

Serendipitous Formation of a Dinuclear Vanadium(III) Amide Complex Containing a Vanadaazacyclobutane Ring. Potassium–Hydrogen Agostic Interactions Holding Together a V_2K_2 Tetrametallic Framework

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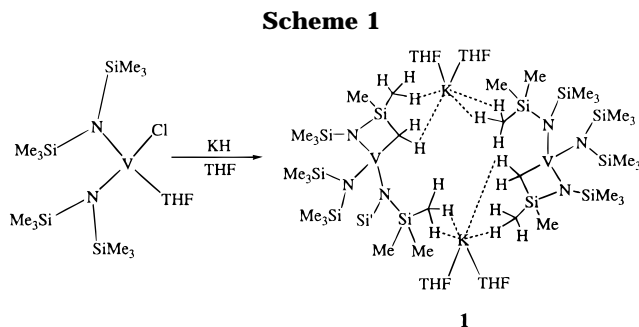
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Summary: Reaction of $[(Me_3Si)_2N]_2V(THF)Cl$ with KH led to the formation of the dinuclear $\{[(Me_3Si)_2N]_2V-[N(SiMe_3)SiMe_2CH_2]\}_2\{K(THF)_2\}_2$ (**1**), whose structure was determined by X-ray analysis. The dinuclear framework is held together via K–H agostic interactions.

The use of anionic organic amides as supporting ligands in transition metal chemistry was pioneered by Bradley and Lappert about 30 years ago.¹ However, the chemistry of early transition metal amides remained relatively undeveloped until only very recently, when a revival of interest in the utilization of these ligands,² as possible alternatives to the tremendously popular Cp systems,³ revitalized research in this field. Several characteristics (tunable steric hindrance, electronic flexibility, variety of bonding modes, and relative inertness) make these anions particularly promising and interesting as an alternative to other more traditional ligand systems.

As a part of an ongoing project in the chemistry of low-valent early transition metals, we have recently studied the synthesis and reactivity of trivalent vanadium amides.⁴ This work has led to the discovery of an unprecedented series of dinitrogen complexes⁵ and to a number of transformations (formation of metallacycles,^{5a,6}



hydrogen transfer,⁷ formation of hydrides,^{8,9} nitrides,⁹ and carbenes,¹⁰ C–H σ -bond metathesis)^{5a,6,10} in which the organic amide side chains were often involved in the reactivity of the metal center.^{6,7,10} We also noticed that the most attractive of these reactions occurred when a vanadium hydride was implicated as a transient intermediate.^{7,8}

In this paper, we describe the serendipitous formation of the dinuclear complex $\{[(Me_3Si)_2N]_2V-[N(SiMe_3)SiMe_2CH_2]\}_2\{K(THF)_2\}_2$ (**1**) obtained during attempts to form unprecedented vanadium hydride amide species.

Results and Discussion

In an attempt to prepare a “ $[(Me_3Si)_2N]_2V-H$ ” species we have reacted $[(Me_3Si)_2N]_2V(THF)Cl$ with a large excess of KH in THF (Scheme 1). The reaction proceeded slowly in THF and at room temperature forming a greenish-brown mixture.

Addition of hexane as a nonsolvent gave a blue-green solution with some insoluble black material. Dark crystals of $\{[(Me_3Si)_2N]_2V-[N(SiMe_3)SiMe_2CH_2]\}_2\{K(THF)_2\}_2$ (**1**) were obtained in moderate yield after filtration of the reaction mixture and allowing the resulting solution to stand several days at $-30\text{ }^\circ\text{C}$. The IR spectrum clearly showed the presence of the ligand as well as the characteristic absorptions of coordinated THF. Qualitative tests showed the presence of potassium and the absence of chlorine. The X-ray fluorescence spectrum clearly indicated the presence of vana-

