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Dimeric and Cyclotrimeric Piano-Stool Vanadium(III) Dihalides with Unusual Differences in V−V Distance and Magnetochemistry. Syntheses, Structures, and Reactivities of (η-$C_5Me_4R)_2V_2(\mu$-$Br)_4$ and the Trivanadium Cluster (η-$C_5Me_4R)_3V_3(\mu$-$Cl)_6$, New Mid-Valent Organovanadium Synthons

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Summary: Reductive oligomerization of $(C_5Me_4R)VX_3$ *or addition of* $(C_5Me_4R)SnBu_3$ *to* VX_3L_3 *(L = thf, tht) yields the (peralkylcyclopentadienyl)vanadium(III) halides* $(\eta^5$-$C_5Me_4R)_2V_2(\mu$-$Br)_4$ *and* $(\eta^5$-$C_5Me_4R)_3V_3(\mu$-$Cl)_6$ *(R = Me, Et), which can be halogenated to afford* $(C_5Me_4R)VX_3$*. Paramagnetic* $(C_5Me_4Et)_2V_2(\mu$-$Br)_4$ *is a four-legged piano-stool dimer in the solid state with a nominal V−V bond (2.565(1) Å), while the spin-frustrated, antiferromagnetic* $(C_5Me_4Et)_3V_3(\mu$-$Cl)_6$ *is a piano-stool cyclotrimer with two* μ*-chlorines per nonbonded V···V edge (3.3732[63] Å).*

Mid- and low-valent polynuclear chemistry of the group 5 transition metals involves two distinct compound classes, inorganic and organometallic. Inorganic compounds include dinuclear[2] and cluster complexes,[3a] while organopolymetallics with various ligands or two cyclopentadienyl groups per metal comprise the second class. Compounds with metal−metal multiple bonds are known for both and exhibit interesting chemistry,[2,3b] but V−V-bonded divanadium/organodivanadium complexes are rare,[2,4] with a tendency for antiferromagnetism and no V−V bonding.[5,6] There is considerable disagreement on the description of V−V bonding in such complexes.[7,8]

We have been developing the chemistry of organodimetallic group 5 compounds which are intermediate between these classes, i.e., mid-valent mono(peralkylcyclopentadienyl)metal halides with potential for M−M multiple bonding and utility as piano-stool synthons.[9] There are no $V(C_5R_5)$ synthons other than the low overall yield, $V(CO)_6$-derived $Cp^*V(CO)_4$ ($Cp^* = C_5Me_5$) and its derivative Cp^*VX_3;[10] therefore, vanadocenes are often used with concomitant cyclopentadienyl loss. We targeted the unknown organodivanadium(III) halides $Cp^*_2V_2X_4$, analogs of the reactive,[11] d^2−d^2, diamagnetic $(C_5Me_4R)_2Ta_2(\mu$-$X)_4$ (R = Me (Cp*), Et). The structures of $(C_5H_5)VX_2$ compounds[9b,12] are unknown. Of particular interest are the number of μ-halides and V−V bond order in $Cp^*_2V_2X_4$, because (1) $Cp_2M_2(\mu$-$X)_4$ complexes may have a $\sigma\delta^*\delta$ MO ordering from δ destabilization by a $(\mu$-$X)_4$ lone pair FMO, and (2) d^2−d^2 complexes may have bond orders of 0, 1, or 2.[13a] Structural possibilities based on analogs[9a,11,13c,14−16] would possess four μ-X groups and a M═M or no M···M bond, two μ-X groups and no M···M bond, or no μ-X groups and a M═M bond. Most studies have involved chlorides, with little recog-

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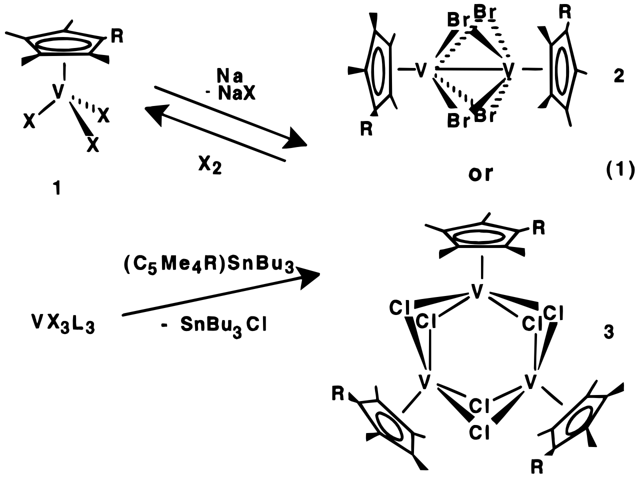
nition of the structural dependence on halide. We report here our studies[17] on piano-stool oligomers of $(C_5Me_4R)VX_2$.

