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# Preparation, Characterization, and Reactivity of the Binuclear Vanadium(III) Compound $\{[(Me_3Si)_2N]V[\mu\text{-}CH_2SiMe_2N(SiMe_3)]\}_2$. C–H σ-Bond Metathesis Promoted by an Amido Function

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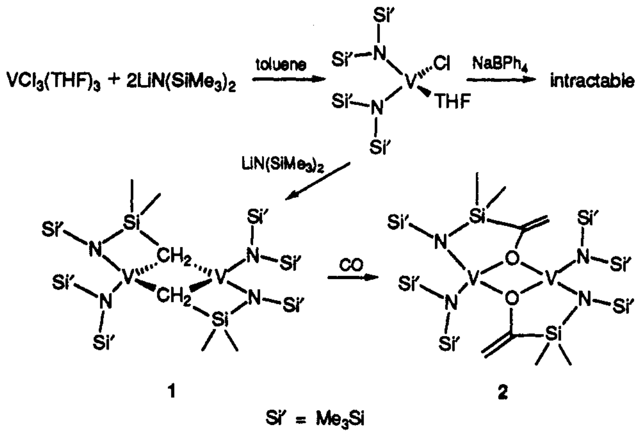
*Summary: C–H σ-bond metathesis promoted by one amido group, during the reaction of $VCl_3(THF)_3$ with 3 equiv of $(Me_3Si)_2NLi$, affords the dimeric $[(Me_3Si)_2NV(\mu\text{-}CH_2Si(Me)_2N(SiMe_3)]_2$ (1). Reaction of 1 with CO takes place at room temperature and atmospheric pressure forming a dinuclear enolate species formally arising from the insertion of CO into the Si–$CH_2$ bond of 1.*

Although low-valent vanadium amides are very rare,[1,2] the vanadium–nitrogen bond of these species is a very promising functionality in terms of chemical reactivity. For example, *in situ* generated V amides have been shown to fragment THF and to stabilize highly reactive moieties such as ethylidene[3] and ynolates.[4] In a previous report, Bradley described the preparation of crystalline, brown, paramagnetic $[(Me_3Si)_2N]_3V$.[5,6] Since the triangular ligand field imposed by the bulky hexamethyldisilazanato ligands is very unusual for a $d^2$ electronic configuration of V(III), we became interested in investigating the reactivity of $[(Me_3Si)_2N]_3V$.

The reaction of $VCl_3(THF)_3$ with 3 equiv of $LiN(SiMe_3)_2$ in toluene proceeds differently than in the case of $VCl_3(Me_3N)_2$.[5] The room-temperature reaction initially affords the emerald green monomeric $[(Me_3Si)_2N]_2VCl(THF)$,[7] which reacts further with 1 equiv of $(Me_3Si)_2NLi$ to form the blue-violet dimer $\{[(Me_3Si)_2N]V[\mu\text{-}CH_2SiMe_2N(SiMe_3)]\}_2$, which can be isolated as a crystalline material in 80% yield[8] (Scheme 1). The reaction can also be conveniently carried out in a one-pot synthesis. Attempts to form 1 via reaction of $[(Me_3Si)_2N]_2VCl(THF)$ with $NaBPh_4$ and formation of NaCl, PhH, and $BPh_3$ gave only intractable mixtures. The IR spectrum of 1 displays broad, intense absorptions at 850 and 1250 $cm^{-1}$, which are characteristic of the Si–N and Si–$CH_3$ stretchings. Elemental analysis and magnetic data ($\mu_{eff}(294\ K) = 2.31\ \mu_B$ per dimer) are in disagreement with the values expected for a monomeric $[(Me_3Si)_2N]_3V$ but support the formulation as provided by the X-ray crystal structure, with two partially coupled vanadium atoms at near V–V bonding distance. The formation of 1 is a clean reaction, and we find no evidence for the presence of any other product in the reaction mixtures. No significant amounts of hydrogen were produced during the formation of 1. Compound 1 is moderately stable, but it decomposes upon reflux in toluene, giving deep brown solutions.

**Scheme 1**



The molecular structure of 1 has been determined by X-ray analysis.[9] The structure is formed by one dimeric unit and a disordered half-molecule of toluene in the lattice (Figure 1). The structure of the divanadium complex consists of two $[(Me_3Si)_2N]V$ moieties bridged by two $\mu$-$CH_2Si(Me)_2N(SiMe_3)$ units. The two terminal amido groups are rather normal, with the expected V–N (V1–N4 = 1.946(5) Å, V2–N3 = 1.944(6) Å) and N–Si (N–$Si_{av}$ = 1.735(6) Å) bond distances and angles (V1–N4–Si5 = 110.0-

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[•] Abstract published in *Advance ACS Abstracts*, February 1, 1994.

