Formation of a vanadium(v) bicyclic carbene–amide complex *via* insertion of alkyne into a V–C bond

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Reaction of $[(Me_3Si)_2N]_2V(thf)(BH_4)$ with excess diphenylacetylene leads to the formation of the bicyclic carbene complex $(Me_3Si)_2NVN(SiMe_3)SiMe_2CH_2C(Ph)C(Ph)C(Ph)$-$C(Ph)$ 1 which is isolated as brown diamagnetic crystals cocrystallized with *trans*-stilbene; the same compound *trans*-stilbene-free is also prepared *via* reaction of $\{[(Me_3Si)_2N]V[\mu\text{-}CH_2SiMe_2N(SiMe_3)]\}_2$ with 4 equiv. of diphenylacetylene.

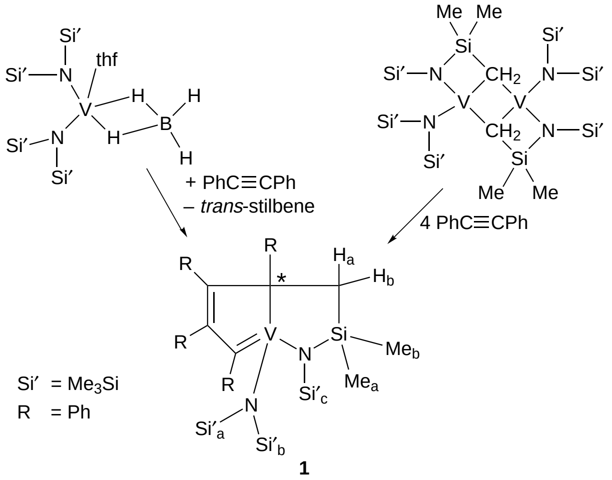
A very large part of the organometallic chemistry of vanadium has been developed with the utilization of cyclopentadienyl ligands[1] with which it is possible to stabilize reactive functions such as carbenes[2] and hydrides.[3] Nitrogen donor based ligands (amides, amidinates) provide a convenient and accessible alternative to the cyclopentadienyl ligand systems, since they significantly enhance the reactivity of the vanadium centre,[4] stabilize rare vanadium species such as dinitrogen,[5] azide,[6] nitride,[7] metallacyclic[8] and alkyl complexes[9] or assist the metal in hydrogen-transfer reactions.[5c,10]

Here we describe the formation and the unusual NMR feature of a unique bicyclic vanadium(v) derivative supported by silazanate ligand, which is also a rare example of a vanadium carbene complex.[2]

According to Scheme 1, the reaction of $[(Me_3Si)_2N]_2V(thf)(BH_4)$[11] with diphenylacetylene in hexane proceeds rapidly at room temperature to yield a brown solution from which dark diamagnetic crystals of **1** were isolated in low yield.† The presence of *trans*-stilbene in the lattice in the ratio 2 : 1, as shown by the X-ray crystal structure,‡ was confirmed by ^{1}H NMR spectroscopy.

The complex is monomeric and features a distorted tetrahedral geometry around the vanadium atom which is combined in two fused five-membered metallacycles (Fig. 1). One intact amide group occupies the fourth coordination site of vanadium. One metallacycle is formed *via* linkage of a CH_2 unit from a trimethylsilylamide function with a carbon atom at one end of the coupled tolane units. The second metallacycle is composed of two diphenylacetylene units forming a tetraphenylvanadacyclopentadiene ring. The geometry around three of the four carbon atoms is trigonal planar, suggesting an sp^2 hybridization for these atoms. Conversely, the fourth carbon atom shared with the first ring is tetrahedral and chiral. The vanadium atom is also chiral and the enantiomer is present as a second molecule in the triclinic cell together with one molecule of stilbene.

At this stage, we are unable to provide a non-speculative explanation for the formation of **1**. However, the production of *trans*-stilbene during the formation of **1** suggests that the first step of the reaction is probably the hydrogenation of diphenylacetylene Complex **1** could also be prepared without *trans*-stilbene and in significantly higher yield (44%)† by reacting the previously reported dinuclear vanadacycloazabutane $\{[(Me_3Si)_2N]V[\mu\text{-}CH_2SiMe_2N(SiMe_3)]\}_2$[8] with 4 equiv. or an excess of diphenylacetylene. In this case, the formation of **1** is simply the result of the insertion of two molecules of diphenylacetylene into the V–CH_2 bond of the metallacycle followed by a tautomeric reorganization of the macrocycle into the bicyclic structure. The formation of **1** from both reactions suggests that perhaps $\{[(Me_3Si)_2N]V[\mu\text{-}CH_2SiMe_2N(SiMe_3)]\}_2$ is produced as a transient intermediate of the reaction of $(Me_3Si)_2N]_2V(thf)(BH_4)$ with diphenylacetylene after the initial formation of *trans*-stilbene. The addition of only



