Insertion *versus* Elimination in the Reaction of Bu^{t}NC with a Azasilavanadacyclobutane Ring supported by Hexamethylsilazanate Ligand

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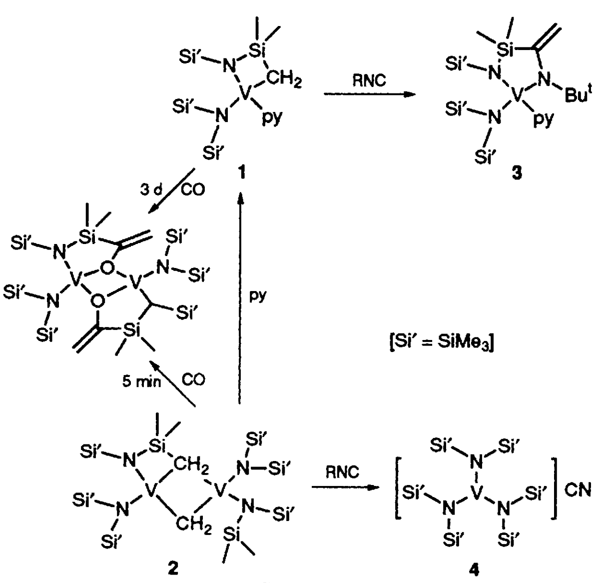
Reaction of the azasilavanadacyclobutane ring of the monomeric $[V\{(Me_3Si)_2N\}\{CH_2SiMe_2N(SiMe_3)\}(py)]$ with isonitrile gave insertion and ring expansion, while the same reaction carried out with the metallacycle of the dimeric $[V\{(Me_3Si)_2N\}\{CH_2SiMe_2N(SiMe_3)\}]_2$ formed an ionic and tetravalent $[V\{(Me_3Si)_2N\}_3]CN$ complex.

The ability of metallacyclobutane rings of early transition metals to exist in equilibrium with carbene species[1a] is probably the key to understanding the very high reactivity and the versatility of these derivatives. Olefin metathesis[1] and polymerization,[2] and incorporation of C_1 moieties[3] (CO, CH_2O, isocyanides) in the metallacycles are rather common transformations which involve carbenes or metallacyclobutanes, and which are widely used in catalysis[4] or for the preparation of a variety of organometallic functions.[5] In particular, the migratory insertion of CO and isonitriles into the M–C and M–H bond of early transition metals and lanthanides to form acyl, formyl and iminoacyl functions, is a very useful and well established process.[6] However, examples of these reactions involving non-cyclopentadienyl complexes remain limited to the coupling of η^2-iminoacyl moieties promoted by complexes of bulky alkoxides.[7] Very little is known about the chemical reactivity of metallacyclobutane moieties with isonitriles.[8]

In this paper, we describe the reaction of an organic isocyanide with a azasilavanadacyclobutane ring supported by a silazanate ligand.

The monomeric $[V\{(Me_3Si)_2N\}\{\mu\text{-}CH_2SiMe_2N(SiMe_3)\}(py)]$[9] **1** and the dimeric $[V\{(Me_3Si)_2N\}\{\mu\text{-}CH_2SiMe_2N(SiMe_3)\}]_2$ **2**,[10] both containing a four-membered azasilavanadacyclobutane group, react with CO to yield the same enolate derivative **3** *via* a formal insertion of CO in the $SiCH_2$ bond of the metallacycle (Scheme 1).[10] By contrast, the reaction of **1** and **2** with Bu^{t}NC took surprisingly different pathways depending on the nuclearity of the starting material (Scheme 1). Treatment of a toluene solution of **1** with 1 equiv. of Bu^{t}NC at room temperature gave a fast reaction with formation of the black crystalline $[V\{(Me_3Si)_2N\}\{N(SiMe_3)Si(CH_3)_2C(=CH_2)NBu^t\}(py)]$ **3** in good yield.† Analytical data formulated the new species as an addition compound and the magnetic moment ($\mu_{eff} = 2.75\ \mu_B$ at room temp.) indicated that the trivalent oxidation state of the metal centre remained unchanged. The IR spectrum showed a broad and intense absorption at 1533 cm^{-1}, possibly indicative of the presence of an olefinic function.



