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Vanadium(III) complexes incorporating the silylamino(disilylamido) ligand $[(Me_3Si)N\{CH_2CH_2N(SiMe_3)\}_2]^{2-}$ $[N\{N''\}_2]^{2-}$. Synthesis and crystal structure of the dimeric, non-metallocene vanadium(III) hydride $[\{V(N\{N''\}_2)\}_2(\mu\text{-}H)_2]$

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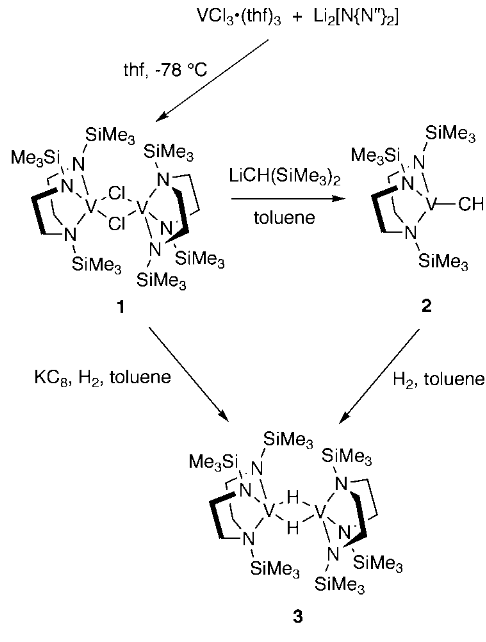
Three vanadium(III) complexes incorporating the chelating silylamino(disilylamido) ligand $[(Me_3Si)N\{CH_2CH_2N(SiMe_3)\}_2]^{2-}$ ($[N\{N''\}_2]^{2-}$) have been reported. Addition of $Li_2[N\{N''\}_2]$ to VCl_3·3THF cleanly yielded the vanadium(III) chloride $[\{V(N\{N''\}_2)Cl\}_2]$ **1**, from which the vanadium(III) hydrocarbyl $[V(N\{N''\}_2)\{CH(SiMe_3)_2\}]$ **2** could be generated by means of salt metathesis. Hydrogenolysis of **2** under dihydrogen produced the thermally stable, dimeric vanadium(III) hydride $[\{V(N\{N''\}_2)\}_2(\mu\text{-}H)_2]$ **3**. The solid state structure of **3** was determined.

Introduction

Much work in the recent chemical literature has been devoted to the study of tervalent vanadium complexes bound to hard donor ligands such as alkoxides, amides, and silylamides.[1] This is due to the interesting and diverse chemistry displayed by these systems, which includes dinitrogen fixation,[2] nitride formation,[3,4] metal–main group element multiple bonding,[5–7] and olefin polymerisation.[8] While the Lewis acidity of vanadium approaches that of the Group III and IV metals,[9] the presence of two or more d electrons on the metal centre allows scope for the activation of small molecules, of which dinitrogen is a prime example.[10] In most of the examples cited above the vanadium centre has been ligated to unidentate, nitrogen-based ligands, and the use of chelating diamide or disilylamide species has been limited.[11] Such ligands may be expected to confer enhanced stability on their derived complexes and allow isolation of otherwise unstable or reactive species. The bulky chelating silylamino(disilylamido) ligand $[(Me_3Si)N\{CH_2CH_2N(SiMe_3)\}_2]^{2-}$ ($[N\{N''\}_2]^{2-}$) has been used in this laboratory and others to generate a series of Group IV metal complexes,[12–14] which display moderate ability as olefin polymerisation catalysts and also includes the unprecedented non-metallocene hydride complex of titanium $[\{Ti(N\{N''\}_2)\}_2(\mu\text{-}H)_2]$;[15] $[N\{N''\}_2]^{2-}$ has also been deployed to stabilise cationic aluminium(III) species.[16,17] The success of this ligand bound to Group III and IV metals was an incentive to apply this approach to vanadium and in this work the chemistry of a series of vanadium complexes incorporating $[N\{N''\}_2]^{2-}$ is reported. Of particular significance is the hydrogenolysis of the vanadium hydrocarbyl $[V(N\{N''\}_2)R]$ ($R = CH(SiMe_3)_2$) to give a rare example of a structurally characterised, dimeric vanadium(III) hydride $[\{V(N\{N''\}_2)\}_2(\mu\text{-}H)_2]$.

