The intriguing structure (I) proposed by Fowles and co-workers for their Zr(III) acetonitrile complexes[2] prompted us to examine reactions of the $[ZrCl_3(py\text{-}R_2]_2$ compounds with trimethylacetonitrile, which we assumed would give soluble and therefore easily characterizable compounds. Thus, the reaction of 1 equiv of trimethylacetonitrile with $[ZrCl_3(py)_2]_2$ in benzene (3 h) gives an orange solution and precipitate. Workup of the reaction, which includes removal of the volatiles under reduced pressure and a hexanes wash of the residue, produces analytically pure $Zr_2Cl_6(py)_3(t\text{-}BuCN)$ as an orange solid in 92% yield.[8]

An X-ray structure determination for $Zr_2Cl_6(py)_3(t\text{-}BuCN)$ revealed that the nitrile is $\pi$ bound to one Zr center (Zr(2)) and $\sigma$ coordinated via nitrogen to the other (Figure 2).[9] The Zr–Zr distance (3.554 (1) Å) is 0.4 Å longer than in $[ZrCl_3(4\text{-}(1\text{-butylpentyl})pyridine)_2]_2$, suggesting that the Zr–Zr bond has been cleaved.[10] The Zr(2)–C(1) distance (2.208 (7) Å) is somewhat short compared to Zr–alkyl bond distances (e.g., Zr–C = 2.262 (11) Å in $ZrMe(N(SiMe_3)_2)_3$).[11] Also, the Zr(2)–N(1) and Zr(1)–N(1) distances (2.245 (5) and 2.112 (6) Å) are significantly shorter than the Zr–N(py) bond distances (average 2.391 (11) Å) and Zr(1)–N(1) is nearly as short as the Zr–N distance in $ZrMe(N(SiMe_3)_2)_3$ (2.080 (5) Å),[11] a molecule in which there is undoubtedly some degree of Zr–N multiple bonding.

The coordinated nitrile C–N bond distance (1.255 (9) Å) is lengthened in comparison to the distance in a free nitrile (1.16 Å), and the $Me_3C$–C–N angle (127.4 (7)°) is close to the value expected for $sp^2$ hybridization. This indicates there is significant population of the nitrile $\pi^*$ orbitals. Raman data also support this notion: the C–N stretch has been assigned to a band at 1612 $cm^{-1}$,[12] which is significantly reduced from the value for free nitrile (2237 $cm^{-1}$) and close to the value observed for the C=N bonds in $R_2C{=}NR$ compounds.[13] Thus, the aggregate of structure and spectroscopic properties suggests it is reasonable to count the nitrile as a formal dianionic ligand and to view the reaction to form $Zr_2Cl_6(py)_3(t\text{-}BuCN)$ as an oxidative addition of *t*-BuCN to the Zr–Zr bond in $[ZrCl_3(py)_2]_2$.

In conclusion, we have presented a convenient synthesis of $[ZrCl_3(py\text{-}R)_2]_2$ complexes and the first definitive structural characterization for this type of compound. We have also shown that *t*-BuCN adds to $[ZrCl_3(py)_2]_2$ in an apparent oxidative addition yielding a nitrile ligand coordinated in a $\sigma,\pi$ fashion. Although several examples of $\pi$-bound nitriles to single metal centers are known,[14] a $\sigma,\pi$ coordination mode like that in $Zr_2Cl_6(py)_3(t\text{-}BuCN)$ appears to be rare.[15] Additional reactivity studies are in progress.

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**Supplementary Material Available:** Tables of crystal data, atomic coordinates, and equivalent isotropic displacement parameters for $[ZrCl_3(4\text{-}(1\text{-butylpentyl})pyridine)_2]_2$ and $Zr_2Cl_6(py)_3(t\text{-}BuCN)$ (4 pages). Ordering information is given on any current masthead page.

