$(TM)_x(MG)_3$ cluster compounds. At one extreme lie the "innocent" $(MG)_2$-containing clusters with no MG···MG interaction, exemplified by $Cp_3Co_3S_2$[40] and $Cp_3Ni_3S_2$.[41] At the other extreme lie clusters with very short intracluster MG···MG contacts exemplified by $E_2[W(CO)_5]_3$ (E = As, Sb, and Bi). The compound $Bi_2W_3(CO)_{15}$ features a Bi···Bi distance of 2.818 Å, which indicates acetylene-like multiple Bi–Bi bonding.[8c] The relationship of 2 to this latter group is further evidenced by its oxidation to form a derivative which has an even shorter Te–Te bond.[17] Finally, we note that the increase in MG–MG bond order upon going from $Cp_3Co_3S_2$ to 2 and then to $Bi_2W_3(CO)_{15}$ is accompanied by a decrease in net M–M bond order.

An alternative view of the bonding in 2 and in related arachno clusters is suggested by a recent report on the structure of Rh-$(P_4)(PPh_3)_2Cl$.[42] In this complex the 14e⁻ $Rh(PPh_3)_2Cl$ fragment
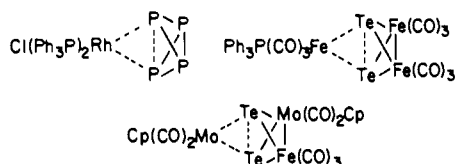
binds in an η^2 fashion to the P_4 tetrahedron, elongating this edge by 0.25 Å. The coordinated P atoms remain mutually bonded, and the elongation of the P–P bond is analogous to that observed for olefin and acetylene coordination. The core of $Fe_2(Te_2)(CO)_6$ is similar structurally and electronically to P_4 as are the As_n-$(Co(CO)_3)_{4-n}$ clusters.[43] From this perspective it is clear that

the "oxidative addition" of $Fe_2(Te_2)(CO)_6$ to $Fe(CO)_3PPh_3$ may be more appropriately described as coordination of largely intact Te–Te bond to the 16e⁻ $Fe(CO)_3PPh_3$ fragment. In the same way, 2 may be considered to be derived from the coordination of $[CpMoFe(\mu-\eta^2-Te_2)(CO)_5]^+$ [17] to $[CpMo(CO)_2]^-$.[44]

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Mononuclear and Binuclear Cationic Complexes of Vanadium(II)

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Abstract: A method for the high-yield synthesis (up to 99%) of the new compounds $[(THF)_3V(\mu-Cl)_3V(THF)_3]AlCl_2R_2$, where R = Et or Me, is described. Compound 1, R = Et, reacts instantaneously with methanol to give a blue solution from which, depending upon the workup, $[V(CH_3OH)_6]Cl_2$ (3) or $VCl_2(CH_3OH)_4$ (2) can be obtained. With trimethylphosphine 1 readily affords $[(PMe_3)_3V(\mu-Cl)_3V(PMe_3)_3]AlCl_2Et_2$ (4). Crystals of 1 diffracted poorly, and the structure could not be satisfactorily refined because of severe disorder in the tetrahydrofuran ligands as well as in the diethyldichloroaluminate anion. The structure was solved, however, and refined sufficiently to define the tri(μ-chloro)hexa(tetrahydrofuran)divanadium(II) cation and the diethyldichloroaluminate anion unambiguously but not accurately. Further characterization came from elemental analysis on all six elements of 1 and its UV spectrum. Compound 3 crystallizes in space group $P2_1/n$ with the following unit cell dimensions: $a = 6.993$ (3) Å, $b = 10.809$ (4) Å, $c = 10.298$ (4) Å, $\beta = 97.00$ (3)°, $V = 764.8$ (9) Å³, $Z = 2$. $[V(MeOH)_6]Cl_2$ represents the first example of a homoleptic vanadium(II) alcoholate to be fully characterized by X-ray crystallography. For compound 4 the orthorhombic unit cell (space group $Pnma$) has the following dimensions: $a = 12.705$ (2) Å, $b = 12.522$ (4) Å, $c = 28.554$ (9) Å, $V = 4543$ (3) Å³, and $Z = 4$. The V–V′ distance in 4 is 3.103 (4) Å.

Our knowledge of the nonaqueous chemistry of vanadium in very low valence states (I, II), but not involving cyclopentadienyl

and/or carbonyl ligands, is still very inadequate. One important reason for this is the lack of suitable (easily prepared, soluble in common organic solvents, etc.) starting materials. For some time it was believed that "$VCl_2(THF)_2$" would be a good choice, but this compound proved, via X-ray crystallographic studies, to be

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$[(THF)_3V(\mu\text{-}Cl)_3V(THF)_3]_2[Zn_2Cl_6]$.[1] Although this material can be used to obtain a number of interesting compounds containing vanadium only, viz., $V_3(\mu_3\text{-}O)(CF_3CO_2)_6(THF)_3$[2] and $[V(\mu\text{-}Cl)(\mu\text{-}dppm)BH_4]_2$,[3] or unusual mixed metal products such as $[VZnO(O_2CPh)_3(THF)]_4\cdot2THF$,[4] $V(THF)_2[ZnCl_3\text{-}(PPh_3)]_2\cdot2CH_2Cl_2$,[5] and $[VZnH_2(BH_4)(PMePh_2)_2]_2$,[6] it is still not as convenient as we should like because it is only sparingly soluble in organic solvents and the presence of zinc may be a potential source of interference with the vanadium chemistry.

