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Symmetrically Bridged Dimeric Vanadium Nitrido Compounds. Synthesis and Characterization of $[(\eta\text{-}C_5Me_5)V(N)Cl]_2$

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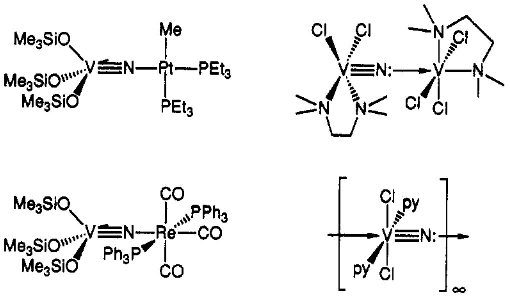
Summary: Reaction of trimethylsilyl azide with $[(\eta\text{-}C_5Me_5)VCl_2]_3$ *produces a dimeric vanadium nitrido compound,* $[(\eta\text{-}C_5Me_5)V(N)Cl]_2$*. Spectroscopic, structural, and reactivity data indicate that this compound possesses stable and symmetric V(N)V interactions in the first example of a* M_2N_2 *compound.*

Nitrido-bridged transition-metal compounds have been the recent target of our efforts,[1,2] as well as those of other research groups,[3,4] to develop synthetic routes to new transition-metal-containing materials. Our approach[1,2,5] has involved parallel exploration of molecular complexes, which serve as models for nitrido-bridged polymers, and chain structures incorporating metal–nitrogen–metal linkages. We have utilized a synthetic route based on the reactivity of the N–Si bonds of silylimido ligands to prepare both bimetallic nitrido-bridged complexes[2] and linear-chain metallonitride polymers.[1] Our work has focused primarily on vanadium-containing nitrido compounds. This stems from our supposition that the smallest group 5 transition-metal element can provide the closest parallel between metallonitride and phosphazene ($[P(N)X_2]_n$)[6] chemistry. Additionally, the availability of reactive vanadium silylimido starting materials[1,7,8] and the utility of ^{51}V NMR spectroscopy[9] make vanadium a logical choice for study. Synthetic, spectroscopic, and reactivity studies, as well as selected X-ray structures, have allowed us to develop a detailed picture of the bridging nitrido ligand in a variety of vanadium nitrido compounds (e.g., Chart I).

Chart I



Unfortunately, the vanadium nitrido derivatives that we[1,2] and others[10] have reported to date—particularly the linear-chain polymers $[V(N)Cl_2L_2]_\infty$, where L is a (substituted) pyridine ligand—are stuck in asymmetrically bridged structures with short, strong $V{\equiv}N$ triple bonds and weak to nonexistent bridging interactions.[11,12] These weak bridging interactions severely limit the utility of $[V(N)Cl_2L_2]_\infty$ and most other metallonitride polymers[13] as materials. Vanadium(V) has a strong tendency to form short, strong triple bonds to nitrogen in a variety of imido[7,14] and nitrido[1,2,10] compounds, and we have previously argued that formation of $V{\equiv}N$ dominates the chemistry available to silylimido and nitrido derivatives of this metal.[15] In contrast, all reported tantalum(V) and niobium(V) nitrido derivatives display bridged structures with symmetrical M(N)M interactions.[3ab,4a,16] Particularly striking are the cyclic organometallic tantalum nitrido trimers $[(\eta\text{-}C_5Me_5)Ta(N)Me]_3$[3a] and $[(\eta\text{-}C_5Me_5)Ta(N)Cl]_3$,[4a] which possess planar Ta_3N_3 rings with delocalized Ta(N)Ta bonding.[12] Furthermore, $[(\eta\text{-}C_5Me_5)Ta(N)Cl]_3$

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(12) For a theoretical description of the bonding in polymeric metallonitrides and other nitrido-bridged compounds, see: Wheeler, R. A.; Whangbo, M.-H.; Hughbanks, T.; Hoffmann, R.; Burdett, J. K.; Albright, T. A. *J. Am. Chem. Soc.* **1986**, *108*, 2222–2236. Wheeler, R. A.; Hoffmann, R.; Strähle, J. *J. Am. Chem. Soc.* **1986**, *108*, 5381–5387.

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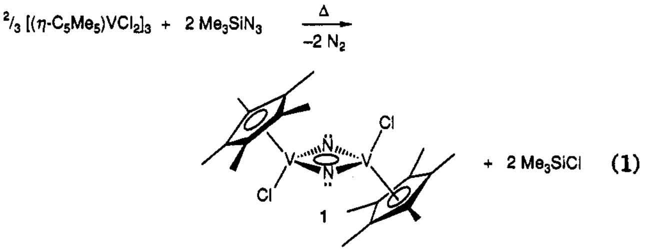
has been reported to undergo ring-opening polymerization to produce a stable and soluble nitrido-bridged polymer.[4b]

To explore the dramatic differences between the group 5 metal nitrido compounds and to determine whether vanadium–nitrogen triple bonding dominates regardless of ligand environment, we recently set out to prepare vanadium analogues of the cyclopentadienyltantalum nitrides. Reported herein is the synthesis and characterization of $[(\eta\text{-}C_5Me_5)V(N)Cl]_2$, the first example of a cyclic M_2N_2 dimer and our first example of a vanadium nitrido compound possessing stable, symmetrical V(N)V interactions.

