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Inorganica Chimica Acta 244 (1996) 37–49

Inorganica Chimica Acta

The role of ligand steric hindrance in determining the stability of very short V–V contacts. Preparation and characterization of a series of V(II) and V(III) amidinates

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Received 2 February 1995; revised 3 July 1995

Abstract

The reaction of $VCl_2(TMEDA)_2$ and of $VCl_3(THF)_3$ with two equivalents of formamidinate lithium salts, respectively, yielded dimeric $\{[CyNC(H)NCy]_2V\}_2$ (**2**), with a very short V–V multiple bond and $\{[CyNC(H)NCy]_2VCl\}_2$ (**4**) which is also dimeric. The formation of **2** proceeded through the intermediate monomeric $[CyNC(H)NCy]_2V(TMEDA)$ (**1**) which was isolated and fully characterized. The dinuclear structure was reversibly cleaved by treatment with pyridine forming the monomeric $[CyNC(H)NCy]_2V(Py)_2$ (**3**). Conversely, similar reactions with acetamidinate anion gave only the monomeric $[CyNC(Me)NCy]_2V(THF)_2$ (**5a**) and $[CyNC(Me)NCy]_2VCl$ (**7**), respectively. Attempts to form a dinuclear structure by either removal of THF from **5a** or reduction of **7** gave only the V(III) compound $[CyNC(Me)NCy]_3V$ (**6**). In the case of the very bulky benzamidinate ligand, similar monomeric complexes $[Me_3SiNC(Ph)NSiMe_3]_2V(THF)_2$ (**5c**) and $[Me_3SiNC(Ph)NSiMe_3]_2VCl$ (**10**) were obtained. However, attempts to form dinuclear species via THF dissociation from **5c** or reduction of **10** gave a novel dinitrogen complex $\{[Me_3SiNC(Ph)NSiMe_3]_2V\}_2$ (**8**). Crystal data are as follows. **1**: $C_{32}H_{62}N_6V$, monoclinic, $P2_1/a$, $a=18.085(3)$, $b=10.737(2)$, $c=18.721(2)$ Å, $\beta=114.37(4)°$, $Z=4$; **2**: $C_{52}H_{92}N_8V_2$, monoclinic, $P2_1$, $a=11.671(3)$, $b=10.371(2)$, $c=22.645(3)$ Å, $\beta=100.65(1)°$, $Z=2$; **5c**: $C_{34}H_{62}N_4Si_4O_2V$, orthorhombic, $Pbcn$, $a=18.133(7)$, $b=12.504(6)$, $c=17.428(4)$ Å, $Z=4$; **6**: $C_{42}H_{75}N_6V$, monoclinic, $P2_1/c$, $a=17.35(1)$, $b=10.854(2)$, $c=22.777(4)$ Å, $\beta=103.04(2)°$, $Z=4$; **7**: $C_{28}H_{50}N_4VCl$, triclinic, $P\text{-}1$, $a=11.132(4)$, $b=13.630(4)$, $c=10.276(2)$ Å, $\alpha=95.92(2)$, $\beta=98.38(2)$, $\gamma=109.29(3)°$, $Z=2$; **8**: $C_{52}H_{92}N_{10}V_2Si_8$, triclinic, $P\text{-}1$, $a=14.181(2)$, $b=18.713(2)$, $c=13.257(2)$ Å, $\alpha=99.48(1)$, $\beta=94.13(2)$, $\gamma=91.87(2)°$, $Z=2$; **10**: $C_{26}H_{46}N_4VClSi_4$, triclinic, $P\text{-}1$, $a=12.781(5)$, $b=13.128(4)$, $c=12.126(5)$ Å, $\alpha=104.85(3)$, $\beta=113.29(4)$, $\gamma=66.80(4)°$, $Z=2$.

Keywords: Crystal structures; Vanadium complexes; Formamidinate complexes; Dinuclear complexes

1. Introduction

Multiple bonds between first row early transition metals are one of the most fascinating and intriguing functionalities of inorganic chemistry. The unusually short metal–metal distances determined in some dinuclear complexes of these metals (the shortest ever found) [1,2] might possibly indicate the existence of fairly strong intermetallic interactions. However, today it is generally recognized that these bonds are paradoxically weak [3], and are unlikely to be able to hold together dinuclear frames in the absence of bridging ligands [4]. They are also easily cleaved to form monomeric species [5], and therefore are very sensitive to ligand features such as electronic configuration, steric hindrance, nature of the donor atom, denticity, shape of the bite, etc. [6].

The employment of three-center chelating ligands (with two donor atoms, three atom bite, four π electrons and a negative charge) has enabled the preparation of divanadium complexes with short [7] and very short vanadium–vanadium bonds [8]. Theoretical work has predicted the existence of V–V triple bonds in these systems, although the single bond configuration was calculated to be considerably more stable than the triply bonded one [8b]. However, these particular ligands have been proved able to promote the formation of very short metal–metal multiple bonds with a variety of metals [1] and metalloids [9], and to possess a unique ability to assemble dimers and to form remarkably short M–M contacts even in the absence of a direct M–M bond [10]. Therefore, it is very difficult to assess the real strength of the V–V multiple bonds. For example, it is not unreasonable to expect that, by analogy with divalent chromium, efficient magnetic couplings (either antiferromagnetism, superex-

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SSDI 0020-1693(95)04757-Z

change or a combination of them) may be the only significant interaction existing between the two vanadium atoms in spite of the remarkable shortness of the intermetallic distance. As for Cr(II), very short M–M distances could be nothing or little more than the result of ligand geometry optimization [11].

The preferred coordination geometry of the transition metal, as imposed by the metal electronic configuration, is a factor able to prevail over the binucleating ability of the ligand [12]. In other words, whereas three-center chelating ligands may easily interface two monomeric square-planar metal complexes, such as in the case of d^4 Cr(II), it is far more difficult to stabilize dimeric structures with divalent and octahedral d^3 vanadium atoms, unless severe distortions occur on the coordination geometry of the bridging donor atom. Such distortions have been observed in two of the three existing examples of divanadium complexes of three-center chelating ligands with short and very short V–V distances [7,8a]. On the other hand, square-planar divalent vanadium, although rare, is documented in two examples of sterically encumbered complexes [13]. Therefore, the employment of sterically demanding three-center chelating ligands might be an interesting synthetic strategy to form divanadium species with very short V–V distances.

Amidinate anions [14] provide a wide choice of three-center chelating ligands where the variety of possible substituents makes possible the fine tuning of steric hindrance, thus allowing clarification of the factors which influence both the nuclearity and the extent of intermetallic separation. In this paper we describe the synthesis, characterization and chemical behavior of a novel series of monomeric and dimeric V(II) and V(III) amidinate complexes.

2. Experimental

All operations were performed under inert atmosphere in a nitrogen-filled dry-box (Vacuum Atmosphere) or by using standard Schlenk techniques. VCl_3THF_3, *trans*-$(TMEDA)_2VCl_2$ (TMEDA = *N,N,N′,N′*-tetramethyl ethylenediamine) [15], $\{[Me_3Si)N]_2C(Ph)\}Li(TMEDA)$ [14] and CyN(H)–(H)C=NCy [16] were prepared according to published procedures. CyN=C=NCy and $(Me_3Si)_2NH$ (Aldrich) were used as received. NMR spectra were recorded on a Varian Gemini 200 and on a Bruker AMX-500 spectrometer by using vacuum-sealed samples prepared in a dry-box. Solvents for NMR spectroscopy were dried over the appropriate drying agents, vacuum-transferred into appropriate ampoules and stored inside a dry-box. IR spectra were recorded on a Mattson 9000 FTIR instrument from Nujol mulls prepared in a dry-box. Samples for magnetic susceptibility measurements were weighed inside a dry-box equipped with an analytical balance, and sealed into calibrated tubes. Magnetic measurements were carried out with a Gouy balance (Johnson Matthey) at room temperature. The magnetic moment was calculated following standard methods [17], and corrections for underlying diamagnetism were applied to the data [18]. Elemental analyses were carried out with a Perkin-Elmer PE2400 CHN analyzer.

2.1. [CyN–C(H)–NCy]Li

A solution of CyN–C(H)–N(H)Cy (13.3 g, 64 mmol) in hexane (160 ml) was treated with a solution of n-BuLi in hexane (26 ml, 2.5 M, 64 mmol) at room temperature. The resulting light yellow solution was allowed to stand overnight at r.t., upon which colorless crystals of [CyN–C(H)–NCy]Li precipitated (11.0 g, 51 mmol, 80%). IR (nujol mull, KBr, cm^{-1}) ν: 1565(s), 1330(s), 1295(s), 1260(m), 1230(m), 1150(w), 1100(m), 1060(m), 1030(w), 990(w), 890(m), 840(m), 805(m), 785(w), 720(m), 600(w), 580(m). ^1H NMR (C_6D_6, 200 MHz, 25 °C) δ: 8.38 (s, 1H, C–H formamidine), 2.81 (pseudo-quintet, 2H, cyclohexyl), 1.89 (m, 4H, cyclohexyl), 1.71–1.24 (series of lines, 16H, cyclohexyl).