We report here a new method of synthesis leading to $[V_2(\mu\text{-}Cl)_3(THF)_6]AlR_2Cl_2$ (R = methyl or ethyl) compounds via $VCl_3(THF)_3$ reduction by $AlR_2(OR)$ in tetrahydrofuran and toluene or hexane. A rich chemistry of these excellently soluble materials is already emerging: $[(THF)_3V(\mu\text{-}Cl)_3V(THF)_3]$-$AlEt_2Cl_2$ reacts immediately with methanol and trimethylphosphine to give $[V(MeOH)_6]Cl_2$ and $[(PMe_3)_3V(\mu\text{-}Cl)_3V(PMe_3)_3]AlEt_2Cl_2$, respectively, which are the first systems of this sort to be completely characterized via X-ray crystallography. We should like to note that the origins of the work reported here go back to the mid-1970's when some of these reactions were first carried out and structures tentatively assigned in the Central Research and Development Laboratories at DuPont.

Experimental Section

All reactions, manipulations, and crystallizations were performed under an atmosphere of dry nitrogen or argon in a Vacuum Atmospheres drybox or on a double-manifold vacuum line equipped with standard Schlenk glassware. Solvents were dried by passage through columns of Linde grade 4A molecular sieves and sparged with nitrogen before use or they were freshly distilled from benzophenone ketyl for THF and hexane and from magnesium for methanol. Elemental analyses were performed by the Physical and Analytical Division of the Central Research and Development Department of DuPont and by Alfred Bernhardt (West Germany). Magnetic susceptibilities were determined at approximately 300 K by the Faraday method. Corrections for diamagnetism were made with Pascal's constants. The UV–visible spectra were measured on a Cary 17D spectrophotometer at room temperature. The numerical data given below and pertaining to the UV–visible spectra are in the following form: λ in nm and in parentheses ϵ in $mol^{-1}\cdot L\cdot cm^{-1}$. Anhydrous VCl_3 was purchased from Ventron Corp. or Strem Chemicals, Inc. $AlEt_2(OEt)$ was purchased as 25 wt % solution in toluene or hexane from Aldrich Chemical Co. or Alpha. $VCl_3(THF)_3$ was prepared by a literature method.[7]

Preparation of $[V_2Cl_3(THF)_6][AlCl_2Et_2]$ with $AlEt_2(OEt)$. To a solution of $VCl_3(THF)_3$ (28 g, 74.9 mmol) in 200 mL of THF was added 130 mL of a 25% solution of $AlEt_2(OEt)$ in hexane or toluene. The solution was stirred for 6 days at room temperature during which time the color changed to a bright green. The solution was then filtered and 300 mL of hexane was added to precipitate a pale green crystalline solid. It was filtered, washed with hexane, and dried. The yield was ca. 27 g. The filtrate was cooled to –30 °C to yield a second crop of green crystals (2.6 g). Alternatively, the clear green reaction mixture after being stirred for 6 days, may be filtered and 300 mL of hexane may be carefully layered on top of the filtrate. Needle-like bright green crystals are formed upon standing in the refrigerator. The yield was 95–99%.

Anal. Calcd for $C_{28}H_{58}AlO_6Cl_5V_2$: C, 42.20; H, 7.34; Cl, 22.24; O, 12.03; V, 12.78; Al, 3.38. Found: C, 41.98; H, 7.41; Cl, 21.97; O, 12.32; V, 12.50; Al, 3.28. Visible spectrum (THF): 392 (18), 405 (26), 435 (14), 635 (15).

Magnetic moment (THF): $X_M = 4.67 \times 10^{-3}$ emu/mol at 303 K; μ_{eff} = 3.38 μ_B.

Preparation of $[V_2Cl_3(THF)_6][AlCl_2Me_2]$ with $AlMe_2(OEt)$. To a solution of $VCl_3(THF)_3$ (1.87 g, 5.0 mmol) in 100 mL of tetrahydrofuran was added a solution of $AlMe_2(OEt)$ in THF, prepared by the slow

addition of EtOH (2.3 g, 50.0 mmol) to $AlMe_3$ (3.60 g, 50 mmol) in 100 mL of THF. The solution was stirred for 48 h during which time the color changed to bright green. The solution was filtered and the solvent reduced in volume by rotary evaporation. Hexane was added and the flask cooled to –40 °C. Pale green crystals separated. They were filtered, washed with hexane, and dried. The yield was 1.34 g (70%).

Anal. Calcd for $C_{26}H_{54}O_6AlCl_5V_2$: C, 40.62; H, 7.07; Cl, 23.06. Found: C, 39.38; H, 6.90; Cl, 23.28.

Preparation of $[V_2Cl_3(THF)_6][AlCl_2Me_2]$ with $AlMe_2(OMe)$. A solution of $AlMe_2(OMe)$ was prepared from $AlMe_3$ (3.60 g, 50 mmol) and MeOH (1.6 g, 50 mmol) in 100 mL THF. The solution of $AlMe_2(OMe)$ was then added to a solution of $VCl_3(THF)_3$ (1.87 g, 5.0 mmol) in 100 mL of THF. After the solution was stirred for 48 h, it was filtered and the solvent reduced in volume by rotary evaporation. Hexane was added and the flask cooled. Green crystals separated; they were filtered and dried. The yield was 1.42 g (74%).

