148 °C (dec). ^1H NMR (CD_3CN, 300 MHz): δ 2.34 (s, 4H, TMEDA-

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C*H*$_2$), 2.19 (s, 12H, TMEDA-C*H*$_3$); a broad, low intensity signal whose maximum lay just downfield of the TMEDA-CH$_2$ signal tailed out to ca. 3 ppm. IR: 1357 (m), 1291 (s), 1236 (s), 1185 (m), 1162 (m), 1130 (m), 1099 (m), 1066 (m), 1037 (s), 1019 (s), 975 (vs), 887 (s), 864 (vs), 842 (vs), 788 (s), 778 (s), 755 (m), 722 (w), 698 (m), 666 (s), 625 (s), 612 (m), 588 (w), 533 (w), 485 (m) cm^{-1}. $\mu_{\mathrm{eff}} = 2.57\ \mu_{\mathrm{B}}$ (CD_3CN). Λ_{M} (MeCN, 1.24×10^{-3} M): 92 S cm^2 mol^{-1}. Anal. Calcd for $C_{26}H_{74}LiN_6Si_4V$: C, 48.71; H, 11.63; N, 13.11. Found: C, 48.44; H, 11.46; N, 13.98.

{[(Me$_3$Si)$_2$N]$_2$VMe}$_2$(*μ*-O). A hexanes solution (40 mL) of [(Me$_3$Si)$_2$N]$_2$VMe(THF) (804 mg, 1.75 mmol) was treated with PhCH(O)CH$_2$ (0.10 mL, 0.88 mmol), giving a forest-green mixture that was stirred for 16 h. The volatiles were removed under reduced pressure, and the solid was extracted with HMDSO (2 × 30 mL). The extracts were filtered and concentrated to ca. 15 mL. Cooling to −25 °C for 24 h afforded 450 mg (65%) of dark crystals, which were dried under vacuum. The crystals dissolved giving forest-green solutions. Mp: 111−113 °C (dec). ^{1}H NMR (0.08 M): δ 1.85 ($\Delta\nu_{1/2}$ ca. 90 Hz). IR: 1264 (m sh), 1251 (s), 882 (s), 858 (s), 786 (m), 750 (m), 709 (s), 672 (m), 657 (s), 643 (m), 557 (m), 503 (m) cm^{-1}. $\mu_{\mathrm{eff}} = 2.46\ \mu_{\mathrm{B}}$ (1.74 μ_{B} per V, C_6D_6). Anal. Calcd for $C_{26}H_{78}N_4OSi_8V_2$: C, 39.55; H, 9.96; N, 7.10. Found: C, 39.32; H, 9.91; N, 6.85.

Generation of [(Me$_3$Si)$_2$N]$_2$V(O)(Me). Method A. A C_6D_6 solution (ca. 0.5 mL) of [(Me$_3$Si)$_2$N]$_2$VMe(THF) (8.6 mg, 0.019 mmol) in a Teflon sealable NMR tube was treated with PhCH(O)CH$_2$ (2.1 *μ*L, 0.018 mmol), giving a green solution. Analysis by ^{1}H NMR spectroscopy showed a mixture of styrene oxide, styrene, [(Me$_3$Si)$_2$N]$_2$V(O)(Me), and {[(Me$_3$Si)$_2$N]$_2$VMe}$_2$(*μ*-O). After 24 h, the solution was a clear yellow and analysis by ^{1}H NMR indicated the presence of only styrene and [(Me$_3$Si)$_2$N]$_2$V(O)(Me) in solution.

Method B. A C_6D_6 solution (ca. 0.5 mL) of {[(Me$_3$Si)$_2$N]$_2$VMe}$_2$(*μ*-O) (22.5 mg, 0.0285 mmol) in a Teflon sealable NMR tube was treated with PhCH(O)CH$_2$ (3.2 *μ*L, 0.028 mmol). After 24 h, the initially green mixture was clear yellow. Analysis by ^{1}H NMR spectroscopy showed only styrene and [(Me$_3$Si)$_2$N]$_2$V(O)(Me). ^{1}H NMR: δ 1.29 (s, 3H, V−*Me*, $\Delta\nu_{1/2}$ ca. 25 Hz), 0.39 (s, 36H, Si*Me*$_3$). ^{51}V NMR (78.94 MHz): δ 222 ($\Delta\nu_{1/2}$ ca. 180 Hz). IR: 1251 (vs), 1093 (w br), 1014 (s, $\nu_{\mathrm{V=O}}$), 900 (s), 846 (vs), 794 (s), 766 (m), 719 (s), 677 (m), 646 (m), 620 (w), 588 (w br), 523 (w), 461 w cm^{-1}.

[(Me$_3$Si)$_2$N]$_2$V(O)(Ph). THF (20 mL) was added to a mixture of [(Me$_3$Si)$_2$N]$_2$VCl(THF) (0.45 g, 0.94 mmol) and MgPh$_2$ (84 mg, 0.47 mmol), giving a deep blue solution. After 10 min, PhCH(O)CH$_2$ (130 *μ*L, 1.14 mmol) was added. The solution at first became green, but over a few seconds it turned clear orange. After 5 min, the volatile materials were removed under reduced pressure, leaving an orange oily residue. Extraction with hexanes (50 mL), filteration of the extract through a frit padded with Celite, and removal of the solvent under vacuum left the product as a dark orange-red oil (355 mg, 81%). ^{1}H NMR: δ 7.78 (s, 2H, *o*-Ph), 6.97 (m, 3H, *m*- and *p*-Ph), 0.38 (s, 36H, −Si*Me*$_3$). ^{51}V NMR (78.94 MHz): δ 101 ($\Delta\nu_{1/2}$ ca. 235 Hz). IR (KBr, neat): 1422 (m), 1405 (m), 1253 (vs), 1113 (m), 1060 (m), 1011 (s), 994 (m), 950 (m), 847 (vs), 766 (m), 720 (s), 694 (m), 677 (m), 646 (m), 620 (w) cm^{-1}.

[(Me$_3$Si)$_2$N]$_2$V(Cl)(N$_2$CPh$_2$). A hexanes solution (40 mL) of [(Me$_3$Si)$_2$N]$_2$VCl(THF) (1.41 g, 2.94 mmol) was added to a flask containing Ph$_2$CN$_2$ (570 mg, 2.93 mmol), resulting in a dark orange-red mixture. After the mixture was stirred for 5 min, the volatile materials were removed under reduced pressure, leaving a sticky residue. Extraction with MeCN (60 mL) and then THF (60 mL) was followed by filtration and concentration of the combined extracts to ca. 20 mL. Cooling the mixture to −25 °C for several days afforded dark red-brown crystals (442 mg, 25%), which were isolated by filtration and dried under vacuum. Mp: 91−95 °C (dec). ^{1}H NMR (400 MHz, 22 °C): δ 7.69 ("d of d", 4H, *o*-Ph and *o*-Ph′), 7.25 (t, 2H, $J = 7.6$ Hz, *m*-Ph), 7.10 (t, 1H, $J = 7.4$ Hz, *p*-Ph), 7.02 (m, 3H, *m*- and *p*-Ph′), 0.42 (s, 36H, −Si*Me*$_3$). ^{1}H NMR (400 MHz, 97 °C): δ 7.71 ("d", 4H, *o*-Ph), 7.21−7.13 (m, 6H, *m*- and *p*-Ph), 0.45 (s, 36H, −Si*Me*$_3$). ^{13}C{^{1}H} NMR (100 MHz, 23 °C): δ 157.5 (N$_2$*C*Ph$_2$), 135.5, 134.8 (*i*-Ph), 131.1 (*o*- or *m*-Ph), 130.9 (*p*-Ph), 130.5 (*p*-Ph′), 129.9 (*o*- or *m*-Ph′), 128.7 (coincident *o*- or *m*-Ph and Ph′), 5.7 (−Si*Me*$_3$). ^{13}C{^{1}H} NMR (100 MHz, 97 °C): δ 135.6 (*i*-Ph), 130.6 (*o*- or *m*-Ph), 130.4 (*p*-Ph), 128.7 (*o*- or *m*-Ph). ^{51}V NMR (78.94 MHz): δ 285 ($\Delta\nu_{1/2}$ ca. 485 Hz). IR: 1331 (m), 1262 (m), 1249 (s), 1218 (w), 1075 (m), 1040 (m), 952 (w), 881 (s), 845 (s), 787 (s), 722 (m), 699 (m), 689 (m), 672 (m), 644 (w), 559 (w) cm^{-1}. Anal. Calcd for $C_{25}H_{46}ClN_4Si_4V$: C, 49.93; H, 7.71; N, 9.32. Found: C, 50.18; H, 7.91; N, 9.26.