Reduction of $(C_5Me_4R)VX_3$ (**1**: R = Me, Et; X = Br, Cl) with Na/Hg (1 equiv) in toluene yields the organo*di*vanadium(III) bromide complex $(C_5Me_4R)_2V_2Br_4$ (**2**; 90% yield) or the organo*tri*vanadium(III) chloride cluster $(C_5Me_4R)_3V_3Cl_6$, (**3**; 71% yield) (eq 1). Both compounds can be prepared more conveniently and directly, without carbonyl precursors, by addition of $Sn(C_5Me_4R)Bu_3$ to a CH_2Cl_2 solution of VX_3L_3 (L = tetrahydrofuran, tetrahydrothiophene; **2**, 60% yield; **3**, 80% yield; eq 1), whereas other Cp* sources gave intractable products.[18] Compounds **2** and **3** differ surprisingly in spectrometric, spectroscopic, and magnetic properties and solid-state structures.



The isolated black bromide **2**[19] is EPR-silent and is dinuclear, as shown by mass spectrometry. ^1H NMR spectra of **2b** (R = Et) are consistent with a symmetric species with equivalent C_5Me_4R ligands bisected by a mirror plane. Compound **2b** was shown to be dinuclear in the solid state by X-ray diffraction, (Figure 1), with four μ-Br atoms (average V−Br = 2.5967[56] Å),[20] an acute V−Br−V angle (average 59.19[3]°), and a V−V distance of 2.565(1) Å in the nominal single-bond range.[2,21]

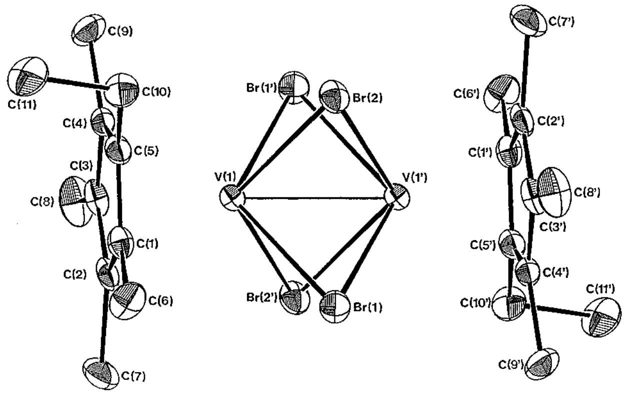


Figure 1. ORTEP diagram of $(C_5Me_4Et)_2V_2(\mu\text{-}Br)_4$ (**2b**) viewed perpendicular to the V−V vector.

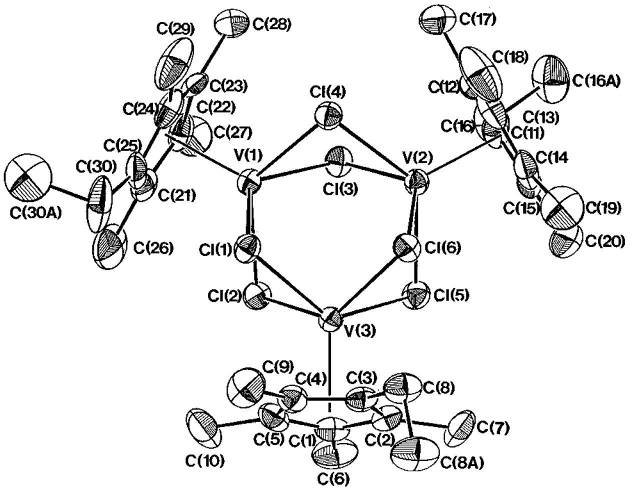


Figure 2. ORTEP diagram of $(C_5Me_4Et)_3V_3(\mu\text{-}Cl)_6$ (**3b**) viewed perpendicular to the V_3 plane, with only one orientation of the two disordered C_5Me_4Et ligands on V(1) shown.

The paramagnetic red-black chloride **3** is also EPR-silent but exhibits a *trinuclear* mass spectral parent ion.[22] The ^1H NMR data are consistent with a symmetric solution structure, with equivalent C_5Me_4R groups bisected by a mirror plane. The solid-state structure of **3b** (R = Et; Figure 2) consists of a non-bonded V_3 equilateral triangular core with long, non-bonded V···V separations (V(1)···V(2), 3.3842(6) Å; V(2)···V(3), 3.3620(6) Å; V(1)···V(3), 3.3733(6) Å; average 3.3732[63] Å) and six Cl bridges (average V--Cl, 2.447[28] Å; average V--Cl--V, 87.29[8]°).