High-yield formation of $[(\eta\text{-}C_5Me_5)V(N)Cl]_2$ (1) is observed upon reaction of the vanadium(III) chloride $[(\eta\text{-}C_5Me_5)VCl_2]_3$[17] with trimethylsilyl azide in refluxing benzene (eq 1).[18] The reaction is conveniently monitored by ^{1}H NMR spectroscopy. At room temperature, disappearance of the broad shifted C_5Me_5 signal for paramagnetic $[(\eta\text{-}C_5Me_5)VCl_2]_3$ is accompanied by the appearance of $ClSiMe_3$ and new broad shifted C_5Me_5 signals for paramagnetic azido intermediate(s); heating this mixture produces 1. Thus, the reaction proceeds via substitution of azide for chloride at vanadium(III), rather than the alternative oxidative addition of Me_3SiN_3.[19]



(1)

Compound 1, which is isolated as a black crystalline solid and dissolves in benzene to produce intensely colored blue-green solutions, possesses a single $(\eta\text{-}C_5Me_5)V$ environment, according to ^{1}H and ^{51}V NMR spectra.[18] The dimeric structure suggested on the basis of solution molecular weight determinations was confirmed by an X-ray structural study.[20] On the basis of the crystal structure (Figure 1), 1 possesses a planar, almost square V_2N_2 core (V–N–V = 92.6(2)°, N–V–N = 87.4(2)°) with symmetric V(N)V interactions (V–N = 1.771(2) Å).[21] The vanadium–nitrogen distance in 1—which is long compared to V≡N triple-bond distances[22] but short compared to that expected for V–N single bonds[23]—is consistent with the expected formal 1.5 V–N bond order. The two d^0 vanadium(V) centers in 1 are quite close (V–V = 2.561(1) Å), but a significant ground-state metal–metal interaction seems unlikely.

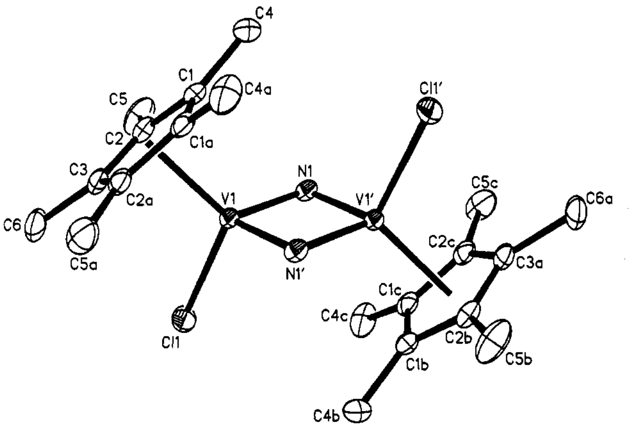


Figure 1. ORTEP drawing of 1 with 50% probability thermal ellipsoids for non-hydrogen atoms.

The structure of 1 indicates multiple bonding of the nitrido ligand to two vanadium atoms. Furthermore, 1 does not react with species capable of attacking unsaturated vanadium(V) centers (pyridine and PMe_3) or terminal nitrido ligands (PMe_3 and $ClSiMe_3$). Overall, these observations indicate that strong, stable V(N)V interactions exist in 1, in sharp contrast to other known vanadium nitrido compounds. Preliminary experiments indicate that the chloride ligands of 1 can be substituted by other anionic groups. For example, reaction with NaO^iPr results in substitution to yield $[(\eta\text{-}C_5Me_5)V(N)(O^iPr)]_2$ (2).[24] The ^{1}H NMR spectrum of $[(\eta\text{-}C_5Me_5)V(N)(O^iPr)]_2$ shows equivalent isopropoxy methyl groups, consistent with a symmetric nitrido-bridged structure.[25] Additionally, NMR monitoring of reaction mixtures suggests that 1 → 2 occurs in a stepwise fashion, via a compound possessing two different cyclopentadienyl environments per isopropoxy ligand (i.e., $(\eta\text{-}C_5Me_5)_2V_2(N)_2Cl(O^iPr)$), supporting the idea that the dimeric nitrido-bridged structure is retained on substitution.

The synthesis of $[(\eta\text{-}C_5Me_5)V(N)Cl]_2$ clearly indicates that it is possible to produce symmetric and stable

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[17] Poli, R. *Chem. Rev.* **1991**, *91*, 509–551. Messerle, L., University of Iowa, personal communication.