2.2. [CyN–C(CH_3)–NCy]Li(Et_2O)

A solution of MeLi in ether (7.3 ml, 1.4 M, 10.2 mmol) was added to a cooled solution (−70 °C) of CyNCNCy (2.1 g, 10.2 mmol) in Et_2O (30 ml). Colorless crystals of [CyN–C(CH_3)–NCy]Li(Et_2O) (2.4 g, 7.9 mmol, 77%) separated from the resulting yellowish solution upon reaching r.t. IR (nujol mull, KBr, cm^{-1}) ν: 1510(vs), 1410(s), 1350(s), 1305(w), 1250(m), 1160(m), 1130(w), 1070(sh), 1050(s), 1020(w), 990(m), 1030(w), 990(w), 950(w), 920(m), 890(m), 840(w), 820(w), 795(m), 720(w), 650(m), 600(m), 570(m), 495(br), 460(w), 410(m). ^1H NMR (C_6D_6, 200 MHz, 25 °C) δ: 3.26 (q, J = 7.0 Hz, 4H, Et_2O), 3.18 (broad s, 2H, cyclohexyl), 1.99 (m, 4H, cyclohexyl), 1.89 (s, 3H, CH_3), 1.85–1.45 (series of multiplets, 16H, cyclohexyl), 1.09 (t, J = 7.0 Hz, 6H, Et_2O).

2.3. [CyN–C(CH_2Ph)–NCy]Li(Et_2O)

A solution of CyNCNCy (4.0 g, 19.4 mmol) in ether (70 ml) was cooled to −40 °C and treated with $PhCH_2Li$(TMEDA) (4.25 g, 19.4 mmol). After standing overnight at r.t., the resulting yellowish solution was concentrated to small volume by evaporation of the solvent in vacuo, and layered with hexane (40 ml). Pale yellow microcrystalline [CyN–C(CH_2Ph)–NCy]Li(Et_2O) (2.8 g, 7.4 mmol, 38%) separated upon standing at −30 °C for 4 days. IR (nujol mull, KBr, cm^{-1}) ν: 3077(sh), 3054(sh), 3020(sh), 2788(sh), 1592(s), 1500(s), 1498(s), 1457(s), 1407(m), 1376(m), 1355(s), 1342(m), 1294(m), 1257(m), 1159(s), 1132(m), 1064(m), 1132(m), 1064(m), 1022(m), 944(s), 887(m), 835(w), 790(m), 771(w), 732(s), 703(s), 651(w), 619(w), 582(br), 543(m). ^1H NMR (C_6H_6, 200 MHz, 25 °C) δ: 7.50, 7.24, 7.05 (m, 5H, phenyl), 3.79 (s, 2H, CH_2benzyl), 3.27 (q, J = 7.0 Hz, 4H, Et_2O), 3.21 (broad s, 2H, cyclohexyl), 1.85 (m, 4H, cyclohexyl), 1.60 (m, 4H, cyclohexyl), 1.31 (m, 4H, cyclohexyl), 1.11 (t, J = 7.0 Hz, 6H, Et_2O).

2.4. Preparation of [CyN–C(H)–NCy]$_2$V(TMEDA) (1)

A suspension of $VCl_2(TMEDA)_2$ (4.44 g, 12.5 mmol) in toluene (100 ml) was stirred and boiled in the presence of [CyN–C(H)–NCy]Li (4.33 g, 20.2 mmol). The resulting deep yellow suspension was cooled to r.t. and filtered to discard the white solid. The resulting dark yellow solution was concentrated to small volume until crystallization of a dark yellow solid started. The suspension was boiled to redissolve the solid and slowly cooled to r.t. Dark yellow air-sensitive crystals of **1** were obtained upon standing for 2 days at r.t. (3.0 g, 5.0 mmol, 40%) IR (nujol mull, KBr, cm^{-1}) ν: 3005(m), 1570(s), 1545(s), 1450(s), 1400(m), 1370(s), 1350(m), 1340(s), 1270(s), 1250(m), 1230(s), 1180(sh), 1160(s), 1155(sh), 1120(s), 1110(s), 1090(br), 1060(m), 1040(w), 1020(m), 1010(m), 980(m), 960(sh), 950(m), 880(s), 840(w), 790(s), 770(w), 720(w), 590(w), 565(w), 475(w), 450(w), 440(w), 390(br). μ_{eff} = 3.88 μ_B. *Anal.* Calc. for $C_{32}H_{62}N_6V$: C, 66.06; H, 10.74; N, 14.44. Found: C, 65.98; H, 10.66; N, 14.11%.

2.5. Preparation of [(CyN–C(H)–NCy)$_2$V]$_2$ (2)

Method A. A suspension of $VCl_2(TMEDA)_2$ (2.23 g, 6.3 mmol) in toluene (100 ml) was refluxed and stirred overnight in the presence of [CyN–C(H)–NCy]Li (2.86 g, 13.4 mmol). The resulting deep yellow suspension was filtered at 80 °C to eliminate a gray solid (0.2 g). The resulting dark yellow solution was concentrated to small volume until crystallization of an emerald-green solid started. The suspension was boiled to redissolve the solid and slowly cooled to r.t. Emerald-green air-sensitive crystals of **2** were obtained upon standing for 2 days (0.4 g, 0.4 mmol, 13%). IR (nujol mull, KBr, cm^{-1}) ν: 2805(s), 1585(s), 1550(m), 1460(s), 1370(m), 1360(m), 1340(s), 1325(s), 1290(m), 1250(m), 1185(w), 1150(s), 1120(m), 1100(s), 1080(m), 1070(sh), 1020(w), 980(m), 890(m), 840(m), 780(w), 725(w), 690(w), 510(m), 490(m), 450(w), 425(s), 390(m). ^1H NMR (C_6D_6, 200 MHz, 25 °C) δ: 9.85 (s, 4H, formamidine), 2.75 (pseudo-quintet, 8H, cyclohexyl), 1.99 (s, 3H, toluene), 1.90 (pseudo-d, 16H, cyclohexyl), 1.75 (pseudo-d, 16H, cyclohexyl), 1.63 (pseudo-d, 8H, cyclohexyl), 1.20 (m, 40H, cyclohexyl). *Anal.* Calc. for $C_{52}H_{92}V_2N_8$: C, 67.07; H, 9.96; N, 12.03. Found: C, 66.98; H, 9.73; N, 11.89%.

Method B. A solution of **4** (1.3 g, 1.3 mmol) in THF (50 ml) was boiled and stirred in the presence of potassium metal (0.14 g, 3.6 mmol) for a few minutes and then stirred overnight at r.t. The deep red color turned dark green. The solvent was evaporated in vacuo and the residual solid was redissolved in toluene (20 ml). The solution was filtered to remove KCl and the filtrate allowed to stand at −30 °C for 2 days, upon which green microcrystals of **2** (0.5 g, 0.54 mmol, 42%) separated.

Method C. A solution of **4** (1.71 g, 1.7 mmol) in THF (50 ml) was boiled and stirred in the presence of potassium metal (0.23 g, 5.9 mmol) and TMEDA (2.0 ml, 13.8 mmol) for a few minutes. After overnight stirring at r.t., the color turned dark green. The solvent was replaced with toluene (25 ml), and microcrystalline **2** (0.7 g, 0.75 mmol, 44%) was obtained by allowing the resulting solution to stand at −30 °C for 2 days.

Method D. A solution of **4** (1.22 g, 1.2 mmol) in toluene (50 ml) was heated for a few minutes while stirring to about 100 °C in the presence of potassium metal (0.14 g, 3.6 mmol). Stirring was continued overnight at r.t. Green microcrystals of **2** (0.6 g, 0.65 mmol, 53%) separated after filtration, concentration to about 20 ml and standing at −30 °C.

Method E. A solution of **1** (1.1 g, 1.9 mmol) in toluene was refluxed overnight. Green crystals of **2** (0.6 g, 0.65 mmol, 68%) were obtained from the resulting dark yellow solution upon standing for 2 days at −30 °C.

Method F. A deep blue solution of **3** (0.3 g, 0.48 mmol) in toluene (20 ml) was refluxed for 30 min. The resulting green solution was concentrated and cooled to −30 °C, yielding green crystals of **2** (47%).

2.6. Preparation of V(CyN–C(H)–NCy)$_2$Py$_2$ (3)

A suspension of **2** (0.6 g, 0.65 mmol) in pyridine (15 ml) was heated at about 100 °C for 30 min. The resulting deep blue solution separated blue crystals of **3** upon slowly cooling to r.t. (0.3 g, 0.48 mmol, 37%). μ_{eff} = 3.81 μ_B. IR (nujol mull, KBr, cm^{-1}): 2747(m), 1664(w), 1565(s), 1480(m), 1453(s), 1436(s), 1376(m), 1364(s), 1344(s), 1311(m), 1258(s), 1228(s), 1171(s), 1145(m), 1118(m), 1088(s), 1064(w), 1040(m), 998(w), 985(w), 956(w), 920(w), 885(m), 842(w), 749(s), 722(w), 685(s), 668(w), 548(w), 455(w). *Anal.* Calc. for $C_{36}H_{56}N_6V$: C, 69.31; H, 9.05; N, 13.47. Found: C, 69.22; H, 8.88; N, 13.38%.