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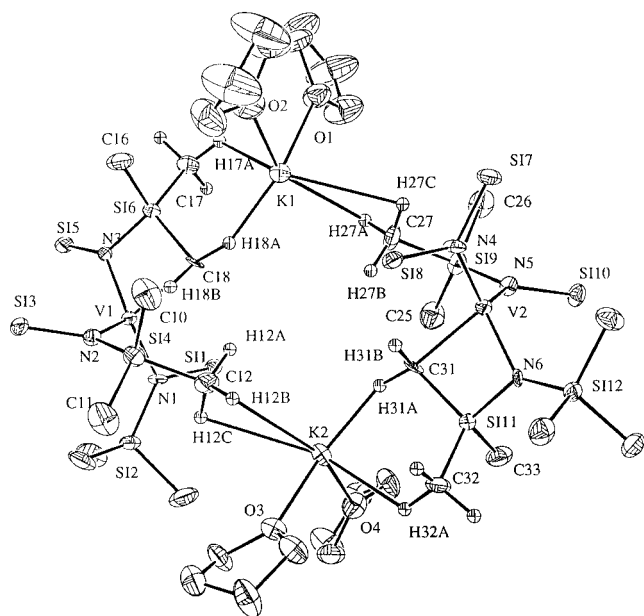
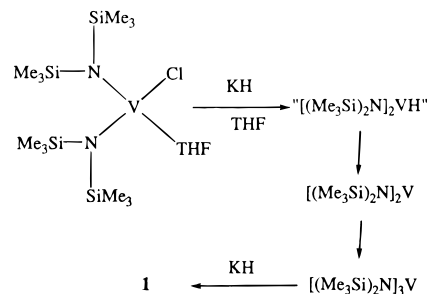


Figure 1. Thermal ellipsoid plot of **1**. Thermal ellipsoids are drawn at the 50% probability level.

dium and potassium in the 1:1 ratio. Unfortunately, the extreme air-sensitivity prevented obtaining significant and reproducible combustion analysis data.

The structure and the molecular connectivity were elucidated by single-crystal X-ray analysis. The complex is composed of two almost identical $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{VN}(\text{SiMe}_3)(\text{SiMe}_2\text{CH}_2)$ moieties connected by two $\text{K}(\text{THF})_2$ units (Figure 1). Each vanadium atom possesses a distorted tetrahedral geometry [$\text{N1}-\text{V1}-\text{N2} = 115.9(2)^\circ$, $\text{N1}-\text{V1}-\text{N3} = 118.9(2)^\circ$, $\text{N1}-\text{V1}-\text{C18} = 112.5(3)^\circ$, $\text{N2}-\text{V1}-\text{N3} = 118.6(2)^\circ$, $\text{N2}-\text{V1}-\text{C18} = 102.2(3)^\circ$, $\text{N3}-\text{V1}-\text{C18} = 80.7(2)^\circ$] defined by three nitrogen atoms of three amide groups [$\text{V1}-\text{N1} = 1.989(5) \text{ \AA}$, $\text{V1}-\text{N2} = 1.971(6) \text{ \AA}$, $\text{V1}-\text{N3} = 1.985(5) \text{ \AA}$], and one CH_2 carbon atoms of one deprotonated Me_3Si group [$\text{V1}-\text{C18} = 2.190(6) \text{ \AA}$], the latter being included in a four-membered vanadaazacyclobutane ring. The geometry parameters of the metallacycle [$\text{V1}-\text{N3}-\text{Si6} = 93.9(3)^\circ$, $\text{N3}-\text{Si6}-\text{C18} = 99.2(3)^\circ$, $\text{V1}-\text{C18}-\text{Si6} = 84.6(3)^\circ$] are similar to those of the previously reported dimeric $\{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{V}[\text{N}(\text{SiMe}_3)]\text{SiMe}_2\text{CH}_2\}_2$ ^{5,6} and monomeric $\{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{V}[\text{N}(\text{SiMe}_3)]\text{SiMe}_2\text{CH}_2\}$ (pyridine).⁷ Each potassium cation bridges the two vanadium-containing moieties. Short contacts between potassium and the hydrogen atoms of the trimethylsilyl groups appear to be the only interatomic contacts present in the bonding range which hold together the polynuclear frame. The shortest contact is seen between potassium and one H atom of the CH_2 group which is engaged in the formation of the metallacycle ($\text{K1}-\text{H18a} = 2.05 \text{ \AA}$). One longer contact is formed with an H atom of another methyl group of the same trimethylsilyl group ($\text{K1}-\text{H17a} = 2.77 \text{ \AA}$). Two longer but comparable distances are also formed with two H atoms from one methyl group of the second vanadium-containing moiety, thus generating the dinuclear framework ($\text{K1}-\text{H27a} = 2.74 \text{ \AA}$, $\text{K1}-\text{H27c} = 2.99 \text{ \AA}$). The second potassium atom forms almost identical contacts, thus completing the overall cyclic structure. Two molecules of THF complete the coordination sphere of each potassium atom [$\text{K1}-\text{O1} = 2.649(5) \text{ \AA}$, $\text{K1}-\text{O2} = 2.600(6) \text{ \AA}$].