Scheme 1

An X-ray crystal structure‡ has revealed the chemical connectivity of compound **3** (Fig. 1). The molecule consists of a vanadium atom placed in the centre of a slightly distorted tetrahedron [N(1)–V–N(2) 113.8(1), N(1)–V–N(3) 95.1(1), N(1)–V–N(4) 107.6(1), N(2)–V–N(3) 121.3(1)°] defined by one nitrogen atom of a silazanate [V–N(2) 1.946(3) Å], one of the coordinated pyridine molecule [V–N(1) 2.103(3) Å] and two of the chelating $NBu^tC(=CH_2)Si(Me)_2N(SiMe_3)$ unit [V–N(3) 1.972(3), V–N(4) 1.946(3) Å] of the metallacycle.

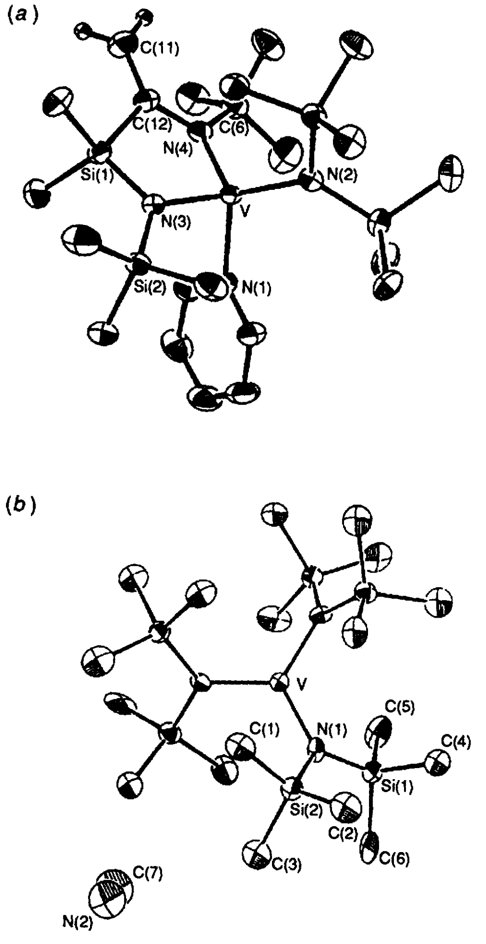


Fig. 1 ORTEP drawings of **3**(*a*) and **4**(*b*) drawn at the 50% probability level. Relevant bond distances (Å) and angles (°). Complex **3**: V–N(1) 2.103(3), V–N(2) 1.946(3), V–N(3) 1.972(3), V–N(4) 1.946(3), C(10)–C(11) 1.346(5), N(4)–C(10) 1.403(4), C(10)–C(11) 1.346(5), N(1)–V–N(2) 113.8(1), N(1)–V–N(3) 95.1(1), N(1)–V–N(4) 107.6(1), N(2)–V–N(4) 117.8(1), N(2)–V–N(3) 121.3(1), N(3)–V–N(4) 97.9(1), V–N(4)–C(10) 111.8(2), N(4)–C(10)–Si(1) 112.1(2), N(4)–C(10)–C(11) 129.6(3), Si(1)–C(10)–C(11) 118.2(3). Complex **4**: V–N(1) 1.91(1), N(1)–Si(1) 1.73(1), N(1)–Si(2) 1.79(1), N(2)–C(7) 1.21(2), N(1)–V–N(1) 119.9(3), V–N(1)–Si(1) 121.7(7), V–N(1)–Si(2) 118.1(7), Si(1)–N(1)–Si(2) 120.2(7).