[18] For 1: Under anaerobic and anhydrous conditions, Me_3SiN_3 (0.350 mL, 2.64 mmol) was added to a sample of $[(\eta\text{-}C_5Me_5)VCl_2]_3$ (0.674 g, 2.62 mmol V) dissolved in benzene (50 mL). The mixture was refluxed for 20 h, the solvent and volatile byproducts were removed under vacuum with heating, and the resulting black solid (>95% crude yield, NMR pure) was recrystallized from a mixture of pentane and toluene: ^{1}H NMR (C_6D_6): δ 2.05; ^{51}V NMR (C_6D_6) δ −144 ($\nu_{1/2}$ = 340 Hz); mp 225 °C dec. Anal. Calcd for $C_{20}H_{30}Cl_2N_2V_2$: C, 50.97; H, 6.42; N, 5.94. Found: C, 51.04; H, 6.53; N, 5.95.

[19] Synthesis of nitrido compounds from metal chlorides plus Me_3SiN_3 or other azido sources is common. See: Dehnicke, K.; Strähle, J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 955–978; **1981**, *20*, 413–426. In contrast, formation of silylimido compounds from metal chlorides plus Me_3SiN_3 is rare. See, for example: Lichtenhan, J. D.; Critchlow, S. C.; Doherty, N. M. *Inorg. Chem.* **1990**, *29*, 439–442.

[20] Crystal data for 1 ($C_{20}H_{30}Cl_2N_2V_2$): a = 8.8097(11) Å, b = 12.122(2) Å, c = 10.5989(13) Å, β = 112.294(9)°, monoclinic, $C2/m$, Z = 2, θ–2θ scan method, Mo Kα radiation (λ = 0.710 73 Å), T = 158 K, data collection $4 < 2\theta < 55°$, solved using 1096 unique data with $|F_o| > 4.0\sigma(|F_o|)$ by direct methods and refined by full-matrix least-squares techniques, R = 4.3%, R_w = 5.1%. Selected bond distances (Å) and angles (deg) not mentioned in text: V(1)–centroid = 1.990, V(1)–Cl(1) = 2.277(1), Cl(1)–V(1)–N(1) = 107.1(1).

[21] Compound 1 sits on a center of symmetry, introducing the possibility that the symmetric V_2N_2 structural model actually results from a disordered asymmetric V_2N_2 structure. Although we cannot unequivocally rule out this possibility, there are no anomalies in the structure to suggest this or indications that the structure is better represented in a lower symmetry space group, and our chemical and spectroscopic data are consistent with symmetric V_2N_2 structures for 1 and 2. Further experiments to test our model (e.g., structural characterization of asymmetrically substituted V_2N_2 derivatives) are being explored.

[22] Distances in vanadium nitrido and imido compounds range from 1.571(7) Å in $[V(N)Cl_2(py)_2]_\infty$[1] to 1.730(5) Å in $(\eta\text{-}C_5Me_5)_2VNPh$ (Gambarotta, S.; Chiesi-Villa, A.; Guastini, C. *J. Organomet. Chem.* **1984**, *270*, C49-C52).

[23] V–N can be estimated as 1.9–2.0 Å on the basis of the covalent radius of nitrogen (0.74 Å), the metallic radius of V (1.35 Å), and the equation $r_{AB} = r_A + r_B - 0.09(\Delta\chi_{AB})$. See: Wells, A. F. *Structural Inorganic Chemistry*; Oxford University Press: Oxford, England, 1984.

[24] For 2: ^{1}H NMR (C_6D_6) δ 5.22 (septet, J = 6 Hz, 1 H), 2.06 (s, 15 H), 1.48 (d, J = 6 Hz, 6 H); ^{51}V NMR (C_6D_6) δ −256 ($\nu_{1/2}$ = 550 Hz); mp 142–146 °C dec. Anal. Calcd for $C_{26}H_{44}N_2O_2V_2$: C, 60.23; H, 8.55; N, 5.40. Found: C, 60.28; H, 8.43; N, 5.24.

[25] The methyl groups of the isopropoxy ligands in 2 would be diastereotopic in a static asymmetrically bridged V_2N_2 structure.

vanadium nitrido-bridged oligomers, given the right ligand environment. Furthermore, it is striking that cyclopentadienyl substitution of the metal center is, thus far, unique in its ability to support cyclic metallonitride oligomers. However, it is by no means clear what factors determine these preferences in structure and bonding, nor is it yet possible to determine how these preferences can be translated into metallonitride polymers with strong M(N)M interactions. Exploration of such questions in the versatile and well-behaved [(cyclopentadienyl)V(N)X]$_n$ system, including examination of the possibility of using 1 and its derivatives as precursors for vanadium nitride polymers, is underway in our laboratories.

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Supplementary Material Available: X-ray diffraction data for 1: text describing experimental procedures and tables of crystal data, atomic coordinates, interatomic distances and angles, anisotropic displacement coefficients, and hydrogen atom coordinates (6 pages). Ordering information is given on any current masthead page.

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