$= 0.49\ \mu_B$/chromium atom) observed in the temperature dependence of $1/\chi_g$.[1] Theoretical calculations[9] have indicated that a poor Cr–Cr δ overlap is the cause of the residual paramagnetism. However, it is not possible, on the basis of the results reported in this paper, to exclude the possibility that the low residual paramagnetism might, in fact, be caused by a small amount of cocrystallized monomer, undetected by the single-crystal X-ray analysis and by elemental analysis (the dimer always retains molecules of solvent in the lattice). Therefore, there is a possibility that the pure dimer could in reality be diamagnetic.

While we did not find evidence that the same cleavage may occur in the isostructural dimer $[(TAA)Mo]_2$,[9] the existence of the monomer/dimer equilibrium in the case of the chromium derivative indicates that the energy of a Cr–Cr multiple bond cannot be greater than twice the energy of a Cr–py bond.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council of Canada (operating grant) and the Petroleum Research Fund, administered by the American Chemical Society.

Supplementary Material Available: Tables listing atomic positional parameters, anisotropic thermal parameters, and complete bond distances and angles, figures showing ORTEP diagrams, and text detailing crystallographic procedures (14 pages); a table listing observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

Department of Chemistry
University of Ottawa
Ottawa, Ontario K1N 6N5, Canada

Shoukang Hao
Jilles H. H. Edema
Sandro Gambarotta*
Corinne Bensimon

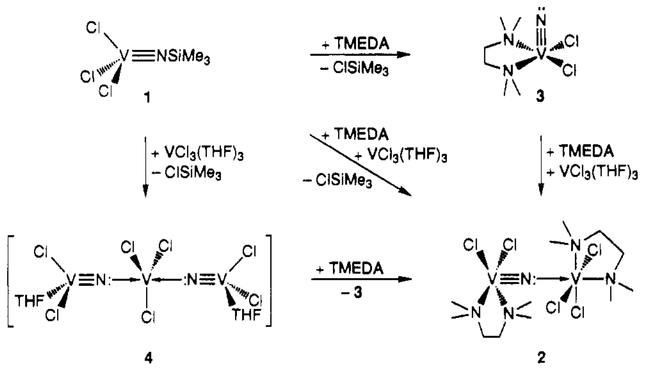
Received September 5, 1991

Mixed-Valence Nitride-Bridged Vanadium Compounds. Synthesis and Structure of $V_2(N)Cl_5(TMEDA)_2$

Nitride-bridged transition-metal complexes have attracted recent attention due to the recognition that the nitride ion can serve as a versatile ligand with which to link metal centers in new materials. For example, we have been developing synthetic methodology aimed at using M(N)M units as building blocks for transition-metal-containing polymers. Using a condensation reaction between metal silylimido and halide complexes, we have prepared examples of solid-state vanadium nitride linear-chain polymers,[1] as well as a family of nitride-bridged vanadium/late-metal model compounds.[2] To date, all of the vanadium-containing nitride-bridged derivatives that we have synthesized possess highly asymmetric structures with strong vanadium–nitrogen triple bonds and relatively weak nitrogen–metal bridging interactions. In contrast, the one previously reported example of a nitride-bridged vanadium compound, $[V_2(N)$(dibenzotetramethyltetraaza[14]annulene$)_2]BPh_4$,[3] was formulated as containing two vanadium(IV) centers, suggesting a symmetric structure,[4] although this was not unambiguously determined.

An understanding of the factors which control formation of asymmetrically versus symmetrically bridged nitrido compounds is important in order to utilize M(N)M units in metal-containing polymers. We therefore set out to examine the reactions of vanadium(V) silylimido derivatives with vanadium(III) chlorides with the aim of exploring whether compounds of the type $V^V{\equiv}N{-}V^{III}$, $V^{IV}{=}N{=}V^{IV}$, $V^{IV}{=}N{=}V^{IV}$, or both would be produced. We report herein the synthesis and characterization of highly localized mixed-valence nitride-bridged di- and trivanadium compounds by this method.