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[7] A similar reaction[6b] has been previously suggested to form dimeric products which contained considerable proportions of chloride and which were resistant to further replacement of chloride. Crystal data for $[(Me_3Si)_2N]_2VCl(THF)$: $C_{16}H_{44}N_2Si_4VClO$, fw = 479.27, green prism, triclinic, $P\bar{1}$, $a = 11.636(3)$ Å, $b = 15.7676(4)$ Å, $c = 8.561(2)$ Å, $\alpha = 94.08(2)°$, $\beta = 108.98(2)°$, $\gamma = 105.55(2)°$, $Z = 2$, $V = 1409.2(6)$ Å$^3$, $D_c = 1.129$ g cm$^{-3}$, $\mu = 6.11$ cm$^{-1}$, $T = 25$ °C, $R = 0.045$, $R_w = 0.046$ for 227 parameters and 3282 reflections out of 4949 unique reflections. Minhas, R.; Gambarotta, S. Unpublished results.

[8] A suspension of $VCl_3(THF)_3$ (10.6 g, 28.4 mmol) in toluene (100 mL) was treated with $LiN(SiMe)_2$ (14.2 g, 85 mmol). The initially emerald green mixture was stirred at room temperature for 24 h, giving a dark blue suspension. The blue-violet crystalline 1 was obtained (4.4 g, 5.9 mmol, 42%) after filtration and by allowing the resulting solution to stand at −25 °C overnight. The mother liquor was concentrated to approximately 40 mL and diluted with an equivalent volume of *n*-hexane. Another crop (3.9 g, 5.2 mmol, 38%) of crystalline 1 was obtained upon standing at −25 °C overnight. The overall yield was 80%. X-ray-quality crystals were obtained from slow cooling of a concentrated toluene solution. IR (Nujol mull, $cm^{-1}$): 1251 (s), 1186 (w), 851 (br), 670 (br). Anal. Calcd (found) for $C_{24}H_{70}N_4Si_8V_2\cdot{}^1/_2$(toluene): C, 41.50 (41.07); H, 9.54 (9.39); N, 7.17 (7.01). $\mu_{eff}(294\ K) = 2.31\ \mu_B$.

[9] Crystal data for 1: $C_{24}H_{70}N_4Si_8V_2\cdot{}^1/_2$(toluene), fw = 775.43, purple prism, triclinic, $P\bar{1}$, $a = 11.700(6)$ Å, $b = 22.131(7)$ Å, $c = 8.893(4)$ Å, $\alpha = 90.70(3)°$, $\beta = 102.04(4)°$, $\gamma = 88.75(4)°$, $Z = 2$, $V = 2251(3)$ Å$^3$, $D_c = 1.144$ g cm$^{-3}$, $\mu = 6.32$ cm$^{-1}$, $T = -155$ °C, $R = 0.061$, $R_w = 0.056$ for 519 parameters and 4633 reflections out of 7889 reflections. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at their idealized positions but not refined.

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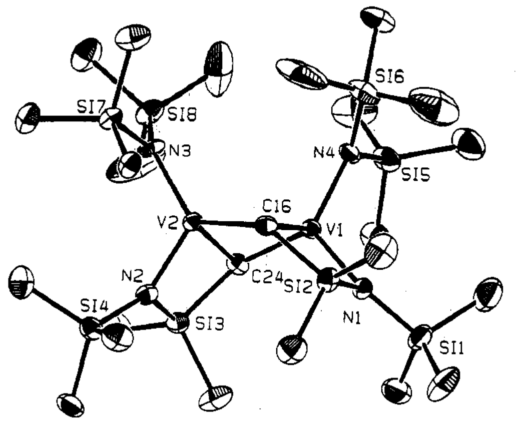

**Figure 1.** ORTEP drawing of 1 showing the labeling scheme. Selected values of bond distances (Å) and angles (deg): V1···V2 = 2.736(2) Å, V1–C16 = 2.221(7), V1–C24 = 2.199(7), V2–C16 = 2.179(7), V2–C24 = 2.216(7), V1–N1 = 1.934(6), V1–N4 = 1.946(5), V2–N2 = 1.921(6), V2–N3 = 1.944(6), N–Si$_{av}$ = 1.733(6), Si3–C24 = 1.894(7), Si2–C16 = 1.892(8); C16–V1–C24 = 98.0(3), C16–V2–C24 = 98.8(3), V1–C16–V2 = 76.9(2), V1–C24–V2 = 76.6(2), V1–N1–Si1 = 138.0(3), V1–N1–Si2 = 94.6(3), V1–N4–Si5 = 110.0(3), V1–N4–Si6 = 128.0(3), V1–C16–Si2 = 81.5(3), Si1–N1–Si2 = 127.4(3), Si5–N4–Si6 = 120.3(3).