Anal. Calcd for $C_{26}H_{54}O_6AlCl_5V_2$: C, 40.62; H, 7.07; Cl, 23.06. Found: C, 40.40; H, 7.05; Cl, 23.89.

Preparation of $[V_2Cl_3(THF)_6][AlCl_2Et_2]$ with $AlEt_2(OMe)$. A solution of $AlEt_2(OMe)$ in THF was prepared from $AlEt_3$ (5.7 g, 50 mmol) and MeOH (1.6 g, 50 mmol). This solution was added to 1.87 g of $VCl_3\text{-}(THF)_3$ dissolved in 100 mL of THF. After being stirred for 48 h, the solution was filtered, and the solvent was reduced in volume by rotary evaporation. Hexane was added, and the flask was cooled to give pale green crystals that were removed by filtration and dried. The yield was 1.55 g (78%).

Preparation of $[V(MeOH)_6]Cl_2$ and $VCl_2(MeOH)_4$ from $[V_2Cl_3\text{-}(THF)_6][AlCl_2Et_2]$. A sample of $[V_2Cl_3(THF)_6][AlCl_2Et_2]$ (3.0 g, 3.7 mmol) was slowly added to 50 mL of methanol. Much gas was evolved, and the solution turned dark blue. After being stirred at room temperature for 0.5 h, the solution was filtered through Celite 545 (Fisher Scientific Co.), and the blue solution was evaporated under vacuum at room temperature to give 1–2 mL of purple-blue solution. Upon standing overnight at room temperature purple-blue X-ray quality crystals (needles) of $[V(MeOH)_6]Cl_2$ were formed in this solution. The yield was 1.2 g (52%).

Visible spectrum of $[V(MeOH)_6]Cl_2$ (MeOH): 375 (1.6), 565 (3.7), 857 (2.0).

If the solution is evaporated at 50–60 °C (moderate vacuum, rotary evaporation, or argon purging), a blue solid, non-crystalline form of $VCl_2(MeOH)_4$ is obtained. The yield was 1.1 g (60%).

Anal. Calcd for $C_4H_{16}Cl_2O_4V$: C, 19.21; H, 6.44; O, 25.58; Cl, 28.36. Found: C, 19.39; H, 6.49; O, 24.43; Cl, 28.46.

Preparation of $[V_2Cl_3(PMe_3)_6][AlCl_2Et_2]$. A sample of $[V_2Cl_3\text{-}(THF)_6][AlCl_2Et_2]$ (3.0 g, 3.7 mmol) was dissolved in 50 mL of THF, and PMe_3 (1.7 g, 22.3 mmol) was added. The solution turned deep red. After being stirred for 1 h the solution was filtered, 50 mL of hexane was added, and the solution was cooled to –30 °C. Red-purple crystals separated. They were filtered and washed with hexane. The yield was 2.34 g (77%).

Anal. Calcd for $C_{22}H_{64}Cl_5AlP_6V_2$: C, 32.20; H, 7.85; Cl, 21.59; P, 22.65. Found: C, 32.53; H, 7.64; Cl, 22.92; P, 21.65.

Magnetic moment (THF): $X_M = 5.7 \times 10^{-3}$ emu/mol at 303 K; μ_{eff} = 3.73 μ_B.

X-ray Crystallography. General. Single-crystal X-ray diffraction analyses were carried out by application of general procedures which have been previously described elsewhere.[8] The unit cell parameters and basic information about data collection and refinement for $[V_2Cl_3(PMe_3)_6]$-$[AlCl_2Et_2]$ (4) and $[V(CH_3OH)_6]Cl_2$ (3) are summarized in Table I. Polarization and Lorentz corrections were applied to the intensity data. In both cases a scan of selected reflections with χ close to 90° at ψ values from 0 to 360° at 10° intervals showed less than 10% changes in intensity and therefore no corrections for absorption were applied.

$[V_2Cl_3L_6][AlCl_2Et_2]$. As had been found in previous studies[1] involving complexes containing the $V_2Cl_3(THF)_6^+$ ion, an extensive disorder of the ligands was found, and in the present case a disorder of the aluminate anion was also observed. There was practically no scattering at high 2θ angles (>30°), and only a relatively small number of reflections could be measured.

For L = THF the following unit cell parameters were found: at 22 °C, orthorhombic (*Pnma*), a = 12.507 (3) Å, b = 13.061 (2) Å, c = 24.867 (4) Å, V = 4062 (2) Å^3, and Z = 4; at –100 °C, monoclinic ($P2_1/c$), a = 13.190 (6) Å, b = 12.150 (4) Å, c = 24.285 (17) Å, β = 90.49 (5)°, V = 3891 (6) Å^3, and Z = 4. In neither case was a complete structural characterization possible. Partially developed structures proved the presence of the $V_2Cl_3(THF)_6^+$ cation, which was analogous to the one previously described.[1]

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(8) See, for example: Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558.