Scheme 1

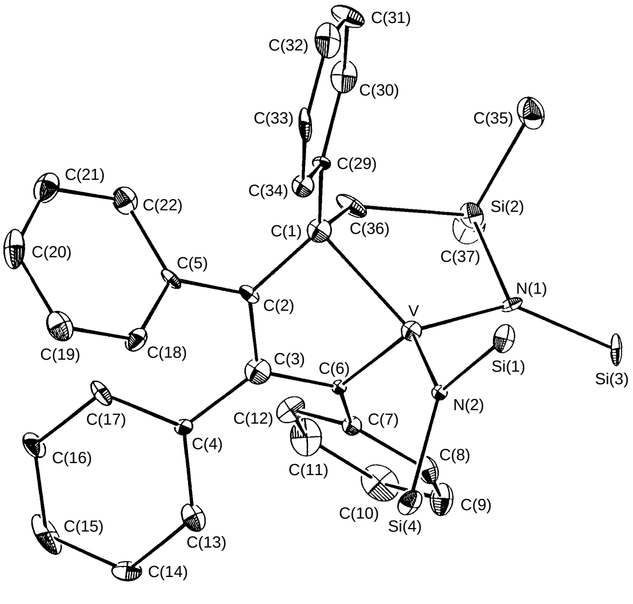


Fig. 1 ORTEP plot of **1**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angles (°): V–N(1) 1.849(5), V–N(2) 1.889(5), V–C(1) 2.092(7), V–C(6) 1.876(7), N(1)–Si(2) 1.729(5), Si(2)–C(36) 1.918(7), C(1)–C(36) 1.541(9), C(1)–C(2) 1.467(9), C(2)–C(3) 1.43(1), C(3)–C(6) 1.406(9); V–N(1)–Si(2) 99.3(3), V–C(1)–C(36) 85.4(4), V–C(1)–C(2) 90.5(4), N(1)–V–N(2) 111.9(2), N(2)–V–C(6) 116.4(3), V–C(6)–C(3) 100.1(5), Si(2)–C(36)–C(1) 123.4(5), C(2)–C(3)–C(6) 117.0(6), C(1)–C(2)–C(3) 119.0(6).

1 equiv. of tolane to $\{[(Me_3Si)_2N]V[\mu\text{-}CH_2SiMe_2N(SiMe_3)]\}_2$ still gave the diamagnetic and pentavalent **1** albeit in lower yield. This behaviour is remarkably different from that of the monomeric pyridine adduct $[(Me_3Si)_2N]V[\mu\text{-}CH_2SiMe_2N(SiMe_3)](py)$, which reacts with diphenylacetylene to give a monoinserted vanadium(iii) paramagnetic species.[10]

The diamagnetism of **1** indicates a formal oxidation state (+5) for the vanadium centre, which implies the existence of a formal V–C double bond. Since the rigid structure observed in the solid state is reasonably expected to be maintained in solution, the crystal structure also provides the key to interpreting the remarkable NMR features of complex **1**. The intact group features two sharp singlets (Si'_a and Si'_b) at δ 0.63 and 0.61, consistent with the fact that the two $SiMe_3$ groups point respectively above and below the folded molecular plane. The $SiMe_3$ of the second amide group (Si'_c) exhibits a rather broad singlet centred at δ −0.05. Remarkably, the two methyl groups of the silicon atom engaged in the formation of the first metallacycle (CH_{3a} and CH_{3b}) give rise to two widely separated signals at δ 0.32 and −0.82. Even more surprising, the two enantiotopic hydrogens of the methylene group (H_a and H_b) produce two doublets positioned far apart from each other at δ 2.85 and −1.43. HQMC experiments clearly indicate that these two protons are attached to the same carbon atom resonating at δ 20.4 in the ^{13}C NMR spectrum. The ^{51}V NMR resonance was located as a rather broad line (1800 Hz) at δ +1318.8.[12] Variable-temperature spectra show the expected broadening of the line (4300 Hz at 210 K) but also a significant downfield shift of about 100 ppm. Some of the hydrogen lines of the ^1H NMR spectrum also significantly broaden and shift at low temperature, suggesting the presence of fluxionality. At low temperature, the line at δ −0.05, attributed to the three methyl groups of the Si'_c group, collapsed and resolved into three sharp resonances at δ 0.39, −0.18 and −0.51. However, under the same conditions, the resonances arising from CH_{3a} and CH_{3b} and the two enantiotopic methylene protons (H_a and H_b) broadened only slightly. In contrast to the minor line broadening, the resonance at δ 2.85 shifted by about 1 ppm to higher field while the resonance at δ −0.82 shifted by only 0.3 ppm in the same direction. The crystal structure showed that one of these two enantiotopic protons is considerably closer to the vanadium centre than the other [V–H(59) 2.73, V–H(60) 3.11 Å]. A similar feature has been observed with the two methyl groups CH_{3a} and CH_{3b}. However, no significant variation of the chemical shift was found over a range of temperature for these two methyl groups.

