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Organometallic Halides: Preparation and Physical and Chemical Properties of Tris[(η-pentamethylcyclopentadienyl)dichlorovanadium], [(η-C_5Me_5)V(μ-Cl)$_2$]$_3$

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The cluster $[(\eta\text{-}C_5Me_5)V(\mu\text{-}Cl)_2]_3$ was synthesized from $VCl_3(thf)_3$ and $Bu^n{}_3SnC_5Me_5$. It was oxidized by O_2 to give $(\eta\text{-}C_5Me_5)VCl_2(O)$, and by NaN_3 to give $[(\eta\text{-}C_5Me_5)VCl(\mu\text{-}N)]_2$. X-ray diffraction showed that $[(\eta\text{-}C_5Me_5)V(\mu\text{-}Cl)_2]_3$ had an equilateral triangle of vanadium atoms (mean V−V 3.367 (2) Å), with each edge of the triangle symmetrically bridged by two chlorine atoms. The cluster contains six core electrons. The cluster $[(\eta\text{-}C_5Me_5)V(\mu\text{-}Cl_2]_3$ had a magnetic moment of 2.92 μ_B at room temperature and showed antiferromagnetic behavior.

Introduction

(Cyclopentadienyl)metal halides are of current interest.[1] They often possess unpaired electrons and associate into clusters showing nondilute magnetic behavior. They also serve as convenient starting materials for the preparation of (cyclopentadienyl)metal chalcogenides and pnictinides. We have prepared a number of (pentamethylcyclopentadienyl)vanadium nitrides[2] and oxides[3,4] and were therefore interested in (pentamethylcyclopentadienyl)vanadium dichloride. The preparation of this compound from $Bu^n{}_3SnC_5Me_5$ and $VCl_3(thf)_3$, and its trimeric nature, have been briefly reported,[1,5] and it has been used to prepare $[(\eta\text{-}C_5Me_5)VCl(\mu\text{-}N)]_2$,[6] but no details are available. We report here the preparation, structure, and chemical and physical properties of $[(\eta\text{-}C_5Me_5)V(\mu\text{-}Cl)_2]_3$. After submission of this paper we learned of the related work by Doherty and co-workers[55] and by Messerle and co-workers.[61]

Results and Discussion

Synthesis of $[(\eta\text{-}C_5Me_5)V(\mu\text{-}Cl)_2]_3$. The reaction between $Bu^n{}_3SnC_5Me_5$ and $VCl_3(thf)_3$ provides a convenient preparation of $[(\eta\text{-}C_5Me_5)VCl_2]_3$ in good (70%) yield (eqs 1 and 2). Excellent syntheses of the starting materials $Bu^n{}_3SnC_5Me_5$[7] and $VCl_3(thf)_3$,[8] which begin with commercially available compounds, are available in the literature. Attempts to replace the toxic $Bu^n{}_3SnC_5Me_5$ with $Me_3SiC_5Me_5$ were not successful; the reaction between $VCl_3(thf)_3$ and $Me_3SiC_5Me_5$ yielded a purple solid which was insoluble in all common solvents.

$$Bu^n{}_3SnCl + LiC_5Me_5 \rightarrow Bu^n{}_3SnC_5Me_5 + LiCl \quad (1)$$

$$3Bu^n{}_3SnC_5Me_5 + 3VCl_3(thf)_3 \rightarrow [(\eta\text{-}C_5Me_5)V(\mu\text{-}Cl)_2]_3 + 9thf + 3Bu^n{}_3SnCl \quad (2)$$

Chemical Properties of $[(\eta\text{-}C_5Me_5)V(\mu\text{-}Cl)_2]_3$. Purple-black $[(\eta\text{-}C_5Me_5)V(\mu\text{-}Cl)_2]_3$ is sensitive to both water and dioxygen. The water sensitivity is presumably similar to that of $\{[(\eta\text{-}C_5Me_5)Nb(\mu\text{-}Cl)(\mu\text{-}O)]_3\}^+$, in which a chloride ligand can be replaced by hydroxide.[9,10] The trimer $[(\eta\text{-}C_5Me_5)V(\mu\text{-}Cl)_2]_3$ reacted readily and cleanly with dioxygen to give $(\eta\text{-}C_5Me_5)VCl_2(O)$ (equation 3).[4,11−13] Green $(\eta\text{-}C_5Me_5)VCl_2(O)$ is obtained in 65% yield by reaction 3, which therefore represents the most convenient and efficient synthesis of this compound (see also refs 55 and 61). Previous preparations involved the oxidation and subsequent chlorination of either $(\eta\text{-}C_5Me_5)_2V$[4,11] or $(\eta\text{-}C_5Me_5)V(CO)_4$.[12,13] Oxidation of the former involves loss of an expensive C_5Me_5 ligand; the latter is difficult to prepare. In turn, $(\eta\text{-}C_5\text{-}$