Table I. Crystallographic Data

	$[V_2Cl_3(PMe_3)_6]AlCl_2Et_2$	$[V(CH_3OH)_6]Cl_2$
formula	$V_2Cl_5P_6C_{22}H_{64}$	$VCl_2O_6C_6H_{24}$
formula wt	820.73	314.10
space group	*Pnma*	$P2_1/n$
systematic absences	$0kl, k + l \neq 2n$	$0k0, k \neq 2n$
	$hk0, h \neq 2n$	$h0l, h + l \neq 2n$
a, Å	12.705 (2)	6.993 (3)
b, Å	12.522 (4)	10.809 (4)
c, Å	28.554 (9)	10.298 (4)
α, deg	90.0	90.0
β, deg	90.0	97.00 (3)
γ, deg	90.0	90.0
V, Å^3	4543 (3)	764.8 (9)
Z	4	2
d_{calcd}, g/cm^3	1.200	1.364
crystal size, mm	$0.3 \times 0.3 \times 0.2$	$0.4 \times 0.2 \times 0.2$
μ(Mo Kα), cm^{-1}	9.356	9.852
data collection instrument	CAD-4	$P\bar{1}$
radiation (monochromated in incident beam)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)
orientation reflections, no., range (2θ)	25; $9.5 \leq 2\theta \leq 34.2$	15; $15.9 \leq 2\theta \leq 28.2$
temp, °C	22	22
scan method	ω–2θ	ω–2θ
data col. range, 2θ, deg	4, 40	4, 50
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	1437	924
	938	785
no. of parameters refined	158	70
R^a	0.077	0.049
$R_w{}^b$	0.095	0.066
quality-of-fit indicator^c	2.351	1.364
largest shift/esd, final cycle	0.05	0.0
largest peak, e/Å^3	0.45	0.46

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o^2|]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^{c}Quality of fit = $[\sum w(|F_o| - |F_c|)^2/(N_{obsd} - N_{parameters})]^{1/2}$.

A complete crystallographic analysis was carried out for the compound with L = PMe$_3$, with the unit cell and space group shown in Table I. The positions of the vanadium atoms in the unit cell belonging to space group *Pnma* were determined by direct methods with the program MULTAN 84. As the structure was being developed by alternating series of least-squares refinements and difference Fourier syntheses an extensive disorder of the methyl carbon atoms and the ligands around Al became evident. Since the lowering of symmetry by removal of the inversion center (space group equivalent to *Pna*2$_1$) did not eliminate the disorder and strong correlations appeared upon refinement, the original centrosymmetric space group was retained. The positions of disordered atoms were derived from a difference Fourier map. Fractional occupancy factors were adjusted by trial and error so as to give comparable values of thermal parameters for related groups of atoms. While the cation, V$_2$Cl$_3$(PMe$_3$)$_6^+$, behaved well upon refinment, the aluminate required special treatment. The distribution of electron density around the Al atom implied the superposition of several orientations of ligands around the central atom. A number of models derived from the difference Fourier map were tried but usually an unacceptable arrangement of atoms was obtained upon unrestrained refinement. The model finally adopted had the minimum number of disordered atoms. The terminal carbon atoms in the Et groups were not refined, while the Al atom and its immediate coordination sphere were included in the full-matrix least-squares refinement. Schematic ORTEP drawings depicting the disordered PMe$_3$ and AlCl$_2$Et$_2^-$ groups are shown in Figure 1. Anisotropic thermal parameters were assigned to the V, Cl, and P atoms in the cation, and to the Al atom.

Crystallization of $[V_2Cl_3(PMe_3)_6][AlCl_2Et_2]$ from a THF/benzene/ hexane mixture afforded a second form of the compound, with benzene molecules in the lattice. The crystals belonged to a tetragonal space group $P4_2/nmc$ (no. 137) with the following unit cell parameters: $a = b = 23.220$ [5] Å, $c = 18.640$ (3) Å, $V = 10049$ (4) Å^3, and $Z = 8$. There were two crystallographically independent V$_2$Cl$_3$(PMe$_3$)$_6^+$ groups located on mm symmetry elements. The AlCl$_2$Et$_2^-$ and C$_6$H$_6$ were positioned on a twofold axis and perpendicular to a mirror plane, respectively. While refinement of the V$_2$Cl$_3$P$_6$ cores presented no difficulty, no well-behaved model representing the disordered PMe$_3$ and aluminate groups was found.

$[V(CH_3OH)_6]Cl_2$ (3). On the basis of the Patterson function the vanadium atom was placed on the inversion center at the origin of the coordinate system. After a scale factor refinement the remaining atoms were located from a difference Fourier map. All atoms were assigned anisotropic thermal parameters.

Tables of observed and calculated structure factors and anisotropic thermal parameters for both compounds are given as the supplementary material.
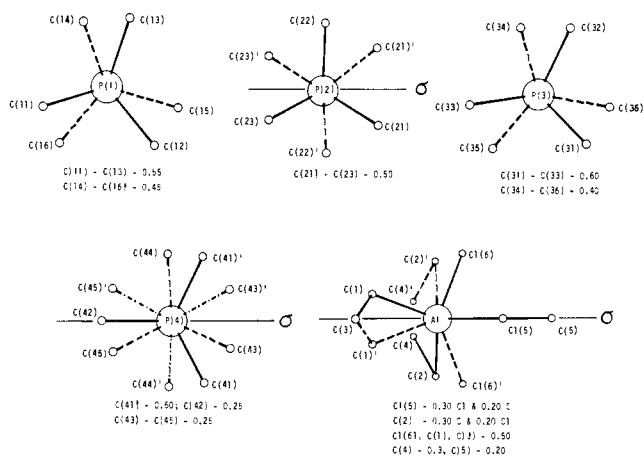

Figure 1. Details of the disordered groups in $[V_2Cl_3(PMe_3)_6]AlCl_2Et_2$. The sizes of spheres representing atoms have been chosen arbitrarily. The numbers underneath each drawing represent fractional occupancy factors.