This work was supported by the National Science and Engineering Council of Canada (NSERC) through a strategic and operating grant. We are grateful to Professor D. Rehder (Hamburg) for helpful discussions.

Footnotes

† *Synthesis and characterisation*: *Method A.* A blue solution of $[(Me_3Si)_2N]_2V(thf)(BH_4)$ (6.26 mmol) in hexane (70 ml) was treated with diphenylacetylene (20.56 mmol) at room temp. The resulting brown mixture was stirred overnight. A light brown material was removed by filtration and the resulting dark brown solution was kept at −30 °C for several weeks. Dark crystals of $\mathbf{1}\cdot 0.5\ C_{14}H_{12}$ were obtained (0.2 g, 0.7 mmol, 8%). Anal. Calc. (found) for $C_{47}H_{61}N_2Si_4V$: C 69.07 (70.40), H 7.52(7.63), N 3.43 (3.20)%.

Method B. A suspension of $\{[(Me_3Si)_2N]V[\mu\text{-}CH_2SiMe_2N(SiMe_3)]\}_2$ (2.0 g, 2.6 mmol) in hexane (50 ml) was reacted with diphenylacetylene (1.86 g, 10.4 mmol) at room temperature. The mixture was stirred overnight at room temperature, during which time the colour had changed to brown. After 24 h, the mixture was filtered to eliminate a small amount of brown insoluble material. The resulting intense red–brown solution was concentrated to approximately 15 ml until incipient crystallization of a brown material. The solution was allowed to stand overnight at 4 °C to yield a crop of brown crystals of $\mathbf{1}\cdot 0.5C_6H_{14}$ (1.66 g, 2.1 mmol, 44%). Spontaneous loss of hexane prevented accurate and reproducible analytical data from being obtained. IR (Nujol, KBr plates) ν/cm^{-1}: 1593s, 1491vs, 1252s, 1112m, 1088m, 1029s, 955vs, 889vs, 870s, 849s, 799s, 700m. Samples were pumped *in vacuo* to eliminate the hexane resonances from the NMR spectra. ^{51}V NMR (C_6D_6, 131.4 MHz, 25 °C: δ 1318.8. ^1H NMR (C_6D_6, 500 MHz, 25 °C): δ 7.59–6.60 (series of m, 20 H, phenyl), 2.85 (d, 1 H, H_a), 0.63 (s, 9 H, Me_3Si_a), 0.61 (s, 9 H, Me_3Si_b), 0.32 (s, 3 H, CH_{3a}), −0.05 (s, 9 H, Me_3Si_c), −0.82 (s, 3 H CH_{3b}), −1.43 (d, 1 H, H_b). ^{13}C NMR (C_6D_6, 125 MHz, 25 °C): δ 318.17 (quat. carbene), 145.95 (quat. C ring), 140.87 (quat. C ring), 135–123 (Ph), 90.10 (quat. chiral C), 20.45 (CH_AH_B), 5.64 (Me_3Si_A, Me_3Si_B), 5.46 (Me_3Si_C), 3.30 (CH_{3A}), 0.47 (CH_{3B}).

‡ *Crystal data*: $\mathbf{1}\cdot 0.5C_{14}H_{12}$: $C_{47}H_{61}N_2Si_4V$, M = 817.30, triclinic, space group $P\bar{1}$, a = 11.505(2), b = 21.527(1), c = 10.228(2) Å, α = 100.39(2), β = 114.72(1), γ = 85.58(3)°, U = 2236(1) Å^3, Z = 2, D_c = 1.199 g cm^{-3}, $F(000)$ = 872, μ = 31.23 cm^{-1}, Cu-Kα (λ = 1.541 78 Å), T = −150 °C, R = 0.065, R_w = 0.077 GOF = 2.69 for 472 parameters and 3929 reflections out of 4668 unique. Non-hydrogen atom positions were located and refined anisotropically with the exception of N(2), C(6) and C(7). Hydrogen atoms were introduced at their idealized positions. Absorption corrections (DIFABS) were applied to the data.

$\mathbf{1}\cdot 0.5C_6H_4$: $C_{40}H_{55}N_2Si_4V$, M = 770.25, triclinic, space group $P\bar{1}$ a = 10.267(1), b = 11.569(1), c = 21.133(2) Å, α = 78.48(1), β = 87.43(1), γ = 65.45(1)°, U = 2235.2(5) Å^3, Z = 2, D_c = 1.144 g cm^{-3}, μ = 3.60 cm^{-1}, Mo-Kα (λ = 0.710 73 Å), T = 298 K, R = 0.057, for 3070 observed independent reflections ($4 \leqslant 2\theta \leqslant 43°$) contributions except those on the solvent molecule which were ignored.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/384.

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Received, 8th October 1996; Com. 6/06904E

Typeset and printed by Black Bear Press Limited, Cambridge, England