

form explosive XeO<sub>3</sub>. The appropriate safety precautions should be observed when these materials are handled.

**Materials and Apparatus.** Xenon and oxygen (Matheson Gas Co.) were used as received. Dioxxygen difluoride, O<sub>2</sub>F<sub>2</sub>, was prepared by photolysis of a 1:1 mixture of F<sub>2</sub> and O<sub>2</sub> in a copper reactor fitted with a sapphire window at -196 °C.<sup>7</sup> Fluorine (Matheson) was treated with NaF to remove HF before use. Volatile materials were manipulated in a stainless steel vacuum line equipped with Kel-F and stainless steel traps, Autoclave Engineers valves, and MKS and Helicoid pressure gauges. prior to use, the vacuum line was thoroughly passivated with ClF<sub>3</sub> and XeF<sub>6</sub> followed by overnight evacuation. Infrared spectra were recorded with a Perkin-Elmer 1500 Fourier transform spectrometer using a 10-cm stainless steel cell fitted with AgCl windows.

**Preparation of XeF<sub>6</sub>.** A modified version of the "hot wire" reactor described by Bezmel'nitsyn and co-workers was used.<sup>8</sup> The reactor consists of a well-passivated stainless steel tube inside which is a resistively heated nickel filament. The reactor is immersed in liquid nitrogen, and the filament is heated to 700–800 °C by a dc power supply. The reactor is connected to a vacuum system that consists of a ballast volume and a metal bellows circulating pump (Metal Bellows Corp., Model 601). In a typical reaction, xenon (15 mmol) was condensed onto the walls of the reactor in 5-mmol increments to ensure that the xenon was evenly distributed along the complete length of the reactor as a thin coating. Fluorine was then introduced into the ballast cans (160 Torr in 22 L, 190 mmol). Following the addition of the xenon and fluorine, the power was turned on and the filament was heated electrically to 700–800 °C. After the filament had reached the desired operating temperature, the fluorine was circulated through the reactor at a nominal pressure of 50–70 Torr. After 1 h, the reactor was shut down and 2.3 g of white solid material was condensed at -78 °C into a stainless steel trap fitted with a sapphire view-point. The material was identified as pure XeF<sub>6</sub> by infrared spectroscopy and its room-temperature vapor pressure.<sup>2</sup> The 2.3 g of XeF<sub>6</sub> recovered represents a 62% yield based on the xenon used as a starting material. The less than quantitative yield most likely is due to layering effects and condensation of xenon in regions of the reactor that are essentially unavailable to filament-generated fluorine atoms.

**Preparation of XeF<sub>4</sub>.** Xenon (3.0 mmol) and a large excess (10-fold or greater) of O<sub>2</sub>F<sub>2</sub> were condensed at -196 °C into a 35-mL stainless steel reaction vessel. A -155 °C cold trap (CF<sub>2</sub>Cl<sub>2</sub>/liquid N<sub>2</sub> slush bath) was placed around the reactor, which then was allowed to warm slowly to -120 °C over a period of 2–4 h. Subsequently, the reactor was warmed to -78 °C by filling the Dewar flask with dry ice. The system was then left overnight at -78 °C, during which time the excess O<sub>2</sub>F<sub>2</sub> decomposed to O<sub>2</sub> and F<sub>2</sub>. The volatile material was then passed through a trap cooled to -196 °C to remove O<sub>2</sub> and F<sub>2</sub>. The -196 °C trap also retained a white solid material. The -196 °C Dewar flask was replaced with one cooled to -78 °C, and the contents of the trap were pumped on for 1 h to remove CF<sub>4</sub>, COF<sub>2</sub>, and SiF<sub>4</sub> impurities. The remaining product was identified as a mixture of XeF<sub>2</sub> and XeF<sub>4</sub> (0.58 g) by its infrared spectrum.<sup>9,10</sup> Following a second treatment of the XeF<sub>4</sub>/XeF<sub>2</sub> mixture with O<sub>2</sub>F<sub>2</sub>, as described above, pure XeF<sub>4</sub> product was isolated in quantitative yield (0.62 g, 3.0 mmol) and identified by its infrared<sup>10</sup> and Raman spectra.<sup>10</sup>