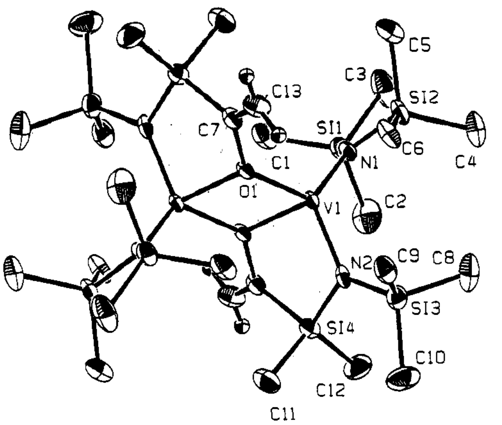

**Figure 2.** ORTEP drawing of 2 showing the labeling scheme. Selected values of bond distances (Å) and angles (deg): V1···V1* = 3.126, V1–O1 = 1.965(4), V1–O1* = 2.032(4), O1–C7 = 1.406(6), C7–C13 = 1.320(8), Si4–C7* = 1.888(6), V1–N1 = 1.927(4), V1–N2 = 1.953(5), N–Si$_{av}$ = 1.737(5); O1–V1–O1* = 77.1(2), V1–O1–V1* = 102.9(2), O1–C7–C13 = 120.8(6), O1–C7–Si4* = 110.1(4), Si4*–C7–C13 = 129.1(5), V1–N1–Si1 = 129.9(2), V1–N1–Si2 = 106.5(2), V1–N2–Si3 = 129.2(3), V1–N2–Si4 = 111.1(4), Si1–N1–Si2 = 123.1(3), Si3–N2–Si4 = 119.7(3).

(3)°, V1–N4–Si6 = 128.0(3)°). The distorted-trigonal-planar geometry around the nitrogen atom, similar to that of the titanium hexamethyldisilazane dinitrogen complexes,[10] suggests the presence of a delocalized V–N–Si $\pi$-system. The two bridging units form almost planar metallaazasilocylobutane rings (V2–N2–Si3–C24 = 7.4(3)° and V1–N1–Si2–C16 = 5.3(3)°) and form the dimeric unit by sharing the $CH_2$ groups with the two vanadium atoms. The V–Si distance is unusually short and is in the bonding range (V–Si = 2.696(3) Å) as a probable result of the strain of the four-membered ring. The $V_2C_2$ core is folded in an overall butterfly conformation (C16–V2–V1–C24 = 149.7(3)°; C16–V1–C24 = 98.0(3)°, C16–V2–C24 = 98.8(3)°, V1–C16–V2 = 76.9(2)°, V1–C24–V2 = 76.6(2)°), forming a fairly short V–V distance (V1–V2 = 2.736(2) Å). In spite of being engaged in the formation of a metallacycle with one metal center, the two bridging carbon atoms are symmetrically placed between the two V atoms (V1–C16 = 2.221(7) Å, V1–C24 = 2.199(7) Å).

Differently from the cases of Zr and Th, where similar metallacyclenes[11] and metallacycles[12] originate from the metathesis of alkyl groups, the formation of 1 arises from a unique case of C–H $\sigma$-bond metathesis promoted by one amido group. At this preliminary stage, it is rather difficult to propose a possible mechanism. However, since the complex $[(Me_3Si)_2N]_3V$ has been reported to be stable, the deprotonation with consequent metallacycle formation must be performed by the third equivalent of $LiN(SiMe_3)_2$ acting as a base rather than a nucleophile.