Results and discussion

Addition of $Li_2[N\{N''\}_2]$ and VCl_3·3THF in THF at low temperature resulted in the immediate appearance of a deep violet colour which persisted upon warming to room temperature. Removal of the THF and recrystallisation from toluene gave violet crystals whose mass spectrum ($m/z = 403$, M^+, 50%) suggested a stoichiometry of $V(N\{N''\}_2)Cl$ **1**, which was confirmed by microanalysis. That **1** is dimeric in solution (presumably doubly chloride-bridged, see Scheme 1) was shown by solution molecular weight studies (cryoscopy in cyclohexane).



Scheme 1

Evidently the chelating diamide ligand is sufficiently bulky to prevent the incorporation of LiCl or THF, which is observed for complexes analogous to **1** but with non-chelating amide ligands of the type $[NR_2]^-$ (R = Cy or $SiMe_3$).[9] The presence of the extra neutral $NSiMe_3$ donor in $[N\{N''\}_2]^{2-}$ also works to the same end in satisfying the Lewis acidity of the metal centre, but preventing salt or THF inclusion. The magnetic moment of **1** as measured by Evans' method ($\mu_{eff} = 2.78\ \mu_B$) is consistent with the spin-only moment for two unpaired electrons. Interestingly, the structurally characterised dimer $[\{V(NCy_2)_2\}_2(\mu\text{-}Cl)_2]$ exhibits a reduced magnetic moment of $\mu_{eff} = 1.79\ \mu_B$ due to strong antiferromagnetic coupling between the metal centres.[9] The reasons for the virtual absence of such an effect in **1** are not clear, although the geometry around the vanadium centres in **1** is very different to that in the former.

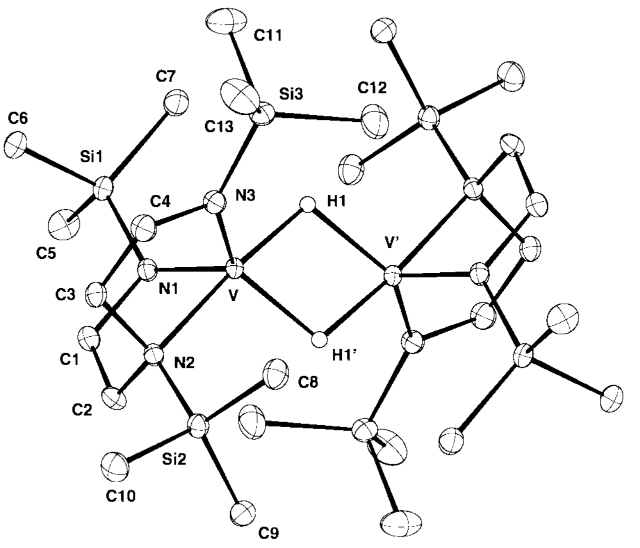


Fig. 1 An ORTEP view of, and numbering scheme for, $[\{V(N\{N''\}_2)\}_2(\mu\text{-}H)_2]$ **3**.