## Results and Discussion

The reaction of xenon with fluorine under conditions of low pressure and high filament temperature in the "hot wire" reactor provides a useful method for the preparation of pure XeF<sub>6</sub>. The use of an excess of fluorine (5–10 times that of xenon) is necessary, since it is likely that some of the fluorine reacts with the reactor walls and hot filament. Excess fluorine also inhibits the formation of XeF<sub>4</sub> and XeF<sub>2</sub> as side products. This reaction, like the reported photochemical reaction for preparing XeF<sub>6</sub>, presumably occurs through formation of fluorine atoms.

Xenon tetrafluoride was prepared in quantitative yield and very high purity at low pressure and temperature. The reaction of O<sub>2</sub>F<sub>2</sub> with xenon initially converts all of the xenon to a mixture of XeF<sub>2</sub> and XeF<sub>4</sub>. Prolonged exposure of this mixture to excess O<sub>2</sub>F<sub>2</sub> further fluorinates the remaining Xe(II) to Xe(IV). This observation is contrary to a previously published report in which only

XeF<sub>2</sub> was observed from the fluorination of xenon with O<sub>2</sub>F<sub>2</sub>.<sup>11</sup> We found no evidence for formation of XeF<sub>6</sub> from the reaction of XeF<sub>4</sub> even with a large excess of O<sub>2</sub>F<sub>2</sub> over a prolonged period of time. In contrast to hot fluorine atoms, as demonstrated by the reaction of F<sub>2</sub> and xenon above, apparently O<sub>2</sub>F<sub>2</sub> is not sufficiently potent to oxidize Xe(IV) to Xe(VI).

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**Registry No.** XeF<sub>4</sub>, 13709-61-0; XeF<sub>6</sub>, 13693-09-9; O<sub>2</sub>F<sub>2</sub>, 7783-44-0; F<sub>2</sub>, 7782-41-4; O<sub>2</sub>, 7782-44-7; Xe, 7440-63-3.

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## Solution and Solid-State Structures of the Monomeric, Piano-Stool Mono(peralkylcyclopentadienyl)vanadium(IV) Trihalides

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Low-valent organovanadium chemistry is dominated by the study of mono- and bis(cyclopentadienyl)vanadium compounds.<sup>2,3</sup> Less studied are compounds with ring alkylation, a derivatization that has been shown to yield reactive compounds such as the highly oxidizing (η-C<sub>5</sub>H<sub>4</sub>Me)VCl<sub>3</sub>.<sup>4</sup> Cyclopentadienyl ring peralkylation has been shown to inhibit (though not completely prevent) intramolecular ring metalation in early-transition-metal chemistry. In our research in low-valent mono(peralkylcyclopentadienyl) group 5 chemistry, we were interested in preparing organodivandium(III) analogues<sup>5</sup> of (η-C<sub>5</sub>Me<sub>4</sub>R)<sub>2</sub>Ta<sub>2</sub>X<sub>4</sub><sup>6</sup> (R = Me, Et; X = Cl, Br) via reductive dimerization in order to examine comparative structure and reactivity<sup>7</sup> between first- and third-row congeners and to develop early-metal-early-metal bonded organodimetallic<sup>8</sup> chemistry. For such studies, a mono(peralkylcyclopentadienyl)vanadium(IV) halide precursor was needed to avoid possible C<sub>5</sub>H<sub>5</sub> or C<sub>5</sub>H<sub>4</sub>Me metalation during reduction; this compound was expected to possess a three-legged piano-stool structure<sup>4</sup> rather than the nonbonded structure of the organoditantalum(IV) compounds (η-C<sub>5</sub>Me<sub>4</sub>R)<sub>2</sub>Ta<sub>2</sub>(μ-X)<sub>2</sub>X<sub>4</sub>.<sup>9</sup>

