Reactivity of a Four-Membered Vanadacycle Ring Supported by Bulky Silazanate. Regioselective Hydrogenation of Pyridine

Pietro Berno and Sandro Gambarotta*

Department of Chemistry, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada

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Summary: The dinuclear $\{[(Me_3Si)_2N]V[\mu\text{-}N(SiMe_3)Si(Me)_2CH_2]\}_2$ *complex, containing a four-membered metallacyclic ring, has been obtained via reaction of* $VCl_3(THF)_3$ *with* $(Me_3Si)_2NLi$. *The reactivity of the metallacycle has been investigated with respect to the coordination of bases, hydrogenation, and insertion of alkynes.*

Although transition-metal amides are today well established[1] and a number of complexes have been discovered and characterized,[2] the current interest in the synthesis of precursors for the preparation of transition-metal nitrides[3] has revitalized synthetic studies in this field. In particular, transition-metal complexes of the bulky disilazanate anion[4] $[(Me_3Si)_2N]^-$ are interesting substrates not only because of their versatility as precursors for MVD but also because the unusual coordination geometries,[5] enforced by the considerable steric bulk of the disilazanate ligand, might be able to enhance the radical- or carbene-like activity of the metal center.

During our synthetic work in the chemistry of low- and medium-valent vanadium amides,[6] we have found that the reaction of $VCl_3(THF)_3$ with $LiN(SiMe_3)_2$ formed the dinuclear metallacyclobutane species $\{[(Me_3Si)_2N]V[\mu\text{-}N(SiMe_3)Si(Me)_2CH_2]\}_2$[7] (**2**) rather than the expected homoleptic tris(amido) complex, previously isolated and characterized using $VCl_3(NMe_3)_2$ as starting material.[8] In this paper, we wish to describe the preparation and characterization of a monomeric vanadacyclobutane species obtained *via* cleavage of **2** and a preliminary study on its chemical reactivity.

Scheme 1 summarizes our findings. Reaction of **2** with 1 equiv of $(Me_3Si)_2NH$ did not yield the expected homoleptic $[(Me_3Si)_2N]_3V$.[8] However, the room-temperature reaction of 2 equiv of pyridine[9] or collidine in toluene cleaved the dinuclear structure, affording the monomeric $[(Me_3Si)_2N]V[N(SiMe_3)Si(Me)_2CH_2]L$ (L = pyridine (**4**), collidine), where the metallacyclic structure has been conserved (Scheme 1).[9] The IR showed a sharp absorption at 1602 cm^{-1} (1622 cm^{-1} for the collidine adduct), characteristic of the aromatic C—C stretching mode of pyridine, while the magnetic moment increased to $\mu_{eff} = 2.89\ \mu_B$ compared to $\mu_{eff} = 2.31\ \mu_B$ *per dimer* found for the parent dinuclear **2**. Complex **4** is chiral at the vanadium atom, and the compound exists as a racemate. In spite of the close similarity of the structural features in the metallacyclic complexes **2** and **4**, the cleavage of the dimeric structure of **2** has important consequences for the reactivity. The reaction of a toluene solution of **4** with CO (1 atm) afforded the same dimeric enolate **3** obtained from carbonylation of **2**.[7] However, the reaction was rapid at room temperature and atmospheric pressure, while in the

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(9) The blue-violet color of a toluene (50 mL) solution of **2** (2.77 g, 3.57 mmol) suddenly changed to ink blue upon addition of neat pyridine (0.6 mL, 7.5 mmol). After the mixture stood at room temperature overnight, the solvent was evaporated in vacuo and the dark red residue was redissolved in *n*-hexane (40 mL). Dark red microcrystalline **4** (1.52 g, 3.15 mmol, 44%) was obtained on cooling the resulting solution at −78 °C. X-ray-quality crystals were obtained by cooling to 4 °C a concentrated *n*-hexane solution. $\mu_{eff} = 2.89\ \mu_B$. IR (Nujol, KBr, cm^{-1}): ν 1602 (sp), 1482 (sp), 1453 (s), 1246 (vs), 980 (vs), 822 (vs), 675 (vs), 632 (m), 614 (m), 479 (m), 434 (w). Anal. Found (calcd) for $C_{17}H_{40}N_3Si_4V$: C, 45.98 (45.39); H, 8.36 (8.96); N, 8.60 (9.34).