$$2[(\eta\text{-}C_5Me_5)V(\mu\text{-}Cl)_2]_3 + 3O_2 \rightarrow 6(\eta\text{-}C_5Me_5)VCl_2(O) \quad (3)$$

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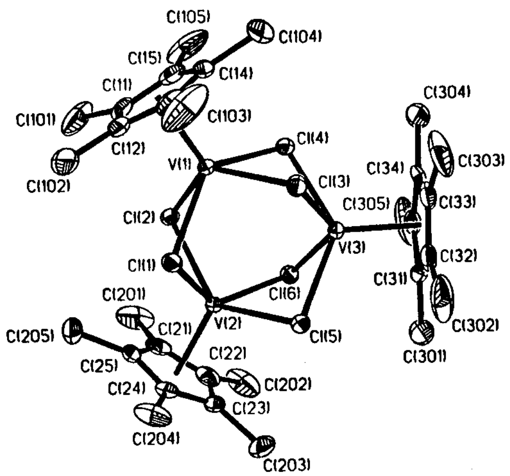

Figure 1. Structure of [(η-C_5Me_5)V(μ-$Cl)_2]_3$.

Table 1. Selected Mean Distances (Å) and Angles (deg) in [(η-C_5Me_5)V(μ-$Cl)_2]_3$[a]

V−V	3.367 (2, 6)	V−Cl−V	86.93 (5, 28)
V−Cl	2.447 (1, 15)	Cl_a−V−Cl_a	82.80 (3, 80)
V−Cp	1.980 (4, 4)	Cl_a−V−Cl_b	77.60 (3, 34)
V_3−Cl	1.533 (1, 16)	Cp−V−Cl	114.4 (1, 6)

[a] The symbols Cp, V_3, Cl_a, and Cl_b are defined in the text.

$Me_5)VCl_2(O)$ may be converted into a variety of alkyl,[13] alkoxide,[13] and sulfide derivatives,[14,15] as well as oxo-bridged compounds such as [(η-C_5Me_5)V(O)(μ-$O)]_3$[16] and [(η-C_5Me_5)VCl(μ-$O)]_4$.[11]

The trimer [(η-C_5Me_5)V(μ-$Cl)_2]_3$ reacted cleanly with azides to form [(η-C_5Me_5)VCl(μ-$N)]_2$ (eq 4). Doherty and

$$2[(\eta\text{-}C_5Me_5)V(\mu\text{-}Cl)_2]_3 + 6RN_3 \rightarrow 3[(\eta\text{-}C_5Me_5)VCl(\mu\text{-}N)]_2 + 6N_2 + 6RCl \quad (4)$$

co-workers used Me_3SiN_3,[6] but we found that NaN_3 is more convenient and gives a good yield (73%). The dimer [(η-C_5Me_5)VCl(μ-$N)]_2$ can be reduced to the cubane [(η-C_5Me_5)V(μ_3-$N)]_4$.[2]

The trimer [(η-C_5Me_5)V(μ-$Cl)_2]_3$ could be reversibly oxidized electrochemically (in tetrahydrofuran solution, with $Bu^t{}_4NBF_4$ as supporting electrolyte), with the oxidation wave centered at 0.5 V. Although the process was reversible, the wave was extremely broad (0.4 V) and may represent several processes, with similar voltages. It was shown previously that {[η-C_6Me_6)Nb-(μ-$Cl)_2]_3\}^+$ could be quasi-reversibly electrochemically oxidized with sequential removal of three electrons.[17]

Structure of [(η-C_5Me_5)V(μ-$Cl)_2]_3$. The structure of [(η-C_5Me_5)V(μ-$Cl)_2]_3$, as determined by X-ray diffraction, is shown in Figure 1, and the important distances and angles are given in Table 1. Within experimental error, the trimer contains an equilateral triangle of vanadium atoms (mean V−V distance 3.367 (2, 6[18]) Å with each edge symmetrically bridged by two chlorine atoms (mean V−Cl distance 2.447 (1,15) Å, mean V−Cl−V angle 86.93 (5, 28)°). The mean Cl_a−V−Cl_a angle between Cl atoms on the same side of the V_3 plane was 82.80 (3, 80)°, the mean Cl_a−V−Cl_b angle between Cl atoms on opposite sides of the V_3 plane was 77.60 (3, 34)°. The mean V−Cp distance, to the centroid of the $C_5(Me_5)$ ring, was 1.980 (4, 4)°, and the planes of the C_5 rings made a mean angle of 90.5° with the V_3 plane.