Previous preparations of mono(cyclopentadienyl)vanadium(IV) halides involved halogenation of CpV(CO)<sub>4</sub> with X<sub>2</sub><sup>10</sup> or SOCl<sub>2</sub><sup>11</sup>

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or of  $Cp_2VCl_2$  with  $SOCl_2$ .<sup>4</sup> The earliest report of a peralkylcyclopentadienyl derivative halide was that of Bottomley et al.,<sup>12</sup> who prepared  $(C_5Me_5)VCl_3$  in very low (unstated) yield from  $(C_5Me_5)_2VCl_2$  and  $SOCl_2$ . Herberhold and co-workers recently reported the high-yield preparation of  $(C_5Me_5) VX_3$  ( $X = Cl, Br, I$ ) by direct halogenation of  $(C_5Me_5)V(CO)_4$ ,<sup>13</sup> a synthesis that is reproducible in our hands and applicable to the preparation of the  $C_5Me_4Et$  analogues. In this note, we report spectroscopic and spectrometric data for the  $C_5Me_5$  and  $C_5Me_4Et$  compounds and the solid-state molecular structure of  $(\eta-C_5Me_4Et)VCl_3$ .

### Experimental Section

**General Experimental Details.** Compounds were manipulated under a dinitrogen/helium or argon atmosphere in a Vacuum Atmospheres glovebox (under continuous atmosphere recirculation and purification) or on a Schlenk line of local design. Reagent grade benzene, toluene, diethyl ether, and tetrahydrofuran were distilled under dinitrogen in greaseless stills from sodium benzophenone ketyl. Hexane was washed several times with 5% nitric/sulfuric acid followed by water, dried over  $CaCl_2$ , and then distilled from sodium/potassium benzophenone ketyl solubilized by tetraglyme.

Bis(diglyme)sodium hexacarbonylvanadate(-I) (Alfa Products, Danvers, MA; Pressure Chemical, Pittsburgh, PA; Strem Chemical, Newburyport, MA) and chlorine (Matheson) were used as received. Bromine (Fisher Scientific) was distilled and stored under argon in a grease-free Schlenk flask. Bromine was handled with Teflon Luer lock, gastight syringes, and flexible, blunt-tipped Teflon needles with Kel-F hubs (Aldrich Chemical). Perdeuteriobenzene (Aldrich) was stored over freshly cut sodium prior to use.

2-Bromo-2-butene,<sup>14</sup> pentamethylcyclopentadiene,<sup>15</sup> tetramethylcyclopentadiene,<sup>16</sup>  $V(CO)_6$ ,<sup>17</sup> and  $(C_5Me_4R)V(CO)_4$  ( $R = Me, Et$ ) were prepared by literature procedures.

Proton NMR spectra were obtained on either a Jeol FX-90Q (89.55 MHz) or Bruker WM-360 (360 MHz) NMR spectrometer operated in the internal  $^2H$ -locked mode; spectra are internally referenced to the residual protio solvent (e.g.,  $C_6D_5H$ ,  $\delta \approx 7.15$ ) impurity. Mass spectra were obtained in the electron impact mode on a VG Instruments ZAB-HF magnetic sector spectrometer; samples were introduced into the spectrometer direct inlet under argon purge via a sampler holder of local design.<sup>18</sup> Single-crystal X-ray diffraction was performed on an Enraf-Nonius CAD-4 diffractometer interfaced to a MicroVAX II minicomputer with Tektronix 4106A color graphics terminals and Talaris laser printer; data were processed with the Enraf-Nonius SDP package.