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(8) $^1H$ NMR ($CD_2Cl_2$): $\delta$ 9.25 (d, 2, $\alpha$-H, $C_5H_5N$), 9.13 (br, 2, $\alpha$-H, $C_5H_5N$), 8.98 (d, 2, $\alpha$-H, $C_5H_5N$), 7.94 (m, 3, $\gamma$-H, $C_5H_5N$), 7.43 (m, 6, $\beta$-H, $C_5H_5N$), 1.25 (s, 9, $Me_3CCN$). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 257.4 ($Me_3CCN$), 152.9 ($\alpha$-C, $C_5H_5N$), 151.7 (br, $\alpha$-C, $C_5H_5N$), 151.4 ($\alpha$-C, $C_5H_5N$), 140.6 (br, $\gamma$-C, $C_5H_5N$), 140.4 ($\gamma$-C, $C_5H_5N$), 140.1 ($\gamma$-C, $C_5H_5N$), 125.5 ($\beta$-C, $C_5H_5N$), 125.2 ($\beta$-C, $C_5H_5N$), 125.1 ($\beta$-C, $C_5H_5N$), 46.5 ($Me_3CCN$), 28.2 ($Me_3CCN$). Anal. Calcd for $C_{20}H_{24}N_4Cl_6Zr_2$: C, 33.57; H, 3.38; N, 7.83. Found: C, 33.39; H, 3.39; N, 7.62.

(9) Crystal data for $C_{20}H_{24}N_4Cl_6Zr_2{\cdot}2CH_2Cl_2$ at −55 (1) °C: orange-red block from cold (−40 °C) $CH_2Cl_2$, 0.70 × 0.45 × 0.40 mm, orthorhombic, space group *Pbca*, $a$ = 13.980 (7) Å, $b$ = 13.743 (9) Å, $c$ = 36.843 (18) Å, $Z = 8$, $d_{calcd}$ = 1.66 g $cm^{-3}$, and $\mu$ = 13.6 $cm^{-1}$. X-ray diffraction data were collected on a Nicolet R3m/V diffractometer using graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å) in the $\omega$ scan mode. Lorentz and polarization corrections and an empirical absorption correction based on $\psi$ scans of 10 reflections having $\chi$ values between 70 and 90° were applied to the data. A total of 4128 reflections were collected in the range $4° < 2\theta < 42°$, and 2823 unique reflections with $I > 3\sigma(I)$ were used in the structure solution. $R(F) = 0.039$; $R_w(F) = 0.035$.

(10) For a different viewpoint on Zr–Zr super long bonds, see: Rohmer, M.-M.; Bénard, M. *Organometallics* **1991**, *10*, 157.

(11) Bradley, D. C.; Chudzynska, H.; Backer-Dirks, J. D. J.; Hursthouse, M. B.; Ibrahim, A. A.; Motevalli, M.; Sullivan, A. C. *Polyhedron* **1990**, *9*, 1423.

(12) The 1612-$cm^{-1}$ band was insensitive to substitution of pyridine by pyridine-$d_5$. The Raman data were obtained via backscattering for a spinning KCl pellet under a $N_2$ atmosphere. See: Czernuszewicz, R. *Appl. Spectrosc.* **1986**, *40*, 571.

(13) Colthup, N. B.; Daly, L. H.; Wiberley, S. E. *Introductions to Infrared and Raman Spectroscopy*, 3rd ed.; Academic: New York, 1990; pp 344–347.

(14) Barrera, J.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **1991**, *113*, 8178 and references therein.

(15) (a) We know of only one other example for group IV metals, $[Ti(2,6\text{-diphenylphenoxide})_2(PhCN)]_2$: Rothwell, I. Private communication. For a related late transition metal example, see: Bassi, I. W.; Benedicenti, C.; Calcaterra, M.; Intrito, R.; Rucci, G.; Santini, C. *J. Organomet. Chem.* **1978**, *144*, 255. For a trinuclear example, see: Andrews, M. A.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1979**, *101*, 7260. (b) While this paper was under review, another low-valent example appeared: Alonso, F. J. G.; Sanz, M. G.; Riera, V. *Organometallics* **1992**, *11*, 801.