X-ray Crystallography. A summary of crystal data, data collection, and refinement for all crystallographically characterized compounds is given in Table 1. A list of selected bond lengths and bond angles is given in Table 2.

[(Me$_3$Si)$_2$N]$_2$VCl$_2$. Red crystals were grown from acetonitrile at −25 °C. A suitable crystal was mounted on a glass capillary under Paratone-N hydrocarbon oil. The crystal was transferred to a Siemens SMART diffractometer/CCD area detector[25] and cooled by a nitrogen-flow low-temperature apparatus which had been previously calibrated by a thermocouple placed at the same temperature as the crystal. A preliminary orientation matrix and unit cell parameters were determined by collecting 60, 10 s frames, followed by spot integration and least-squares refinement. A hemisphere of data was collected using 0.3° ω scans at 10 s per frame. The raw data were integrated (*XY* spot spread = 1.60°; *Z* spot spread = 0.60°), and the unit cell parameters were refined (7930 reflections with $I > 10\sigma(I)$) using SAINT.[26] The acentric, orthorhombic space group $P2_12_12_1$ (No. 19) was uniquely defined by the systematic absences. Preliminary data analysis and a semiempirical ellipsoidal absorption correction ($T_{\mathrm{min}} = 0.755$; $T_{\mathrm{max}} = 0.841$; merging R_{int} before/after correction = 0.0334/0.0302) were performed using XPREP.[27] Of the 9928 reflections measured, 3479 were unique and 3039 had $I > 3\sigma(I)$ and were used in the refinement. Redundant reflections were averaged. The data were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied. The structure was solved by direct methods using the TEXSAN software package[28] on a Digital microvax workstation and refined using standard least-squares and Fourier techniques. A conformational disorder involving V and the N(2) amide ligand across a virtual mirror plane passing through N(1), N(2), and Cl(2) was refined, resulting in partial occupancies of 0.844 for V(1), Si(3), Si(4), and C(8). The occupancies of V(2), Si(5), Si(6), and Cl(3) were constrained to sum to full occupancy. The position of the low-occupancy carbon atom near Cl(1) was not resolved. All of the full occupancy non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms for the ordered −N(SiMe$_3$)$_2$ group were fixed at idealized positions (C−H = 0.95 Å). Assignment of the correct enantiomorph was indicated by refinement of the Flack parameter to −0.0404(83). Neutral atomic scattering factors were taken from Cromer and Waber,[29] and anomalous dispersion effects[30] were included in F_{c}. The final residuals for 202 variables refined against 3039 data for which $I > 3\sigma(I)$ were $R = 0.0381$, $R_{\mathrm{w}} = 0.0570$, and GOF = 2.083.

[Li(TMEDA)$_2$]{[(Me$_3$Si)$_2$N]$_2$VCl$_2$}. Data collection and integration were carried out as described above. The space group $P2_1/c$ (No. 14) was uniquely defined by the systematic

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

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

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

(28) *TEXSAN: Crystal Structure Analysis Package*; Molecular Structure Corp.: 1992.

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

(30) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

Table 1. Summary of X-ray Diffraction Data: $[N] = N(SiMe_3)_2$; $[Li] = Li(TMEDA)_2$

	$[N]_2VCl_2$	$[Li]\{[N]_2VCl_2\}$	$[Li]\{[N]_2VMe_2\}$	$[N]_2VCl(N_2CPh_2)$
formula	$C_{12}H_{36}Cl_2N_2Si_4V$	$C_{24}H_{68}Cl_2LiN_6Si_4V$	$C_{26}H_{74}LiN_6Si_4V$	$C_{25}H_{46}ClN_4Si_4V$
mol wt	442.62	681.97	641.14	601.40
source, color, habit	MeCN, red, tabular	hexanes, purple, acicular	ether, blue, equant	hexanes, red-brown, equant
cryst size (mm)	0.36 × 0.25 × 0.13	0.39 × 0.35 × 0.25	0.49 × 0.35 × 0.30	0.34 × 0.30 × 0.28
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$P2_12_12_1$	$P2_1/c$	$P2_1/c$	$P2_1/n$
T (°C)	−145	−157	−122	−117
a (Å)	12.5250(2)	19.2175(2)	21.2683(1)	9.4017(3)
b (Å)	13.2145(1)	22.4030(1)	13.5551(2)	32.088(6)
c (Å)	14.6238(3)	19.4357(3)	29.0793(2)	11.5636(3)
α (deg)	90	90	90	90
β (deg)	90	96.749(1)	93.113(1)	107.050(1)
γ (deg)	90	90	90	90
vol (Å^3)	2420.40(8)	8309.61(15)	8371.00(25)	3335.23(23)
Z	4	8	8	4
ρ_{calcd} (g cm^{-3})	1.22	1.00	1.02	1.20
μ (cm^{-1})	8.25	4.44	3.73	5.41
diffractometer	Siemens, CCD/ area detector	Siemens, CCD/ area detector	Siemens, CCD/ area detector	Siemens, CCD/ area detector
radiation (λ)	Mo Kα (0.710 73 Å)	Mo Kα (0.710 73 Å)	Mo Kα (0.710 73 Å)	Mo Kα (0.710 73 Å)
scan mode	ω (0.3° scans)	ω (0.3° scans)	ω (0.3° scans)	ω (0.3° scans)
collcn range	hemisphere	hemisphere	hemisphere	hemisphere
total no. of reflcns	9928	34 748	34 349	14 090
no. of unique reflns	3479	12 274	12 508	4888
R_{int}	0.038	0.0327	0.0427	0.0281
abs type	semiempirical, XPREP	semiempirical, XPREP	semiempirical, XPREP	none
transm coeff	0.755−0.841	0.828−0.893	0.730−0.885	NA
structure soln	direct methods, TEXSAN	direct methods, TEXSAN	direct methods, TEXSAN	direct methods, TEXSAN
no. of obs (n_o), $I > 3\sigma(I)$	3039	8561	7259	3910
no. of params refined (n_v)	202	685	660	500
final R,[a] R_w[b]	0.0381, 0.0570	0.0451, 0.0575	0.0820, 0.1038	0.0298, 0.0421
GOF[c]	2.083	2.051	3.471	1.764