2.7. Preparation of {V[CyN–C(H)–NCy]$_2$Cl}$_2$ (4)

A suspension of VCl_3 THF_3 (8.25 g, 22.1 mmol) in THF (100 ml) was boiled in the presence of [CyN–C(H)–NCy]Li (9.33 g, 43.6 mmol). After stirring overnight, the solvent was evaporated in vacuo and the resulting deep red solid was extracted from hexane yielding **4** as a red microcrystalline solid (7.6 g, 7.6 mmol, 69%). ^1H NMR (C_6D_6, 200 MHz, 25 °C) δ: 9.4 (1H, $\Delta\nu_{1/2}$ = 40 Hz, C–H_{form}), 6.6 (2H, $\Delta\nu_{1/2}$ = 63 Hz, cyclohexyl), 6.2 (2H, $\Delta\nu_{1/2}$ = 50 Hz, cyclohexyl), 2.8 (4H, $\Delta\nu_{1/2}$ = 15 Hz, cyclohexyl), 2.1 (2H, $\Delta\nu_{1/2}$ = 15 Hz, cyclohexyl), 1.88 (2H, $\Delta\nu_{1/2}$ = 9 Hz, cyclohexyl), 1.6 (4H, $\Delta\nu_{1/2}$ = 20 Hz, cyclohexyl), 1.3 (4H, $\Delta\nu_{1/2}$ = 10 Hz, cyclohexyl), 0.8 (4H, $\Delta\nu_{1/2}$ = 20 Hz, cyclohexyl). IR (nujol mull, KBr, cm^{-1}): 1558(s), 1529(s), 1454(s), 1411(m), 1374(s), 1364(sh), 1350(m), 1334(m), 1313(m), 1260(s), 1228(s), 1189(m), 1151(m), 1118(m), 1096(s), 1082(sh), 1064(m), 1046(w), 1020(m), 992(w), 968(w), 920(w), 887(m), 845(m), 803(w), 788(w), 764(w), 728(s), 694(m), 680(m), 510(m), 478(w), 464(w), 454(w), 432(s). $\mu_{eff} = 1.22$ μ_B per dimer. *Anal.* Calc. for $C_{26}H_{46}N_4ClV$: C, 62.32; H, 9.25; N, 11.18. Found: C, 62.19; H, 9.13; N, 11.01%.

2.8. *Preparation of [CyNC(Me)NCy]$_2$V(THF)$_2$ (5a)*

A suspension of VCl_3THF_3 (2.95 g, 7.9 mmol) in THF (70 ml) was stirred overnight at r.t. in the presence of [CyNC(Me)NCy]Li(Et_2O) (4.77 g, 15.8 mmol). Thinly smashed metallic lithium (0.06 g, 8.5 mmol) was added to the resulting blood-red solution. The flask was evacuated and sealed under Ar and stirring was continued for an additional 24 h. The resulting brown solution was boiled and filtered while warm to remove the excess of lithium. Light green crystals of **5a** (2.4 g, 3.7 mmol, 46%) were obtained upon standing at r.t. overnight. $\mu_{eff} = 3.85$ μ_B. IR (nujol mull, KBr, cm^{-1}) ν: 1380(s), 1360(m), 1340(s), 1255(s), 1190(m), 1170(s), 1140(br), 1080(sh), 1050(sh), 1000(s), 920(m), 890(m), 840(m), 820(m), 705(m), 720(s), 650(s), 570(sh), 495(s). *Anal.* Calc. for $C_{34}H_{62}N_4O_2V$: C, 66.96; H, 10.25; N, 9.19. Found: C, 66.85; H, 10.17; N, 9.09%.

2.9. *Preparation of [CyNC(CH$_2$Ph)NCy]$_2$V(THF)$_2$ (5b)*

A suspension of $VCl_2(TMEDA)_2$ (2.3 g, 6.5 mmol) in toluene (60 ml) was stirred and boiled for a few minutes in the presence of [CyNC(CH_2Ph)NCy]$_2$Li(Et_2O) (4.9 g, 13.0 mmol). The resulting yellowish-green suspension was filtered while hot, concentrated to small volume (30 ml) and layered with hexane. Emerald-green crystals of **5b** (1.8 g, 2.3 mmol, 35%) separated upon standing for 2 days at r.t. $\mu_{eff} = 3.81$ μ_B. IR (nujol mull, KBr, cm^{-1}) ν: 1650(br), 1605(m), 1500(sh), 1375(sh), 1365(sh), 1310(s), 1265(m), 1240(s), 1200(m), 1170(sh), 1140(s), 1075(br), 1030(m), 1000(s), 935(m), 900(m), 890(sh), 875(s), 840(m), 785(sh), 740(sh), 725(sh), 705(sh), 690(m), 655(m), 600(m). *Anal.* Calc. for $C_{48}H_{74}N_4O_2V$: C, 72.97; H, 9.44; N, 7.09. Found: C, 72.91; H, 9.38; N, 7.00%.

2.10. *Preparation of [(Me$_3$Si)NC(Ph)N(SiMe$_3$)]$_2$V(THF)$_2$ (5c)*

A suspension of VCl_2TMEDA_2 (2.0 g, 5.6 mmol) in THF (60 ml) was stirred for 3 h at r.t. in the presence of [(Me_3Si)NC(Ph)N($SiMe_3$)]Li·TMEDA (4.03 g, 11.3 mmol). The resulting orange–brown suspension was boiled to redissolve the orange microcrystalline solid formed during the stirring, and very slowly cooled to r.t. Orange crystals of **5c** (3.0 g, 4.5 mmol, 80%) were obtained upon standing overnight at r.t. $\mu_{eff} = 3.77$ μ_B. IR (nujol mull, KBr, cm^{-1}) ν: 1255(s), 1240(sh), 1175(m), 1075(s), 1050(sh), 1000(m), 975(sh), 915(sh), 885(s), 830(br), 790(m), 750(br), 720(s), 700(sh), 670(m), 600(sh), 495(sh). *Anal.* Calc. for $C_{34}H_{62}N_4O_2Si_4V$: C, 56.55; H, 8.65; N, 7.76. Found: C, 56.45; H, 8.58; N, 7.61%.

2.11. *Preparation of [CyNC(Me)NCy]$_3$V (6)*

Method A. A suspension of VCl_2TMEDA_2 (1.8 g, 5.1 mmol) in toluene (100 ml) was refluxed and stirred overnight in the presence of [CyN–C(Me)–NCy]Li(Et_2O) (3.06 g, 10.1 mmol). After filtration, the resulting brown–orange solution was allowed to stand overnight at −30 °C, upon which dark orange crystals of **6** (1.5 g, 2.1 mmol, 41%) separated. $\mu_{eff} = 2.78$ μ_B. IR (nujol mull, KBr, cm^{-1}): 1490(sh), 1450(vs), 1375(sh), 1360(s), 1340(m), 1310(w), 1290(s), 1270(s), 1235(w), 1190(sh), 1180(sh), 1140(m), 1080(sh), 1000(s), 900(m), 890(w), 880(m), 840(w), 820(m), 800(m), 650(m), 600(w), 570(w), 500(w). *Anal.* Calc. for $C_{42}H_{75}N_6V$: C, 70.55; H, 10.57; N, 11.75. Found: C, 70.41; H, 10.38; N, 11.69%.

Method B. A suspension of $VCl_3(THF)_3$ (3.83 g, 10.3 mmol) in THF (120 ml) was stirred at room temperature for 5 h in the presence of [CyN–C(Me)–NCy]Li(Et_2O) (6.17 g, 20.4 mmol). The resulting deep red solution was boiled for 30 min, cooled to r.t. and evaporated to dryness. The residual solid was redissolved in toluene (50 ml) and the insoluble material was eliminated by filtration. After the addition of potassium (0.50 g, 12.8 mmol), the mixture was stirred at 80 °C overnight. The dark yellow suspension was filtered at ~60 °C and slowly cooled to r.t. Brown needles of **6** (3.4 g, 4.8 mmol, 46%) were obtained upon standing for a few days at r.t. $\mu_{eff} = 2.88$ μ_B. IR (nujol mull, KBr, cm^{-1}) ν: 1490(s), 1460(s), 1360(s), 1340(s), 1330(m), 1310(w), 1250(m), 1240(m), 1190(s), 1170(s), 1140(w), 1080(s), 1000(m), 890(w), 880(m), 840(m), 820(m), 800(m), 650(m), 600(w), 570(w), 500(w).

2.12. *Preparation of [CyNC(Me)NCy]$_2$VCl (7)*

A suspension of VCl_3THF_3 (2.3 g, 6.2 mmol) in THF (75 ml) was stirred overnight at r.t. in the presence of [CyNC(Me)NCy]Li(Et_2O) (3.75 g, 12.4 mmol). The resulting blood-red solution was evaporated to dryness and the residual solid was redissolved in toluene (40 ml). After filtration, the solution was concentrated and layered with hexane. Red crystals of **7** (0.8 g, 1.5 mmol, 24%) separated upon standing for 2 days at r.t. $\mu_{eff} = 2.77$ μ_B. *Anal.* Calc. for $C_{28}H_{50}N_4ClV$: C, 63.56; H, 9.53; N, 10.59. Found: C, 63.49; H, 9.48; N, 10.50%.