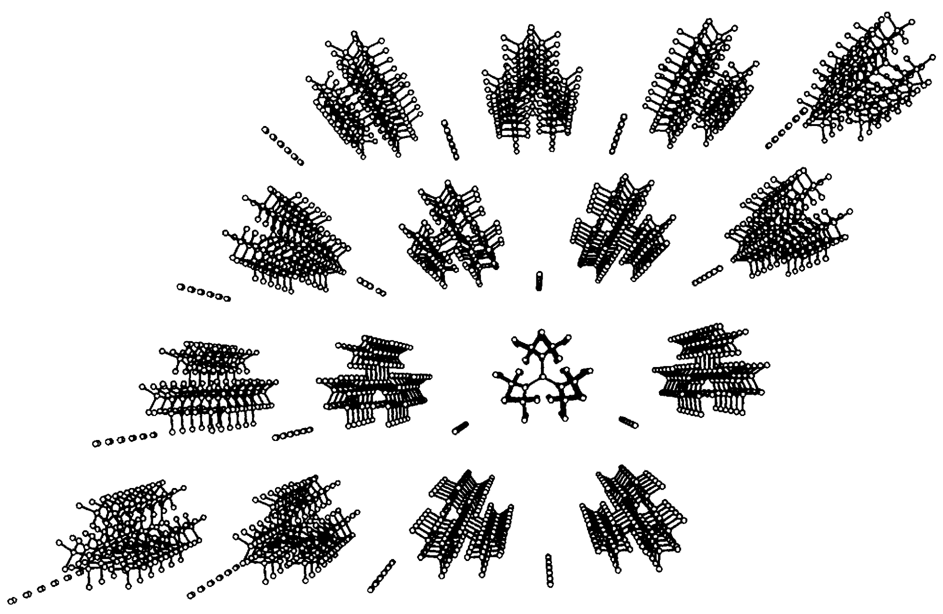


Fig. 2 Packing diagram of complex **4** showing the columnar arrangement

The metallacycle [N(3)–V–N(4) 97.9(1)°] is planar as a result of the trigonal-planar coordination geometry of both nitrogen donor atoms [V–N(4)–C(10) 111.8(2), V–N(3)–Si(1) 106.8(1)°] and of the C atom used in the formation of the C=CH_2 group [C(10)–C(11) 1.346(5) Å, Si(1)–C(10)–N(4) 112.1(2)°]. The vanadium atom is chiral and the two enantiomeric molecules are present in the unit cell as two crystallographically independent molecules.

The vinyl group of complex **3** arises from the formal insertion of Bu^{t}NC carbon atom into the Si–CH_2 bond of the metallacycle of **1**. The consequent formation of the enamido group during this anomalous insertion[8] is rather surprising because eneamines, although widely used, are well-known for their instability and high reactivity, which has not allowed these species to be isolated. On the other hand, the V–N π bond is conjugated with the olefinic moiety, probably introducing a considerable amount of stabilization energy. Furthermore the formation of a transition metal enamide moiety provides the thermodynamic driving force for some unusual transformations recently described, such as 1,2-hydrogen migration,[11] regioselective pyridine hydrogenation[9] and dehydrogenation of aliphatic groups.[12] Therefore, the formation of the enamido group in complex **3** is likely to be the factor determining the unusual insertion mode of the isonitrile.

Reaction of **2** with Bu^{t}NC, carried out under identical reaction conditions, proceeded in a remarkably different manner. The reaction afforded a brown-black crystalline compound **4** which showed a very intense and sharp resonance in the IR spectrum at 2159 cm^{-1}.§ Both the analytical data and the presence of a mixture of isobutene and isobutane in the mother-liquor indicated that an elimination reaction, rather than the expected insertion had taken place in this case. Once again the chemical connectivity has been elucidated by an X-ray crystal structure.¶ The molecule is composed of two separate ionic fragments. The cation is a trigonal-planar vanadium atom [N(1)–V–N(1a) 119.95(3)°] surrounded by three symmetrically placed silazanate groups [V–N(1) 1.91(1) Å]. The geometry around the amide nitrogen atoms is trigonal planar [V–N(1)–Si(1) 121.7(7), V–N(1)–Si(2) 118.1(7), Si(1)–N(1)–Si(2) 120.2(7)°] with the planes of the three amido ligands skewed with respect to each other, conferring an overall propeller shaped geometry to the vanadium atom. The CN^- counter anion [N(2)–C(7) 1.21(2) Å] does not form any bonding contact with the metal centre.

The formation of **4** is probably just part of a more complicated reaction requiring a major molecular rearrangement, where one amido group was acquired by the metal centre. However, attempts to isolate other species in the reaction mixture were unsuccessful.

The ionic structure of **4** is somewhat surprising. In fact the small size of the V^{IV} cation and the large steric encumbrance of the silazanate ligand alone cannot justify an ionic structure, especially in the view of the small dimension of the CN^- anion {for example, the closely related Ti^{IV} derivative [TiCl{($Me_3Si)_2N\}_3$] is tetrahedral}.[13] Therefore, the d^1 electronic configuration of the vanadium atom has to be responsible for the unusual ionic structure. An EHMO calculation, performed on the model cation $[V\{N(SiH_3)\}_3]^+$ using the geometrical parameters obtained from the crystal structure, has shown the presence of three almost degenerate HOMOs (at −7.78, −7.79 and −7.80 eV) with 1/3 occupancy and which basically are the d_{z^2}, d_{zx} and d_{zy} orbitals. The other two $d_{x^2-y^2}$ and d_{xy} orbitals are the LUMO and are also almost degenerate (−7.12 and −6.98 eV). Although the HOMO/LUMO gap is rather small, the geometry and the orientation of the LUMO appears unfavourable to accommodate the CN^- anion, therefore resulting in the observed ionic structure.