Scheme 2



Complex **1** is paramagnetic, and its $^1\text{H-NMR}$ spectrum showed the presence of several slightly broad singlets whose positions greatly changed as a result of the variation in the sample concentration. The magnetic moment, calculated on the basis of the formula obtained from the X-ray analysis, was significantly lower than expected for the d^2 electronic configuration of two V(III) metal centers ($\mu_{\text{eff}} = 2.70 \mu_{\text{B}}$). This is rather puzzling in the view of the fact that in the solid-state structure the two vanadium atoms are placed 7.8 \AA apart. On the other hand, it is impossible to draw definite conclusions about the hydrogen atom positions and consequently about the oxidation state of the vanadium center. Since degradation experiments ruled out the presence of hydrides, on the basis of the geometrical parameters obtained from the crystal structure, a structure with two trivalent vanadium atoms seems to be the most reasonable proposal.

The formation of **1** is not a straightforward process since it requires at least three separate steps. First, while the overall oxidation state of the metal center was conserved, the vanadium atom has acquired one additional amide group. Second, the formation of the metallacycle implies deprotonation of one methyl group. Finally, an amount of H_2 close to the stoichiometry is formed during the reaction (measured with a Toepler pump). These observations suggest a possible pathway for the formation of complex **1**. As speculated in Scheme 2, the process might be envisioned with the initial replacement of one chloride atom by hydride and subsequent reductive elimination to a V(II) amide complex.

These species are well-known to be unstable¹¹ and highly reactive and to rapidly disproportionate toward higher oxidation states^{4,12} and colloidal vanadium. Reaction of the trivalent vanadium $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{V}$ ¹³ with KH may well form the final compound via simple C-H σ -bond metathesis.¹⁰

Experimental Section

All operations were performed under inert atmosphere by using standard Schlenk techniques. $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{V}(\text{THF})\text{Cl}$ was prepared according to published procedures.⁶ An emulsion of KH in mineral oil (Aldrich) was washed with hexane, dried, and sealed in ampules under nitrogen. Infrared spectra were recorded on a Mattson 9000 FTIR instrument from Nujol mulls

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prepared in a drybox. Samples for magnetic susceptibility measurements were weighed inside a drybox equipped with an analytical balance and sealed into calibrated tubes. Magnetic measurements were carried out with a Gouy balance (Johnson Matthey) at room temperature. The magnetic moment was calculated by following standard methods,¹⁴ and corrections for underlying diamagnetism were applied to data.¹⁵ Elemental analyses were carried out with a Perkin-Elmer 2400 CHN analyzer. Ratios between heavy atoms were determined by X-ray fluorescence by using a Philips 2400 instrument.

Synthesis of 1. A solution of $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{VCl}(\text{THF})$ (2.0 g, 4.17 mmol) in THF (60 mL) was stirred for 6 days at room temperature in the presence of KH (0.8 g, 20.9 mmol), giving a green-brown mixture. The solvent was removed *in vacuo*, and hexane (200 mL) was added to the solid residue. The resulting blue-green solution was filtered in order to remove a small amount of black insoluble material and allowed to stand at $-30\text{ }^\circ\text{C}$, upon which dark, extremely air-sensitive crystals of **1** were formed (0.6 g, 0.4 mmol, 22%). IR (Nujol, cm^{-1}): ν 1248 (vs, symmetric CH_3 deformation), 1029 (vs, symmetric Si–N–Si stretching), 1025 (s), 949 (vs, antisymmetric Si–N–Si stretching), 831 (br, rocking of the Si–C stretching), 666 (vs), 618 (m). Combustion analysis determinations were severely affected by the extreme air-sensitivity of the complex. Anal. Calcd (found) for $\text{C}_{52}\text{H}_{138}\text{N}_6\text{Si}_{12}\text{V}_2\text{K}_2\text{O}_4$: C, 43.71 (42.95); H, 9.74 (9.05); N, 5.88 (4.91). $^1\text{H-NMR}$ (C_6D_6 , 500 MHz, $25\text{ }^\circ\text{C}$): δ 19.54 (broad), 5.0 (very broad), 3.5 (singlet THF), 2.3 (very broad), 1.5 (singlet THF), 0.5 (broad).