The isolation of compound **1** constitutes a facile entry into vanadium(III) chemistry, and the presence of a halide ligand allowed for further elaboration. Treatment of **1** with $Li[CH(SiMe_3)_2]$ in toluene at −78 °C resulted in the formation of a deep red solution and a grey precipitate. Work-up and recrystallisation from pentane gave large, violet crystals with apparently good mass recovery. Unfortunately, they were unsuitable for a single crystal X-ray diffraction experiment, but the mass spectrum led to a formulation of $[V(N\{N''\}_2)\{CH(SiMe_3)_2\}]$ **2** ($m/z = 527$, 52% $[M]^+$; 368, 98% $[M - CH(SiMe_3)_2]^+$) as anticipated (Scheme 1). Combustion analysis supports the proposed formula, as does the solid state magnetic susceptibility of **2** ($\mu_{eff} = 2.60\ \mu_B$ at 298 K) which is consistent with the spin-only value for a monomeric species with two unpaired electrons. In the absence of structural data, a tetrahedral geometry is assumed for **2**, with the central silylamine donor completing the tetrahedral array (Scheme 1), as is found in the solid state for the monomeric titanium(III) analogue.[15] Such facial geometry can also be demonstrated unequivocally in solution by ^1H NMR spectroscopy for the related Group IV complexes, $[M(N\{N''\}_2)R_2]$ (M = Ti or Zr; R = hydrocarbyl).[13,14]

The hydrocarbyl species **2** can subsequently be treated as a pentane solution under 1–2 atm dihydrogen; filtration and slow cooling to −50 °C yielded brown crystals. The mass spectrum exhibited a strong signal centred at $m/z = 738$, leading to a formulation of $[\{V(N\{N''\}_2)\}_2(\mu\text{-}H)_2]$ **3** (Scheme 1). Compound **2** had evidently undergone hydrogenolysis, a reaction typical of early transition and f-element metal hydrocarbyl complexes,[18] presumably with the elimination of $H_2C(SiMe_3)_2$. Interestingly, **3** could also be prepared by slurrying **1** with stoichiometric KC_8 in toluene under dihydrogen (Scheme 1). The identity of **3** was subsequently confirmed unequivocally by a low temperature, X-ray diffraction experiment and the structure is presented in Fig. 1; selected bond lengths and bond angles are listed in Table 1.

The dimeric nature of compound **3** is clearly evident, as are the bridging hydrides which were located and refined. The vanadium centre lies in a slightly distorted trigonal bipyramidal environment with N(1), N(3) and H(1′) equatorial and N(2) and H(1) in the axial positions (*cf.* N(1)–V–N(3) 115.27(10), N(3)–V–H(1′) 126.4(9)°, N(1)–V–H(1′) 117.7(9), N(2)–V–H(1) 174.4(9), N(2)–V–H(1′) 96.5(9)°, N(3)–V–H(1) 102.0(9)°). The metal–silylamide distances (N(1)–V 1.917(2), N(3)–V 1.924(2)Å) are equivalent to the distances reported for other vanadium(III) centres bound to silylamide donors.[20–24] The vanadium–silylamine distance (N(2)–V 2.203(2)Å) is substantially longer than V–N(1) and V–N(3) as expected for a neutral nitrogen donor and constitutes a dative interaction;[20] likewise the N(2)–Si(2) distance of 1.801(2)Å is longer than N(1)–Si(1) and N(3)–Si(3) (1.735(2) and 1.728(3)Å respectively), which possibly indicates some degree of delocalisation of the formal negative charge on the silylamide nitrogen to the vacant d orbitals on the adjacent silicon, thereby shortening the N–Si bond. The V ··· V′ separation of 2.852(1) in **3** is long but does not preclude interaction between the vanadium centres and can be compared with the Ti–Ti distance in the isostructural $[\{Ti(N\{N''\}_2)\}_2(\mu\text{-}H)_2]$ which is 2.931Å.[15] The V–(μ-H-H′)–V′ bridge can be considered symmetrical, with distances V–H(1) (1.85(3) Å) and V–H(1′) (1.83(3) Å); these distances are similar to the V–H distances in the dimeric $[\{V(PMe_3)_3\}_2(\mu\text{-}H)_3]^+$.[25]

Table 1 Selected bond lengths (Å) and bond angles (°) in $[\{V(N\{N''\}_2\}_2(\mu\text{-}H)_2]$ **3**