2.13. *Preparation of {[Me$_3$SiNC(Ph)NSiMe$_3$]$_2$V}$_2$(N$_2$) (8)*

A solution of **10** (6.35 g, 10.4 mmol) in toluene (60 ml) was treated with $NaHBEt_3$ (10.5 ml, 1 M in toluene). The color rapidly turned brown during a vigorous gas evolution. The suspension was stirred overnight at r.t., during which time a slow gas uptake occurred. The mixture was filtered, evaporated to dryness and the residual solid was redissolved in hexane. Dark green crystals of **8** separated almost immediately (2.69 g, 43%). Satisfactory combustion analysis data were obtained. $\mu_{eff} = 0.91 \mu_B$ per dimer. ^{1}H NMR (200 MHz, C_6D_6, 25 °C) δ: 7.69 (5H, $\Delta\nu_{1/2} = 66$ Hz, phenyl), 0.36 (18H, $\Delta\nu_{1/2} = 84$ Hz, Me_3Si). IR (nujol mull, KBr, cm^{-1}) ν: 3060(w), 1500(sp), 1248(s), 1173(m), 1073(w), 1001(s), 982(vs), 912(m), 843(vs), 763(vs), 701(vs), 604(m), 522(s), 498(m), 443(w). *Anal.* Calc. for $C_{52}H_{92}N_{10}Si_8V_2$: C, 52.75; H, 7.83; N, 11.17. Found: C, 52.66; H, 7.71; N, 11.01%.

2.14. Preparation of [(Me$_3$Si)NC(Ph)N(SiMe$_3$)]VCl$_2$(TMEDA) (9)

A suspension of $VCl_3(THF)_3$ (13.19 g, 35 mmol) in toluene (200 ml) was treated with [(Me_3Si)NC(Ph)N($SiMe_3$)]Li·TMEDA (13.6 g, 35 mmol). A greenish-yellow color developed almost immediately and stirring was continued overnight at r.t. The mixture was heated to ~100 °C and filtered while hot. The resulting green solution was concentrated to about half of the initial volume and Et_2O was added (100 ml). Green microcrystalline **9** (11.62 g, 66%) separated upon standing overnight at −30 °C. $\mu_{eff} = 2.66 \mu_B$. IR (nujol mull, KBr, cm^{-1}) ν: 1247(s), 1067(sp), 1016(sp), 1000(sp), 981(s), 954(sp), 843(vs, br), 805(sp), 784(m), 768(br), 704(s), 511(s). *Anal.* Calc. for $C_{19}H_{39}N_4Si_2Cl_2V$: C, 45.50; H, 7.84; N, 11.17. Found: C, 45.44; H, 7.78; N, 11.07%.

2.15. Preparation of [(Me$_3$Si)NC(Ph)N(SiMe$_3$)]$_2$VCl (10)

A suspension of $VCl_3(THF)_3$ (5.1 g, 13.7 mmol) in toluene (100 ml) at r.t. was treated with [(Me_3Si)NC(Ph)N($SiMe_3$]Li(TMEDA) (10.6 g, 27.4 mmol). The color turned greenish-yellow upon mixing and stirring was continued overnight. The solvent was evaporated to dryness and the residual solid was heated in vacuo at 120–130 °C for 3 h, during which time the solid became a brick-red powder. The solid was redissolved in toluene (100 ml) and the resulting clear orange solution, obtained after filtration, was concentrated until a solid started to crystallize. Addition of hexane (100 ml) and standing at −30 °C overnight completed the crystallization of **10** (6.35 g, 10.4 mmol, 76%). $\mu_{eff} = 2.95 \mu_B$. IR (nujol mull, KBr, cm^{-1}) ν: 3060(w), 1508(s), 1248(s), 1169(m), 1075(w), 1008(w), 973(vs), 923(w), 842(vs), 764(vs), 727(m), 704(s), 615(w), 535(s), 445(w). *Anal.* Calc. for $C_{26}H_{46}N_4Si_4ClV$: C, 50.91; H, 7.56; N, 9.13. Found: C, 50.85; H, 7.44; N, 9.02%.

2.16. X-ray crystallography

Data were collected in the temperature range −157 to −167 °C (the only exception being complex **2** whose crystals did not show diffraction patterns at temperatures below −60 °C) using the ω–2θ scan technique in the range $3.5 < 2\theta < 50.0°$, for suitable air-sensitive crystals mounted on glass fibers. Cell constants and orientation matrices were obtained from the least-squares refinement of 25 carefully centered high-angle reflections. Redundant reflections were removed from the data set. The intensities of three representative reflections were measured after every 150 reflections to monitor crystal and instrument stability. Data were corrected for Lorentz and polarization effects but no absorption corrections were necessary. The structures were solved by either Patterson or direct methods. The non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were located in the difference Fourier maps and when possible refined isotropically. The final cycle of full-matrix least-squares refinement was based on the number of observed reflections with $I > 2.5\sigma(I)$. Neutral atomic scattering factors were taken from Cromer and Waber [19]. Anomalous dispersion effects were included in F_{calc}. All calculations were performed using the TEXSAN package on a Digital VAX station. Details on data collection and structure refinement are reported in Table 1. Selected bond distances and angles are given in Table 2. See also Section 5.

3. Results

The lithium amidinates were prepared by either amidine deprotonation with bases or addition of alkyl lithium reagents to CyN=C=NCy. This second method is rather general and allows the preparation of a consistent series of amidinate lithium salts of formula [CyNC(R)NCy]Li (R = Me, Ph, Bz, 2-(Me_2NCH_2)Ph).

The room temperature reaction of $VCl_2(TMEDA)_2$ (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine) with two equivalents of [(Cy)NC(H)N(Cy)]Li formed a dark red very air-sensitive solution from which dark yellow air-sensitive crystals of the monomeric, paramagnetic [(Cy)NC(H)N(Cy)]$_2$V(TMEDA) (**1**) were isolated in good yield (Scheme 1). Analytical data and magnetic moment were in accord with the formulation demonstrated by the X-ray diffraction analysis. Although complex **1** is indefinitely stable at room temperature in both solid state and solution, a fast reaction occurred in boiling toluene. The thermolysis gave a deep brown solution from which light green diamagnetic crystals of the dimeric lantern-type {[(Cy)NC(H)N(Cy)]$_2$V}$_2$ (**2**) were isolated in good yield. The diamagnetism of **2** was determined in both solid state and solution and a well-resolved NMR spectrum was obtained for this compound. In addition no significant change of the chemical shift was observed in the temperature range −80 to +80 °C. The dinuclear frame of **2** was reversibly cleaved by treatment with pyridine, forming the thermally robust, blue, paramagnetic and monomeric [(Cy)NC(H)N(Cy)]$_2$V(pyridine)$_2$ (**3**). Reflux of **3** in toluene reformed green crystals of **2**. Complex **2** may also be conveniently prepared using $VCl_3(THF)_3$ as the starting mate-

Table 1
Crystal data and structural analysis results for complexes **1**, **2**, **5c**, **6**, **7**, **8**, **10**

	1	**2**	**5c**	**6**
Formula	$C_{32}H_{62}N_6V$	$C_{52}H_{92}V_2N_8$	$VO_2N_4Si_4C_{34}H_{62}$	$C_{42}H_{75}N_6V$
Formula weight	581.82	931.24	722.17	715.04
Crystal system	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/a$	$P2_1$	*Pbcn*	$P2_1/c$
a (Å)	18.085(3)	11.671(3)	18.133(7)	17.35(1)
b (Å)	10.737(2)	10.371(2)	12.504(6)	10.854(2)
c (Å)	18.72(2)	22.645(3)	17.428(4)	22.777(4)
α (°)	90	90	90	90
β (°)	114.37(4)	100.65(1)		103.04(2)
γ (°)	90	90	90	90
V (Å^3)	3311(2)	2694(1)	3951(4)	4178(2)
Z	4	2	4	4
Radiation (Mo Kα) (Å)	0.71069	0.71069	0.71069	0.71069
T (°C)	−160	−30	−161	−160
D_{calc} (g cm^{-3})	1.167	1.148	1.214	1.137
μ_{calc} (cm^{-1})	3.17	3.73	3.94	2.62
R, R_w	0.059, 0.065	0.075, 0.076	0.046, 0.059	0.057, 0.075

	7	**8**	**10**
Formula	$C_{28}H_{50}ClVN_4$	$C_{52}H_{92}Si_8V_2N_{10}$	$C_{26}H_{46}Si_4VN_4Cl$
Formula weight	529.12	1183.93	613.41
Crystal system	triclinic	triclinic	triclinic
Space group	*P*-1	*P*-1	*P*-1
a (Å)	11.132(4)	14.181(2)	12.781(5)
b (Å)	13.630(4)	18.713(2)	13.128(4)
c (Å)	10.276(2)	13.257(2)	12.126(5)
α (°)	95.92(2)	99.48(1)	104.85(3)
β (°)	98.38(2)	94.13(2)	113.29(4)
γ (°)	109.29(3)	91.87(2)	66.80(4)
V (Å^3)	1437(2)	3458(2)	1705(3)
Z	2	2	2
Radiation (Mo Kα) (Å)	0.71069	0.71069	0.71069
T (°C)	−160	−157	−151
D_{calc} (g cm^{-3})	1.223	1.137	1.194
μ_{calc} (cm^{-1})	4.49	4.34	5.18
R, R_w	0.047, 0.063	0.050, 0.056	0.030, 0.044

$R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$; $R_w=[(\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o{}^2)]^{1/2}$.

rial. The reaction of $VCl_3(THF)_3$ in toluene with two equivalents of [(Cy)NC(H)N(Cy)]Li led in this case to the dimeric and almost diamagnetic {[(Cy)NC(H)N(Cy)]$_2$-VCl}$_2$ (**4**) which was isolated as orange, air-stable crystals [1]. Reduction of **4** with metallic potassium in either THF or toluene/TMEDA gave the diamagnetic green **2**.