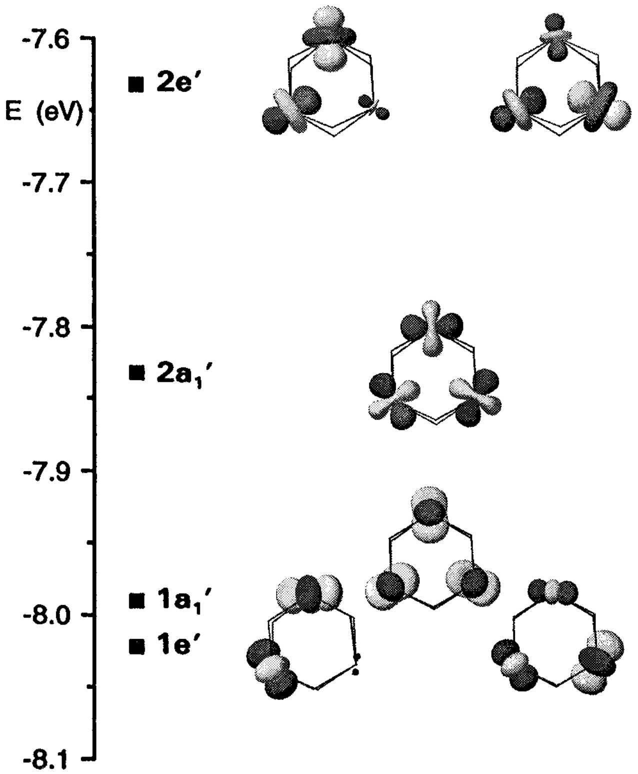

Figure 2. Energy levels and contours of the cluster orbitals of [(η-C_5Me_5)V(μ-$Cl)_2]_3$.

The trimer [(η-C_5Me_5)V(μ-$Cl)_2]_3$ is one of a small number of [(η-arene)M(μ-X)(μ-$Y)]_3$ trimers which are listed in Table 2. All have the same geometries, and even similar metrical parameters, when the differences in the atomic radii of the metal and X or Y atoms are taken into account. In particular, there is no correlation between the magnitude of the M−X−M and X−M−X angles and the identity of M or the number of electrons in the cluster (i.e., with the formal oxidation number of the metal). The molecular orbital model for compounds of this type, first proposed for {[(η-C_5Me_5)Re(μ-$O)_2]_3\}^{2+}$ by Hofmann, Rösch, and Schmidt on the basis of extended Hückel and Xα-SW calculations,[19] and extended to {[(η-C_5Me_5)Nb(μ-Cl)(μ-$O)]_3\}^+$ and {[(η-C_5Me_5)-$Mo]_3$(μ-$OH)_n$(μ-$O)_{6-n}\}^{2+}$ by ourselves on the basis of EXHUD and INDO calculations,[9,20] shows that the cluster electrons reside in nonbonding orbitals which are derived from the metal d-orbitals (Figure 2). There are no localized M−M bonds. The M−M distances are determined primarily by the nature of X and Y. When X = Y = Cl the mean M−M distance (3.351 (4, 16) Å) is independent of M. The differences in the M−Cl distances (mean 2.501 (2, 54) Å) are compensated by

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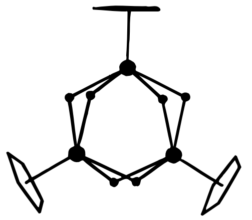
Table 2. Compounds of Type [(η-arene)M(μ-A)(μ-B)]$_3$