Results and Discussion

Syntheses. The reaction between VCl$_3$(THF)$_3$ and diethylaluminum ethoxide in tetrahydrofuran and toluene or hexane at room temperature for six days furnishes bright green needle-like crystals (in yields of up to 99%) proved by partial X-ray studies to contain $[(THF)_3V(\mu\text{-Cl})_3V(THF)_3]^+$ and AlEt$_2$Cl$_2^-$ moieties. Additional support for the assigned formula comes from elemental analyses for all elements involved (C, H, Cl, O, V, and Al) as well as from the UV spectrum in dichloromethane/tetrahydrofuran. The latter is identical with the UV spectra already described for two compounds containing the tri(μ-chloro)hexa(tetrahydrofuran)divanadium(II) cation;[1] in particular, it exhibits characteristic narrow bands at 405 and 395 nm which we have postulated to be due to a double spin-flip transition.[1b]

The use of dimethylaluminum ethoxide, dimethylaluminum methoxide, or diethylaluminum methoxide in tetrahydrofuran leads to the same type of green compound, $[(THF)_3V(\mu\text{-Cl})_3V-(THF)_3][AlR_2Cl_2]$, where R = Et or Me. The yields of these reactions are in the range of 70–80%. These compounds are
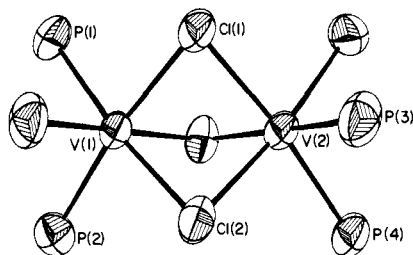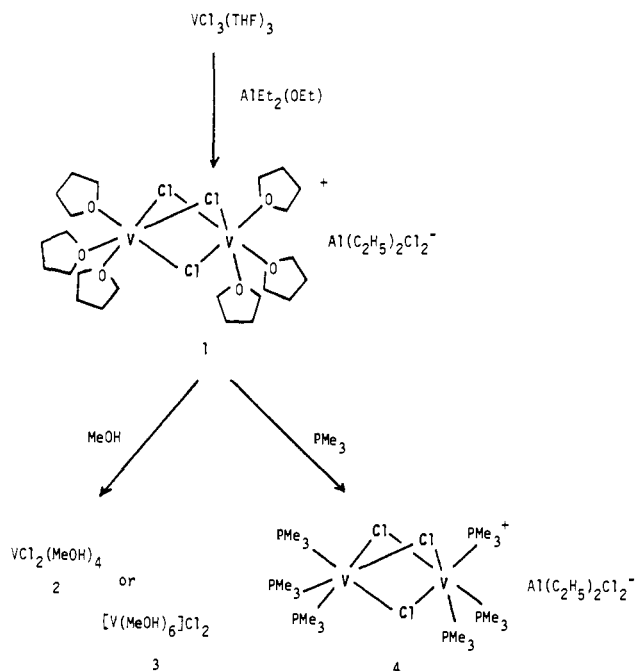
Figure 2. An ORTEP drawing of the $[V_2Cl_3(PMe_3)_6]^+$ ion without the disordered CH_3 groups. Thermal ellipsoids enclose 40% of electron density. A crystallographic mirror plane incorporates both vanadium atoms, Cl(1), P(2), and P(4).

Scheme I

excellently soluble in tetrahydrofuran, and the derivative with R = Et was selected to study the reactivity of this class of complexes. The overall general reaction patterns are depicted in Scheme I.

When $[(THF)_3V(\mu\text{-}Cl)_3V(THF)_3][AlCl_2Et_2]$ (**1**) is slowly added to methanol, ethane is given off and a dark blue solution is formed immediately. $VCl_2(MeOH)_4$ (**2**) or $[V(MeOH)_6]Cl_2$ (**3**) may be isolated from this solution after appropriate workup of the reaction mixture (See Experimental Section). The composition of **2** was established by elemental analysis; compound **3** was also fully characterized by X-ray crystallography; details of the structure will be discussed below. The reaction of **1** with an excess of methanol is a novel process wherein a compound containing two vanadium atoms in a confacial bioctahedral structure and an aluminum atom is used to form a mononuclear complex of vanadium only. The attempted replacement of the THF ligands by the more strongly coordinating MeOH ligands proceeds further and leads to complete destruction of the face-sharing bioctahedron structure. The reaction is smooth, clean, and immediate as compared to the already described electrochemical process for $VX_2(MeOH)_n$ (X = Cl, n = 2, 4; X = Br, n = 2, 4, 6; X = I, n = 4, 6) preparation.[9]

The compound $[(THF)_3V(\mu\text{-}Cl)_3V(THF)_3][AlEt_2Cl_2]$ (**1**) reacts readily with trimethylphosphine in tetrahydrofuran to give a red-purple crystalline product, that has been shown by X-ray analysis to be the compound $[(PMe_3)_3V(\mu\text{-}Cl)_3V(PMe_3)_3]\cdot[AlEt_2Cl_2]$ (**4**). This composition is also substantiated by elemental analysis. A detailed structural description is given below.