V–N(1)	1.917(2)	V–N(2)	2.203(2)
V–N(3)	1.924(2)	V–H(1)	1.85(3)
V–H(1′)	1.83(3)	V ··· V′	2.852(1)
Si(1)–N(1)	1.735(2)	Si(2)–N(2)	1.801(2)
Si(3)–N(3)	1.728(3)		
N(1)–V–N(3)	115.27(10)	N(1)–V–H(1′)	117.7(9)
N(3)–V–N(2)	82.55(9)	N(3)–V–H(1′)	126.4(9)
N(3)–V–H(1)	102.0(9)	V–H(1)–V′	102(1)
N(1)–V–N(2)	82.21(9)	N(1)–V–H(1)	98.5(9)
N(2)–V–H(1)	174.4(9)	N(2)–V–H(1′)	96.5(9)
H(1)–V–H(1′)	78(1)		

While compound **3** is paramagnetic and NMR spectroscopy cannot therefore be employed to determine structure, measurement of μ_{eff} by Evans' method was used as a probe of solution structure. The observed value of $\mu_{eff} = 1.76\ \mu_B$ per vanadium at 293 K is much too low to be consistent with a d^2 metal centre in solution, and is in fact more typical of a system with a single unpaired electron. This suggests that the dimer retains its integrity in solution and the two d^2 metal centres in **3** undergo considerable antiferromagnetic coupling, resulting in a reduced magnetic moment. Similar behaviour was also observed for the analogous titanium hydride $[\{Ti(N\{N''\}_2)\}_2(\mu\text{-}H)_2]$ which is essentially diamagnetic yet formally contains two d^1 metal centres.[15] The dimeric nature of **3** in solution was confirmed by a solution molecular weight study (cryoscopy in cyclohexane).

In this paper the utility of the chelating $[N\{N''\}_2]^{2-}$ ligand for V^{III} has been demonstrated. Not only does $[N\{N''\}_2]^{2-}$ provide a suitable co-ordination environment for tervalent vanadium, but its built-in silylamine donor allows isolation of base-free complexes, in contrast to other vanadium(III) complexes incorporating unidentate amide ligands.[9,21] While the reaction of the hydrocarbyl species **2** under dihydrogen follows well established patterns,[18] the reaction of **1** with KC_8 under dihydrogen is intriguing; the intermediacy of a vanadium(II) species such as $[\{V(N\{N''\}_2)\}_n]$, which subsequently activates dihydrogen, is implied.

Experimental

All experiments were carried out under dry, oxygen free argon or dinitrogen by means of Schlenk techniques, or in a MBraun glove-box (<2 ppm H_2O, <1 ppm O_2). Tetrahydrofuran (THF), toluene, and *n*-pentane were pre-dried over sodium wire, distilled from sodium–potassium alloy or sodium, and stored over potassium mirrors. The compounds $VCl_3\cdot3THF$, $Li_2[N\{N''\}_2]$, KC_8, and $Li[CH(SiMe_3)_2]$ were prepared according to literature methods.[14,26–28] Dihydrogen (99.997%) was supplied by Matheson. Mass spectra (EI) were recorded by a Kratos MS80RF spectrometer. Elemental analyses were carried out by Mikroanalytisches Labor Pascher, Remagen, Germany. Solid state magnetic susceptibility values were measured by a MSB-MK1 balance. Solution state magnetic susceptibility was measured by Evans' method on a Bruker DPX 300 instrument in potassium-dried d_6-benzene.[29,30]

Preparations

[V(N{N″}$_2$)Cl] 1. To a slurry of $VCl_3 \cdot 3THF$ (3.00 g, 8.0 mmol) in THF (30 cm^3) was added a solution of $Li_2[N\{N''\}_2]$ (2.66 g, 8.0 mmol) in THF (20 cm^3) dropwise at −78 °C. With the first drop of ligand a deep violet colour was observed in solution which persisted upon warming to room temperature. The reaction mixture was stirred for 2 h, after which time it was filtered through Celite and the THF was removed. The violet residue was dissolved in toluene (10 cm^3), and this violet solution was cooled to −50 °C to yield violet crystals of [V(N{N″}$_2$)Cl] **1** (2.56 g, 80%) (Found: C, 38.70; H, 8.75; N, 10.20. $C_{13}H_{35}ClN_3Si_3V$ requires C, 38.64; H, 8.73; N, 10.40%); *m*/*z* 403 (M^+, 50%); μ_{eff} (d_6-benzene) = 2.78 μ_B; *M* (cyclohexane) 795 ± 40.