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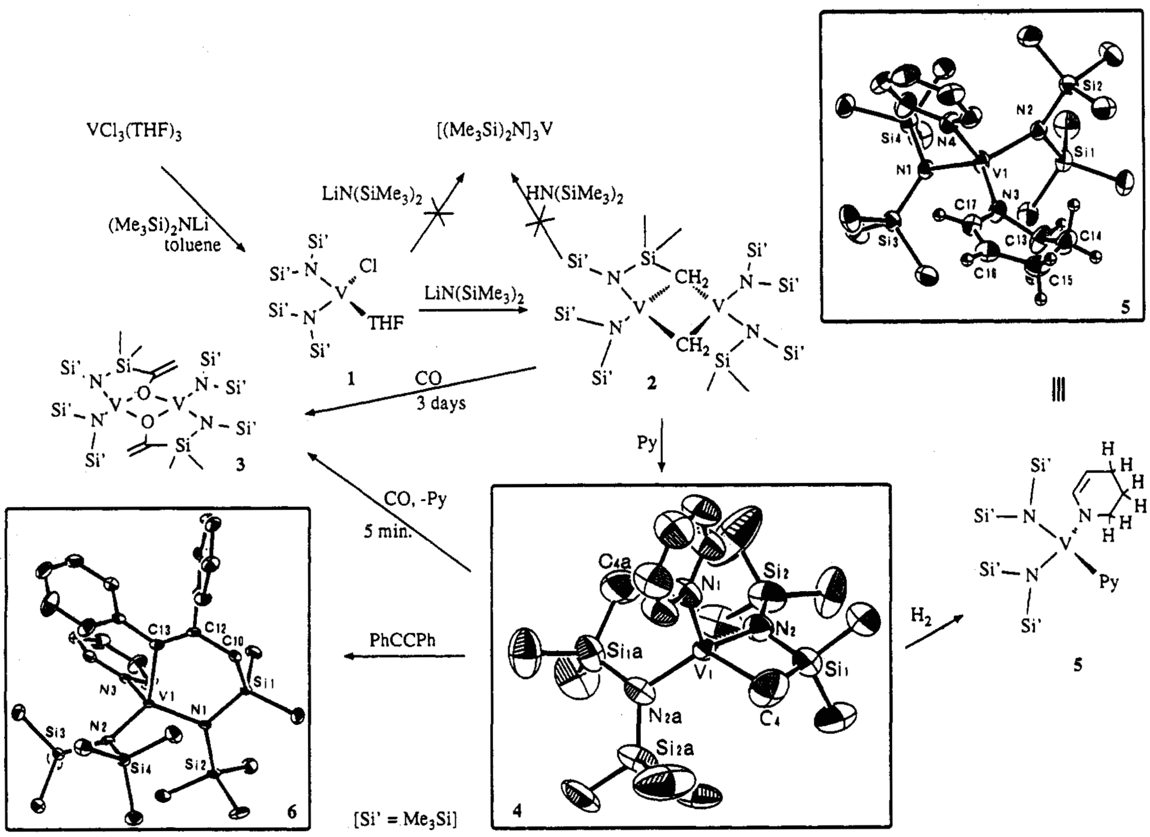
Scheme 1 [a]



[a] ORTEP Drawings of 4–6 are drawn at the 50% probability level. Selected values of bond distances (Å) and angles (deg) are as follows. 4: V1—N1 = 2.07(2), V1—N2 = 1.94(2), V1—C4 = 2.15(1), Si1—N2 = 1.735(4), Si1—C4 = 1.835(6); N1—V1—C4 = 98.5(8), N1—V1—N2 = 112.3(8), V1—C4—Si1 = 81.6(5), C4—Si1—N2 = 102.4(2), V1—N2—Si1 = 113.1(4). 5: V1—N1 = 1.986(2), V1—N2 = 1.961(2), V1—N3 = 1.935(2), V1—N4 = 2.099(2), N3—C13 = 1.467(4), N3—C17 = 1.382(3), C16—C17 = 1.336(4), C13—C14 = 1.495(4); N1—V1—N2 = 121.25(9), N1—V1—N3 = 102.37(9), N1—V1—N4 = 99.70(9), N2—V1—N3 = 109.36(9), N2—V1—N4 = 109.86(9), N3—V1—N4 = 90.18(9). 6: V1—N1 = 1.938(2), V1—C13 = 2.093(3), V1—N2 = 1.952(2), V1—N3 = 2.095(2), C13—C12 = 1.350(4), C12—C10 = 1.511(4), C10—Si1 = 1.875(3), N1—Si1 = 1.734(2); N1—V1—N2 = 119.5(1), N1—V1—N3 = 104.4(1), N2—V1—N3 = 113.4(1), N1—V1—C13 = 107.4(1), V1—C13—C12 = 123.9(2), C10—C12—C13 = 123.6(3), V1—N1—Si1 = 113.9(1).

case of 2 the same reaction requires at least 3 days to be completed. Complex 3 was the only product which could be isolated in 70% yield.