Scheme I



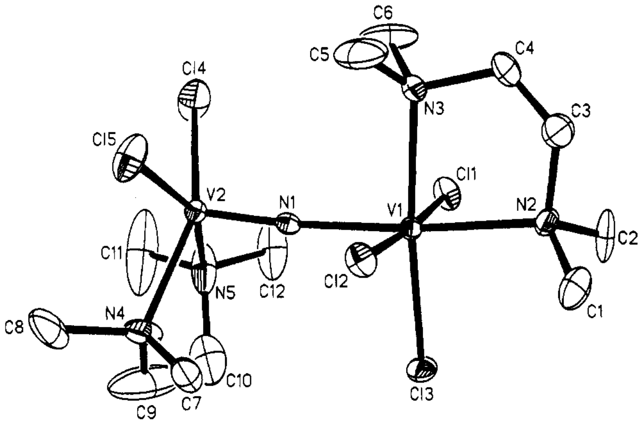


Figure 1. ORTEP drawing of $V_2(N)Cl_5(TMEDA)_2$ (**2**) with 40% thermal ellipsoids for non-hydrogen atoms. Selected bond distances (Å) and angles (deg) not mentioned in text: V(1)–N(2), 2.238 (4); V(1)–N(3), 2.248 (5); V(2)–N(4), 2.188 (5); V(2)–N(5), 2.156 (6); V(1)–Cl(1), 2.336 (2); V(1)–Cl(2), 2.329 (2); V(1)–Cl(3), 2.346 (2); V(2)–Cl(4), 2.235 (2); V(2)–Cl(5), 2.242 (2); N(1)–V(1)–N(2), 174.0 (2); N(1)–V(1)–N(3), 92.8 (2); N(1)–V(1)–Cl(1), 89.7 (1); N(1)–V(1)–Cl(2), 87.7 (1); N(1)–V(1)–Cl(3), 92.9 (1); N(1)–V(2)–N(4), 100.7 (2); N(1)–V(2)–N(5), 97.8 (2); N(1)–V(2)–Cl(4), 105.8 (2); N(1)–V(2)–Cl(5), 103.2 (2).

$V(NSiMe_3)Cl_3$[1a,5] (**1**) reacts immediately with $VCl_3(THF)_3$[6] in benzene solution in the presence of ≥2 equiv of tetramethylethylenediamine (TMEDA) to produce $V_2(N)Cl_5(TMEDA)_2$ (**2**) (Scheme I). $ClSiMe_3$ and THF are detected in the ^1H NMR spectra of reactions performed in C_6D_6 in sealed NMR tubes. Paramagnetic **2** precipitates from benzene as an orange solid in greater than 80% yield and can be crystallized as orange prisms from dichloromethane.

An X-ray structural determination indicates that **2** contains two distinct vanadium centers (Figure 1).[7] V(2) clearly forms a multiple bond to the bridging nitride: the short V(2)–N(1) distance (1.588 (4) Å) is typical of the triple bonds in vanadium(V) nitrido complexes,[1a,2a,8] and the distorted square pyramidal

---

(1) (a) Critchlow, S. C.; Lerchen, M. E.; Smith, R. C.; Doherty, N. M. *J. Am. Chem. Soc.* **1988**, *110*, 8071–8075. (b) Critchlow, S. C.; Smith, R. C.; Doherty, N. M. In *Atomic and Molecular Processing of Electronic and Ceramic Materials: Preparation, Characterization, and Properties*; Aksay, I. A., McVay, G. L., Stoebe, T. G., Wager, J. F., Eds.; Materials Research Society: Pittsburgh, PA, 1988; pp 153–158.