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Table II. Positional and Isotropic Equivalent Thermal Parameters for $[V_2Cl_3(PMe_3)_6]AlCl_2Et_2$ (**4**)[a]

atom	x	y	z	B (Å²)
V(1)	0.1480 (3)	0.250	−0.0718 (2)	4.6 (1)
V(2)	−0.0413 (3)	0.250	−0.1404 (2)	5.2 (1)
Cl(1)	0.1486 (5)	0.250	−0.1590 (3)	7.7 (2)
Cl(2)	0.0046 (4)	0.1174 (5)	−0.0798 (2)	6.7 (1)
P(1)	0.2836 (4)	0.4003 (5)	−0.0704 (2)	7.5 (2)
P(2)	0.1183 (7)	0.250	0.0163 (3)	6.6 (2)
P(3)	−0.0682 (4)	0.0997 (6)	−0.1990 (2)	7.9 (2)
P(4)	−0.2303 (6)	0.250	−0.1109 (3)	6.9 (2)
C(11)	0.235 (3)	0.533 (3)	−0.080 (1)	10 (1)*
C(12)	0.372 (3)	0.431 (3)	−0.019 (1)	10 (1)*
C(13)	0.379 (3)	0.386 (3)	−0.122 (1)	7 (1)*
C(14)	0.327 (3)	0.453 (4)	−0.133 (1)	7 (1)*
C(15)	0.411 (3)	0.375 (3)	−0.040 (1)	7 (1)*
C(16)	0.232 (3)	0.524 (4)	−0.046 (2)	8 (1)*
C(21)	0.201 (3)	0.174 (3)	0.057 (2)	10 (1)*
C(22)	0.106 (3)	0.377 (3)	0.044 (1)	7 (1)*
C(23)	−0.003 (3)	0.188 (3)	0.036 (1)	9 (1)*
C(31)	−0.197 (3)	0.072 (3)	−0.229 (1)	8 (1)*
C(32)	0.008 (3)	0.119 (3)	−0.255 (1)	9 (1)*
C(33)	−0.031 (4)	−0.037 (4)	−0.179 (2)	15 (2)*
C(34)	0.051 (4)	0.059 (4)	−0.230 (2)	8 (1)*
C(35)	−0.121 (4)	−0.023 (5)	−0.173 (2)	8 (2)*
C(36)	−0.157 (4)	0.130 (4)	−0.249 (2)	8 (1)*
C(41)	−0.262 (3)	0.128 (3)	−0.077 (1)	7 (1)*
C(42)	−0.342 (4)	0.250	−0.156 (2)	5 (1)*
C(43)	−0.249 (4)	0.307 (4)	−0.055 (2)	3 (1)*
C(44)	−0.284 (5)	0.121 (6)	−0.105 (2)	7 (2)*
C(45)	−0.351 (4)	0.310 (5)	−0.144 (2)	4 (2)*
Al	−0.013 (1)	0.250	0.3583 (5)	12.2 (4)
Cl(5)	0.043 (1)	0.250	0.4308 (5)	12.2 (4)*
Cl(6)	−0.091 (1)	0.401 (1)	0.3725 (6)	16.1 (6)*
C(1)	0.104 (4)	0.197 (4)	0.314 (2)	13 (2)*
C(2)	−0.100 (2)	0.114 (2)	0.341 (1)	10.4 (8)*
C(3)	0.206 (3)	0.250	0.322 (1)	15*
C(4)	−0.165 (6)	0.206 (6)	0.303 (3)	15*
C(5)	−0.052 (7)	0.250	0.467 (3)	15*

[a] Asterisked atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table III. Important Interatomic Distances (Å) and Angles (deg) for the $V_2Cl_3(PMe_3)_6^+$ Cation[a]

A. Distances			
V(1)–V(2)	3.103 (4)	V(2)–Cl(1)	2.469 (5)
Cl(1)	2.492 (6)	Cl(2)	2.468 (4)
Cl(2)	2.476 (4)	P(3)	2.540 (5)
P(1)	2.553 (5)	P(4)	2.546 (6)
P(2)	2.543 (7)		

B. Angles			
Cl(1)–V(1)–Cl(2)	84.8 (2)	Cl(1)–V(2)–Cl(2)	85.4 (1)
P(1)	90.7 (2)	P(3)	89.4 (2)
P(2)	171.6 (2)	P(4)	173.1 (2)
Cl(2)–V(1)–Cl(2)′	84.2 (2)	Cl(2)–V(2)–Cl(2)′	84.6 (2)
P(1)	173.1 (2)	P(3)	89.7 (1)
P(1)′	90.2 (1)	P(3)′	172.6 (2)
P(2)	89.0 (2)	P(4)	89.5 (2)
P(1)–V(1)–P(1)′	95.0 (2)	P(3)–V(2)–P(3)′	95.6 (3)
P(2)	94.9 (2)	P(4)	95.2 (2)
		V(1)–Cl(1)–V(2)	77.4 (2)
		V(1)–Cl(2)–V(2)	77.7 (1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Crystal Structure of $[V_2Cl_3(PMe_3)_6][AlCl_2Et_2]$ (4). The positional and isotropic equivalent thermal vibration parameters are listed in Table II. Important interatomic distances and angles for the $[V_2Cl_3(PMe_3)_6]^+$ cation are given in Table III. Complete listings of bond distances and angles are included in the supplementary material. An ORTEP drawing of the $V_2Cl_3P_6$ core is shown in Figure 2.