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## Reversible Cleavage of the Cr–Cr Multiple Bond in $[(TAA)Cr]_2$ (TAA = Tetramethyldibenzotetraaza[14]annulene)

Until the recent discovery that a dichromium moiety with a very short Cr–Cr distance may exist in $[(TAA)Cr]_2$ (TAA = tetramethyldibenzotetraaza[14]annulene) in the absence of any bridging interaction,[1] extremely short Cr–Cr contacts had been found in a particular class of compounds containing bridging three-center chelating ligands[2] and in a few organometallic dimers with bridging carbon donor atoms.[3] The extremely short M–M distances and the magnetic properties of the complexes initially suggested that a strong M–M multiple bond[4] (thought to be quadruple) was the thermodynamic driving force for the dimer formation. However, more recent experimental[5] and theoretical[6] work has established that Cr–Cr quadruple) bonds are para-

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(1) Edema, J. J. H.; Gambarotta, S.; van der Sluis, P.; Smeets, W. J. J.; Spek, A. L. *Inorg. Chem.* **1989**, *28*, 3782.

(2) (a) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; J. Wiley & Sons: New York, 1982 and references cited therein. (b) Cotton, F. A.; Walton, R. A. Metal-Metal Multiple Bonds in Dinuclear Clusters. *Struct. Bonding (Berlin)* **1985**, *62*, 1. (c) Cotton, F. A.; Feng, X.; Kibala, P. A.; Matusz, M. *J. Am. Chem. Soc.* **1988**, *110*, 2807 and references cited therein. (d) Cotton, F. A.; Koch, S.; Millar, M. *Inorg. Chem.* **1978**, *17*, 2084. (e) Cotton, F. A.; Koch, S. *Inorg. Chem.* **1978**, *17*, 2021. (f) Bino, A.; Cotton, F. A.; Khaim, W. *Inorg. Chem.* **1979**, *18*, 3566. (g) Cotton, F. A.; Koch, S.; Millar, M. *Inorg. Chem.* **1978**, *17*, 2087.

(3) (a) Hursthouse, M. B.; Malik, K. M. A.; Sales, K. D. *J. Chem. Soc., Dalton Trans.* **1978**, 1314. (b) Koschmieder, S. U.; McGillan, B. S.; McDermott, G.; Arnold, J.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1990**, 3427. (c) Krausse, J.; Mark, G.; Schoedl, G. *J. Organomet. Chem.* **1970**, *21*, 159. (d) Krausse, J.; Schoedl, G. *J. Organomet. Chem.* **1971**, *27*, 59.

(4) Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 225.

(5) (a) Larkworthy, L. F.; Tabatabai, J. M. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 427. (b) Sneeden, R. P.; Zeiss, H. H. *J. Organomet. Chem.* **1973**, *47*, 125. (c) Salt, J. E.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1986**, 1141. (d) Wilson, L. M.; Cannon, R. D. *Inorg. Chem.* **1988**, *27*, 2382. (e) Cannon, R. D. *Inorg. Chem.* **1981**, *20*, 2341.

(6) Hall, M. B. *Polyhedron* **1987**, *6*, 679 and references cited therein.

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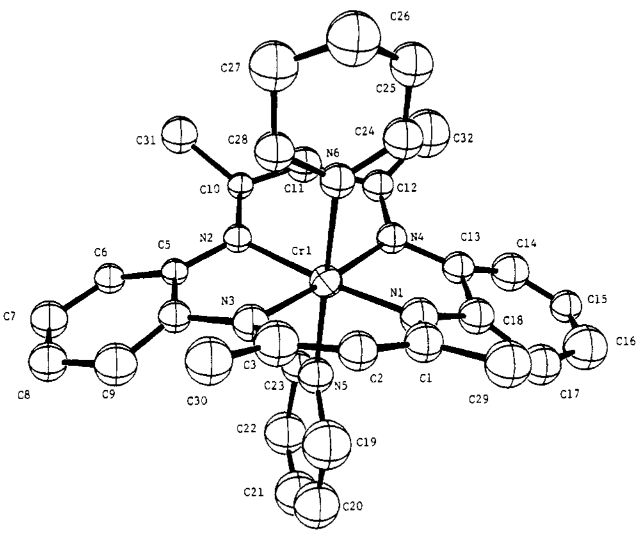


**Figure 1.** ORTEP plot of the monomeric unit of **2**, showing the labeling scheme. Selected values of bond distances (Å) and angles (deg): Cr(1)-N(1) = 1.95 (3), Cr(1)-N(5) = 2.138 (18), Cr(1)-N(6) = 2.059 (19); N(5)-Cr(1)-N(6) = 176.9 (18), N(1)-Cr(1)-N(5) = 86.0 (12), N(1)-Cr(1)-N(6) = 91.9 (12).