The monomeric nature of 4 was elucidated by an X-ray crystal structure.[10] The tetrahedral coordination geometry of the vanadium atom is defined by the nitrogen and the carbon atom of the metallacylcobutane ring, the nitrogen atom of the amido group, and the pyridine molecule (Scheme 1). The vanadium atom was found disordered over two positions with 50% occupancies and as a result of that, the metallacycle may be formed with equal probability with either one of the two amide groups. This disorder is likely to be the result of the presence of a racemic mixture.

Complex 4 reacts with H_2, slowly at room temperature and 1 atm or rapidly in an autoclave (400 psi),[11] to give the unprecedented enamido[12] complex $[(Me_3Si)_2N]_2V$-(2,3-didehydropiperidinato)(pyridine) (5) in reasonable yield. This species arises from the formal uptake of two molecules of H_2, with resulting cleavage of the V—CH_2 bond and hydrogenation of the positions 4, 5, and 6 of the pyridine ring. The formation of 5 is likely to proceed *via* an intermediate $[(Me_3Si)_2N]_2V(H)$(pyridine) hydride complex which, upon transferring the hydride to the pyridine ring, reacts with a second molecule of H_2 to further hydrogenate the ring. The presence of the residual double bond in the piperidine ring has been unambiguously demonstrated by an X-ray structure (Scheme 1).[13]

The formation of 5 is a very rare example of regioselective hydrogenation of pyridine achieved with a homogeneous system. At this stage it is difficult to imagine why the

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[10] Crystal data for 4: $C_{17}H_{40}N_3Si_4V$, fw = 449.81, black cube, monoclinic, $P2/n$, a = 10.682(4) Å, b = 11.121(4) Å, c = 11.645(2) Å, β = 103.30(2)°, Z = 2, V = 1346(1) Å^3, D_c = 1.117 g/cm^3, μ = 6.32 cm^{-1}, T = −157 °C, R = 0.059, R_w = 0.071 for 142 parameters and 1598 reflections out of 2384. Non-hydrogen atom positions were refined anisotropically. Hydrogen atoms were introduced at their idealized positions but not refined. After the molecule was expanded over the symmetry operation, the vanadium atom was disordered over three positions (two general and one special) with occupancies of 0.25 and 0.50, respectively. The carbon atoms of one of the two trimethylsilyl groups were also found disordered over two positions. The disorder was modeled by equally splitting the occupancy of each carbon atom over the two positions. The significant improvement of the refinement confirmed the goodness of the model.

[11] A burgundy red solution of 4 (2.54 g, 5.65 mmol) in toluene (20 mL) was pressurized with H_2 (400 psi). After 2 days at room temperature, a brown solution was obtained, which was evaporated to dryness. The brown residue was redissolved in hexane (30 mL); this solution was allowed to stand at −78 °C overnight, from which brown crystals of 5 (1.09 g, 2.0 mmol, 36%) separated. μ_{eff} = 2.91 μ_B. IR (Nujol, KBr, cm^{-1}): ν 1627 (sp), 1259 (vs), 1093 (vs), 1022 (vs), 800 (br, vs). Anal. Found (calcd) for $C_{22}H_{49}N_4Si_4V$: C, 49.31 (49.58); H, 8.88 (9.27); N, 9.97 (10.51).

[12] Duchateau, R.; Williams, A. J.; Gambarotta, S.; Chiang, M. Y. *Inorg. Chem.* **1991**, *30*, 4863.

[13] Crystal data for 5: $C_{22}H_{49}N_4Si_4V$: fw = 532.94, brown cube, triclinic, $P\bar{1}$, a = 11.216(4) Å, b = 16.873(6) Å, c = 8.878(4) Å, α = 102.35(3)°, β = 105.35(3)°, γ = 73.47(3)°, Z = 2, V = 1536(2) Å^3, D_c = 1.152 g/cm^3, μ = 4.81 cm^{-1}, T = −151 °C, R = 0.039, R_w = 0.052 for 477 parameters and 4402 reflections out of 5069. Non-hydrogen atom positions were refined anisotropically. Hydrogen atoms were introduced at their idealized positions but not refined.

reaction does not proceed further toward the complete ring hydrogenation or why is not catalytic.[14] Moreover, the presence in complex **5** of a second, intact pyridine completing the tetrahedral geometry of the vanadium atom suggests that the reaction pathway might be rather complex and that other unidentified species might be present in the reaction mixture. We suggest that the regioselectivity of the hydrogenation is the result of a fairly high stability of the vanadium enamido moiety caused by the conjugation of the C═C π-bond with the vanadium center through the trigonal-planar coordination geometry of the nitrogen atom. This idea is supported by theoretical calculations, carried out on a 1,2,3,4-tetrahydropyridine model compound,[15] which predict an increase of stabilization energy when the conjugation of the C═C with the nitrogen lone pair is enhanced by the presence of bulky substituents on the nitrogen equatorial position.