[V(N{N″}$_2$){CH(SiMe$_3$)$_2$}] 2. To a solution of compound **1** (0.300 g, 0.74 mmol) in toluene (5 cm^3) at −78 °C was added a solution of $Li[CH(SiMe_3)_2]$ (0.124 g, 0.74 mmol) in toluene (5 cm^3). The solution was warmed to room temperature at which point a grey powder precipitated. After stirring for 1 h the solvent was removed and the residue dissolved in pentane (10 cm^3). This solution was passed through a glass fibre filter and concentrated to 4 cm^3. Slow cooling to −50 °C yielded [V(N{N″}$_2$)-{CH(SiMe$_3$)$_2$}] **2** as violet crystals (0.229 g, 60%) (Found: C, 44.55; H, 10.19; N, 7.96. $C_{20}H_{54}N_3Si_5V$ requires C, 44.59; H, 10.31; N, 7.96%); *m*/*z* 527 (M^+, 52%), 368 ($M - CH(SiMe_3)_2$, 98); μ_{eff} (solid) = 2.60 μ_B.

[{V(N{N″}$_2$)}$_2$(μ-H)$_2$] 3. (i) A degassed solution of compound **2** (0.200 g, 0.38 mmol) in *n*-pentane (20 cm^3) in a high-pressure ampoule (100 cm^3 volume) was charged with dihydrogen to a pressure of 2 bar. Upon addition of the gas a deep brown colour was observed, and after 12 h the gas was vented and the solvent removed. The brown-red residue was dissolved in *n*-pentane (5 cm^3), and this solution filtered through a glass fibre filter. Slow cooling to −50 °C yielded [{V(N{N″}$_2$)}$_2$(μ-H)$_2$] **3** as brown crystals (0.132 g, 95%) (Found: C, 41.84; H, 9.93; N, 11.16. $C_{13}H_{36}N_3Si_3V$ requires C, 42.24; H, 9.82; N, 11.37%); *m*/*z* 738 (M^+, 52%) and 368 ($M - C_{13}H_{37}N_3Si_3V$, 98); μ_{eff} (d_6-benzene) = 1.76 μ_B; *M* (cyclohexane) 745 ± 40.

(ii) A degassed slurry of compound **1** (0.100 g, 0.24 mmol) and KC_8 (0.033 g, 0.24 mmol) in toluene (20 cm^3) in a high-pressure ampoule (100 cm^3 volume) was charged with dihydrogen to a pressure of 2 atm. Work-up as before gave brown crystals of **3** (0.055 g, 60%).

Crystal structure determination of compound 3

Single crystals of [{V(N{N″}$_2$)}$_2$(μ-H)$_2$] were recrystallised from pentane, mounted in mineral oil, and transferred to the cold gas stream of an Enraf-Nonius CAD4 diffractometer.

Crystal data. $C_{26}H_{72}N_6Si_6V_2$, $M = 739.3$, monoclinic, space group $P2_1/n$ (non-standard no. 14), $a = 10.562(5)$, $b = 18.902(2)$, $c = 11.236$ Å, $\beta = 113.73°$, $U = 2053.5(10)$ Å^3, $T = 173$ K, $Z = 2$, μ(Mo-Kα) = 0.66 mm^{-1}, 5193 reflections measured, 4946 unique ($R_{int} = 0.0506$) which were used in all calculations, $R1 = 0.048$. The final $wR(F^2)$ was 0.126 (all data).

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See http://www.rsc.org/suppdata/dt/1999/3345/ for crystallographic files in .cif format.

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