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

Table 2. Selected Metrical Data for Crystallographically Characterized Compounds

$[(Me_3Si)_2N]_2VCl_2$		$[Li(TMEDA)_2]\{[(Me_3Si)_2N]_2VCl_2\}$		$[Li(TMEDA)_2]\{[(Me_3Si)_2N]_2VMe_2\}$		$[(Me_3Si)_2N]_2V(Cl)(N_2CPh_2)$	
			Bond Distances (Å)				
V(1)−N(1)	1.847(4)	V(1)−Cl(1)	2.311(1)	V(1)−N(1)	2.031(6)	V−Cl	2.2454(7)
V(1)−N(2)	1.842(4)	V(1)−Cl(2)	2.309(1)	V(1)−N(2)	2.011(6)	V−N(1)	1.851(1)
V(1)−Cl(1)	2.211(2)	V(1)−N(1)	1.936(3)	V(1)−C(1)	2.096(8)	V−N(2)	1.879(2)
V(1)−Cl(2)	2.222(2)	V(1)−N(2)	1.949(3)	V(1)−C(2)	2.124(8)	V−N(3)	1.683(2)
N(1)−Si(1)	1.774(4)	V(2)−Cl(3)	2.299(1)	N(1)−Si(1)	1.711(6)	N(3)−N(4)	1.328(3)
N(1)−Si(2)	1.796(4)	V(2)−Cl(4)	2.306(1)	N(1)−Si(2)	1.722(6)	N(4)−C(13)	1.295(3)
N(2)−Si(3)	1.772(4)	V(2)−N(3)	1.946(3)	N(2)−Si(3)	1.709(6)	C(13)−C(14)	1.487(4)
N(2)−Si(4)	1.807(4)	V(2)−N(4)	1.949(3)	N(2)−Si(4)	1.729(6)	C(13)−C20)	1.483(4)
N(2)−Si(5)	1.84(1)	Li(1)−N$_{av}$	2.13(1)				
N(2)−Si(6)	1.75(1)	Li(2)−N$_{av}$	2.13(2)				
			Bond Angles (deg)				
N(1)−V(1)−N(2)	118.5(2)	Cl(1)−V(1)−Cl(2)	103.42(5)	N(1)−V(1)−N(2)	124.0(2)	Cl−V−N(1)	106.89(7)
N(1)−V(1)−Cl(1)	103.1(1)	Cl(1)−V(1)−N(1)	109.1(1)	N(1)−V(1)−C(1)	101.4(3)	Cl−V−N(2)	113.75(7)
N(1)−V(1)−Cl(2)	111.2(1)	Cl(1)−V(1)−N(2)	107.5(1)	N(1)−V(1)−Cl2)	111.2(3)	Cl−V−N(3)	106.10(7)
N(2)−V(1)−Cl(1)	113.0(1)	Cl(2)−V(1)−N(1)	103.2(1)	N(2)−V(1)−C(1)	112.5(3)	N(1)−V−N(2)	117.79(9)
N(2)−V(1)−Cl(2)	102.2(1)	Cl(2)−V(1)−N(2)	114.5(1)	N(2)−V(1)−C(2)	104.0(3)	N(1)−V−N(3)	105.5(1)
Cl(1)−V(1)−Cl(2)	108.83(7)	N(1)−V(1)−N(2)	118.0(1)	C(1)−V(1)−C(2)	101.8(3)	N(2)−V−N(3)	105.9(1)

absences. The structure was solved and refined as above. The final residuals for 685 variables refined against 8561 data for which $I > 3\sigma(I)$ were $R = 0.0451$, $R_w = 0.0575$, and GOF = 2.051.

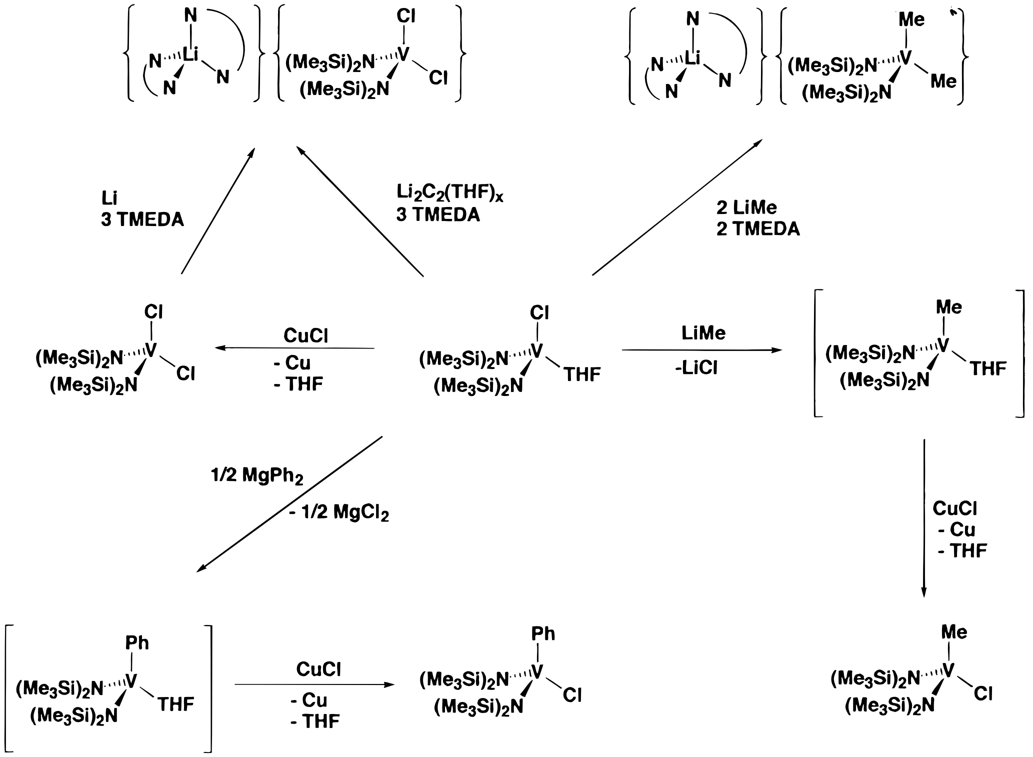
$[Li(TMEDA)_2]\{[(Me_3Si)_2N]_2VMe_2\}$. All aspects, from data collection to solution and refinement of the structure, were as described above. The space group $P2_1/c$ was uniquely defined by the systematic absences. The molecule crystallized as well-separated cations and anions with two molecules per asymmetric unit ($Z = 8$). In one of the anions, there existed a conformational disorder (analogous to that described for $[(Me_3Si)_2N]_2VCl_2$) across a virtual mirror plane defined approximately by N(7), N(8), and the midpoint of the vector joining V(2) and V(3). A model employing major (75%) and minor (25%) conformations was employed with moderate success, as indicated by the final agreement factors. The Li(TMEDA) cations and the ordered anion were well-behaved. All non-hydrogen atoms (except the silicon and carbon atoms of the disordered $-N(SiMe_3)_2$ ligand) were refined with anisotropic thermal parameters. Hydrogen atoms were included on the three ordered $-N(SiMe_3)_2$ ligands and on the TMEDA ligands at idealized positions. The final residuals for 660 variables refined against 7259 data for which $I > 3\sigma(I)$ were $R = 0.0820$, $R_w = 0.1038$, and GOF = 3.471.

$[(Me_3Si)_2N]_2VCl(N_2CPh_2)$. All aspects, from data collection to solution and refinement of the structure, were as described above. The space group $P2_1/n$ (No. 14) was uniquely defined by the systematic absences. All non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were located and refined with isotropic thermal parameters. The final residuals for 500 variables refined against 3910 data for which $I > 3\sigma(I)$ were $R = 0.0298$, $R_w = 0.0421$, and GOF = 1.764.

Results and Discussion

Neutral V(IV) Species. Drawing from established research on vanadocene systems, where Cp_2VCl_2 may

Scheme 1



be obtained[31] by reaction of Cp_2VCl with CuCl, $[(Me_3Si)_2N]_2VCl(THF)$ underwent one-electron oxidation by CuCl to yield $[(Me_3Si)_2N]_2VCl_2$ (Scheme 1). Likewise, $[(Me_3Si)_2N]_2VR(THF)$ (R = Me, Ph[32]) reacted with CuCl to yield the methyl−chloride and phenyl−chloride V(IV) organometallic products (Scheme 1). We note that $Cp_2V(Cl)(Me)$ is the lone example of a mixed halide−hydrocarbyl that is stable within the Cp_2V ligand system.[33,34]

The redox reactions proceeded rapidly in THF, as a color change from blue to red along with precipitation of elemental copper were immediately apparent on mixing the reactants. The red products are exceedingly soluble in hydrocarbons and were crystallized from MeCN to afford the first crops of material in 40−60% yields. This latter point highlights the decreased reactivity of these V(IV) hydrocarbyls relative to V(III) species of the type $[(Me_3Si)_2N]_2VRL$ which rapidly add their V−C bonds across the C−N bonds of both nitriles and isocyanides.[13,35] Solution-state magnetic moments of 1.7 μ_B are indicative of a d^1electronic configuration and are consistent with the products as formulated. The X-ray crystal structure of $[(Me_3Si)_2N]_2VCl_2$ has been determined (see below). Similar to other structurally characterized early metal $-N(SiMe_3)_2$ complexes, the amides are planar at nitrogen, indicating that they are probably acting as three-electron donors ($1\sigma + 2\pi$) toward the metal center, resulting in a formal electron count about the vanadium of 13 in these species.[36]