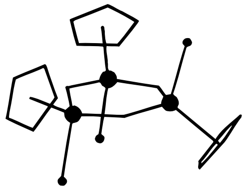
compound	cluster electrons	M−M (Å)	M−X (Å)	X−M−X (deg)	M−X−M (deg)	ref
$[(\eta\text{-}C_5Me_5)V(\mu\text{-}Cl)_2]_3$	6	3.367 (2)	2.447 (1)	82.8 (3)	86.9 (1)	this work
$\{[(\eta\text{-}C_6Me_6)Nb(\mu\text{-}Cl)_2]_3\}^+$	8	3.347 (2)	2.508 (2)	83.1 (1)	84.3 (1)	51, 52
$\{[(\eta\text{-}C_6Me_6)Nb(\mu\text{-}Cl)_2]_3\}^{2+}$	7	3.335 (9)	2.494 (3)	83.4 (2)	83.8 (1)	53
$\{[\eta\text{-}C_6Me_6)Zr(\mu\text{-}Cl)_2]_3\}^{2+}$	4	3.354 (2)	2.555(2)	85.1(1)	82.0(1)	59
$\{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_n(\mu\text{-}O)_{6-n}\}^{2+}$	5/6/7	2.78 (1)	2.02 (4)	87.9 (18)	87.0 (16)	19
$\{[(\eta\text{-}C_5Me_5)Re(\mu\text{-}O)_2]_3\}^{2+}$	4	2.747 (2)	1.96 (2)	88.4 (1)	88.9 (1)	60
$\{[(\eta\text{-}C_5Me_5)Nb(\mu\text{-}Cl)(\mu\text{-}O)]_3\}^+$	2	2.876 (1)	2.542 (1) (Cl) 1.937 (3) (O)	79.2 (5) (Cl) 95.5 (1) (O)	68.8 (3) (Cl) 95.9 (1) (O)	9
$\{[(\eta\text{-}C_5Me_5)Nb]_3(\mu\text{-}Cl)_2(\mu\text{-}OH)(\mu\text{-}O)_3\}^+$	2	2.853 (5) (×2) 2.807 (4)	2.530 (10) (Cl) 1.920 (20) (O) 2.145 (20) (OH)	77.1 (3) (Cl) 94.4 (9) (O)	68.6 (3) (Cl) 95.3 (O) 81.7 (7) (OH)	10

variations in the M−Cl−M angle (mean 84.3 (1, 29)°). When X = O and Y = O, Cl, or OH, the mean M−M distance is 2.810 (4, 66) Å. The larger maximum deviation from the mean, compared to the case where X = Y = Cl, is caused by the variation in the M−O−M angle as a consequence of the accompanying oxide, chloride, or hydroxide bridge.

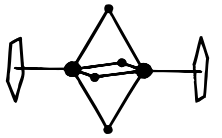
The trimeric structure **1a** adopted by $[(\eta\text{-}C_5Me_5)V(\mu\text{-}Cl)_2]_3$ and the other seven compounds listed in Table 2 is very unusual for a $(\eta\text{-}C_5R_5)MXY$ complex. There are other trimers such as $[(\eta\text{-}C_5Me_5)TiCl(\mu\text{-}O)]_3$,[21] $[(\eta\text{-}C_5Me_5)V(O)(\mu\text{-}O)]_3$,[16] and $[(\eta\text{-}C_5Me_5)TaCl(\mu\text{-}N)]_3$,[22] but they have the structure **1b**. A few $(\eta\text{-}C_5R_5)MX_2$ derivatives of the early transition metals are oligomeric (for example, $[(\eta\text{-}C_5Me_5)ScCl_2]_n$[23]) or tetrameric (for example $[(\mu_2\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2)(TiCl)_2]_2(\mu\text{-}O)_4$,[24] and $[(\eta\text{-}C_5Me_5)VCl(\mu\text{-}O)]_4$).[11] However, most $(\eta\text{-}C_5R_5)MXY$ compounds are dimeric. A few, for example $[(\eta\text{-}C_5Me_4Et)V]_2(\mu\text{-}Br)_4$,[1,5,25,26] $\{[(\eta\text{-}C_6H_3Me_3)Nb]_2(\mu\text{-}I)_4\}^{n+}$ ($n = 0, 1$),[27] $[(\eta\text{-}C_5Me_5)Ta]_2(\mu\text{-}Br)_4$,[28] $[(\eta\text{-}C_5Me_5)W]_2(\mu\text{-}Cl)_4$,[29] and several $[(\eta\text{-}C_5R_5)Mo]_2(\mu\text{-}X)_4$ (X = halogen),[1,25,26,30−34] adopt the structure **2a**. The majority adopt the structure **2b**, for example, $[(\eta\text{-}C_5H_2(SiMe_3)_3)TiCl(\mu\text{-}O)]_2$,[35] $[(\eta\text{-}C_5Me_5)MX(\mu\text{-}Cl)]_2$ (X = Cl; M = Cr,[1,36,37] Re,[38] Ru,[39,40] Rh,[41] Ir;[42] X = Me; M = Cr[43,44]), $[(\eta\text{-}C_5R_5)M(O)(\mu\text{-}O)]_2$ (M = Cr,[45] Mo[46]), and $[(\eta\text{-}C_5R_5)M(E^1)(\mu\text{-}E^2)]_2$ (M = Mo, W; E^1 = O, S; E^2 = S, Se[47−49]). In addition to the molecular orbital analyses of the trimers with structure **1a** noted above, there has been an analysis of $[(\eta\text{-}C_5H_5)TaMe(\mu\text{-}N)]_3$ with structure **1b**[50] and detailed analyses of $[(\eta\text{-}C_5H_5)MX_2]_2$ with structures **2a** and **2b**.[26] An important conclusion from these analyses is that, in the dimers of both structures **2a** and **2b**, the lowest energy metal-based orbital represents a metal−metal σ-bonding interaction. For dimers of structure **2a**, the orbital of the next highest energy represents a metal−metal δ-antibonding interaction, whereas for **2b**, it represents a π-bonding interaction.[26] For the trimers with structure **1a** or **1b**, all of the metal-based orbitals are essentially nonbonding.[9,19,20,50] Thus, when the metal has d-electrons to occupy the M−M σ-bonding orbitals, there is a definite gain in energy for either of the dimeric structures compared to the trimers. A direct comparison between structures **1a** and **2a** or **1b** and **2b** can be made, because in each pair there are the same number and type of M−X bonds. The presence of metal−metal bonds in dimers of structure **2a** and their absence in the trimers