(2) (a) Doherty, N. M.; Critchlow, S. C. *J. Am. Chem. Soc.* **1987**, *109*, 7906–7908. (b) Hoffman, N. W.; Prokopuk, N.; Robbins, M. J.; Jones, C. M.; Doherty, N. M. *Inorg. Chem.* **1991**, *30*, 4177–4181. (c) Jones, C. M. Ph.D. Dissertation, University of Washington, 1990.

(3) Goedken, V. L.; Ladd, J. A. *J. Chem. Soc., Chem. Commun.* **1981**, 910–911.

(4) (a) Wheeler, R. A.; Whangbo, M.-H.; Hughbanks, T.; Hoffmann, R.; Burdett, J. K.; Albright, T. A. *J. Am. Chem. Soc.* **1986**, *108*, 2222–2236. (b) Wheeler, R. A.; Hoffmann, R.; Strähle, J. *J. Am. Chem. Soc.* **1986**, *108*, 5381–5387.

(5) Schweda, E.; Scherfise, K. D.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1985**, *528*, 117–124.

(6) Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 135–140.

(7) Crystallographic data for $C_{12}H_{32}Cl_5N_5V_2$ (fw = 525.6): orthorhombic, *Pbca* (No. 61), $a = 10.7921$ (9) Å, $b = 15.5364$ (14) Å, $c = 27.031$ (3) Å, $V = 4532.3$ (7) Å^3, $Z = 8$, $D_{calcd} = 1.54$ g cm^{-3}, $T = -100$ °C, λ(Mo Kα) = 0.71073 Å, $\mu = 1.401$ mm^{-1}, transmission coefficient = 0.4327–0.4699, $R(F_o) = 0.052 = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w(F_o) = 0.067 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ where $w^{-1} = \sigma^2(|F_o|) + 0.0005(|F_o|)^2$.

0020-1669/92/1331-2678$03.00/0

structure has the equatorial chlorides and TMEDA nitrogens bent away from the axial multiply-bonded nitride, as expected.[9] V(1) resides in an approximately octahedral environment defined by three chlorides, two TMEDA nitrogens, and the bridging nitride. The V(1)–N(1) distance (2.092 (4) Å) is consistent with a single bond, although shortened compared to other vanadium(III)–nitrogen donor distances[10,11] (also compare V(1)–N(2) and V(1)–N(3), Figure 1) as might be expected[12,13] due to the sp hybridization of the nitride ion (V(1)–N(1)–V(2) = 172.0 (3)°). A closely related asymmetrically bridged $\mathrm{V^{IV}(N)V^{III}}$ derivative has recently been reported.[14]

The structure indicates that **2** is best viewed as consisting of a neutral vanadium(V) nitride, $\mathrm{V(N)Cl_2(TMEDA)}$ (**3**), coordinated to a vanadium(III) center via a dative interaction, $\mathrm{V^{V}{\equiv}N{:}\!\rightarrow V^{III}}$.[15] The magnetic properties of this compound further support this picture. Molar susceptibilities for **2** measured between 6 and 300 K on a SQUID susceptometer show Curie–Weiss behavior consistent with an isolated d^2 vanadium(III) center ($g = 1.81$, $\mu_{\mathrm{eff}} = 2.54\ \mu_{\mathrm{B}}$ at 300 K).[16] We can prepare **3** independently by the fast reaction of **1** with TMEDA in benzene and find that it reacts immediately with $\mathrm{VCl_3(THF)_3}$ plus TMEDA, producing **2** (Scheme I). This suggests that formation of **2** from **1**, $\mathrm{VCl_3(THF)_3}$, and TMEDA proceeds via **3** rather than by a condensation reaction between the silylimido ligand of **1** and a chloride ligand of a $\mathrm{VCl_3}$ derivative.