A low-temperature ( $-35^\circ C$ ) refrigerator in the glovebox was used for compound recrystallizations. Crystals for X-ray diffraction were grown in layered cosolvent/solution mixtures in 5-mm-o.d. glass tubes; crystals were inspected by using a stereomicroscope mounted on the glovebox window and placed in appropriately sized glass capillaries, which were then stoppered with a rubber septum and flame sealed with a microtorch.

**Synthesis of  $(C_5Me_4Et)VCl_3$ .** A solution of  $(C_5Me_4Et)V(CO)_4$  (1.00 g, 3.20 mmol) dissolved in hexane (50 mL) in a 100-mL Schlenk flask was reacted with a gentle chlorine gas stream (in excess) for 0.5 h. The orange solution quickly yielded a gray-purple precipitate, which was filtered out, washed with hexane, and dried in vacuo to give 0.88 g of  $(C_5Me_4Et)VCl_3$  (90% yield). The compound is conveniently recrystallized from toluene/hexane cosolvent mixtures cooled to  $-35^\circ C$ . Anal.

**Table I.** Crystallographic Data for  $(C_5Me_4Et)VCl_3$

$VC_{11}H_{17}Cl_3$	fw 306.2
$a = 6.608$ (5) Å	space group $P2_1/m$ (No. 11)
$b = 11.408$ (3) Å	$\lambda = 0.71073$ Å
$c = 9.284$ (3) Å	$\rho_{\text{calcd}} = 1.467$ g cm <sup>-3</sup>
$\beta = 96.26$ (4) $^\circ$	$\mu = 12.91$ cm <sup>-1</sup>
$V = 695.642$ Å <sup>3</sup>	transm coeff = 0.904–1.000
$Z = 2$	$R(F_o) = 0.030$
$T = 22^\circ C$	$R_w(F_o^2) = 0.047$

**Table II.** Positional and Thermal Parameters and Their Estimated Standard Deviations

atom	x	y	z	$B^a$ Å <sup>2</sup>
V(1)	0.58575 (8)	0.250	0.30043 (6)	3.02 (1)
Cl(1)	0.7089 (2)	0.250	0.5339 (1)	4.44 (2)
Cl(2)	0.7529 (1)	0.10114 (8)	0.21386 (9)	5.21 (2)
C(1)	0.3077 (5)	0.250	0.1352 (4)	3.18 (7)
C(2)	0.2926 (4)	0.1493 (2)	0.2240 (3)	3.04 (4)
C(3)	0.2751 (3)	0.1877 (2)	0.3666 (3)	2.81 (4)
C(4)	0.3168 (7)	0.250	-0.0249 (4)	5.0 (1)
C(5)	0.2787 (5)	0.4754 (3)	0.1731 (3)	4.56 (6)
C(6)	0.2473 (4)	0.1120 (3)	0.4939 (3)	4.20 (6)
C(7)	0.1041 (8)	0.250	-0.1056 (5)	6.2 (1)
H(4)	0.393	0.303	-0.052	5.3*
H(5A)	0.257	0.512	0.264	5.2*
H(5C)	0.409	0.501	0.149	5.2*
H(5B)	0.177	0.496	0.102	5.2*
H(6A)	0.149	0.094	0.513	4.7*
H(6B)	0.305	0.149	0.599	4.7*
H(6C)	0.316	0.046	0.458	4.9*
H(7A)	0.121	0.250	0.795	7.3*
H(7B)	0.030	0.182	-0.079	6.9*

<sup>a</sup> Starred  $B$  values are for atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as  $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$ .

(combustion with  $WO_3/V_2O_5$ ). Calcd for  $C_{11}H_{17}Cl_3V$ : C, 43.09; H, 5.60; Cl, 34.69. Found: C, 42.84; H, 5.51; Cl, 33.98.