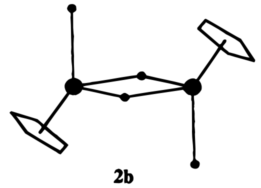
1a



1b



2a



2b

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of structure **1a** is shown by the M−M distances. For example, the V−V distance in $[(\eta\text{-}C_5Me_4Et)V]_2(\mu\text{-}Br)_4$ is 2.565 (1) Å,[26] whereas in $[(\eta\text{-}C_5Me_5)V(\mu\text{-}Cl)_2]_3$ it is 3.367 (2) Å; in $\{[\eta\text{-}C_6H_3Me_3)Nb]_2(\mu\text{-}I)_4\}^{n+}$ the Nb−Nb distances are 2.855 (1) Å for $n = 0$ and 2.828 (4) Å for $n = 1$,[27] whereas in $\{[(\eta\text{-}C_6Me_6)Nb(\mu\text{-}Cl)_2]_3\}^{n+}$ the distances are 3.347 (2) Å for $n = 1$[51,52] and 3.335 (9) Å for $n = 2$.[53]

The nonbonded repulsive interactions between the hydrogen atoms of the $\eta\text{-}C_nMe_n$ ligands also favor the dimeric over the trimeric structures. In the dimeric structures, the planes of the $\eta\text{-}C_nMe_n$ rings lie parallel to one another, giving a minimum C···C distance between CH_3 groups of 6.0 Å. In the trimers, the planes of the $\eta\text{-}C_nMe_n$ rings intersect, so that the CH_3 groups on adjacent $\eta\text{-}C_nMe_n$ ligands abut one another. The shortest C···C distance in $[(\eta\text{-}C_5Me_5)V(\mu\text{-}Cl)_2]_3$ is 4.2 Å. There will be an attractive interaction between the hydrogen atoms of the $\eta\text{-}C_nMe_n$ ligand and the X or Y atom of $[(\eta\text{-}C_nMe_n)MXY]_n$, which will favor the structures with a terminal X atom **1b** and **2b**. The interaction will be weak, as are all such C−H···X hydrogen bonds.[54]

The dimers of structure **2a** contain a $M(\mu\text{-}X)_4M$ unit, which is a distorted octahedron with apical M and equatorial X atoms. The trimers of structure **1a** contain a $M(\mu\text{-}X)_2M$ unit, which is a distorted tetrahedron (butterfly). The M−M distances in **2a** are shorter than those in **1a**. Thus, the nonbonded repulsive interactions between the bridging halide (X) atoms will be greater in **2a** than in **1a**, and this repulsion will increase with the size of X. It is therefore surprising to find that $(\eta\text{-}C_5Me_4Et)VBr_2$ and $\{[(\eta\text{-}C_6H_3Me_3)NbI_2\}^{n+}$ adopt structure **2a**[26,51−53] but $(\eta\text{-}C_5Me_5)VCl_2$ adopts structure **1a**.