Since reactions between VCl_4 and strong alkylating reagents can be highly dependent on the reaction conditions and countercations, we view these transformations as mild, oxidative routes to $(R_2N)_2VX_2$ or $(R_2N)_2VXR$ vanadium(IV) species that may not be cleanly obtainable from reactions of V(IV) sources with highly reducing $-NR_2$ anions. Hoffman and co-workers have reported congeneric group 5 species that are obtained using different synthetic methodologies. The Nb(IV) dihalide $[(Me_3Si)_2N]_2NbCl_2$,[14,15] available from $NbCl_4(THF)_2$ and $LiN(SiMe_3)_2$, may be converted to $[(Me_3Si)_2N]_2Nb(Cl)(Ph)$[37] on treatment with $ZnPh_2$. Reduction of Andersen's $[(Me_3Si)_2N]_2TaCl_3$[38] with Na/Hg affords $[(Me_3Si)_2N]_2TaCl_2$[16,17] in 64% yield. It is noteworthy that bis(amide)titanium(IV) alkyl iodides have recently been prepared by substitution of a $-NMe_2$ with I or by monoalkylation of a bis(amide)titanium(IV) diiodide.[39]

We assume the mechanism of the above reactions involves initial oxidation of $[(Me_3Si)_2N]_2VX(THF)$ (X = Cl, Me, Ph) to $\{[(Me_3Si)_2N]_2VX(THF)\}^+$, followed by an associative displacement of THF by chloride. In an attempt to synthesize cationic $\{[(Me_3Si)_2N]_2VMe(THF)\}^+$ by using a less nucleophilic anion, a THF solution of the neutral V(III)−methyl was treated with $AgBPh_4$ in THF. Although the reaction was immediate, a pure

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[31] Gladyshev, E. N.; Bayushkin, P. Y.; Cherkasov, V. K.; Sokolov, V. S. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1979**, *28*, 1070.

[32] Although the V(III)−Ph complex could not be isolated as a stable solid, persistent blue solutions formed from the reaction of $[(Me_3Si)_2N]_2VCl(THF)$ and 0.5 equiv of $MgPh_2$ in THF behave as if they contain "$[(Me_3Si)_2N]_2VPh(THF)$". It is likely that the instability of the complex stems from facile dissociation of THF followed by metallation of a $-N(SiMe_3)_2$ ligand. Gerlach, C. P.; Arnold, J. Manuscript in preparation.

[33] Razuvaev, G. A.; Korneva, S. P.; Vyshinskaya, L. I.; Mar'in, V. P.; Cherkasov, V. K. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1978**, *27*, 605.

[34] Razuvaev, G. A.; Bayushkin, P. Y.; Cherkasov, V. K.; Gladyshev, E. N.; Phokeev, A. P. *Inorg. Chim. Acta* **1980**, *44*, L103.

[35] Gerlach, C. P.; Arnold, J. Manuscript in preparation.

[36] The covalent convention is followed in counting electrons. See: Crabtree, R. H. *The Organometallic Chemistry of the Elements*, 2nd ed.; Wiley: New York, 1994.

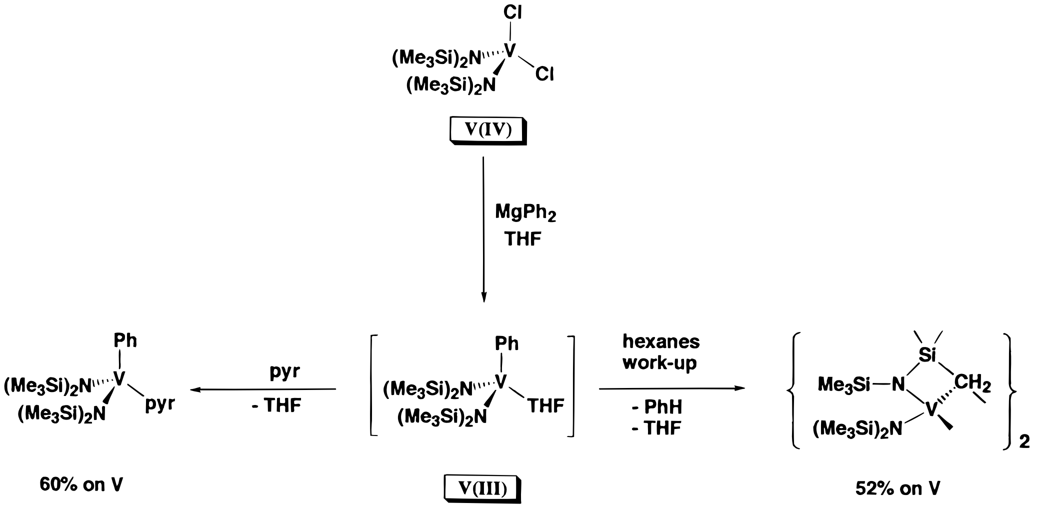
[37] Bott, S. G.; Hoffman, D. M.; Rangarajan, S. P. *J. Chem. Soc., Dalton Trans.* **1996**, 1979.

[38] Andersen, R. A. *Inorg. Chem.* **1979**, *18*, 3622.

[39] Johnson, A. R.; Davis, W. M.; Cummins, C. C. *Organometallics* **1996**, *15*, 3825.

[40] While a persistent color change from green-blue to blue was observed on treating $[(Me_3Si)_2N]_2VCl(THF)$ with sources of Et^-, we have no evidence that indicates the identity of the product one way or another and have not been successful in isolating either a product or product-derivative from these mixtures.

Scheme 2



product could not be isolated from the dark brown mixture. Blue solutions of putative $[(Me_3Si)_2N]_2VEt(THF)$,[40] from alkylation of $[(Me_3Si)_2N]_2VCl(THF)$ with EtMgCl or $MgEt_2$, also reacted quickly with CuCl in THF, but the expected $[(Me_3Si)_2N]_2V(Cl)(Et)$ could not be isolated. Our inability to isolate either a V(III)− or V(IV)−alkyl with β-hydrogens in this system may be compared to the decomposition of Cp_2VXR complexes when the R group contains β-hydrogen atoms.[41]

Our initial attempts at synthesizing dialkyl, diaryl, or mixed alkyl−aryl V(IV) species suggested that the reactions were solvent and temperature dependent, as indicated above for alkylations of VCl_4. For example, reaction of $[(Me_3Si)_2N]_2VCl_2$ with $MgPh_2$ in THF at room temperature (Scheme 2) gave a blue solution that most likely contained "$[(Me_3Si)_2N]_2VPh(THF)$". Work-up of the reaction mixture in hexanes led to violet mixtures from which the known[42] dimeric $\{[(Me_3Si)_2N]V[\mu\text{-}CH_2SiMe_2NSiMe_3]\}_2$ was isolated in 55% yield. Given the crowded coordination sphere about the metal center in four-coordinate $[(Me_3Si)_2N]_2V$ species, it is likely that loss of THF in $[(Me_3Si)_2N]_2VPh(THF)$ generates three-coordinate "$[(Me_3Si)_2N]_2VPh$", which then metalates a $-N(SiMe_3)_2$ ligand, loses benzene, and dimerizes. Addition of pyridine (pyr) to blue solutions of "$[(Me_3Si)_2N]_2VPh(THF)$" formed the stable $[(Me_3Si)_2N]_2VPh(pyr)$ (Scheme 2), which is more conveniently prepared from $[(Me_3Si)_2N]_2VCl(THF)$, 0.5 equiv of $MgPh_2$, and pyr.[35] In contrast, $[(Me_3Si)_2N]_2VCl_2$ and $MgPh_2$ react in cold (−60 °C) diethyl ether to give red mixtures that may contain the V(IV)−diphenyl complex; unfortunately, extreme solubility in hydrocarbon solvents has hampered adequate purification and characterization of the material (the compound separates from MeCN as an oil). Difficulties have also been noted in attempts to prepare Ta(IV) dialkyls from $[(Me_3Si)_2N]_2TaCl_2$;[17] nonetheless, the synthesis of $[(Me_3Si)_2N]_2TaPh_2$ in 65% yield was successful. Thus, as a class of compounds, d^1 $[(Me_3Si)_2N]_2MR_2$ species remain rare.