In the absence of TMEDA, **1** and $\mathrm{VCl_3THF_3}$ react in a 2:1 ratio, producing a black crystalline solid, $\mathrm{V_3(N)_2Cl_7(THF)_2}{\cdot}x\mathrm{THF}$ (**4**·xTHF) (x = 0.33–0.50, on the basis of elemental analyses). Compound **4** is very labile in solution, decomposing on attempts to purify by recrystallization and reacting rapidly with TMEDA to form **2** plus **3** (Scheme I) and with pyridine to form $\mathrm{[V(N)Cl_2(py)_2]_n}$[1,17] together with $\mathrm{VCl_3(py)_3}$.[11] On the basis of this reactivity and by analogy to **2**, we propose that **4** consists of two vanadium(V) nitrido complexes coordinated to a vanadium(III) center (Scheme I) in a structure reminiscent of that observed for $\mathrm{VCl_3(NMe_3)_2}$.[10]

For the variety of vanadium-containing nitride-bridged compounds that we have studied, the propensity of vanadium(V) to form strong short triple bonds to the nitride ion dominates the observed chemistry. This is again the case for the mixed-valence vanadium nitrido compounds described here. We now need to explore whether these asymmetrically substituted, asymmetrically bridged metallonitrides can be converted to symmetrically substituted, symmetrically bridged species via manipulation of the vanadium coordination environment.

Acknowledgment. We gratefully acknowledge support of this work by the Air Force Office of Scientific Research, Air Force Systems Command, USAF (Grant No. AFOSR-87-0362). Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We express our thanks to Professor Frank J. Feher for his assistance with the magnetic studies and to Professor Christopher Reed for providing access to a SQUID susceptometer at the University of Southern California. We also thank Dr. Susan C. Critchlow for a preliminary X-ray study of **2**. N.M.D. thanks the Alfred P. Sloan Foundation for a fellowship (1990–1992).

Supplementary Material Available: A textual presentation of the spectroscopic and analytical data for **2**–**4** and magnetic data for **2** (including experimental and simulation procedures), a plot of experimental and simulated magnetic data and a table of SQUID data for **2**, and X-ray crystal data for **2**, including a textual description of experimental procedures and tables of crystal data, atomic coordinates and equivalent isotropic displacement coefficients, interatomic distances, interatomic angles, anisotropic displacement coefficients, and hydrogen atom coordinates and isotropic displacement coefficients (12 pages); a listing of observed and calculated structure factors for **2** (14 pages). Ordering information is given on any current masthead page.

Department of Chemistry
University of Washington
Seattle, Washington 98195

Kate L. Sorensen
Megan E. Lerchen

Department of Chemistry
University of California
Irvine, California 92717

Joseph W. Ziller
Nancy M. Doherty*

Received April 1, 1992

---

(8) Willing, W.; Christophersen, R.; Müller, U.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1987**, *555*, 16–22.

(9) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988; pp 155–158.

(10) Greene, P. T.; Orioli, P. L. *J. Chem. Soc. A* **1969**, 1621–1624.

(11) (a) Fowles, G. W. A.; Greene, P. T. *J. Chem. Soc. A* **1967**, 1869–1874. (b) Characterization by X-ray diffraction: Sorensen, K. L.; Ziller, J. W.; Doherty, N. M. To be submitted for publication.

(12) See, for example: Pestana, D. C.; Power, P. P. *Inorg. Chem.* **1991**, *30*, 528–535 and references therein.

(13) We have used analogous arguments to explain the short nitrogen–phosphorus bond distances observed in some metal phosphiniminato complexes: (a) Schomber, B. M.; Ziller, J. W.; Doherty, N. M. *Inorg. Chem.* **1991**, *30*, 4488–4490. (b) Lichtenhan, J. D.; Ziller, J. W.; Doherty, N. M. *Inorg. Chem.*, companion paper in this issue.

(14) Sable, D. B.; Armstrong, W. H. *Inorg. Chem.* **1992**, *31*, 161–163.

(15) NMR spectra for **2** have been obtained, but provide only limited information. In $\mathrm{CD_2Cl_2}$, we observe equally broad ^{1}H and ^{13}C NMR signals for paramagnetic **2** and diamagnetic **3**, with no resolvable H–H coupling in the ^{1}H NMR spectra of either compound. Additionally, decomposition of **2** (faster) and **3** (slower) is observed in dichloromethane solution, as well as in all other solvents in which these compounds are soluble. These observations preclude meaningful assignment of the NMR spectra for **2**.