Attempts to carry out similar hydrogenolysis of the V—CH_2 bond of the metallacycle of **2**, under high pressure and at room temperature in the absence of pyridine, failed since only unreacted starting materials could be isolated together with a small amount of intractable products.

The unusual insertion mode of CO into the Si—CH_2 bond of **4**[7] prompted us to investigate the reactivity of the vanadacyclobutane ring with respect to the insertion of unsaturated substrates. Alkynes, such as diphenylacetylene and $Me_3SiCCSiMe_3$, inserted into the V—CH_2 bond[16] to give ring expansion and formation of the monomeric and paramagnetic $[(Me_3Si)_2N]V[\mu\text{-}N(SiMe_3)Si(Me)_2CH_2C(R){=}C(R)]Py$ (R = Ph (**6**), $SiMe_3$ (**7**)) containing a six-membered metallacyclic ring (Scheme 1).[17]

In summary, this preliminary work has shown that the vanadacyclobutane ring of complex **4** possesses a promising reactivity. Further work to identify and characterize V–hydride species and their possible application in catalytic processes is in progress at the moment.

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Supplementary Material Available: Text giving details of the structure determination, ORTEP drawings showing the full labeling schemes, and tables listing atomic positional parameters, anisotropic thermal parameters, complete bond distances and angles, and torsion or conformation angles for **4**–**6** (68 pages). Ordering information is given on any current masthead page.

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(14) Experiments carried out under pressure of H_2 (400 psi) and in the presence of a large excess of pyridine (20 equiv) did not show formation of any product other than **5** in significant amount.

(15) Buchrach, S. M.; Liu, M. *Tetrahedron Lett.* **1992**, *33*, 6771.

(16) Solid diphenylacetylene (1.48 g, 8.31 mmol) was added to a solution of **4** (3.74 g, 8.26 mmol) in hexane (100 mL). The color slowly changed to dark brown upon standing 3 days at room temperature. Large crystals of **6** (2.62, 4.17 mmol, 50%) were grown by partial evaporation of the solvent and standing at room temperature. $\mu_{eff} = 2.70\ \mu_B$. IR (Nujol, KBr, cm^{-1}): ν 3064 (sp), 1593 (sp), 1555 (sp), 1250 (vs), 851 (br, vs), 780 (vs), 762 (vs), 668 (vs), 525 (sp), 495 (sp), 463 (sp). Anal. Found (calcd) for $C_{31}H_{50}N_3Si_4V$: C, 58.93 (59.29); H, 7.76 (8.02); N, 6.38 (6.69). Compound **7** was prepared in an identical procedure by using $Me_3SiCCSiMe_3$ (yield 36%). $\mu_{eff} = 2.93\ \mu_B$. IR (Nujol, KBr, cm^{-1}): ν 1604 (s), 1459 (s), 1444 (vs), 1247 (br vs), 1066 (m), 1014 (m), 908 (vs), 879 (sp), 840 (vs, vb), 782 (s), 758 (s), 694 (vs), 669 (vs). Anal. Found (calcd) for $C_{25}H_{58}Si_6N_3V$: C, 48.42 (48.41); H, 10.01 (9.43); N, 6.97 (6.78).

(17) Crystal data for **6**: $C_{31}H_{50}N_3Si_4V$, fw = 628.04, green cube, triclinic, $P\bar{1}$, $a = 10.368(3)$ Å, $b = 18.708(4)$ Å, $c = 9.823(3)$ Å, $\alpha = 95.30(2)°$, $\beta = 110.79(2)°$, $\gamma = 89.72(3)°$, $Z = 2$, $V = 1773(2)$ Å^3, $D_c = 1.176$ g/cm^3, $\mu = 4.25$ cm^{-1}, $T = -150$ °C, $R = 0.045$, $R_w = 0.063$ for 353 parameters and 4233 reflections out of 4739. Non-hydrogen atom positions were refined anisotropically. Hydrogen atoms were introduced at their idealized positions but not refined.