V(III) Anions. Given the stability of the 14-electron species $[(Me_3Si)_2N]_2VXL$, it seemed reasonable that 14-electron V(III) anions of the type $\{[(Me_3Si)_2N]_2VX_2\}^-$ would be accessible via the one-electron reduction of $[(Me_3Si)_2N]_2VX_2$ or by nucleophilic attack of X^- on $[(Me_3Si)_2N]_2VXL$. Thus, reaction between $[(Me_3Si)_2N]_2VCl(THF)$ and 2 equiv of LiMe in the presence of TMEDA afforded $[Li(TMEDA)_2]\{[(Me_3Si)_2N]_2VMe_2\}$ in 66% yield as highly air-sensitive, deep-blue crystals (Scheme 1). While the salt formed an oily suspension in benzene, it was soluble in acetonitrile or ethereal solvents giving ink-blue solutions. ^1H NMR spectra measured in CD_3CN showed sharp signals for the TMEDA ligand as well as a broad low intensity signal in the range 2.5−3.0 ppm, presumably for the anionic portion of the molecule. Magnetic susceptibility measurements made in this same solvent indicated a high spin d^2 electronic configuration ($\mu_{eff} = 2.57\ \mu_B$). The molar conductivity of acetonitrile solutions ($\Lambda_M = 92$ S $cm^2\ mol^{-1}$) was in accord with the behavior of a 1:1 electrolyte.[43] X-ray quality crystals of the complex were obtained on recrystallization from diethyl ether, and the experiment verified our proposed connectivity. The molecule crystallized as well-separated cations and anions as discussed below. Variable, low yields of an extremely air-sensitive, blue, paramagnetic compound were isolated when the reaction was carried out in the absence of TMEDA; however, due to the low yield and irreproducibility of the reaction, characterization of this material was not possible.

Attempts to extract hydride from $\{[(Me_3Si)_2N]_2VMe_2\}^-$ to give the V(V) methyl−methylidene complex with Ph_3CPF_6 or Et_3OBF_4 led to an as yet uncharacterized paramagnetic product in the first case and no reaction in the second.[44] Reaction with $B(C_6F_5)_3$ in C_6D_6 apparently led to abstraction of Me^- to generate the unstable intermediate $[(Me_3Si)_2N]_2VMe$, which, via metalation of a bis(silyl)amide ligand and loss of CH_4, gave dimeric $\{[(Me_3Si)_2N]V[[\mu\text{-}CH_2SiMe_2N(SiMe_3)]\}_2$ as the only detectable product by ^1H NMR spectroscopy.[45]

Attempts to prepare a lithiated vanadium acetylide in one step by reaction of Li_2C_2 wtih $[(Me_3Si)_2N]_2VCl(THF)$ led instead to the dichloride anion analog of the dimethyl complex discussed above. Purple needles

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[41] Sustmann, R.; Kopp, G. *J. Organomet. Chem.* **1988**, *347*, 325.

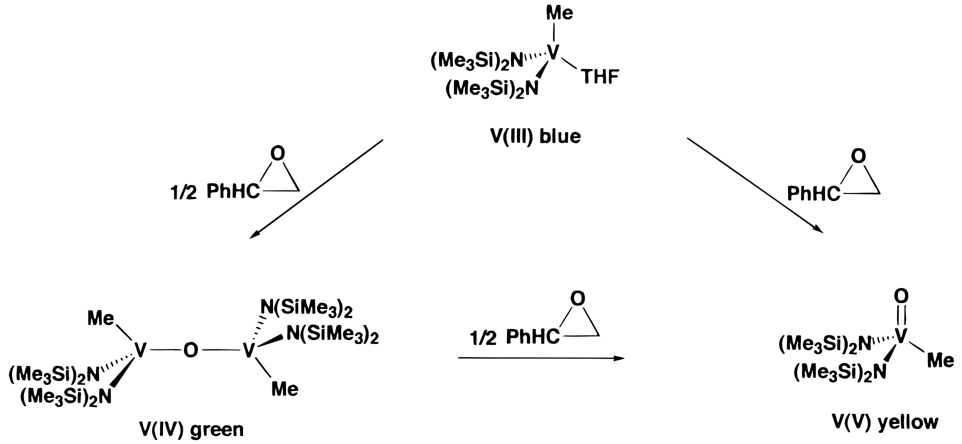
[42] Berno, P.; Minhas, R.; Hao, S.; Gambarotta, S. *Organometallics* **1994**, *13*, 1052.

[43] Angelici, R. J. *Synthesis and Technique in Inorganic Chemistry*; University Science Books: Mill Valley, CA, 1986.

[44] Conversely, the extraction of H^+ from cationic transition metal dimethyl complexes has successfully been used to synthesize methyl−methylidene complexes. See: Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98. Dawson, D. Y.; Arnold, J. *Organometallics* **1997**, *16*, 1111.

[45] Although the dimer is paramagnetic, C_6D_6 solutions show several low-intensity resonances in the ^1H NMR spectrum that are indicative of the complex. ^1H NMR (300 MHz, C_6D_6): δ 0.96, 0.64, 0.39, 0.21, −1.2.

Scheme 3



of $[Li(TMEDA)_2]\{[(Me_3Si)_2N]_2VCl_2\}$ were isolated in 40% yield based on vanadium from the reaction of $[(Me_3Si)_2N]_2VCl(THF)$ with 1 equiv of $Li_2C_2(THF)_x$ in the presence of TMEDA. Recrystallization of the complex from diethyl ether afforded purple, prismatic crystals which dissolved in hydrocarbon solvents to give blue solutions. In the absence of TMEDA, the reaction was messy and it is clear that the presence of the diamine assists in the chloride redistribution that has taken place during the course of the reaction. The lithium reduction of $[(Me_3Si)_2N]_2VCl_2$ in the presence of TMEDA also yielded the dichloride anion, although the product was not as clean as that isolated from the above route.

In contrast to the low solubility of the dimethyl anion, the dichloride salt dissolves in benzene, giving a solution magnetic moment of 2.64 μ_B at ambient temperature. Conductivity measurements indicated that it is a 1:1 electrolyte in acetonitrile ($\Lambda_M = 92$ S cm^2 mol^{-1}). In contrast to the ^{1}H NMR spectrum measured in C_6D_6, which showed two broadened signals at ca. 5.0 and 1.9 ppm, in CD_3CN sharp signals for the $Li(TMEDA)_2$ cation were observed at δ 2.32 (CH_2) and 2.17 (CH_3), along with a broadened signal ($\Delta\nu_{1/2}$ ca. 200 Hz) centered at ca. δ 2.8 for the anion. A crystallographic study (see below) verified the proposed connectivity shown in Scheme 1. We note that related "ate" complexes of Ti(III) have recently been reported where the Cl and Me ligands form bridges between bis(amide)titanium and Li(TMEDA) units.[39,46] The successful isolation of bis(amide)Ti and bis(amide)V halide ate complexes may be contrasted with the metallocene systems, where $[Cp_2MCl_2]^-$ (M = Ti, V) and $[Cp_2VCl]^-$ are rapidly susceptible to loss of Cl^-.[47]

Oxidations with $PhCH(O)CH_2$. We have previously shown that the V(III) bromide derivative $[(Me_3Si)_2N]_2VBr(THF)$ reacts with styrene oxide to yield $[(Me_3Si)_2N]_2V(O)(Br)$ as the kinetic product.[12] Curious as to whether organovanadium oxo complexes could be prepared in a similar manner, we investigated the reaction between $[(Me_3Si)_2N]_2VR(THF)$ (R = Me, Ph) and styrene oxide.

Treatment of a hexanes solution of $[(Me_3Si)_2N]_2VMe(THF)$ with 1 equiv of styrene oxide (Scheme 3) resulted in an immediate color change from blue to green and eventually clear yellow. Removal of the solvent yields $[(Me_3Si)_2N]_2V(O)(Me)$ as a dark-orange oil. Monitoring the reaction by ^{1}H NMR spectroscopy (C_6D_6) showed a broad signal at δ 1.85 that we attribute to the green intermediate (see below), which over several hours gave way to only signals for free styrene and $[(Me_3Si)_2N]_2V(O)(Me)$. The oxo−methyl complex was characterized by a sharp singlet at δ 0.39 for the $-SiMe_3$ groups and a singlet at δ 1.29 ($\Delta\nu_{1/2} = 25$ Hz) for the methyl group, broadened due to coupling to the quadropolar ^{51}V nucleus ($I = {}^7/_2$). A singlet in the ^{51}V NMR spectrum at δ 222 is consistent with a +5 oxidation state of the vanadium, and we assign a strong absorbance in the IR spectrum at 1014 cm^{-1} to the $\nu_{V=O}$.