The compound is composed of discrete $[V_2Cl_3(PMe_3)_6]^+$ cations and $[AlCl_2Et_2]^-$ anions. Both species reside on crystallographic

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Table IV. A Comparison of Selected Interatomic Dimensions in the $V_2Cl_3L_6^+$ Ions

	L = PMe$_3$	L = C$_4$H$_8$O
	Interatomic Distances, Å	
V–V'	3.103 (4)	2.993 (1)
V–Cl	2.475 [4]	2.478 [3]
V–L	2.546 [3]	2.147 [7]
	Bond Angles, deg	
Cl–V–Cl'	84.2–85.4	87.02–87.45
V–Cl–V'	77.4–77.7	74.24–74.53
L–V–L'	94.9–95.6	85.86–89.55
trans Cl–V–L	171.6–173.1	175.73–178.56

Table V. Positional and Isotropic Equivalent Thermal Parameters for [V(CH$_3$OH)$_6$]Cl$_2$ (3)^a

atom	x	y	z	B (Å^2)
V	0.000	0.000	0.000	2.71 (2)
Cl	−0.0208 (2)	−0.2442 (2)	0.3755 (2)	4.53 (3)
O(1)	−0.0459 (6)	−0.0164 (4)	0.2003 (4)	4.3 (1)
O(2)	−0.2911 (6)	0.0654 (4)	−0.0400 (4)	4.12 (9)
O(3)	0.1083 (6)	0.1843 (4)	0.0285 (4)	4.5 (1)
C(1)	−0.035 (1)	0.0768 (7)	0.3007 (7)	6.2 (2)
C(2)	−0.402 (1)	0.0799 (6)	−0.1674 (6)	4.6 (2)
C(3)	0.014 (1)	0.2987 (6)	−0.0111 (7)	4.7 (1)

^{a} Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

**Table VI.** Bond Distances (Å) and Angles (deg) in the V(CH$_3$OH)$_6^{2+}$ Cation^a

A. Distances			
V–O(1)	2.132 (4)	O(1)–C(1)	1.439 (8)
V–O(2)	2.128 (4)	O(2)–C(2)	1.444 (7)
V–O(3)	2.137 (4)	O(3)–C(3)	1.434 (8)

B. Angles			
O(1)–V–O(2)	88.0 (2)	V–O(1)–C(1)	129.5 (4)
O(1)–V–O(3)	92.0 (2)	V–O(2)–C(2)	126.6 (4)
O(2)–V–O(3)	91.4 (2)	V–O(3)–C(3)	128.7 (4)

^{a} Numbers in parentheses are estimated standard deviations in the least significant digits.

mirror planes. The former is positioned so that the two vanadium atoms as well as Cl(1), P(2), and P(4) are in the plane. The cation has a structure analogous to that of the [V$_2$Cl$_3$(THF)$_6$]$^+$ ion.[1] It is a confacial bioctahedron with a *fac* disposition of the ligands around each of the metal atoms, which share a common Cl$_3$ face. In Table IV a comparison of some relevant interatomic dimensions in both ions is presented. While the average V–Cl bond lengths are practically identical in both species, the metal–metal distance is a little longer in the phosphine complex. This elongation results in more acute Cl–V–Cl' angles and more obtuse V–Cl–V' angles with respect to the THF adduct. Distortions of the octahedral environment around the metal atoms (see Table IV) indicate that steric factors are the primary reason for the changes in the central V(μ-Cl)$_3$V region. Spatial crowding of PMe$_3$ molecules causes the VP$_3$ pyramid to be flattened in comparison to the VO$_3$ one; thus the repulsive forces between Cl and P atoms do not allow as close an approach of the V atoms.

Crystal Structure of [V(CH$_3$OH)$_6$]Cl$_2$ (3). The positional and isotropic equivalent thermal vibration parameters are listed in Table V. Bond distances and angles in the [V(CH$_3$OH)$_6$]$^{2+}$ cation are presented in Table VI. ORTEP drawings of the cation and of the unit cell are shown in Figures 3 and 4.