Whether $(\eta\text{-}C_nR_n)MXY$ compounds adopt the dimeric structure **2a** or **2b**, or the trimeric **1a** or **1b**, appears to depend on the opposing forces of the formation of metal−metal bonds in **2a** and **2b**, but not in **1a** or **1b**, versus the increased nonbonded repulsions between the X and Y atoms in **2a** (and to a lesser extent **2b**), compared to **1a** and **1b**. The only clear case is that in which the $(\eta\text{-}C_nR_n)MXY$ compound has zero d-electrons, since no metal−metal bond can be formed and the trimeric structures will be preferred. In fact, all $(\eta\text{-}C_nR_n)MXY$ compounds with zero d-electrons do adopt the trimeric structure **1b**, except $[(\eta\text{-}C_5H_2(SiMe_3)_3)TiCl(\mu\text{-}O)]_2$, which has the dimeric structure **2b**.[35] The $\{[(\eta\text{-}C_5Me_5)Nb(\mu\text{-}O)]_3(\mu\text{-}Cl)_2(\mu\text{-}X)\}^+$ compounds in Table 2 do not have enough d-electrons to form Nb−Nb bonds as dimers, and are also trimers. It is not clear why other $(\eta\text{-}C_nR_n)MXY$ compounds exist as trimers or dimers.

There is the possibility that different oligomers of $(\eta\text{-}C_5Me_5)VCl_2$ coexist. Doherty and co-workers found that an insoluble purple material was formed, along with $[(\eta\text{-}C_5Me_5)V(\mu\text{-}Cl)_2]_3$, when the preparation was run at elevated temperatures. They formulated this material as a higher oligomer $[(\eta\text{-}C_5Me_5)VCl_2]_n$.[55] We also observed small quantities of this insoluble purple material. However, when pure $[(\eta\text{-}C_5Me_5)V(\mu\text{-}Cl)_2]_3$ was refluxed in xylenes (∼140 °C) for several days, no precipitate formed and there was no change in the color of the solution or in the NMR spectrum. We concluded that $[(\eta\text{-}C_5Me_5)V(\mu\text{-}Cl)_2]_3$ does not convert into another oligomer under the conditions of the experiments described here and that the purple oligomer is a product of a side reaction occurring in the formation of $[(\eta\text{-}C_5Me_5)V(\mu\text{-}Cl)_2]_3$ from $VCl_3(thf)_3$ and $Bu^n{}_3SnC_5Me_5$.

Magnetic Behavior of $[(\eta\text{-}C_5Me_5)V(\mu\text{-}Cl)_2]_3$. The extended Hückel calculations shown in Figure 2 suggest that the ground state of $[(\eta\text{-}C_5Me_5)V(\mu\text{-}Cl)_2]_3$ should be the diamagnetic $(1e')^4(1a_1)'^2(2a_1')^0(2e')^0$. At room temperature, the ^1H NMR spectrum showed a single broad resonance at −7.0 ppm, with a line width at half-height of 52 Hz, indicating a paramagnetic compound. In $CDCl_3$ solution at 291 K, the magnetic moment by the Evans NMR method[56,57] (200 MHz, field strength 47 kG) was 2.8 μ_B. In the solid state at 293 K, the moment was 2.92 μ_B by the Faraday method. Using a SQUID instrument at a field strength of 20 kG, the moment was 2.78 μ_B at 300 K and decreased with temperature, indicating antiferromagnetic behavior. The detailed magnetic behavior is unusual and complicated, and we are presently investigating and interpreting the data for this and other trimers of type **1a**. This will be reported elsewhere.