The green intermediate was isolated cleanly from preparative-scale reactions between (i) 0.5 equiv of styrene oxide and $[(Me_3Si)_2N]_2VMe(THF)$ (Scheme 3) or (ii) $[(Me_3Si)_2N]_2VMe(THF)$ and $[(Me_3Si)_2N]_2V(O)(Me)$. The μ-O dimer is converted smoothly to $[(Me_3Si)_2N]_2V(O)(Me)$ on treatment with an additional equivalent of styrene oxide. Although extremely soluble in hexanes, the dimer crystallized nicely from HMDSO (65%) and the crystal structure confirmed the connectivity.[13] We tentatively assign a strong absorbance at 709 cm^{-1} in the IR spectrum to the linear V−O−V unit. The dimer is paramagnetic, and its magnetic moment of 2.46 μ_B (1.74 μ_B per V) indicates that, at least at room temperature in solution, there is negligible coupling of the unpaired spins and that the μ-oxo core is best described as bridging two V(IV), d^1 centers. Crystallographic data also rules out a mixed valence ground state, i.e., a V(V) oxo acting as a dative donor to a V(III) center, as the molecule crystallized with a C_2-axis passing through the μ-O resulting in one independent V−O distance of 1.7943(4) Å.[13] This contrasts with the μ-N derivatives of vanadium, which may possess both long and short V−N bonds,[48−51] and also with $[Cp_2TaMe]_2(\mu\text{-}S)$,[52] which is described as diamagnetic and possibly in equilibrium with $Cp_2Ta(Me)(S)$ and "Cp_2TaMe", i.e., Ta(V) and Ta(III) species. A broad signal at δ 1.85 in the ^{1}H NMR spectrum of the isolated material matches that for the observed intermediate in

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(46) Scoles, L.; Minhas, R.; Duchateau, R.; Jubb, J.; Gambarotta, S. *Organometallics* **1994**, *13*, 4978.

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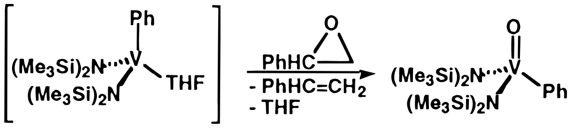
the one-step transformation of $[(Me_3Si)_2N]_2VMe(THF)$ to $[(Me_3Si)_2N]_2V(O)(Me)$.

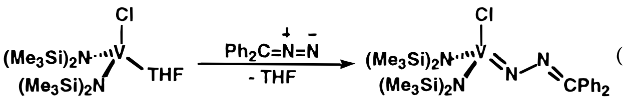
In regard to the kinetics of the reactions in Scheme 3, once $[(Me_3Si)_2N]_2V(O)(Me)$ is formed it must react with $[(Me_3Si)_2N]_2VMe(THF)$ faster than does styrene oxide. Nucleophilic addition of vanadium(V) oxo complexes to unsaturated Ti[53] species has recently been studied by Cummins and co-workers, and there is also precedent for this type of reaction between two vanadium centers in the literature.[54]

While the reaction of 0.5 equiv of styrene oxide with $[(Me_3Si)_2N]_2VPh(THF)$ gave persistent green mixtures, on workup the color changed to brown and the putative $\{[(Me_3Si)_2N]_2VPh\}_2(\mu\text{-}O)$ was not isolated. However, treatment of $[(Me_3Si)_2N]_2VPh(THF)$ with a full equivalent of styrene oxide yielded $[(Me_3Si)_2N]_2V(O)(Ph)$ as a dark red-orange oil in 81% yield (eq 1). ^1H and ^{51}V NMR data are consistent this formulation, and a strong absorbance at 1011 cm^{-1} in the IR spectrum is indicative of a terminal V=O functionality. At this point, we have no reasonable explanation for why an intermediate $\{[(Me_3Si)_2N]_2VPh\}_2(\mu\text{-}O)$ does not appear to be stable in the solid state, and attempts to isolate $[(Me_3Si)_2N]_2VMe(\mu\text{-}O)VPh[N(SiMe_3)_2]_2$ by reaction of $[(Me_3Si)_2N]_2V(O)(R)$ with $[(Me_3Si)_2N]_2VR'(THF)$ were also unsuccessful.



(1)

Reaction of $[(Me_3Si)_2N]_2VCl(THF)$ with Ph_2CN_2. Reaction of $[(Me_3Si)_2N]_2VCl(THF)$ with diphenyldiazomethane in hexanes gave a deep-red solution from which $[(Me_3Si)_2N]_2V(Cl)(N_2CPh_2)$ was isolated (eq 2).



(2)

The compound is extremely soluble in hydrocarbon solvents, but crystallization from a mixture of MeCN/THF afforded a crop of analytically pure material in 30% yield. X-ray structural data (see below) suggest that the vanadium center has been oxidized to the +5 state concomitant with a two-electron reduction of the diazoalkane moiety to an alkylidenehydrazido.[55] Sharp resonances in the ^1H, $^{13}C\{^1H\}$, and ^{51}V NMR spectra also indicate the species is best described as a d^0, diamagnetic compound.

A signal for the diazo-bound carbon was observed in the $^{13}C\{^1H\}$ NMR spectrum at δ 157.5. The aryl carbon signals for the two phenyl rings are inequivalent at room temperature (i.e., Ph and Ph′), indicating a slow rotation about one or more of the bonds in the $V{=}N{-}N{=}CPh_2$ unit. On warming the sample, the signals coalesced at 55 °C. Further heating to 95 °C sharpened the signals such that a single set of four phenyl ^{13}C resonances is observed in the spectrum. Although metallodiazoalkane complexes have long been recognized as precursors to alkylidenes via loss of dinitrogen,[56–59] no evidence for this type of reactivity was found in the present case. $[(Me_3Si)_2N]_2V(Cl)(N_2CPh_2)$ showed no sign of decomposition in C_6D_6, even after prolonged periods of heating (>100 °C) or photolysis. Reaction between (i) $[(Me_3Si)_2N]_2VMe(THF)$ and Me_3SiCHN_2 or Ph_2CN_2 or (ii) $[(Me_3Si)_2N]_2VCl(THF)$ and Me_3SiCHN_2 also proceeded rapidly to afford deep red mixtures, however, in these cases the products could not be isolated as crystalline solids and appear to be very low melting materials that were difficult to isolate and purify in good yields.

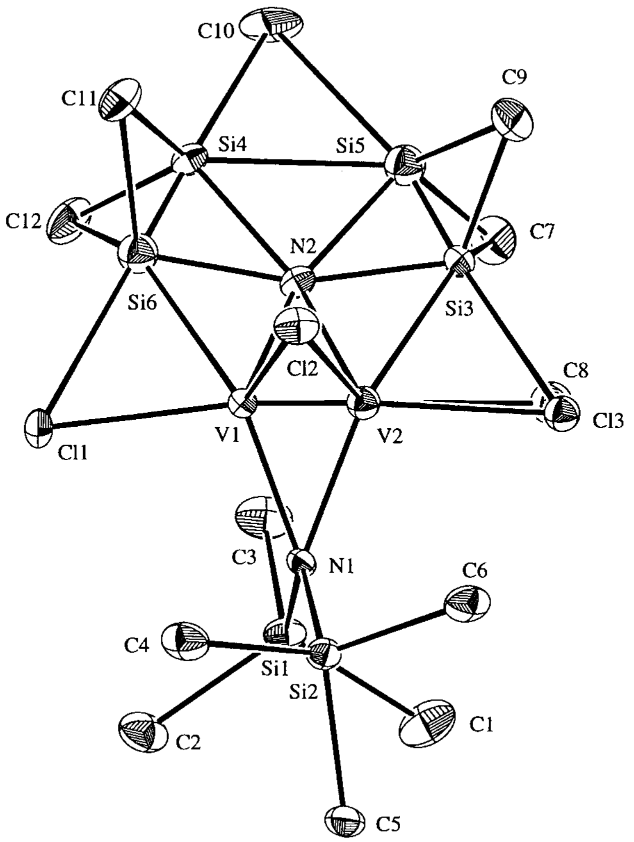


Figure 1. ORTEP drawing (50% ellipsoids) of $[(Me_3Si)_2N]_2VCl_2$. V(2), Si(5), Si(6), and Cl(3) are at 16% occupancy, while V(1), Si(3), Si(4), and C(8) are at 84% occupancy. The position of the (minor occupancy) carbon atom near Cl(1) was not resolved.