**Synthesis of  $(C_5Me_4Et)VBr_3$ .** A solution of bromine (2 mL, 9.7 mmol) in hexane (30 mL) was added dropwise to a stirring solution of  $(C_5Me_4Et)V(CO)_4$  (1.56 g, 5.00 mmol). During the course of the addition a gray precipitate formed; upon completion of the addition, the mixture was stirred for 1 h. The precipitate was then filtered out, washed with hexane, and dried in vacuo to yield solid  $(C_5Me_4Et)VBr_3$  (1.89 g, 86% yield). The compound is soluble in aromatic solvents, resulting in dark green solutions.  $^1H$  NMR ( $\delta$ ,  $C_6D_6$ , 89.56 MHz): -27.2 and -26.4 (broad singlets, 12 H,  $C_5Me_4Et$  ring Me, Me'), -12.24 (singlet, 2 H,  $CH_2$ ), -0.06 (singlet, 3 H, Me of Et group).

**Synthesis of  $(C_5Me_5)VCl_3$ .** To a solution of excess  $Cl_2$  in 100 mL of diethyl ether ( $Cl_2$  bubbled continuously through a gas dispersion adapter) was added a solution of  $(C_5Me_5)V(CO)_4$  (1.45 g, 4.86 mmol) in diethyl ether (40 mL). The orange color of the carbonyl reactant quickly changed to purple upon chlorination. The mixture was filtered and the solid washed with hexane to give 1.19 g (83% yield) of  $(C_5Me_5)VCl_3$ .  $^1H$  NMR ( $\delta$ ,  $C_6D_6$ , 89.56 MHz): -27.7 (broad singlet,  $\Delta\nu_{1/2} = 65$  Hz).

**Synthesis of  $(C_5Me_5)VBr_3$ .** To a solution of  $Br_2$  (1.6 mL, 7.76 mmol) in diethyl ether (200 mL) was added dropwise a solution of  $(C_5Me_5)V(CO)_4$  (2.25 g, 7.54 mmol) in ether (50 mL). A dark green precipitate quickly formed during the course of the addition. Upon completion the mixture was filtered and the solid washed with hexane and dried in vacuo to yield 2.25 g (73%) of dark green solid  $(C_5Me_5)VBr_3$ .  $^1H$  NMR ( $\delta$ ,  $C_6D_6$ , 89.56 MHz,  $30^\circ C$ ): -24.7 (broad singlet,  $\Delta\nu_{1/2} = 52$  Hz). Mass spectrum ( $m/e$ ): 425 ( $P^+$ ,  $^{79}Br^{79}Br^{81}Br$  isotopomer of  $Br_3$  isotope pattern), 346 ( $P^+ - Br$ ,  $^{79}Br^{81}Br$  isotopomer of  $Br_2$  isotope pattern), 264 ( $P^+ - Br - HBr$ ,  $^{79}Br$  isotopomer of  $Br_1$  isotope pattern).

**Crystallographic Data Collection and Structural Refinement.** Crystals of  $(C_5Me_4Et)VCl_3$  were grown by slow diffusion of hexane layered over a saturated toluene solution in a 5-mm-o.d. glass tube placed in a  $-35^\circ C$  glovebox freezer. A crystal with dimensions 0.26 mm  $\times$  0.17 mm  $\times$  0.44 mm was sealed in a glass capillary under  $N_2$  and mounted on the diffractometer. A preliminary set of reflections from a rotational photo were centered and yielded a primitive monoclinic cell, which was confirmed by axial photographs. Crystal data are given in Table I. Scaling factors and Lorentz, polarization, and empirical absorption (range 0.904–1.00) corrections were applied to the data, 4885 reflections ( $2\theta_{\text{max}} = 50^\circ$ ,  $\omega/2\theta$  scan,  $\pm h, \pm k, \pm l$ ) collected at 295 K. A total of 1034 reflections after averaging with  $I \geq 3\sigma(I)$  were used in the structure de-

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**Table III.** Bond Distances (Å) in  $(C_5Me_4Et)VCl_3^a$ 