Experimental Section

General Information. All manipulations were performed using a standard double-manifold vacuum line, under argon or vacuum. Samples were transferred in a dinitrogen-filled glovebag. All solvents were dried by standard methods. The starting materials $Bu^n{}_3SnCl$ and C_5Me_5H were purchased from Aldrich Chemical Co. and used as received. The other starting materials, $Bu^n{}_3SnC_5Me_5$,[7] and $VCl_3(thf)_3$,[8] were prepared by the methods in the literature cited. Instruments used were a Varian XL200 for ^1H NMR spectra, and for the magnetic moment in solution by the Evans' method, Perkin-Elmer 683 for infrared spectra (as Nujol mulls or KBr disks) and Kratos MS50 for mass spectra (EI). Extended Hückel and INDO calculations were performed using the CAChe system. Microanalyses (C, H, Cl) were performed by Beller Laboratorium, Göttingen, Germany. Magnetic susceptibilities of powdered samples were measured using a Quantum Design (MPMS) SQUID magnetometer.

Preparation of $[(\eta\text{-}C_5Me_5)V(\mu\text{-}Cl)_2]_3$. To a warm (60 °C), stirred, solution of $VCl_3(thf)_3$ (6.0 g, 16.1 mmol) in toluene (100 cm^3) was added $Bu^n{}_3SnC_5Me_5$ (6.7 cm^3, 17.7 mmol). The mixture was stirred for 12 h. The toluene was removed under vacuum, while the solution was maintained at 35 °C, leaving a red-brown oily residue. This was washed twice with hexane (80 cm^3 portions), dried under vacuum, and extracted with hot (80 °C) toluene (100 cm^3). The hot mixture was filtered and the filtrate reduced to a volume of 20 cm^3 under vacuum. On cooling to −25 °C, adding hexane (80 cm^3), and setting aside (at −25°) for 12 h, purple-black microcrystals of $[(\eta\text{-}C_5Me_5)V(\mu\text{-}Cl)_2]_3$ formed. Yield: 2.9 g, 70%. Anal. Found: C, 46.4; H, 6.0; Cl, 28.2. Anal. Calcd for $C_{30}H_{45}Cl_6V_3$: C, 46.7; H, 5.9; Cl, 27.6. ^1H NMR (200 MHz, $C_6{}^2H_6$ solution): −7.0 ppm ($\Delta\nu_{1/2}$ 52 Hz). Mass spectrum (*m/e*, % abundance, assignment): 257, 43, $\{C_{10}H_{16}V^{35}Cl_2\}^+$ ($\{(C_5Me_5)VCl_2H\}^+$); 221, 100, $\{C_{10}H_{15}V^{35}Cl\}^+$ ($\{(C_5Me_5)VCl\}^+$). The compound was also characterized by X-ray diffraction (see below).

Oxidation of $[(\eta\text{-}C_5Me_5)V(\mu\text{-}Cl)_2]_3$ with O_2: Formation of $(\eta\text{-}C_5Me_5)VCl_2(O)$. A solution of $[(\eta\text{-}C_5Me_5)V(\mu\text{-}Cl)_2]_3$ (2.1 g, 2.7 mmol) in tetrahydrofuran (100 cm^3) was incubated, with

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stirring, under a mixture of argon and dioxygen (Ar/O_2, 4:1; total volume, 1500 cm^3; total pressure, 1 atm) for 1.5 h. The pressure was maintained at 1 atm by addition of pure dioxygen at intervals. The solution changed from dark red to blue-green as the reaction proceeded. The solvent was removed under vacuum leaving an oily green residue. This was extracted with toluene (120 cm^3); the extract was filtered (leaving a purple residue) and reduced in volume to 30 cm^3. Hexane (100 cm^3) was added. On setting aside at −25 °C for 12 h, bright green crystals of (η-C_5Me_5)$VCl_2(O)$ were obtained. These were collected by filtration and dried under vacuum. Yield: 1.45 g, 65%. The product was characterized by comparison of its spectroscopic properties to those reported in the literature. ^1H NMR (C^2HCl_3 solution): 2.31 (s) (lit. 2.32,[15] 2.33[55]) ppm; ^{13}C NMR: 13.3 (s, $C_5(CH_3)_5$), 133.5 (s, $C_5(CH_3)_5$) (lit.[11,15] 13.3, 133.7) ppm. Infrared: 967 (ν(V=O)) (lit. 965,[11] 967[55]) cm^{-1}. Mass spectrum: *m/e* 272 ($\{(C_5Me_5)V^{35}Cl_2O\}^+$).