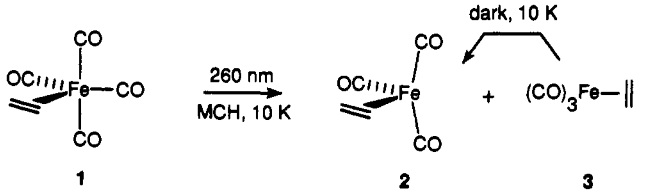
(16) (a) Carlin, R. L. *Magnetochemistry*; Springer-Verlag: Berlin, 1986. (b) Mabbs, F. E.; Machin, D. J. *Magnetism and Transition Metal Complexes*; Chapman & Hall: London, 1973. (c) Drago, R. S. *Physical Methods in Chemistry*; Saunders: Philadelphia, PA, 1977; Chapter 11.

(17) Schomber, B. M. Ph.D. Dissertation, University of Washington, 1991.

Isomerism in Coordinatively Unsaturated $\mathrm{Fe(CO)_3(\eta^2\text{-ethene})}$ Complexes

Despite continuing experimental[1-5] and theoretical[3,6-8] interest in the structure and reactivity of $\mathrm{Fe(CO)_3L}$ complexes, the geometry of $\mathrm{Fe(CO)_3(\eta^2\text{-ethene})}$ remains uncertain. Hayes and Weitz recently reported evidence that $\mathrm{Fe(CO)_3(\eta^2\text{-ethene})}$ possesses a triplet ground state, but they could not address the issue of molecular geometry.[2] We now report direct observation of geometric isomerism in coordinatively unsaturated $\mathrm{Fe(CO)_3(\eta^2\text{-ethene})}$ complexes (**2** and **3**) using matrix-isolation spectroscopy.

Photolysis (260 ± 10 nm, 30 min) of $\mathrm{Fe(CO)_4(\eta^2\text{-}C_2H_4)}$ (**1**),[9,10] matrix-isolated in either argon or methylcyclohexane at 10 K,[11]



---

(1) Nayak, S. K.; Burkey, T. J. *Inorg. Chem.* **1992**, *31*, 1125–1127.

(2) Hayes, D. M.; Weitz, E. *J. Phys. Chem.* **1991**, *95*, 2723–2727.

(3) Weiller, B. H.; Miller, M. E.; Grant, E. R. *J. Am. Chem. Soc.* **1987**, *109*, 352–356.

(4) Wuu, Y.-M.; Bentsen, J. G.; Brinkley, C. G.; Wrighton, M. S. *Inorg. Chem.* **1987**, *26*, 530–540.

(5) Ellerhorst, G.; Gerhartz, W.; Grevels, F.-W. *Inorg. Chem.* **1980**, *19*, 67–71.

(6) Albright, T. A.; Clemens, P. R.; Hughes, R. P.; Hunton, D. E.; Margerum, L. D. *J. Am. Chem. Soc.* **1982**, *104*, 5369–5379.

(7) (a) Burdett, J. K. *Coord. Chem. Rev.* **1978**, *27*, 1–58. (b) Burdett, J. K. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 1599–1613.

(8) (a) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058–1076. (b) Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801–3812.

(9) Solutions of $\mathrm{Fe(CO)_4(\eta^2\text{-}C_2H_4)}$ in methylcyclohexane were prepared as described by Wrighton.[4] $\mathrm{Fe(CO)_4(\eta^2\text{-}C_2H_4)}$, as the pure material, was synthesized by the method of Murdoch and Weiss.[10]

(10) Murdoch, H. D.; Weiss, E. *Helv. Chim. Acta* **1963**, *46*, 1588–1594.

0020-1669/92/1331-2679$03.00/0