V(1)–Cl(1)	2.2341 (9)	C(1)–C(2)	1.426 (3)
V(1)–Cl(1)	2.2341 (9)	C(1)–C(2)	1.426 (3)
V(1)–Cl(2)	2.2260 (6)	C(1)–C(4)	1.496 (4)
V(1)–Cl(2)	2.2260 (6)	C(1)–C(4)	1.496 (4)
V(1)–C(1)	2.264 (3)	C(2)–C(3)	1.413 (3)
V(1)–C(1)	2.264 (3)	C(2)–C(5)	1.501 (3)
V(1)–C(2)	2.299 (2)	C(3)–C(3)	1.425 (4)
V(1)–C(2)	2.299 (2)	C(3)–C(6)	1.493 (3)
V(1)–C(3)	2.318 (2)	C(4)–C(7)	1.520 (5)
V(1)–C(3)	2.318 (2)	C(4)–C(7)	1.520 (5)

<sup>a</sup>Numbers in parentheses are estimated standard deviations in the least significant digits.

**Table IV.** Bond Angles (deg) in  $(C_5Me_4Et)VCl_3^a$ 

Cl(1)–V(1)–Cl(2)	102.02 (3)	C(2)–C(1)–C(4)	126.1 (2)
Cl(1)–V(1)–Cl(2)	102.02 (3)	C(1)–C(2)–C(3)	108.1 (2)
Cl(1)–V(1)–CNT	115.13 (9)	C(1)–C(2)–C(5)	126.1 (4)
Cl(2)–V(1)–Cl(2)	99.69 (4)	C(3)–C(2)–C(5)	125.6 (3)
Cl(2)–V(1)–CNT	117.65 (5)	C(2)–C(3)–C(3)	108.1 (2)
Cl(2)–V(1)–CNT	117.65 (5)	C(2)–C(3)–C(6)	126.4 (3)
C(2)–C(1)–C(2)	107.6 (3)	C(3)–C(3)–C(6)	125.4 (2)
C(2)–C(1)–C(4)	126.1 (2)	C(1)–C(4)–C(7)	110.8 (2)

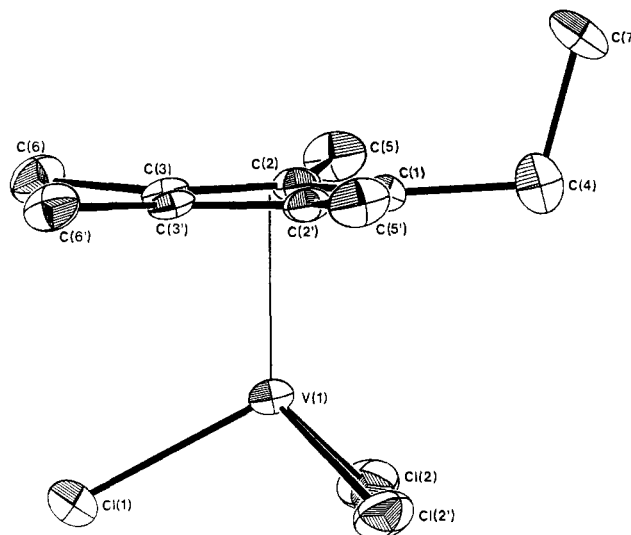
<sup>a</sup>Numbers in parentheses are estimated standard deviations in the least significant digits.

termination, which was solved by direct methods (MULTAN) and refined by blocked full-matrix least-squares techniques to  $R = 0.030$  and  $R_w = 0.047$ . Several hydrogen atoms were found via difference maps (after anisotropic convergence of all nonhydrogen atoms), with the remaining calculated via the program HYDRO, and all placed in fixed positions, followed by several cycles of refinement. Positional and equivalent isotropic thermal parameters are listed in Table II.