The magnetic moment of **4** is also intriguing. The dependence of the magnetic susceptibility with temperature in the rangee 5.82–307 K showed a perfect agreement with the Curie law, with a very small antiferromagnetic deviation at low temperature (θ = 1 K). Variable-field measurement (0–6 G) at 5.82 K showed slight ferromagnetic behaviour as well. However, the resulting magnetic moment [μ_{eff} = 2.37 μ_B] is significantly higher than expected for a d^1 electronic configuration of V^{IV}. A possible explanation may be obtained by analysing the unique crystal packing of **4** which shows that the triangular $[V\{(Me_3Si)_2N\}_3]$ cations are parallel to each other assembling pillars (Fig. 2). The cationic pillars which compose the crystal lattice are also parallel to each other and are surrounded by parallel and linear arrays of cyanide anions placed according the trigonal symmetry of the crystal. This packing is even more surprising considering that there are no bonding contacts between the vanadium atoms of the parallel triangular cations within each pillar [V···V 8.520(2) Å]. We tentatively suggest that, similar to the case of [VO(salpn)] [H_2salpn = *N,N′*-propane-1,3-diylbis(salicylideneimine)],[14] the overall magnetic moment of this compound is the result of two contrasting factors: antiferromagnetic exchange across the pillars and ferromagnetism alongside the pillars with a small prevalence of ferromagnetism.

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Footnotes

† *Preparation* of **3**: The addition of neat Bu^{t}NC (0.9 ml, 8.0 mmol) to a purple solution of **1** (3.6 g, 8.0 mmol) in toluene (50 ml) turned the colour dark green. The solution was evaporated to dryness and the dark green residue was redissolved in hexane (50 ml) by stirring and gentle heating to 50 °C. After removal of the insoluble material by filtration, black microcrystals of **3** formed at room temp. (2.1 g, 3.9 mmol, 49%). Crystals suitable for X-ray analysis were obtained from the mother-liquor upon concentration and standing at −25 °C (0.9 g, 1.7 mmol, 21%). (μ_{eff} = 2.75 μ_B at room temp.). IR ($\tilde{\nu}$/cm^{-1}, Nujol mull) 3072sp, 1600w, 1533br, 1484sp, 1444s, 1396w, 1378sp, 1357sp, 1246s, 1217sp, 1192sp, 1041m, 979vs, 900vs, 846br, vs, 794s, 767s, 708s, 673m, 639m, 511w, 464w, 430w. Satisfactory combustion analysis data were obtained.

‡ *Crystal data* for complex **3**: Two chemically equivalent but crystallographically independent molecules were found in the unit cell. $C_{44}H_{98}N_8Si_8V_2$, M = 1065.88, triclinic, space group $P\bar{1}$, a = 16.165(1), b = 17.898(2), c = 10.953(2) Å, α = 98.89(1), β = 98.11(2), γ = 96.04(2)°, V = 3073(1) Å^3, Z = 2, R = 0.039, R_w = 0.052, GOF = 2.29 for 560 parameters and 6618 out of 7782 unique reflections. Non-hydrogen atom were refined anisotropically. Hydrogen atoms were introduced at their calculated positions.

§ *Preparation of* **4**: Neat Bu^{t}NC (0.40 ml, 3.3 mmol) was added by syringe to a blue-violet solution of **2** (1.2 g, 1.7 mmol) in hexane (30 ml). The colour immediately turned dark green. The solution was allowed to stand for 2 days at room temperature, during which time the colour turned dark brown. After evaporation to one half of the initial volume and cooling to −30 °C, dark brown–black crystals of **4** separated (0.2 g, 0.3 mmol, 20%). μ_{eff} = 2.37 μ_B at room temp. IR ($\tilde{\nu}$/cm^{-1}, Nujol mull) 3077sp, 2159vs, 1516br, 1357sp, 1246vs, 1198vs, 1040m, 978vs, 926vs, 846br, vs, 763vs, 705s, 672s, 639m, 512sp, 462sp. Satisfactory combustion analysis data were obtained.

¶ *Crystal data* for complex **4**: $C_{19}H_{54}N_4Si_6V$, M = 558.12, trigonal, space group $P\bar{3}$, a = 16.053(4), c = 8.520(2) Å, V = 1897.0(8) Å^3, Z = 2, R = 0.057, R_w = 0.070, GOF = 2.44 for 79 parameters and 477 out of 711 unique reflections. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at their calculated position. The CN group was found to be disordered over two positions along the three-fold axis. The disorder was modelled by equally splitting the occupancy over the two positions. The significant improvement of the refinement confirmed the goodness of the model.

Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at The Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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