Oxidation of $[(\eta\text{-}C_5Me_5)V(\mu\text{-}Cl)_2]_3$ with NaN_3: Formation of $[(\eta\text{-}C_5Me_5)VCl(\mu\text{-}N)]_2$. A solution of $[(\eta\text{-}C_5Me_5)V(\mu\text{-}Cl)_2]_3$ (2.43 g, 3.16 mmol) in tetrahydrofuran (100 cm^3) was added to NaN_3 (0.63 g, 9.69 mmol) (the NaN_3 was dried and deareated by grinding slowly with a Teflon stir bar under dynamic vacuum for 0.5 h). The mixture was stirred for 12 h at 40 °C in a flask equipped with a pressure equalizing valve, since N_2 is evolved (eq 4). The solution changed from dark red to green-blue. The solvent was then removed under vacuum, leaving an oily black residue. This was extracted with hot (80 °C) toluene (150 cm^3), and the resultant solution filtered twice through acid-free Celite to remove sodium chloride. The toluene solvent was removed under vacuum and hexane (50 cm^3) added. On setting aside for 12 h at −25 °C, black microcrystals of $[(\eta\text{-}C_5Me_5)VCl(\mu\text{-}N)]_2$ were deposited. These were collected by filtration and dried under vacuum. Yield: 1.61 g, 72%. The product was characterized by comparison of its spectroscopic properties with these reported in the literature. ^1H NMR ($C_6{}^2H_6$ solution): 2.05 (s) (lit.[6] 2.05) ppm; ^{51}V NMR: −144 (s) (lit.[6] −144) ppm. Mass spectrum: *m/e* 470 ($\{(C_5Me_5)_2V_2N_2{}^{35}Cl_2\}^+$). Infrared: 720 cm^{-1}; since all other bands in the spectrum can be assigned to vibrations of the (η-C_5Me_5)V unit, we assign this band to ν(V−N−V); however, a band assigned to ν(Ta−N−Ta) in $[(\eta\text{-}C_5Me_5)TaX(\mu\text{-}N)]_3$ appears at 960 cm^{-1} for X = Cl[22] or Me,[50] and 964 cm^{-1} for $\{[(\eta\text{-}C_5Me_5)TaMe(\mu\text{-}N)]_3\}^-$.[50]

X-ray Crystallography. Large thin platelike crystals were obtained by setting aside saturated solutions of $[(\eta\text{-}C_5Me_5)V(\mu\text{-}Cl)_2]_3$ in ether at 4 °C for several days. The gross structure of the trimer was determined by processing data obtained from a crystal of dimensions 0.50 × 0.10 × 0.75 mm using an Enraf-Nonius CAD4 diffractometer with Mo Kα radiation. However, refinement did not proceed below $R = 0.12$, and there were several unreasonable thermal parameters, among other problems. After several abortive attempts at obtaining data from similar crystals, samples were examined using a Siemens P4/SMART diffractometer with a rotating anode generator and a CCD detector. This revealed that the plates were in fact stacked sheets, each sheet rotated by a small angle with respect to its neighbor. A less platelike crystal of dimensions 0.6 × 0.6 × 0.25 mm was used for data collection.

Crystal data for $C_{30}H_{45}Cl_6V_3$ ($M_r = 771.18$): triclinic, $P\bar{1}$; $a = 11.8187$ (1) Å, $b = 11.8395$ (1) Å, $c = 16.0141$ (1) Å, $\alpha = 68.361$ (1)°, $\beta = 70.896$ (1)°, $\gamma = 60.160$ (1)°; $Z = 2$; $D_c = 1.44$ Mg m^{-3}; Mo $K\alpha$ radiation, $\lambda = 0.710\,73$ Å; $T = 290$ K; $\theta = 1.39$ - 26.38°; 10 s/frame exposure; 0.3°/frame; 14 394 reflections collected, 6611 unique reflections. Full matrix refinement[58] of 355 parameters (including one disordered η-C_5Me_5 group, with 80/20% occupancy in two positions) on F^2 gave $R1 = 0.039$, $wR2 = 0.093$, GoF 1.136. Max ΔF 0.345 e Å^{-3}, min −0.256 e Å^{-3}. An absorption correction based on multiple redundant data analysis was applied (maximum transmission factor 0.85, minimum 0.73).

Full details are given in the Supporting Information with selected distances and angles in Table 1.

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Supporting Information Available: X-ray diffraction data for $[(\eta\text{-}C_5Me_5)V(\mu\text{-}Cl)_2]_3$: tables of crystal data, atomic coordinates, thermal parameters, hydrogen atom coordinates, and interatomic distances and angles (19 pages). Ordering information is given on any current masthead page.

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