Electron-Deficient Vanadium Alkyl Complexes: Synthesis and Molecular Structure of the Vanadium(III) Dinitrogen Complex $[(Me_3CCH_2)_3V]_2(\mu\text{-}N_2)$

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Summary: The vanadium(III) dinitrogen-bridged complex $[(Me_3CCH_2)_3V]_2(\mu\text{-}N_2)$ (1), obtained from reaction of $VCl_3(THF)_3$ and Me_3CCH_2Li under nitrogen, is converted to the vanadium(V) oxo complex $OV(CH_2CMe_3)_3$ (3) by reaction with styrene oxide. Both 1 and 3 decompose at ambient temperature to give neopentane and species which are active in the ring-opening metathesis polymerization of norbornene.

Sterically demanding alkyl groups lacking β-hydrogens (e.g. neopentyl, neophyl) have played an important role in the development of early-transition-metal olefin metathesis[1] and ring-opening metathesis polymerization[2] (ROMP) catalysts. Although a number of vanadium complexes incorporating these alkyl groups are known,[3] metathesis activity has been mentioned in one case only.[3k] Here we wish to report a new vanadium(III) alkyl species with a bridging dinitrogen moiety, $[(Me_3CCH_2)_3V]_2(\mu\text{-}N_2)$ (1), and some aspects of its reactivity.

When $VCl_3(THF)_3$ is reacted with 3 mol of $MeCCH_2Li$ in diethyl ether under nitrogen, the bridged dinitrogen complex $[(Me_3CCH_2)_3V]_2(\mu\text{-}N_2)$ (1) can be isolated in 45% yield (eq 1).[4,5]

1 is a red-brown crystalline diamagnetic complex, poorly soluble in aliphatic and aromatic hydrocarbons and extremely air sensitive (pyrophoric). An X-ray structure determination[6] shows (Figure 1) that 1 consists of two identical tris(neopentyl)vanadium fragments linked by a bridging dinitrogen ligand, the molecule possessing $\bar{3}$ symmetry. The vanadium atoms have a tetrahedral environment; three of the coordination sites are occupied by neopentyl groups and the remaining position is taken by the μ-N_2 ligand. The V—C bond distances, all