Simple replacement of the formamidinic hydrogen atom by a methyl group introduced a significant modification in the reactivity patterns of the two vanadium halides. As shown in Scheme 2, the reaction of $VCl_2(TMEDA)_2$ with two equivalents of the acetamidinate lithium salt [(Cy)-NC(Me)N(Cy)]Li·Et$_2$O formed the paramagnetic, monomeric and octahedral *trans*-(THF)$_2$V[(Cy)NC(Me)N-(Cy)]$_2$ (**5a**) which was isolated in good yield as light green crystals. This reaction seems to be rather general since compounds **5b** and **5c** possess analogous structures. However, attempts to obtain other dinuclear lanthern-type compounds via thermal dissociation of one or two molecules of coordinated THF from **5a** yielded only the monomeric V(III) complex [(Cy)NC(Me)N(Cy)]$_3$V (**6**). The same compound was obtained when the reaction of $VCl_2(TMEDA)_2$ with two equivalents of lithium acetamidinate salt was carried out in toluene. Consistent results were obtained by using $VCl_3(THF)_3$ as starting material. In contrast to the case of formamidine which gave a dinuclear compound **4**, the reaction yielded the monomeric and paramagnetic [(Cy)NC(Me)N(Cy)]$_2$VCl (**7**). Once again, reduction of **7** with finely dispersed potassium in toluene gave **6**, while reduction in THF yielded **5a**. The presence of an intermediate during the formation of **6**, probably a tetracoordinated square-planar complex, is suggested by the initial deep brown color which rapidly turned bright orange upon heating at 40 °C. Attempts to isolate the intermediate species at low temperatures were unsuccessful.

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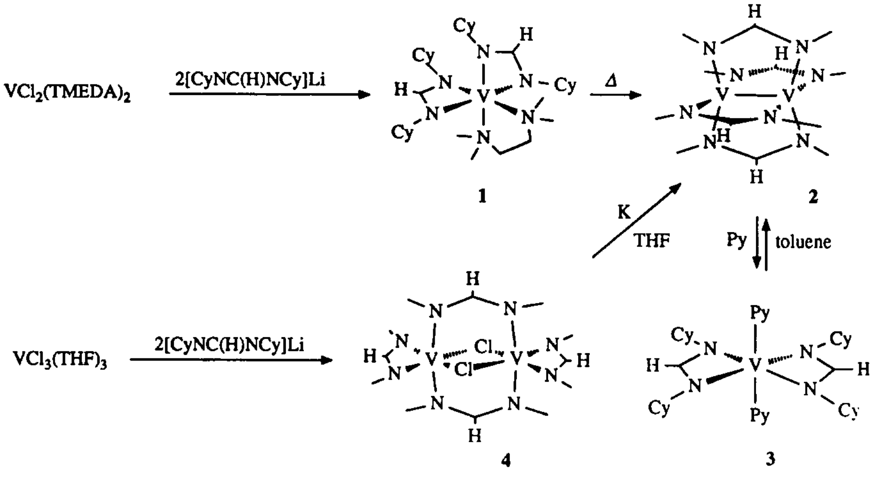
[1] Crystal data for **4**: orthorhombic *Fddd*, $a=27.295$, $b=28.761$, $c=15.716$ Å, $D_c=0.950$, $\mu=4.808$, $R=9.7$, $R_w=10.8$, $GOF=3.84$ for 168 parameters and 1722 observations; V1–V1a = 2.81(2) Å.

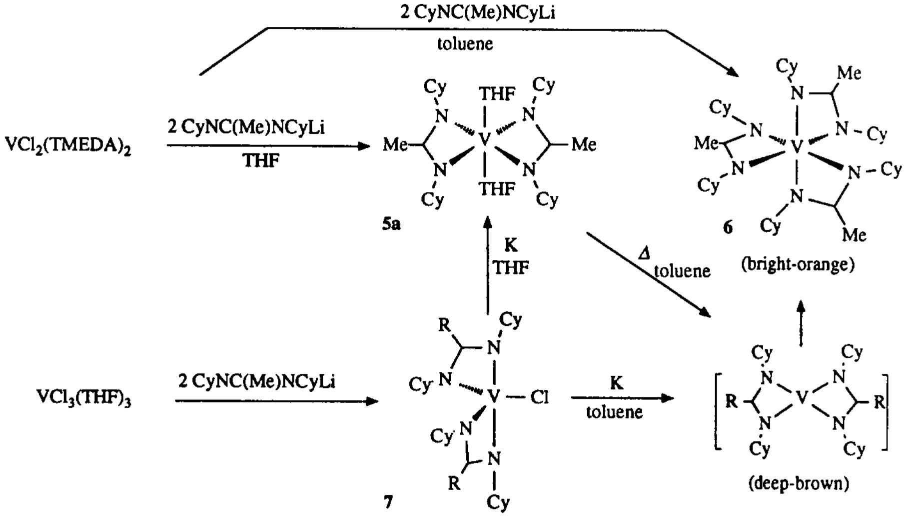
Table 2
Selected bond distances (Å) and angles (°)

1	2	5c	6
V1–N1 = 2.164(3)	V1–V2 = 1.968(2)	V1–N1 = 2.221(4)	V1–N1 = 2.099(3)
V1–N2 = 2.137(3)	V1–N1 = 2.075(7)	V1–N2 = 2.232(3)	V1–N2 = 2.091(3)
V1–N3 = 2.282(3)	V1–N3 = 2.142(7)	V1–O1 = 2.174(4)	V1–N3 = 2.075(3)
V1–N4 = 2.296(3)	V1–N5 = 2.080(6)	V1–O2 = 2.147(4)	V1–N4 = 2.091(4)
V1–N5 = 2.260(3)	V1–N6 = 2.106(7)	Si1–N1 = 1.729(4)	V1–N5 = 2.110(4)
V1–N6 = 2.256(3)	V2–N2 = 2.076(7)	O1–V1–O2 = 180.0	V1–N6 = 2.091(4)
N1–V1–N2 = 94.5(1)	V2–N4 = 2.099(7)	N1–V1–N2 = 61.4(1)	N1–V1–N2 = 63.7(1)
N1–V1–N5 = 61.9(1)	V2–N7 = 2.115(6)	N1–V1–O1 = 86.01(9)	N3–V1–N4 = 63.5(1)
N3–V1–N4 = 80.3(1)	V2–N8 = 2.142(6)	N1–V1–N1 = 172.0(2)	N5–V1–N6 = 63.6(1)
N2–V1–N6 = 61.6(1)	V1–V2–N4 = 93.9(2)	N1–C10–N2 = 118.1(4)	N1–V1–N5 = 91.9(1)
N1–V1–N6 = 100.7(1)	V1–V2–N2 = 94.2(2)	Si1–N1–C10 = 130.8(3)	N1–C1–N2 = 112.1(3)
N1–V1–N3 = 166.1(1)	V1–V2–N7 = 92.8(2)	Si2–N2–C10 = 128.1(3)	N3–C2–N4 = 112.2(4)
N1–C25–N5 = 119.3(4)	V1–V2–N8 = 93.1(2)		N5–C29–N6 = 112.5(4)
N2–C26–N6 = 117.3(4)	N3–C2–N4 = 122.7(8)		C5–N1–C1 = 123.3(3)
C1–N2–C26 = 122.5(3)	N1–C1–N2 = 120.6(8)		C17–N2–C1 = 122.9(3)
C7–N1–C25 = 118.9(3)	N5–C15–N7 = 121.5(7)		
	N6–C52–N8 = 122.1(6)		
	C1–N1–C3 = 112.6(7)		
	C1–N2–C28 = 114.4(7)		
	C2–N3–C22 = 114.8(7)		
	C2–N4–C46 = 117.4(7)		
	V1–N1–C1 = 112.9(5)		
	V2–N2–C1 = 113.3(6)		
7	**8**	**10**	
V1–Cl1 = 2.300(1)	V1–N1 = 1.756(5)	V1–Cl1 = 2.306(2)	
V1–N1 = 1.944(2)	V2–N2 = 1.757(5)	V1–N1 = 2.005(3)	
V1–N2 = 2.158(2)	N1–N2 = 1.235(6)	V1–N3 = 1.969(3)	
V1–N3 = 1.960(2)	V1–N7 = 2.074(5)	V1–N2 = 2.111(2)	
V1–N4 = 2.147(2)	V1–N8 = 2.137(5)	V1–N4 = 2.114(2)	
Cl1–V1–N1 = 123.00(8)	V1–N9 = 2.051(5)	N1–V1–N3 = 106.9(1)	
Cl1–V1–N2 = 95.47(7)	V1–N10 = 2.137(5)	Cl1–V1–N1 = 139.71(8)	
Cl1–V1–N3 = 123.57(7)	N7–V1–N9 = 116.0(2)	Cl1–V1–N3 = 113.40(9)	
Cl1–V1–N4 = 96.50(7)	N7–V1–N1 = 129.2(2)	Cl1–V1–N4 = 91.82(8)	
N1–V1–N3 = 113.4(1)	N1–V1–N9 = 114.7(2)	Cl1–V1–N2 = 95.69(8)	
N1–V1–N2 = 64.84(9)	N1–V1–N8 = 97.4(2)	N1–C7–N2 = 114.4(3)	
N3–V1–N4 = 64.60(9)	N1–V1–N10 = 97.7(2)	N3–C8–N4 = 114.1(3)	
N2–V1–N4 = 167.77(8)	N8–V1–N10 = 164.9(2)	Si1–N3–C8 = 132.2(2)	
N1–C15–N2 = 11.6(2)	N7–V1–N8 = 64.9(2)	Si4–N4–C8 = 130.8(2)	
N3–C7–N4 = 123.0(2)	N9–V1–N10 = 65.3(2)	Si2–N2–C7 = 132.7(2)	
C1–N3–C7 = 123.8(2)	V1–N1–N2 = 173.7(4)	Si3–N1–C7 = 129.0(2)	
C7–N4–C9 = 122.9(2)	V2–N2–N1 = 179.3(4)		
C15–N1–C17 = 123.7(2)	N7–C27–N8 = 116.5(5)		
C15–N2–C23 = 122.3(2)	N9–C38–N10 = 116.2(5)		
	Si5–N8–C27 = 132.1(4)		
	Si6–N7–C27 = 132.1(4)		