In order to probe the V−V interactions in **2** and **3**, we examined the solution and solid-state susceptibilities as a function of T and H. We expected that **2** would possess an antiferromagnetic V−V interaction and **3** would exhibit frustrated paramagnetism[23] for an odd number of $S = 1$ (d^2) centers. Comparative solid-state

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(17) Messerle, L. Presented at the 201st National Meeting of the American Chemical Society, Atlanta, GA, April 19, 1991; INOR 467 (synthetic, and preliminary structural details for **2** and **3**).

(18) (a) Synthesis of **2a**: $VBr_3(tht)_3$ (3.00 g, 5.40 mmol) was dissolved in CH_2Cl_2 (200 mL) in a 250 mL round-bottom flask under an inert atmosphere. $(C_5Me_5)SnBu_3$ (2.30 g, 5.40 mmol) was added with stirring and the mixture stirred for 7 h. The mixture was rotavapped to dryness, redissolved in toluene (150 mL), and filtered to remove insoluble byproducts. After concentration *in vacuo* followed by cooling to −40 °C, three crops were collected by filtration and recrystallized from toluene: total = 1.12 g (60% yield). (b) Synthesis of **3a**: $VCl_3(thf)_3$ (4.00 g, 10.7 mmol) and $(C_5Me_5)SnBu_3$ (4.55 g, 10.7 mmol) were reacted in CH_2Cl_2 as described above, and the mixture was stirred for 12 h. Upon concentration of the reaction mixture filtrate to 30 mL, a large first crop of reasonably pure **3a** was recovered by filtration, provided filtration was performed quickly. The mother liquor was rotavapped to dryness, redissolved in toluene (150 mL), and filtered. After concentration *in vacuo* and cooling, three crops were collected: total 2.19 g (80% yield). Recrystallization from toluene is necessary to obtain **3a** in high purity. (c) For the corresponding chemistry with Cp sources, see: Niemann, J.; Teuben, J. H.; Huffmann, J. C.; Caulton, K. G. *J. Organomet. Chem.* **1983**, *255*, 193.

(19) **2a**: Anal. Calcd for $C_{10}H_{15}Br_2V$: C, 34.72; H, 4.37; Br, 46.19. Found: C, 34.85; H, 4.46; Br, 43.72. ^1H NMR (δ, 25 °C, 360 MHz, C_6D_6): 1.68; 1.54 at 90 MHz. EPR (C_6H_5Me, 77 K): silent. MS (EI): *m*/*e* 688, $^{79}Br_4$ isotopomer, M^+. Crystal data for **2b**: monoclinic, $P2_1/n$, $a = 14.807(4)$ Å, $b = 8.301(4)$ Å, $c = 10.623(4)$ Å, $\beta = 99.55(2)°$, $Z = 2$, $R = 0.023$, $R_w = 0.028$.

(20) The value in brackets, the standard deviation of the mean, equals $[(\Sigma_m \Delta_i^2)/m(m-1)]^{1/2}$ with Δ_i defined as the deviation from the mean of the *i*th value in a set of *m* values.

(21) Dean, N.; Bartley, S.; Streib, W. E.; Lobkovsky, E.; Christou, G. *Inorg. Chem.* **1995**, *34*, 1608.

(22) **3a**: Anal. Calcd for $C_{10}H_{15}Cl_2V$: C, 46.72; H, 5.88; Cl, 27.58. Found: C, 46.60; H, 6.04; Cl, 27.09. ^1H NMR (δ, 25 °C, 360 MHz, C_6D_6): −7.9. EPR (C_6H_5Me, 77 K): silent. MS (EI): *m*/*e* 810, $^{35}Cl_6$ isotopomer, M^+. Crystal data for **3b**: triclinic, $P\bar{1}$, $a = 11.865(4)$ Å, $b = 12.046(4)$ Å, $c = 15.992(4)$ Å, $\alpha = 76.95(2)°$, $\beta = 71.95(2)°$, $\gamma = 60.34(2)°$, $Z = 2$, $R = 0.040$, $R_w = 0.062$.

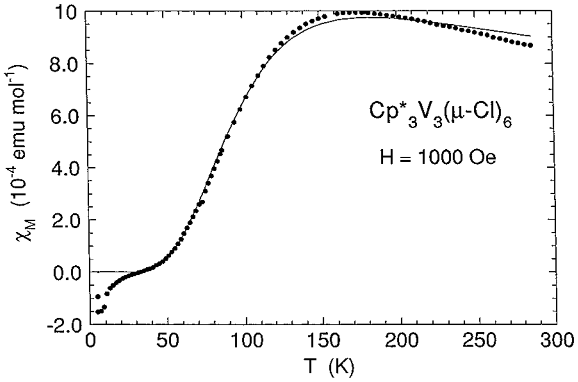

Figure 3. Plot of bulk molar susceptibility vs *T* for **3a**.