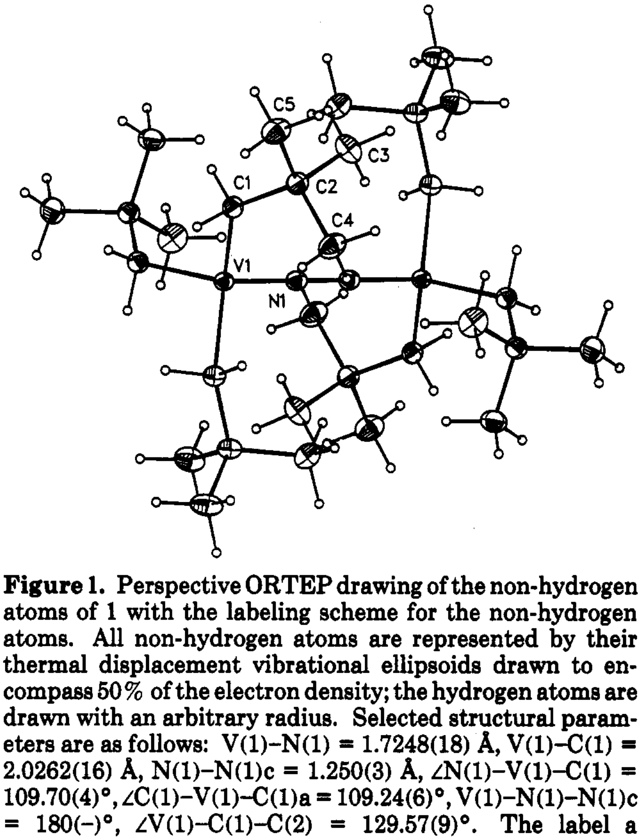

Figure 1. Perspective ORTEP drawing of the non-hydrogen atoms of 1 with the labeling scheme for the non-hydrogen atoms. All non-hydrogen atoms are represented by their thermal displacement vibrational ellipsoids drawn to encompass 50% of the electron density; the hydrogen atoms are drawn with an arbitrary radius. Selected structural parameters are as follows: V(1)–N(1) = 1.7248(18) Å, V(1)–C(1) = 2.0262(16) Å, N(1)–N(1)c = 1.250(3) Å, ∠N(1)–V(1)–C(1) = 109.70(4)°, ∠C(1)–V(1)–C(1)a = 109.24(6)°, V(1)–N(1)–N(1)c = 180(-)°, ∠V(1)–C(1)–C(2) = 129.57(9)°. The label a indicates the symmetry operation $1 - y$, $1 + x - y$, z. The label c indicates the symmetry operation $^2/_3 - x$, $^4/_3 - y$, $^1/_3 - z$.

$$\mathrm{VCl_3(THF)_3 + 3Me_3CCH_2Li \xrightarrow[Et_2O]{N_2}} \qquad \mathrm{{}^1/_2}\underset{\mathbf{1}}{\mathrm{[(Me_3CCH_2)_3V]_2(\mu\text{-}N_2)}} \mathrm{+ 3LiCl + 3THF} \quad (1)$$

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(4) Onto a mixture of $VCl_3(THF)_3$ (2.67 g, 7.14 mmol) and Me_3CCH_2Li (1.67 g, 21.44 mmol), 40 mL of ether was condensed at −196 °C. The mixture was thawed out and warmed to 20 °C while being stirred. After 1 h the solvent was pumped off from the brown mixture. The residue was extracted twice with 25 mL of pentane. Concentrating and cooling the extract to −25 °C yielded 0.90 g (1.62 mmol, 45% based on V) of red-brown crystalline 1. IR (ν, cm^{-1}): 2775 (w), 2688 (w), 2681 (w), 1363 (m), 1257 (w), 1234 (s), 1076 (m), 1058 (m), 931 (w), 858 (m), 752 (m), 563 (m), 490 (m). Anal. Calcd for $C_{30}H_{66}V_2N_2$: C, 64.72; H, 11.95; V, 18.29. Found: C, 62.49; H, 11.51; V, 18.49. Carbon and hydrogen data are low, probably due to explosive burning of the described compound in an oxygen/nitrogen mixture.

(5) 1: ^1H NMR (C_6D_6) δ 2.13 (CH_2, $\Delta\nu_{1/2}$ = 33 Hz), 1.21 (CMe_3); ^{13}C NMR δ 118–108 (CH_2CMe_3), 37.6 (CH_2CMe_3), 34.0 (CH_2CMe_3); ^{51}V NMR δ 1237 (quintet, average ^{51}V–^{14}N coupling constant 48 Hz). **2**: ^{51}V NMR δ 1237 (triplet, average ^{51}V–^{15}N coupling constant 76 Hz). **3**: ^1H NMR (toluene-d_8) δ 1.73 (CH_2, $\Delta\nu_{1/2}$ = 92 Hz), 1.08 (CMe_3); ^{13}C NMR δ 120–107 (CH_2CMe_3), 37.6 (CH_2CMe_3), 34.0 (CH_2CMe_3); ^{51}V NMR δ 1212 ($\Delta\nu_{1/2}$ = 50 Hz); IR (Nujol, ν, cm^{-1}) 984 (V═O).

(6) 1 crystallizes in the trigonal space group $R\bar{3}$, with $a = 10.072(1)$ Å, $c = 29.494\ (1)$ Å (130 K), and $Z = 3$. Reflections (1131) with $I \geq 2.5\sigma(I)$ were considered observed. All hydrogen atoms were located from the Fourier difference map and refined isotropically. $R = 0.027$ and $R_w = 0.030$ ($w = 1/\sigma^2(F)$) for 97 refined parameters.

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2.0262(16) Å, are among the shortest reported for V—C single bonds.[7] The V—N distances (1.7248(18) Å) are shorter than those found in the V^{II}—(μ-N_2) complex (μ-N_2){[(*o*-Me_2NCH_2)C_6H_4]$_2$V(py)}$_2$(THF)$_2$[9] (1.833(3)/1.832(3) Å) but are relatively long compared to most known V═N bonds in V(IV) or V(V) systems (usually 1.60–1.68 Å).[10] The perfectly linear arrangement of the V—(μ-N_2)—V unit and the rather long N—N distance (1.250(3) Å) indicate extensive electronic delocalization over the V_2(μ-N_2) group.