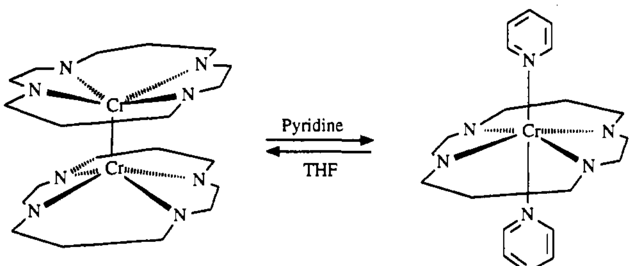
doxically weak. We even question whether or not these Cr–Cr interactions are sufficient to be termed a chemical bond.[7]

The crystal structure of $[(TAA)Cr]_2$[1] (**1**) has shown that it is possible to form Cr–Cr bonds sufficiently strong to hold together the dimetallic unit, when the metal is "pyramidalized"[8] by a "small-hole" macrocyclic ligand. Since complex **1** has a very short Cr–Cr distance and the characteristic residual low paramagnetism, questions again arise about how strong this M–M bond should be. Theoretical calculations[9] carried out on **1** have indicated the presence of a Cr–Cr triple bond. Conversely, a quadruple bond has been calculated in the diamagnetic and isostructural dimolybdenum derivative, although the energy levels of the M–M bond orbitals are comparable in the two complexes.

We felt that it was important to try to evaluate experimentally the strength of the Cr–Cr multiple bond of **1** and to provide a comparison with the isostructural molybdenum derivative. In this paper we describe the reversible cleavage of $[(TAA)Cr]_2$ by pyridine to form an octahedral, low-spin monomeric $[(TAA)Cr(py)_2]\cdot py$ complex.

When the deep-red dimeric $[(TAA)Cr]_2$ (**1**) was recrystallized from pure pyridine, a black-brown needle-shaped crystalline solid was formed.[10] Analytical results were consistent with the formulation $[(TAA)Cr(py)_2]\cdot py$ (**2**).[10] The paramagnetism of **2**, consistent with a low-spin $d^4$ electronic configuration ($\mu_{eff} = 2.79$ $\mu_B$) strongly suggests that a major molecular reorganization occurred in pyridine solution. Conversely, when complex **2** was redissolved in either hot toluene or THF, the deep-red dimer **1** was re-formed in moderate yield and analytically pure form (Scheme I). This result indicates that a chemical equilibrium exists between the two species, and its position is probably determined by the amount of pyridine in solution. Unfortunately, attempts to grow suitable crystals of **2** failed, due to unfavorable crystal shape. However, a curious phenomenon of cocrystallization was observed when a pyridine solution of **2** was layered with a mixture of THF/hexane. The IR spectrum of the resulting large brown lozenges showed the same spectrum as could be obtained by the overlap of the spectra of the pure **1** and **2**.

**Scheme I**



The X-ray crystal structure[11] revealed one dimeric $[(TAA)Cr]_2$ and two monomeric octahedral $(TAA)Cr(py)_2$ molecules. Two molecules of THF and one disordered molecule of pyridine were found also in the lattice. The dimeric unit is identical to that of the previously reported dimer[1] with the expected geometrical parameters and very similar Cr–Cr distance [Cr(1)–Cr(1a) = 2.075 (7) Å]. The monomeric molecule is somewhat surprising. The octahedral geometry of chromium (Figure 1) with the two pyridines trans with respect to the macrocycle plane is unusual[12] for a Cr(II) $d^4$ electronic configuration, which usually prefers square-planar or square-pyramidal geometries.[13] Moreover, this octahedral geometry is unique among the TAA–transition metal derivatives, where the characteristic saddle shape of the ligand imposes pyramidal geometries on the transition metal, with or without an additional ligand on the apical position. The deviation of the macrocycle from the planarity is probably responsible for the small difference in the Cr–N distances [Cr(1)–N(5) = 2.138 (18), Cr(1)–N(6) = 2.059 (19) Å] formed by the two axial pyridine molecules.