### Results and Discussion

The  $C_5Me_4Et$  analogues of  $(C_5Me_5) VX_3$  are easily prepared in high yield by the halogenation procedure developed by Herberhold et al.<sup>13</sup> as based on the original work of Fischer et al.<sup>10</sup> The Herberhold synthetic route will lead to the development of lower valent, non-carbonyl mono( $\eta$ -alkyltetramethylcyclopentadienyl)vanadium chemistry, with the only impediment being the moderate yields and multiple steps involved in the synthesis and purification of  $(C_5Me_4R)V(CO)_4$ ; we are currently examining more direct routes to  $(C_5Me_4R) VX_3$ . Proton NMR spectroscopy of  $(C_5Me_4R) VX_3$  in  $C_6D_6$  showed paramagnetic broad singlets for the  $C_5Me_5$  analogues ( $X = Cl$ ,  $\delta = -27.7$ ;<sup>19</sup>  $X = Br$ ,  $\delta = -28$ ), and spectra of the  $C_5Me_4Et$  analogues demonstrated that a plane of symmetry passes through the peralkylcyclopentadienyl ligand, as expected for a three-legged piano-stool structure. Mass spectra of the  $C_5Me_5$  compounds show a parent ion with the correct halogen isotope pattern.

A single-crystal X-ray diffraction study of  $(C_5Me_4Et)VCl_3$  shows that the molecule adopts a three-legged piano-stool structure (Figure 1) in the solid state, as would be expected by comparison to the known structure of  $(C_5H_4Me)VCl_3$ .<sup>4a</sup> A crystallographically imposed mirror plane passes through the molecule. Experimental details, fractional coordinates, bond distances, and bond angles are listed in Tables I–IV, respectively. The V–Cl distances, 2.2341



**Figure 1.** ORTEP diagram of  $(C_5Me_4Et)VCl_3$ . A crystallographically imposed mirror plane passes through V(1), Cl(1), C(1), C(4), and C(7); symmetry-related atoms are indicated with a prime.

(9) Å for V–Cl(1) and 2.2260 (6) Å for V–Cl(2), are slightly longer than those found in  $(C_5H_4Me)VCl_3$ , 2.187 (4)–2.208 (4) Å.<sup>4a</sup> The Cl–V–Cl angles, 102.02 (3)° for Cl(1)–V–Cl(2) and 99.69 (4)° for Cl(2)–V–Cl(2'), are similar to the Cl–M–Cl angles in the three-legged piano-stool halo monomers  $CpTiCl_3$  (102.2 (2)–104.1 (2)°)<sup>20</sup> and  $(C_5H_4Me)VCl_3$  (98.7 (1)–103.3 (1)°).<sup>4a</sup> The V–C<sub>ring</sub> distances in  $(C_5Me_4Et)VCl_3$  average 2.29 [3] Å.<sup>21</sup> The CNT–V–Cl angles, where CNT is the calculated centroid of the  $C_5Me_4Et$  ring carbons, are CNT–V–Cl(1) = 115.13° and CNT–V–Cl(2) = 117.65°. The V–CNT distance of 1.957 Å is longer though statistically similar to the 1.93 (1)-Å distance in  $(C_5H_4Me)VCl_3$ .<sup>4a</sup>

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**Supplementary Material Available:** A complete table of crystal data, measurement conditions, and refinement details and listings of thermal parameters (2 pages); a table of calculated and observed structure factors (4 pages). Ordering information is given on any current masthead page.

(19) The <sup>1</sup>H chemical shift value for  $(C_5Me_5)VCl_3$  of  $\delta = -27.7$  (fwhm 65 Hz) is essentially the same as that reported by Bottomley et al.<sup>12</sup> ( $\delta = -28.7$ , solvent unspecified).

(20) Engelhardt, L. M.; Papasergio, R. I.; Raston, C. L.; White, A. H. *Organometallics* **1984**, *3*, 18–20.

(21) Variances in averaged values, indicated by the square brackets, were calculated by the formula  $[\sum(x - \bar{x})^2 / (N - 1)]^{1/2}$ .