X-ray Crystal Structures. $[(Me_3Si)_2N]_2VCl_2$. Selected bond distances and angles for this as well as the other crystallographically characterized compounds are collected in Table 2. As described in the Experimental Section, the molecule crystallized as a mixture of major (85%) and minor (15%) conformers that are related by a virtual mirror plane that passes roughly through the amide nitrogens, Cl(2), C(10), and the midpoint of the vector that connects the two partial occupancy vanadium nuclei. This is illustrated in Figure 1, which includes all full and partial occupancy atoms. The following points refer to the major conformer, of which an ORTEP drawing is shown in Figure 2. The $VNSi_2$ units are virtually planar, with all of the angles about

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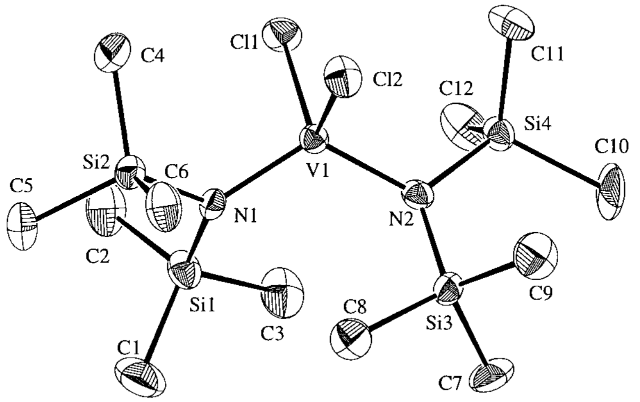

Figure 2. ORTEP drawing (50% ellipsoids) of the major conformer of $[(Me_3Si)_2N]_2VCl_2$.

the amide nitrogen being ca. 120°. As in the other complexes that we have crystallographically studied that contain the $\{[(Me_3Si)_2N]_2V\}^{n+}$ fragment, the largest angle about the metal center is between the two amide ligands (N(1)−V(1)−N(2) = 118.5(2)°). The remainder of the angles about the metal span the range 102.2(1)°−113.0(1)° (Table 2). Relative to $[(Me_3Si)_2N]_2VCl(THF)$,[19] the V−Cl bond lengths in $[(Me_3Si)_2N]_2VCl_2$ (V(1)−Cl(1) = 2.211(2) Å; V(1)−Cl(2) = 2.222(2) Å) are slightly shorter due to the smaller V(IV) in the present case.

There are some interesting differences between this vanadium structure and that of $[(Me_3Si)_2N]_2TaCl_2$,[16] with which the intermediate niobium complex is apparently isostructural.[15] Despite the smaller radius of V(IV), the distortion of the N_2VCl_2 core from idealized C_{2v} symmetry is not nearly as pronounced as that observed in $[(Me_3Si)_2N]_2TaCl_2$. For example, the dihedral angle between the VN_2 and VCl_2 deviates by ca. 6° from the ideal value of 90°, versus a value of 17° in the Ta analog. Furthermore, the Ta complex possesses a rather compressed Cl−Ta−Cl angle (95.7(2)°) compared to a more normal Cl−V−Cl angle of 108.83(7)° in the major conformer. Equivalent V−N bond lengths (V(1)−N(1) = 1.847(4) Å, V(1)−N(2) = 1.842(4) Å) contrast with the unsymmetrical Ta−N bond lengths, the latter due to steric repulsion between a chlorine and amide methyl groups. On the basis of the wide range of dihedral angles we have observed between the two N_2V planes in structures having the $\{[(Me_3Si)_2N]_2V\}^{n+}$ fragment (e.g., see below), the apparently soft potential-energy surface for rotation about the V−N bonds may not exist in the third-row congener, particularly if N(pπ)−M(dπ) overlap assists in "locking" the amides in a particular conformation. In other words, facile rotation about V−N bonds in complexes of $\{[(Me_3Si)_2N]_2V\}^{n+}$ may allow the molecules to avoid unfavorable, intramolecular steric repulsions in the solid state. A shallow potential-energy curve for bending the Nb−N−Si angles in $[(Me_3Si)_2N]_2NbBr_2$ has been noted, a point perhaps related to the ability of the $-N(SiMe_3)_2$ ligand to metalate via γ-hydrogen elimination.

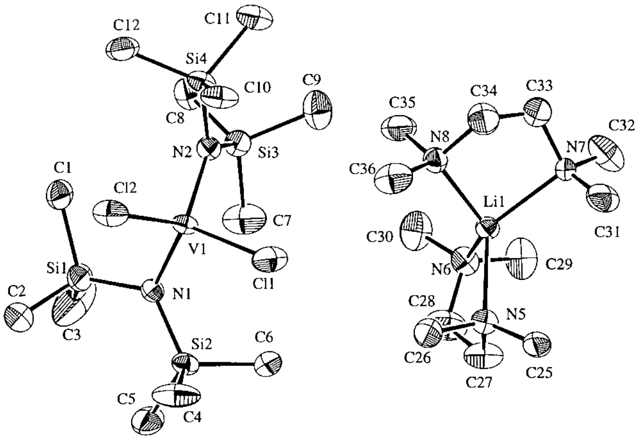

Figure 3. ORTEP drawing (50% ellipsoids) of one of the crystallographically independent molecules of $\{Li(TMEDA)_2\}\{[(Me_3Si)_2N]_2VCl_2\}$.

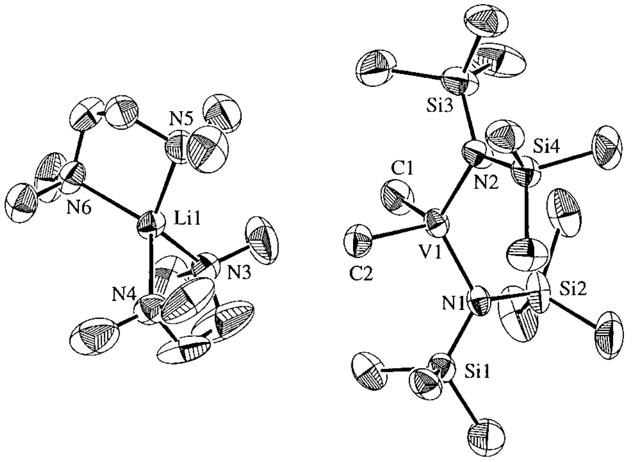

Figure 4. ORTEP drawing (50% ellipsoids) of one of the crystallographically independent molecules of $[Li(TMEDA)_2]\{[(Me_3Si)_2N]_2VMe_2\}$.

$[Li(TMEDA)_2]\{[(Me_3Si)_2N]_2VCl_2\}$. The molecule crystallized as well-separated cations and anions, the closest intramolecular contact (excluding hydrogen atoms) being the C(9)−C(30) distance of 3.333(7) Å. There are two molecules per asymmetric unit, and an ORTEP drawing of one of them is shown in Figure 3. The metrical parameters of the Li(TMEDA) cations are unremarkable. The vanadium−ligand bond lengths ($V-N_{av}$ = 1.945(5) Å, $V-Cl_{av}$ = 2.306(2) Å) are elongated by ca. 0.1 Å when compared with those of neutral $[(Me_3Si)_2N]_2VCl_2$ above and, as expected, are slightly shorter than those in the analogous Ti species.[60,61] The angles about the vanadium center are virtually identical in the two crystallographically independent molecules, however, a subtle difference between the anions exists. While the $-N(SiMe_3)_2$ groups are all planar at nitrogen, the dihedral angle between the two $VNSi_2$ planes measures 99° in the V(1) anion versus a value of 83° in the V(2) anion, again indicative of a low activation energy for rotation about the V−N bonds in this system.