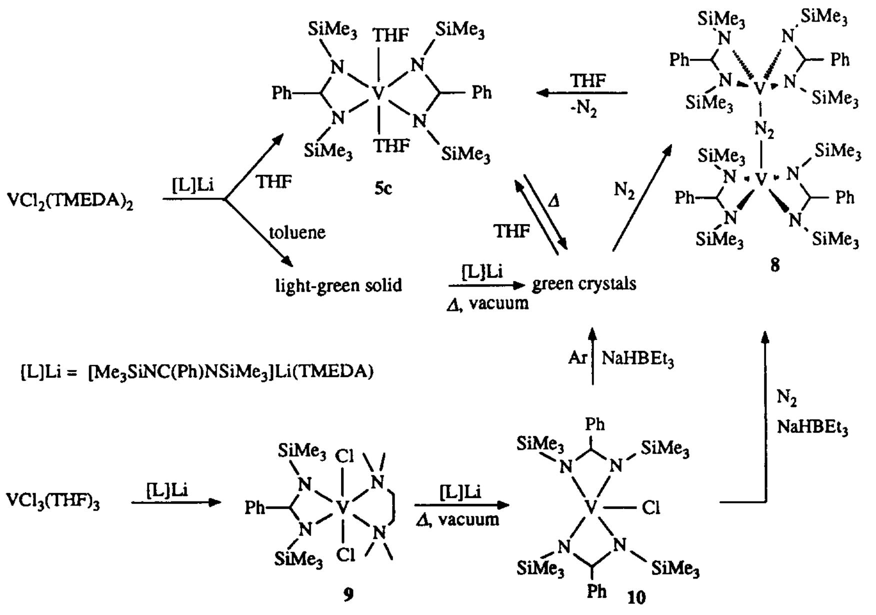
Although the series of results obtained from the reactions of vanadium halides with the sterically demanding $[Me_3SiNC(Ph)NSiMe_3][Li(TMEDA)]$ was consistent with those found in the case of the acetamidinate, a few significant differences can be seen (Scheme 3). Reaction of $VCl_2(TMEDA)_2$ with $[Me_3SiNC(Ph)NSiMe_3][Li(TMEDA)]$ yielded the monomeric and paramagnetic V(II) derivative $[Me_3SiNC(Ph)NSiMe_3]_2V(THF)_2$ (**5c**) isostructural with **5a** and **5b**. Even in this case, dissociation of THF was achieved by heating in vacuum. However, we found no evidence that in this case the reaction might lead to oxidation and formation of the $[Me_3SiNC(Ph)NSiMe_3]_3V$ analogue of **6**. The reaction rather produced a green crystalline material which was indefinitely stable while kept under Ar, but which rapidly turned brown upon exposure to N_2 even in solid state. Recrystallization from toluene under N_2 allowed the isolation and characterization of the new V(II) dinitrogen complex $\{[Me_3SiNC(Ph)NSiMe_3]_2V\}_2(\mu\text{-}N_2)$ (**8**). A similar result was obtained by carrying out the reaction of $VCl_2(TMEDA)_2$ with $[Me_3SiNC(Ph)NSiMe_3]Li(TMEDA)$ in toluene rather than in THF. The formation of the same green complex, which upon exposure to N_2 formed



Scheme 1.



Scheme 2.



Scheme 3.

the dinitrogen complex **8**, was observed even in this case. However, in order to obtain the chlorine-free green crystalline material the reaction mixture had to undergo a prolonged heating at 120 °C in vacuum in solid state after removal of the solvent in vacuo. The unusual procedure is probably necessary to assure the complete removal of TMEDA. Employment of $VCl_3(THF)_3$ as a starting material gave a thermally robust $[Me_3SiNC(Ph)NSiMe_3]VCl_2(TMEDA)$ (**9**) complex[2] which yielded the monomeric and paramagnetic $[Me_3SiNC(Ph)NSiMe_3]_2VCl$ (**10**) only after reaction with a second equivalent of $[Me_3SiNC(Ph)NSiMe_3]Li(TMEDA)$, evaporation of the solvent in vacuo, heating for 3 h at 120 °C in vacuo, and recrystallization of the residue from toluene. The reduction of **10**, carried out under Ar with a solution of $NaHBEt_3$ in toluene, originated the same green crystalline precursor of the dinitrogen complex. Even in this case, recrystallization of the green solid under N_2 gave good yield of the N_2 complex. Complex **8** could be conveniently prepared in good yield and in one-pot synthesis by carrying out the reduction of **10** under N_2.

Complex **10** is one of the rare cases where coordination of dinitrogen on a V(II) metal center occurs with a non-organometallic complex [20]. The coordination of dinitrogen appears to be quite labile since simple treatment with THF released almost quantitatively N_2 during chemical degradation experiments carried out with a Toepler pump.

3.1. Description of the crystal structures

3.1.1. Complex 1

The structure of complex **1** consists of discrete monomeric units. The coordination geometry around the vanadium atom is distorted octahedral, with the two chelating formamidine ligands and the TMEDA molecule imposing an overall propeller-shape configuration (Fig. 1) (N1–V1–N2 = 94.5(1)°, N1–V1–N5 = 61.9(1)°, N3–V1–N6 = 93.0(1)°, N4–V1–N5 = 94.3(1)°, N1–V1–N6 = 100.7(1)°, N4–V1–N6 = 93.0(1)°, N1–V1–N4 = 93.0(1)°). The two formamidine fragments are almost coplanar with vanadium forming slightly puckered four-membered rings (torsion angles V1–N2–C26–N6 = 9.1(4)°, N1–V1–N5–C25 = 4.9(2)°). The V–N distances (V1–N1 = 2.164(3) Å, V1–N2 = 2.137(3) Å, V1–N3 = 2.282(3) Å, V1–N4 = 2.296(3) Å, V1–N5 = 2.260(3) Å, V1–N6 = 2.256(3) Å) are as expected. Short H...H contacts are observed between the formamidinic hydrogen atoms and some of the hydrogens of the cyclohexyl rings (H50...H49 = 2.06 Å, H50...H12 = 2.15 Å, H51...H52 = 2.09 Å, H52...H2 = 2.24 Å).

3.1.2. Complex 2

The structure of the complex shows the typical dimeric arrangement (lantern-type) observed in all the complexes formed by formamidinate anions with several transition metals (Fig. 2). Each formamidinate ligand adopts the classical three-center chelating geometry where each of the two donor atoms of one ligand molecule binds one of the two metal centers, forming a five-membered ring with the V_2 unit. The four vanadacycles rings are slightly puckered (V1–N5–C15–N7 = 8.0(1)°, V2–N7–C15–N5 = 7.0(1)°). The coordination geometry of the two vanadium atoms is distorted square-planar (N1–V1–N3 = 173.0(3)°, N5–V1–N6 = 171.7(2)°, N1–V1–N5 = 91.2(3)°) with the vanadium atom slightly elevated above the plane defined by the four nitrogen atoms (V2–V1–N angles ranging from 93.1(3) to 97.6(4)°). The V–V distance (V1–V2 = 1.968(2) Å) is a rare case of a very short V–V distance and the shortest ever found so far. The V–N bonding distances are normal (V1–N1 = 2.057(7) Å, V1–N3 = 2.142(7) Å, V1–N5 = 2.080(6) Å, V1–N6 = 2.106(7) Å) and compare well with those of other

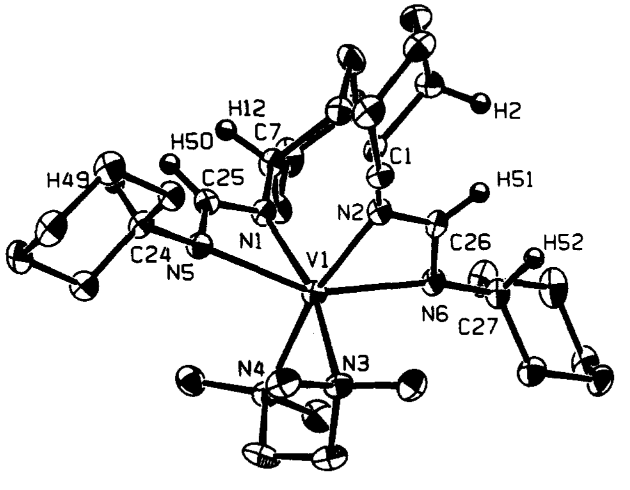


Fig. 1. ORTEP plot of **1**. Thermal ellipsoids are drawn at the 50% probability level.