X-ray Crystallography. Data were collected at $-153\text{ }^\circ\text{C}$. An air-sensitive crystal was mounted on a glass fiber inside a drybox and transferred under the liquid-nitrogen stream of the cooling system of a AFC6S Rigaku X-ray diffractometer. The ω - 2θ scan technique was used. Data were collected until 100 deg of 2θ obtaining a reflection/parameter ratio 23/1. Cell constants and orientation matrices were obtained from the least-squares refinement of 25 centered reflections. The intensities of three standard reflections, measured after every 150 reflections, showed no statistically significant decay over the duration of the data collections. Data were corrected for Lorentz and polarization effects and for absorption (ψ scan). The structure was solved by direct methods resulting in locating all the non-hydrogen atoms. Their positions were refined anisotropically. Hydrogen atom positions were calculated but not refined. Not surprisingly, some of the carbon atoms of the coordinated THF molecules and of the methyl groups attached to the peripheral silicon atoms showed some large thermal parameters possibly indicative of some minor disorder. However, attempts to model the disorder did not improve the thermal parameters and the quality of the refinement. The data were processed using the NRCVAX

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Table 1. Crystal Data and Structure Analysis Results for 1

formula	$\text{C}_{52}\text{H}_{138}\text{N}_6\text{Si}_{12}\text{V}_2\text{O}_4\text{K}_2$
formula weight	1428.81
space group	$P2_1/c$
a (Å)	10.681(5)
b (Å)	35.100(6)
c (Å)	22.268(3)
β (deg)	92.44(3)
V (Å ³)	8341(1)
Z	4
radiation (Cu K α ; Å)	1.540 56
T (°C)	-153
D_{calcd} (g cm ⁻³)	1.139
μ_{calcd} (cm ⁻¹)	48.0
$R,^a R_w,^a \text{GoF}$	0.049, 0.069, 1.97

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad R_w = [(\sum (|F_o| - |F_c|)^2 / \sum wF_o^2)]^{1/2}.$$

Table 2. Selected Bond Distances (Å) and Angles (deg) for 1

V1–N1	1.989(5)	K1–H27c	2.99
V1–N2	1.971(6)	V2–N4	1.999(6)
V1–N3	1.985(5)	V2–N5	1.997(6)
K1–O1	2.649(5)	V2–N6	1.956(5)
K1–O2	2.600(6)	V2–C31	2.192(7)
K1–H18a	2.05	K2–H31a	2.13
K1–H17a	2.77	K2–H32a	2.735
V1–C18	2.190(6)	K2–H12b	2.99
K1–H27a	2.74	K2–H12c	2.98
N1–V1–N2	115.9(2)	N3–Si6–C18	99.2(3)
N1–V1–N3	118.9(2)	N4–V2–N5	121.0(2)
N1–V1–C18	112.5(3)	N4–V2–N6	115.5(2)
N2–V1–N3	118.6(2)	N4–V2–C31	111.1(3)
N2–V1–C18	102.2(3)	N5–V2–N6	118.2(2)
N3–V1–C18	80.7(2)	N5–V2–C31	99.9(3)
V1–N3–Si6	93.9(3)	N6–V2–C31	80.8(2)
V2–C31–Si11	83.4(3)	V2–N6–Si11	94.4(3)
V1–C18–Si6	84.6(3)	N6–Si11–C31	98.2(3)

software packages on a Silicon Graphics workstation. Refinements were carried out by using full-matrix least-squares techniques on F minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$ and F_o and F_c are the observed and calculated structure factors. Atomic scattering factors and anomalous dispersion terms were taken from the usual sources (Cromer and Waber).¹⁶ Details on the data collections and structure refinement are listed in Table 1. The final atomic coordinates are given as Supporting Information. Selected bond distances and angles are given in Table 2.

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Supporting Information Available: Listing of X-ray data, atomic coordinates, thermal parameters, and bond distances and angles for **1** (17 pages). Ordering information is given on any current masthead page.

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