Unlike the V(II) complex (μ-N_2){[(*o*-Me_2NCH_2)-C_6H_4]$_2$V(py)}$_2$(THF)$_2$[11] (N—N = 1.228(4) Å) or the M(III) dinitrogen-bridged complexes [{M(S_2CNEt_2)$_3$}$_2N_2$][12] (M = Nb (N—N = 1.252(16) Å), Ta) **1** does not produce ammonia or hydrazine upon protonation with HCl. Instead, neopentane is produced while the complexed dinitrogen is liberated quantitatively. It appears that, despite the fact that the dinitrogen ligand is considerably reduced and therefore expected to be readily protonated,[13] proton attack occurs at the peripheral methylene groups of the neopentyl ligands in this sterically congested molecule.

The reactivity of **1** is dominated by loss of dinitrogen. With PMe_3, pyridine, and *t*-BuCN **1** reacts to give dinitrogen and the corresponding paramagnetic Lewis base adducts (Me_3CCH_2)$_3$V·L (L = Lewis base). Reversible coordination of dinitrogen is observed in THF. When **1** is dissolved in THF, dinitrogen is liberated quantitatively (Töpler pump determinations). Replacement of dinitrogen by $^{15}N_2$ gives crystalline [(Me_3CCH_2)$_3$V](μ-$^{15}N_2$) (**2**) upon cooling.[5]

Reaction of **1** with styrene oxide produces yellow crystalline OV(CH_2CMe_3)$_3$ (**3**)[5] (eq 2), a rare example of the vanadium(V) oxo complexes OVR_3 (R = alkyl,[3a] aryl[8]).

$$\underset{\mathbf{1}}{[(Me_3CCH_2)_3V]_2(\mu\text{-}N_2)} + 2PhCHCH_2O \rightarrow \underset{\mathbf{3}}{2OV(CH_2CMe_3)_3} + N_2 + 2PhCH{=}CH_2 \quad (2)$$

The ^{51}V NMR spectra[5] of the trisalkyl complexes show resonances at very low field, reflecting the electron deficiency of the metal atom.[3i] In **1** and **2** one- and two-bond coupling of ^{51}V to nitrogen is observed. The one- and two-bond coupling constants seem to be equal,[14] but the width of the resonances precludes accurate determination. The ^{51}V NMR spectrum of **1** shows a moderately resolved quintet at δ 1237 ppm with an apparent ^{51}V–^{14}N coupling constant of 48 Hz. For **2** a moderately resolved triplet with an apparent ^{51}V–^{15}N coupling constant of 76 Hz is obtained.

In agreement with observations made by Schrock *et al.* on M–(μ-N_2)–M systems (M = Mo, W)[15] an absorption with medium intensity at 858 cm^{-1} in the IR spectrum of **1** can be assigned to a V═N stretch. It shows the expected shift to lower energy when $^{14}N_2$ is replaced by $^{15}N_2$ (839 cm^{-1} in **2**).

1 and **3** decompose thermally in solution at 20 °C ($t_{1/2}$ = 4–6 h), giving neopentane and species which are moderately active in the ring-opening metathesis polymerization of norbornene ((1–2 mol norbornene/mol of V)/h).

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Supplementary Material Available: Text giving experimental details, analytical and spectral data for all compounds, and details of the structure determination and tables of crystal data, anisotropic thermal displacement parameters, atomic coordinates, bond lengths, bond angles, and torsion angles for **1** (11 pages). Ordering information is given on any current masthead page.

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(7) For comparison, the V–C distances in (2,4,6-$Me_3C_6H_2$)$_3$VO are in the range 2.022(4)–2.079(3) Å[8] and those in Li[(*t*-Bu_3SiN)$_2VMe_2$] are 2.043(5) and 2.057(8) Å.[3j]

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(14) Similar behavior has been observed in [W(C_5Me_5)Me_3]$_2$(μ-$^{15}N_2$), with the one- and two-bond coupling constants of ^{15}N to tungsten being 125 and 104 Hz, respectively.[15a]

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