The facile dimer dissociation, the paramagnetism of the monomeric complex, and its ability to cocrystallize with the dimer prompted us to reconsider the residual paramagnetism of **1** ($\mu_{eff}$

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(7) Edema, J. J. H.; Gambarotta, S. *Comments Inorg. Chem.* **1991**, *11*, 195.

(8) Losada, J.; Alvarez, S.; Novoa, J. J.; Mota, F.; Hoffmann, R.; Silvestre, J. *J. Am. Chem. Soc.* **1990**, *112*, 8998.

(9) Cotton, F. A.; Czuchajowska, J.; Feng, X. *Inorg. Chem.* **1990**, *29*, 4329.

(10) Preparation of $[(TAA)Cr(py)_2]\cdot py$: $[(TAA)Cr]_2$ (2.0 g, 2.5 mmol) was added to freshly distilled dry pyridine (50 mL). The resulting suspension was boiled and filtered hot. Black-brown very fine needles separated upon slow cooling at room temperature (1.3 g, 2.1 mmol; yield 42%). Anal. Calcd (found) for $C_{37}H_{37}N_7Cr$: C, 70.35 (70.06); H, 5.90 (5.89); N, 15.52 (15.01); Cr, 8.23 (7.97). IR [KBr, Nujol mull, cm$^{-1}$]: 1570 (m), 1540 (m), 1450 (s), 1390 (vs), 1270 (w), 1195 (s), 1180 (s), 1030 (m), 980 (s), 725 (m), 640 (s), 610 (s), 515 (w), 490 (w). ($\mu_{eff} = 2.79$ $\mu_B$). Preparation of $[(TAA)Cr(py)_2][(TAA)Cr]_2\cdot py\cdot THF$: A saturated solution of $[(TAA)Cr(py)_2]\cdot py$ in pyridine (15 mL) was layered with THF and hexane in a 70-cm Schlenk tube. Large brown lozenges were obtained upon slow diffusion (2 months).

(11) The crystal structure was hampered by several difficulties including weak scattering (probably caused by ready loss of interstitial solvent), the large number of atoms, and a positional disorder of the interstitial molecule of pyridine. However, the quality of the crystal structure was sufficient to demonstrate the chemical composition: Monoclinic, *C*2, $Cr_4N_{21}C_{121}H_{153}O_2$, fw = 2141.66, $a = 27.089$ (16) Å, $b = 15.125$ (5) Å, $c = 14.449$ (5) Å, $\beta = 103.35$ (4)°, $V = 5760$ (4) Å$^3$, $Z = 2$, $R = 0.117$ ($R_w = 0.132$), for 286 parameters and 2446 significant reflections with $I > 2.5\sigma(I)$ out of 4540. Data were collected at room temperature ($T = 298$ K) on a ASFC6 Rigaku diffractometer using Mo K$\alpha$ radiation ($\lambda = 0.709\,30$ Å). Intensities of three standard reflections were measured every 150 reflections showing no significant decay. The structure was solved by direct methods using the NRCVAX structure solution package. Chromium atoms were anisotropically refined. All the other atoms were refined isotropically due to the unfavorable observation/parameter ratio. Hydrogen atoms were introduced at calculated positions but not refined. The nitrogen atom position of the interstitial pyridine could not be determined with certainty; therefore, each ring atom was treated as $^1/_6$ N and $^5/_6$ C.

(12) (a) Girolami, G. S.; Salt, J. E.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Am. Chem. Soc.* **1983**, *105*, 5954. (b) Girolami, G. S.; Wilkinson, G.; Galas, A. M. R.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1985**, 1339. (c) Scheidt, W. R.; Brinegar, A. C.; Kirner, J. F.; Reed, C. A. *Inorg. Chem.* **1979**, *18*, 3610.