and solution[24] magnetic behavior of both are more complex, with low moments necessitating considerable care in SQUID background corrections. Compound **2a** behaved as a simple *paramagnet* in the solid state, with no field dependence of χ_M, a linear χ_M vs T^{-1} plot, and a low μ_{eff} value of 0.19 μ_B per vanadium. These data are consistent with a diamagnetic ground state (possible $\sigma^2\delta^{*2}$ configuration with no V−V bond rather than $\sigma^2\delta^{*1}\delta^1$ or $\sigma^2\delta^2$) for **2** and a small amount (<0.5%) of paramagnetic V(III) impurity. PE spectra with cross-sectional analysis of the He I and He II data are needed to assess the V−V MO ordering and bonding in **2**. ^{1}H NMR spectra of impure **2** exhibit an extra resonance at δ −6.4 consistent with a trinuclear bromide; thus, a mononuclear species (e.g., Cp*VBr_2(solvate)) may be the paramagnetic impurity.

The solid-state susceptibility of **3a** is consistent with antiferromagnetic behavior, with a ground-state singlet and nearby triplet excited state(s) (Figure 3). Approximate curve fitting of the data with two parameters to an HDVV model[25] for three $S = 1$ centers gave $J = -119$ cm^{-1} and $g = 1.87$. In solution, the Cp* ^{1}H NMR shift for **3a** is neither concentration nor field dependent, and the solution χ_M value parallels the temperature dependence of the solid-state χ_M value.

We do not understand the reasons for the nuclearity dependence on halide. In both structures the vanadiums adopt four-legged piano-stool geometries, with similar X−V−X angles (X = Br, 76.0°; X = Cl, 77.5° average between chlorides bridging to the same vanadium). The isolated compounds may be kinetic products, as suggested by the possibly trinuclear species in impure **2**. Intramolecular van der Waals (VDW) interactions between μ-halides (e.g., Br(1)···Br(2) in **2b**, 3.90 Å; within the range of twice the VDW radius[26] of Br, 1.80−2.00 Å), a maximization of V−X versus V−V bonding, and/or differences in π-bonding capabilities of Cl and Br may play a role in determining the nuclearity. Molecular orbital calculations[27] to address this point are in progress.

Most importantly, both **2** and **3** are useful synthons for the development of organovanadium and organodivanadium[28] chemistry. Halogenation of **2** or **3** gave $(C_5Me_4R)VX_3$ (**1**) in good yield (95%, X = Br; 70%, X = Cl), which represents a new, non-carbonyl route[11] to these understudied organovanadium(IV) synthons. Both **2a** and **3a** polymerize ethylene at room temperature in toluene to high-molecular-weight polyethylene,[29] using methylalumoxane as cocatalyst.

In conclusion, the piano-stool oligomers $(C_5Me_4R)_2V_2(\mu\text{-}Br)_4$ (**2**) and $(C_5Me_4R)_3V_3(\mu\text{-}Cl)_6$ (**3**) are easily prepared by two routes, and the nuclearity is surprisingly halide dependent. Both compounds display interesting and differing solid-state and solution magnetochemistry and are new, useful synthons for the elaboration of organovanadium piano-stool chemistry.

Note Added in Proof. Articles by Doherty and co-workers (see p 1994 of this issue) and Bottomley and co-workers (see p 1865 of this issue) describe alternate reaction conditions for the preparation of $(C_5Me_5)_3V_3(\mu\text{-}Cl)_6$, its use to prepare $(C_5Me_5)VOCl_2$ and $[(C_5Me_5)VCl(\mu\text{-}N)]_2$, its molecular structure and electrochemistry, and preliminary details of its magnetochemistry. We thank these authors for providing preprints.

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Supporting Information Available: Text and figures giving magnetochemistry experimental details and data for **2a** and **3a** and tables giving crystal data, diffractometry conditions, refinement details, fractional coordinates, thermal parameters, bond lengths, and bond angles for **2b** and **3b** (23 pages). Ordering information is given on any current masthead page.

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(24) (a) The Evans method[24b] susceptibility, chemical shift, and line width data vs temperature for **2a** shows a nonlinear dependence of χ_M and δ on T^{-1} for the Cp* ^{1}H resonance at higher *T* (linewidth and δ approach diamagnetic values at low *T*) and a field-dependent δ consistent with a paramagnetic V(III) component in an equilibrium mixture with a diamagnetic component, a concentration-independent δ value consistent with a rapid equilibrium between oligomers, a μ_{eff} value of 1.31 μ_B (333 K), and a spin-only value at 297 K of 0.5 e$^-$ per **2a**. (b) Bartle, K. D.; Dale, B. J.; Jones, D. W.; Maricic, S. *J. Magn. Reson.* **1973**, *12*, 286.

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