$[Li(TMEDA)_2]\{[(Me_3Si)_2N]_2VMe_2\}$. The molecule crystallized in the same manner as the dichloride above, i.e., in $P2_1/c$ with two molecules per asymmetric unit. Diffraction data verified the connectivity in the paramagnetic molecule, but a severe disorder in one of the anions (analogous to that described for $[(Me_3Si)_2N]_2VCl_2$, but not nearly as well-behaved) limits the usefulness of the metrical data. An ORTEP view of the ordered molecule is shown in Figure 4. The dihedral angle between the $VNSi_2$ planes is 96°, close to that observed in the V(1) anion of $[Li(TMEDA)_2]\{[(Me_3Si)_2N]_2VCl_2\}$ to which the present structure is closely related. The V−C bond lengths in the ordered anion (V(1)−C(1) = 2.096(8)

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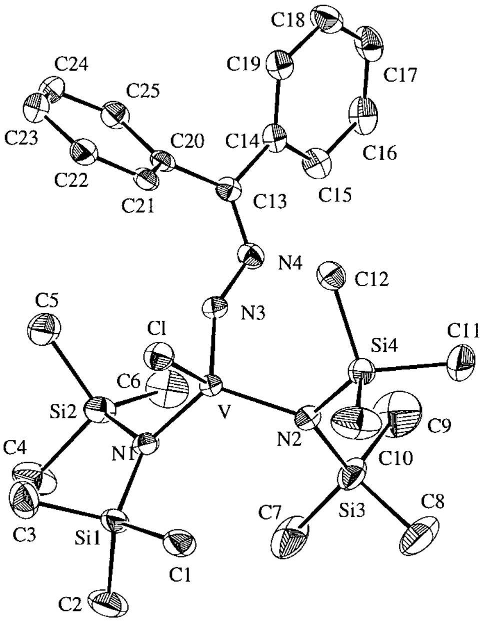
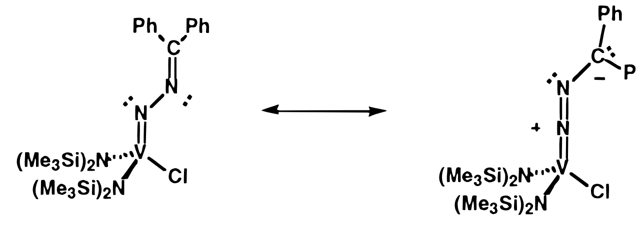


Figure 5. ORTEP drawing (50% ellipsoids) of $[(Me_3Si)_2N]_2V(Cl)(N_2CPh_2)$.

Å, V(1)−C(2) = 2.124(8) Å) are the same within experimental error as that in the neutral V(III) complex $[(Me_3Si)_2N]_2VMe(THF)$.[13]

$[(Me_3Si)_2N]_2VCl(N_2CPh_2)$. An ORTEP drawing of the structure is shown in Figure 5. The distorted tetrahedral geometry about the metal is such that the angle between the amide nitrogens and vanadium is 117.79(9)° and that between the N-bound Ph_2CN_2 and the remaining three ligands are all ca. 106°. The sum of the angles about N(1) (357.5(2)°) and N(2) (358.3(2)°) again establish planarity at nitrogen for the amide ligands. The V−N(1), V−N(2), and V−Cl bond lengths (1.851(2), 1.879(2), and 2.2454(7) Å, respectively) are all unremarkable.

The most interesting structural feature is the geometry of the coordinated Ph_2CN_2 ligand. Consistent with a reduction of the diazoalkane to a $Ph_2CN_2^{2-}$ ligand, or alkylidenehydrazido, is the short V−N(3) bond length of 1.683(2) Å. Although marginally longer, the V−N(3) distance is comparable to the V−N triple bonds found in other four-coordinate, V(V) imido complexes, such as $(Ph_3SiS)_3V{\equiv}NBu^t$ (V−N = 1.622(2) Å, V−N−C = 170.7(2)°),[62] $(Me_3SiO)_3V{\equiv}NAdm$ (Adm = adamantyl; V−N = 1.614(2), V−N−C = 175.8(2)°),[63] $Me_3SiN{\equiv}VCl_3$ (V−N = 1.59(1) Å, V−N−Si = 177.5(7)°),[64] and $(RAr_FN)_2VI({\equiv}NMes)$ (R = $C(CD_3)_2Me$, Ar_F = 2,5-C_6H_3FMe, Mes = 2,4,6-$C_6H_2Me_3$; V−N = 1.645(7) Å, V−N−C = 175.7(7)°).[65] In view of the large distortion of the V−N(3)−N(4) angle (152.8(2)°) from 180°, the V=N− linkage is analogous to that in a bent imido consisting of a double bond between the vanadium and nitrogen (i.e., a two-electron donor). The N(3)−N(4) distance (1.328(3) Å) is intermediate to a N=N double and N−N single bond,[66] while the N(4)−C(13) distance (1.295(3) Å) is as expected for a N=C double bond.[67] Along with the N(3)−N(4)−C(13) angle of 121.9(2)°, which indicates sp^2 hybridization of N(4), it follows that the best Lewis structure is resonance structure **A**, shown below, with a smaller contribution from **B**. Of the numerous binding modes that have been well-documented for transition metal diazoalkane complexes,[68] this doubly-bent form is rare;[57] the other example being $Mo_2(OPr^i)_6(N_2CPh_2)_2(py)$[69] whose solid-state structure features Mo−N−N angles of 155(1)° and 164(1)°, with corresponding N−N−C angles of 124(1)° and 122(1)°.



Summary. We have demonstrated that V(III) species of the type $[(Me_3Si)_2N]_2VX(THF)$ are easily oxidized by CuCl to give $[(Me_3Si)_2N]_2V(Cl)(X)$ products. As in alkylation reactions of Cp_2VCl_2, attempts to use these V(IV) compounds as the starting material for bis(hydrocarbyl) complexes of V(IV) showed that care must be taken in order to minimize reduction of the metal. Styrene oxide affects the two-electron oxidation of $[(Me_3Si)_2N]_2VR(THF)$ (R = Me, Ph), and in the case of R = Me, it was shown that the reaction proceeded through a dimeric V(IV) intermediate bridged by a single O^{2-} ligand. Barring a trimolecular transfer of oxygen from the epoxide to two V(III) centers, the formation and lifetime of $\{[(Me_3Si)_2N]_2VMe\}_2(\mu\text{-}O)$ in the presence of excess $PhCH(O)CH_2$ suggests that nucleophilic addition of $[(Me_3Si)_2N]_2V(O)(Me)$ to $[(Me_3Si)_2N]_2VMe(THF)$ is faster than than the transfer of oxygen from $PhCH(O)CH_2$ to $[(Me_3Si)_2N]_2VMe(THF)$. In a related oxidation reaction, Ph_2CN_2 was formally reduced to a $Ph_2CN_2^{2-}$ ligand by $[(Me_3Si)_2N]_2VCl(THF)$ to give an “alkylidenehydrazido” in which the N_2 unit was neither thermally or photolytically labile under the conditions we have examined thus far. The crystal structure of $[(Me_3Si)_2N]_2VCl(N_2CPh_2)$ showed the $PhCN_2^{2-}$ unit bound in a rare, doubly-bent, two-electron donor mode.

Acknowledgment. We thank the National Science Foundation for support and the Alfred P. Sloan Foundation for a fellowship (to J.A.).

Supporting Information Available: Tables of bond distances and angles, atomic coordinates, and anisotropic thermal parameters, packing diagrams for $[(Me_3Si)_2N]_2VCl_2$, $[Li(TMEDA)_2]\{[(Me_3Si)_2N]_2VCl_2\}$, $[Li(TMEDA)_2]\{[(Me_3Si)_2N]_2VMe_2\}$, and $[(Me_3Si)_2N]_2VCl(N_2CPh_2)$, and an ORTEP drawing showing the disorder in $[Li(TMEDA)_2]\{[(Me_3Si)_2N]_2VMe_2\}$ (47 pages). Ordering information is given on any current masthead page.

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