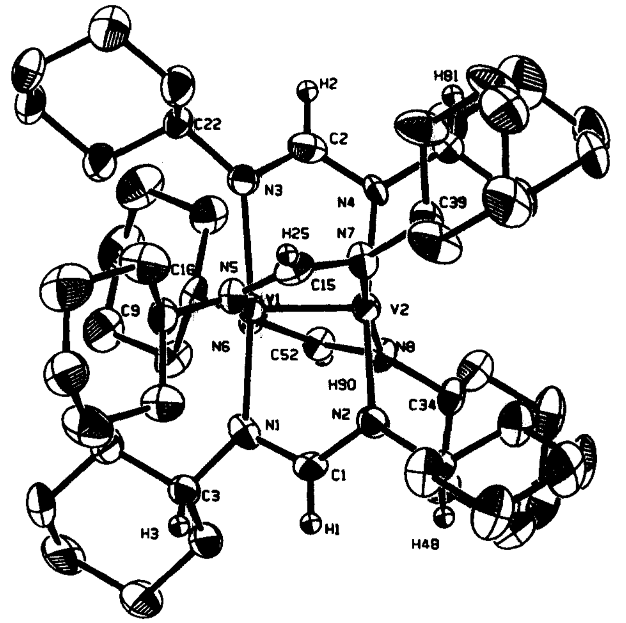


Fig. 2. ORTEP plot of **2**. Thermal ellipsoids are drawn at the 50% probability level.

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[2] Crystal data for **9**: monoclinic, $P2_1/c$, $a = 10.171$, $b = 12.966$, $c = 20.185$ Å, $\beta = 92.41°$, $D_c = 1.250$, $\mu = 6.625$, $R = 9.3$, $R_w = 11.1$, $GOF = 4.84$ for 113 parameters and 3483 observations.

monomeric V(II) complexes reported in this work. Short H...H contacts are observed between the formamidinic hydrogen atoms and some of the hydrogens of the cyclohexyl rings (H2...H81 = 1.89 Å, H1...H3 = 1.93 Å, H1...H48 = 2.01 Å).

3.1.3. Complex 5c

The complex is monomeric with the vanadium atom placed in the center of a regular octahedron (Fig. 3) generated by a two-fold crystallographic axis and defined by four nitrogen atoms of the two equatorial benzamidinate ligand (N1–V1–N2 = 61.4(1)°, N1–V1–N1a = 172.0(2)°) and the two oxygens of two axial molecules of THF placed in *trans* with respect to each other (O1–V1–O2 = 180.0°, O1–V1–N1 = 86.01(9)°, O1–V1–N2 = 92.52(9)°). The V–N (V1–N1 = 2.221(4) Å, V1–N2 = 2.232(3) Å) and the V–O (V1–O1 = 2.714(4) Å, V1–O2 = 2.147(4) Å) bond distances compare well with those of the other amidinate complexes reported in this work. The four-membered rings formed by the chelating benzamidinate ligands are almost planar (V1–N1–C10–N2 = 4.0(4)°).

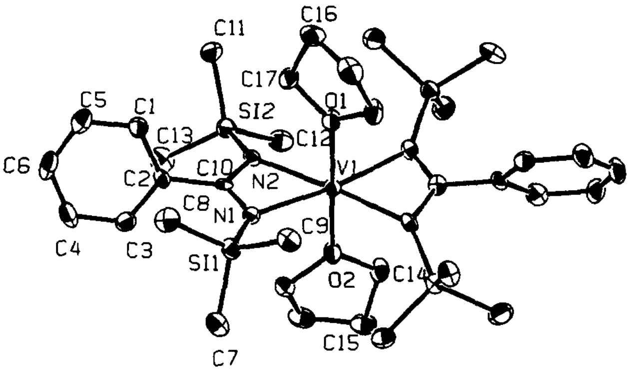


Fig. 3. ORTEP plot of **5c**. Thermal ellipsoids are drawn at the 50% probability level.

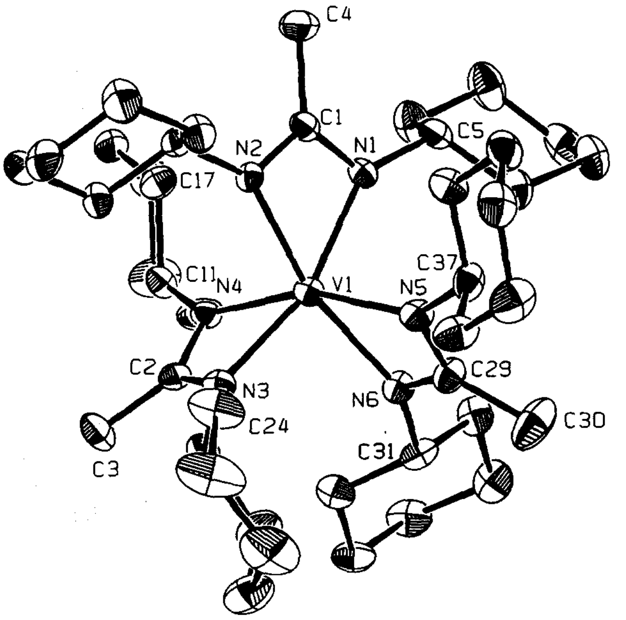


Fig. 4. ORTEP plot of **6**. Thermal ellipsoids are drawn at the 50% probability level.

3.1.4. Complex 6

The monomeric complex is formed by a vanadium atom placed in the center of a distorted octahedron (Fig. 4) bound by the six nitrogen atoms of three acetamidine ligands (N1–V1–N2 = 63.7(1)°, N3–V1–N4 = 63.5(1)°, N5–V1–N6 = 63.6(1)°). The three metallacycles are planar (V1–N1–C1–N2 = 1.3(3)°, V1–N3–C2–N4 = 3.5(3)°, N5–V1–C29–N6 = 1.1(2)°) and impose to the central vanadium atom an overall propeller-shape geometry. The angles subtended at the acetamidinate carbon atoms deviate from the normal value expected for an sp^2 carbon atom as a probable result of the H...H short non-bonding contacts formed by the central methyl hydrogen atoms and some of the hydrogens of the cyclohexyl groups (av. H...H = 1.94 Å).

3.1.5. Complex 7

The coordination geometry of the vanadium atom in this monomeric complex may be described in terms of a severely distorted trigonal bipyramid (Fig. 5) with one chlorine and two nitrogen atoms from two acetamidinate ligands defining the equatorial plane (Cl1–V1–N1 = 123.00(8)°, Cl1–V1–N3 = 123.75(7)°, Cl1–V1–N4 = 96.50(7)°, Cl1–V1–N2 = 95.47(7)°) and the other two nitrogen atom sited on the two apical sites (N2–V1–N4 = 167.77(8)°). The angle

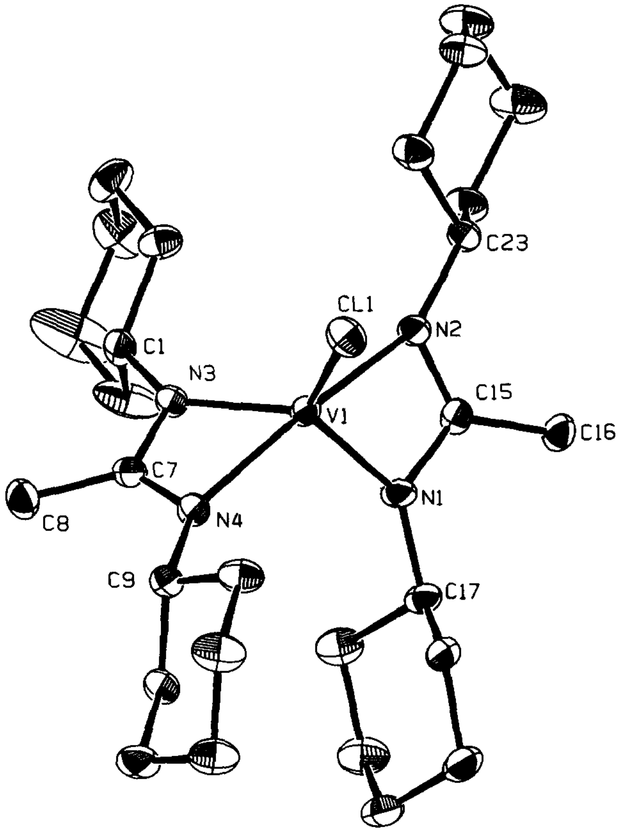


Fig. 5. ORTEP plot of **7**. Thermal ellipsoids are drawn at the 50% probability level.