The chemical reactivity of complex 1 has been preliminarily explored with CO (Scheme 1). The reaction proceeds slowly at room temperature and atmospheric pressure, forming a deep blue solution from which deep blue crystals of a new compound can be isolated in 55% yield.[13] The IR spectrum of this new species is almost identical with that of the starting material, except for the presence of two sharp absorptions at 1589 and 1162 cm$^{-1}$, which may be associated with the C═C and C—O stretching modes. No resonances indicative of formation of acyl groups from insertion of CO into the V—C bond were detected. Elemental analysis and gas volumetric measurements indicated that 2 equiv of CO per dimeric unit have been taken up.

The crystal structure of complex 2[14] revealed an unprecedented V(III) dinuclear enolate complex. The molecule is a centrosymmetric dimer (Figure 2) and is very similar to the starting dimer with comparable bond distances and angles of the terminal amide groups (V1–N1 = 1.927(4) Å, N1–Si1 = 1.738(5) Å, V1–N1–Si1 = 129.9(2)°, V1–N1–Si2 = 106.5(2)°, Si1–N1–Si2 = 123.1(3)°). The two enolate moieties form puckered five-membered rings with the two vanadium atoms and, by sharing the two oxygens, compose the dimeric unit. The O–C and C–C distances and the O–C–C angle within the enolate fragment (O1–C7 = 1.406(6) Å, C7–C13 = 1.320(8) Å, O1–C7–C13 = 120.8(6)°) are similar to those found in the other TMS-substituted enolates.[12,15–17] The V–V distance (V1–V1* = 3.126 Å) is significantly longer than in complex 1 and is also in agreement with the higher magnetic moment

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[13] A violet solution of 1 (2.5 g, 3.4 mmol) in toluene (50 mL) was exposed to CO gas (1 atm). The color of the solution changed to deep green-brown during the 3 days of stirring. The solution was evaporated to a small volume and added to *n*-hexane (20 mL). The blue microcrystalline 2 (1.49 g, 1.87 mmol, 55%) was obtained upon standing 2 days at –25 °C. Recrystallization from ether at 4 °C gave crystals suitable for X-ray analysis. IR (Nujol mull, cm$^{-1}$): 1589 (sh), 1251 (s), 1162 (s), 958 (vs), 926 (vs), 850 (vs), 769 (s), 710 (m), 670 (m), 639 (w), 551 (sh), 476 (sh), 443 (m), 415 (m). Anal. Calcd (found) for $C_{28}H_{70}N_4O_2Si_8V_2$: C, 39.16 (39.98); H, 8.85 (8.76); N, 7.03 (6.91). $\mu_{eff}$ = 3.86 $\mu_B$ at 294 K.

[14] Crystal data for 2: $C_{28}H_{70}Si_8N_4O_2V_2$, fw = 797.43, blue plate, monoclinic, *C*2/*c*, *a* = 23.123(8) Å, *b* = 9.700(8) Å, *c* = 20.402(5) Å, $\beta$ = 99.17(6)°, *Z* = 4, *V* = 4518(7) Å$^3$, $D_c$ = 1.172 g cm$^{-3}$, $\mu$ = 6.34 cm$^{-1}$, *T* = –150 °C, *R* = 0.056, $R_w$ = 0.068, GOF = 2.25 for 331 parameters and 2860 reflections out of 4239 reflections. Non-hydrogen atoms were refined anisotropically; hydrogen atom positions were calculated but not refined.

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($\mu_{eff}$(294 K) = 3.86 $\mu_B$ per dimeric unit) which, however, is still lower than expected for a high-spin $d^2$ electronic configuration of V(III).

The formation of the enolates arises from the formal insertion of CO into the Si–$CH_2$ bond under remarkably mild conditions. This kind of transformation, which is rather desirable for the functionalization of silanes, has (to the best of our knowledge) only a few precedents in the literature of group 4 metals[15,16] and actinides.[12,17] Although the reaction might be rationalized in terms of the same carbenoid mechanism,[12] a more complex pathway probably takes place, since the reactions of 1 with *t*-BuNC and with $(Me_3Si)N_3$ led to the formation of $\{[(Me_3Si)_2N]_3V\}\{CN\}$ and $[(Me_3Si)_2N]_3V{=}N(SiMe_3)$ rather than to the expected insertion products.[18]

**Acknowledgment.** This work was supported by the Natural Sciences and Engineering Research Council of Canada (operating grant).

**Supplementary Material Available:** Text giving details of the X-ray crystal structure determinations and tables giving crystal data, atomic positional parameters, anisotropic thermal parameters, complete bond distances and angles, and torsion angles for 1 and 2 (47 pages). Ordering information is given on any current masthead page.

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[18] Berno, P.; Gambarotta, S. Manuscript in preparation.