(13) (a) Murray, B. D.; Hope, H.; Power, P. P. *J. Am. Chem. Soc.* **1985**, *107*, 169. (b) Hermes, A. N.; Girolami, G. S. *Inorg. Chem.* **1988**, *27*, 1775. (c) Hermes, A. R.; Morris, J. R.; Girolami, G. S. *Organometallics* **1988**, *7*, 2372. (d) Edema, J. J. H.; Gambarotta, S.; van Bolhuis, F.; Smeets, W. J. J.; Spek, A. L. *Inorg. Chem.* **1989**, *28*, 1407. (e) Edema, J. J. H.; Gambarotta, S.; van Bolhuis, F.; Spek, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 2142. (f) Edema, J. J. H.; Gambarotta, S.; Smeets, W. J. J.; Spek, A. L. *Inorg. Chem.* **1991**, *30*, 1380. (g) Edema, J. J. H.; Gambarotta, S.; Meetsma, A.; Smeets, W. J. J.; Spek, A. L.; Khan, S. I. *Inorg. Chem.* **1991**, *30*, 3639. (h) Edema, J. J. H.; Gambarotta, S.; Meetsma, A.; van Bolhuis, F.; Spek, A. L.; Smeets, W. J. J. *Inorg. Chem.* **1990**, *29*, 2147. (i) Edema, J. J. H.; Gambarotta, S.; Bolhuis, F.; Smeets, W. J. J.; Spek, A. L.; Chiang, M. Y. *J. Organomet. Chem.* **1990**, *389*, 47.

= 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 $\delta$ 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.

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**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.

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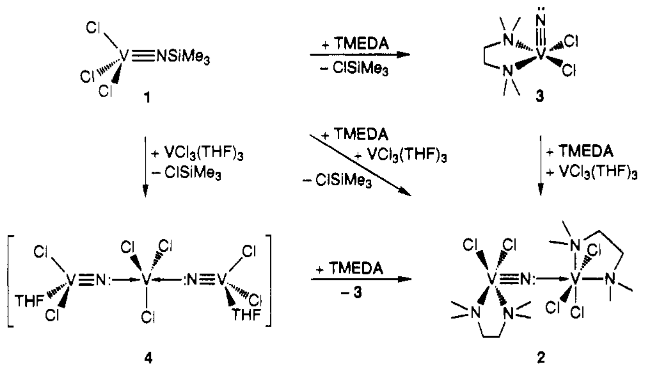
## Mixed-Valence Nitride-Bridged Vanadium Compounds. Synthesis and Structure of $V_2(N)Cl_5(TMEDA)_2$

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, $[V_2(N)(\text{dibenzotetramethyltetraaza[14]annulene})_2]BPh_4$,[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



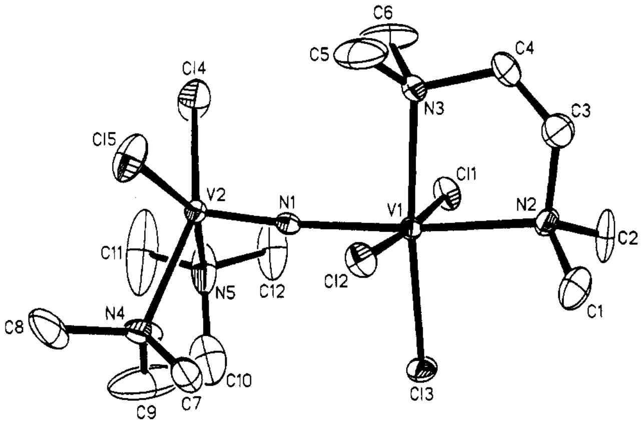


**Figure 1.** ORTEP drawing of $V_2(N)Cl_5(TMEDA)_2$ (**2**) with 40% thermal ellipsoids for non-hydrogen atoms. Selected bond distances (Å) and angles (deg) not mentioned in text: V(1)–N(2), 2.238 (4); V(1)–N(3), 2.248 (5); V(2)–N(4), 2.188 (5); V(2)–N(5), 2.156 (6); V(1)–Cl(1), 2.336 (2); V(1)–Cl(2),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

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(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 $w^{-1} = \sigma^2(|F_o|) + 0.0005(|F_o|)^2$.

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