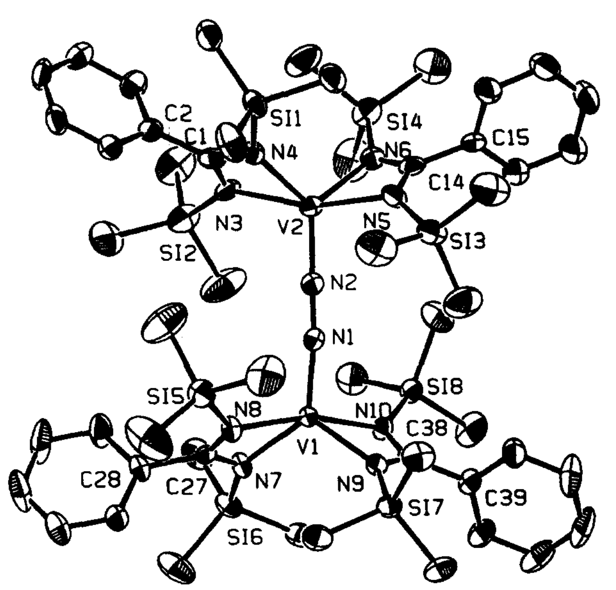


Fig. 6. ORTEP plot of **8**. Thermal ellipsoids are drawn at the 50% probability level.

submitted at the formamidinic carbon atom by the two nitrogens (N1–C15–N2 = 111.6(2)°, N3–C7–N4 = 111.2(3)°) is significantly narrower than in the formamidinic complexes as a probable result of the H...H non-bonding contacts formed by the two methyls of the acetamidinic groups with the cyclohexyl groups.

3.1.6. Complex 8

The molecule is a dimeric dinitrogen complex where two $[Me_3SiNC(Ph)NSiMe_3]_2V$ units are linked by an end-on bridging dinitrogen molecule (Fig. 6). The $V–N_2–V$ array is almost linear (V1–N1–N2 = 173.7(4)°, V2–N2–N1 = 179.3(4)°) forming rather short V–N distances (V1–N1 = 1.756(5) Å, V2–N2 = 1.757(5) Å) which might indicate significant reduction of the dinitrogen molecule. The short N–N distance (N1–N2 = 1.235(6) Å) also indicates that partial reduction of the N–N multiple bond occurred. Considering the vanadium atom lying on the center of a distorted square-pyramid, the basal plane is bound by the four nitrogen atoms of two benzamidine groups (N2–V2–N3 = 98.9(2)°, N2–V2–N4 = 127.5(2)°, N2–V2–N5 = 97.3(2)°, N2–V2–N6 = 119.4(2)°) with the vanadium atom significantly elevated above the basal plane (distance of V2 from the N3–N4–N5–N6 plane = 0.73(6) Å).

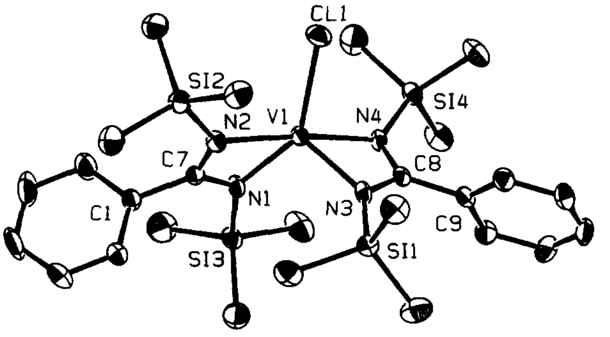


Fig. 7. ORTEP plot of **10**. Thermal ellipsoids are drawn at the 50% probability level.

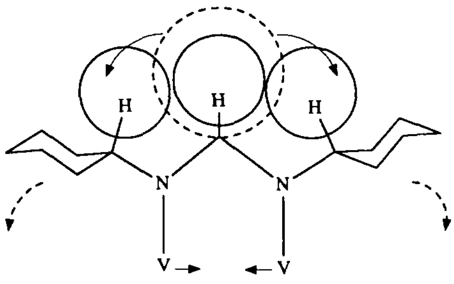
3.1.7. Complex 10

The complex is monomeric with the vanadium atom placed in the center of a trigonal bipyramid (Fig. 7). The equatorial plane is defined by one chlorine atom (V1–Cl1 = 2.306(2) Å) and two nitrogen atoms (V1–N1 = 2.005(3) Å, V1–N3 = 1.969(3) Å) of two benzamidinate anions (Cl1–V1–N1 = 139.71(8)°, Cl1–V1–N3 = 113.40(9)°, N1–V1–N3 = 106.9(1)°) while the remaining two nitrogen atoms occupy the axial positions (Cl1–V1–N2 = 139.71(8)°, Cl1–V1–N4 = 91.82(8)°, N2–V1–N4 = 171.59(9)°).

4. Discussion

The simple replacement of the formamidinic hydrogen atom with the methyl group of the acetamidine has a profound repercussion on the structure of the corresponding V(II) complex. The fact that one molecule of TMEDA is retained in the formamidine derivative **1**, while a complete replacement by two molecules of THF is observed in the amidinate **5**, can be ascribed only to the larger steric hindrance of the acetamidine and benzamidine ligands since the reaction conditions employed in the three reactions are identical. The most remarkable difference between **1** and **5** in terms of chemical behavior is provided by the fact that while the dinuclear species **2** is easily formed from **1** through thermal dissociation of TMEDA or reduction of the corresponding V(III) complex **4**, no dimeric structures with a V–V bond were obtained in the case of the acetamidine and benzamidine derivatives. The two reactions rather gave an oxidation to the trivalent $[CyNC(Me)NCy]_3V$, probably via disproportionation. Conversely, in the case of the benzamidinate, where the very large steric hindrance prevents the formation of $[Me_3SiNC(Ph)NSiMe_3]_3V$, the reaction from both $VCl_2(TMEDA)_2$ and $VCl_3(THF)_3$ yielded the precursor of the dinitrogen complex **8**. Although a full characterization of this complex could not be obtained, due to its enormous reactivity, given the result of the reaction with N_2, we tentatively propose a tetrahedrally distorted square-planar structure similar to that of the Cr(II) derivative $[Me_3SiNC(Ph)NSiMe_3]_2Cr$ [21].

The diamagnetism of **2** together with the very short V–V contact (the shortest ever found for a divanadium unit) might indicate the existence of a direct M–M bond with high degree of multiplicity (triple). Since the replacement of the formamidinic hydrogen with the methyl group of the acetamidine ligand cannot be reasonably expected to significantly modify the electronic configuration of the complex, it is evident that only the larger steric hindrance may be responsible for the failure of the acetamidinate ligand to stabilize a dimeric species. On the other hand, complex **2** has an intermetallic distance (V–V = 1.968(2) Å) which is even shorter than in $[(p\text{-tolylformamidinate})_2V]_2$ (V–V = 1.978(2) Å). This



Scheme 4.

suggests that, similar to the case of the lantern-type compounds of divalent chromium, the increase of ligand steric hindrance results in shorter M–M bonds rather than longer [6], as could be expected on the basis of the behavior of multiple bonds between main group elements (larger steric bulk within the molecule usually results in stretched bonds). The X-ray crystal structure of **2** has pointed out the presence of short H...H non-bonding contacts between the formamidinic hydrogen and other hydrogen atoms of the cyclohexyl groups (H...H ranging from 1.89 to 2.01 Å). The same contacts have also been observed in the monomeric $[(Cy)NC(H)N(Cy)]_2V(TMEDA)$ (H...H ranging from 2.06 to 2.24 Å). In biscyclopentadienyl dinuclear species, these H...H non-bonding contacts have shown energy profiles as a function of the distance which sharply rise up to 38 Kcal mol^{-1} when the distance becomes shorter [22]. Assuming that a comparable destabilization energy arises from the H...H non-bonding contacts of **2**, and given that the cyclohexyl–cyclohexyl hydrogen atom contacts are definitely longer (ranging from 2.5 to 3.15 Å), it is obvious that the stability of the complex is determined primarily by the shortest H...H contacts, i.e. the contacts formed by the formamidinic hydrogen with the two cyclohexyl methyne hydrogens. The increase of steric hindrance introduced by the methyl group of the acetamidic ligand pushes apart the two cyclohexyl 'wings' (Scheme 4) thus resulting in a considerable distortion of the N–C–N framework (confirmed by the X-ray analysis of the monomeric **5a**, **6** and **7**) [23]. The V–V multiple bond obviously does not provide enough stabilization energy to prevail over the destabilization introduced by the H...H interactions since simple treatment with pyridine *reversibly* cleaved the dinuclear structure of **2** forming **3**. In contrast, the dinuclear and almost diamagnetic **4** with far longer V–V distance (V–V = 2.871 Å) could not be cleaved by similar treatment with pyridine under similar conditions.

In conclusion, the results described in this paper provide the first example where a relatively minor modification of ligand steric hindrance is shown to be capable of modifying the nuclearity and the chemistry of vanadium complexes. In the absence of a detailed theoretical analysis, it is obviously impossible to identify which factors, affected by the steric hindrance of the ligand (orientation of the orbitals used by the ligand donor atoms for bonding the metals, distortion of the normal hybridization angles, more or less efficient orbital overlaps, or a combination of them), determine the relative stabilization or destabilization of the monomeric structures with respect to the dimeric ones. Nevertheless, this work clearly shows that: (i) the existence of the V–V multiple bonds is determined by the nature of the ligand and its steric bulk; (ii) V–V very short bonds possess an intrinsic weakness which is in contrast to the shortness of the intermetallic distance. The striking parallelism between this behavior and that of the quadruply bonded dichromium complexes suggests that even in this case the very short intermetallic contacts might be just artifacts of the binucleating ability of the particular ligands employed for the stabilization of the dimetallic frame.

5. Supplementary material

Tables listing atomic positional parameters, temperature factors, torsion angles, bond angles and distances, and hydrogen atom positional parameters associated with complexes **1**, **2**, **5c**, **6**, **7**, **8** and **10** are available from the authors on request.

Acknowledgements

This work was supported by the Natural Sciences and Engineering Research Council of Canada (operating grant).

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