The unit cell of compounds 3 consists of two [V(CH$_3$OH)$_6$]$^{2+}$ ions residing on crystallographic inversion centers and four uncoordinated chloride ions. Each cation is surrounded in the lattice by a distorted octahedron of Cl$^-$ ions (Cl–V–Cl' angles in the range 77 to 102°) located 4.6 to 4.7 Å from the V atom. The VO$_6$ unit has only slight distortions from the ideal octahedral geometry with an average V–O distance equal to 2.132 [3] Å.
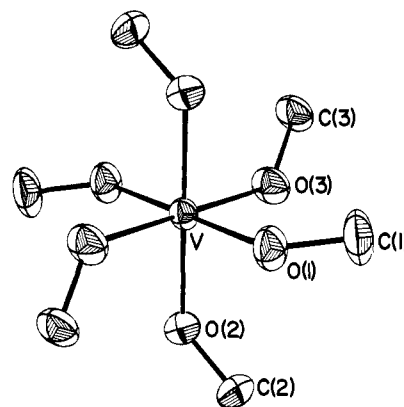
Figure 3. An ORTEP drawing of the [V(CH$_3$OH)$_6$]$^{2+}$ cation. Thermal ellipsoids enclose 40% of electron density. The V atom resides on an inversion center which relates the halves of the molecule.
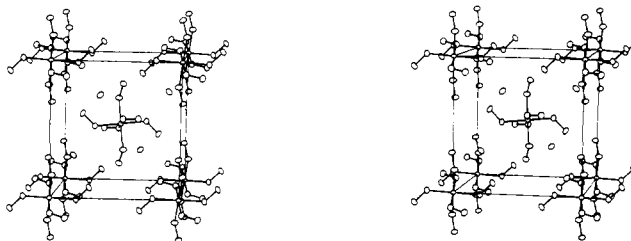
Figure 4. A stereoscopic view of the unit cell of [V(CH$_3$OH)$_6$]Cl$_2$.
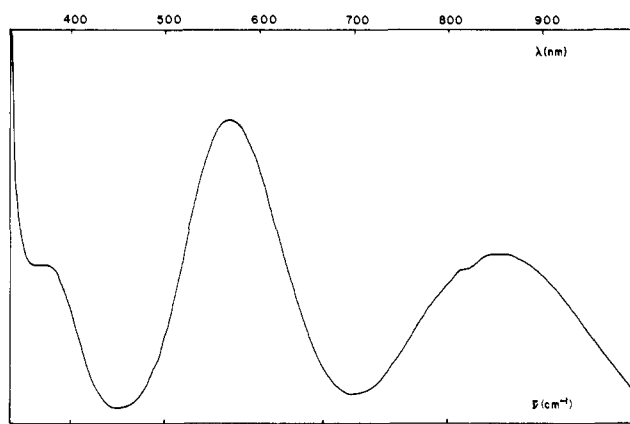
Figure 5. The visible spectrum of [V(CH$_3$OH)$_6$]Cl$_2$ in the region 340–1000 nm; 0.07 M solution in CH$_3$OH.

A similar value of the V–O bond length, equal to 2.15 [2] Å, is found in the [V(H$_2$O)$_6$]$^{2+}$ cation present in the Tutton salt, (NH$_4$)$_2$[V(H$_2$O)$_6$](SO$_4$)$_2$.[10]

Spectrum and Electronic Structure of the [V(CH$_3$OH)$_6$]$^{2+}$ Ion. The blue-purple color of [V(CH$_3$OH)$_6$]Cl$_2$ is consistent with its composition and structure if we recall that compounds containing the [V(H$_2$O)$_6$]$^{2+}$ ion are characteristically purple or violet in color. The electronic absorption spectrum is shown in Figure 5. It is very similar to that of the [V(H$_2$O)$_6$]$^{2+}$ ion and can be similarly assigned.[11] The spectrum we have recorded is in good agreement with that previously reported[12] (only in the form of numerical values of band energies) for a solution of "VCl$_2$" in methanol. The band energies suggest a slightly weaker ligand field for six methanol ligands compared to six water molecules, as might have been expected. There is a slight inflection on the high-energy site of the $^4A_{2g} \rightarrow {}^4T_{2g}$ transition which is probably attributable to

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the spin-forbidden $^4A_{2g} \rightarrow {}^2E_{1g}, {}^2T_{1g}$ transitions.

The compound $V(CH_3OH)_4Cl_2$ has not been structurally characterized since we have not yet found a way to obtain suitable crystals. Judging by its color and composition we assume that it too contains octahedrally coordinated vanadium(II). This compound has been mentioned previously[12] without any indication of its preparation. It was reported to have essentially a spin-only magnetic moment with but slight temperature dependence, from which the conclusion was drawn that it consists of discrete $VCl_2(CH_3OH)_4$ molecules.

Concluding Remarks. Even though severe difficulties with crystallographic disorder have made it impossible for us to obtain complete or accurate structures for $[V_2Cl_3(THF)_6][AlCl_2R_2]$ compounds, the presence of the dinuclear cation, very similar to that in $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$, was established and there are other physical data to show that it is the same species in all compounds. The visible spectra of both $[V_2Cl_3(THF)_6][AlCl_2R_2]$ compounds in CH_2Cl_2 and THF are identical with that of $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$. In addition, the magnetic moment of $[V_2Cl_3(THF)_6][AlCl_2Et_2]$ at 303 K is 3.38 μ_B; this is equivalent to 2.39 μ_B per metal ion, which is well below the spin-only value of 3.85 μ_B that would be expected for independent high-spin d^3 ions. It is consistent with the strong antiferromagnetic coupling ($J = -75$ cm^{-1}) found by Teuben et al.[1c] in $[V_2Cl_3(THF)_6]_2$-$[Zn_2Cl_6]$. The appearance of strong, double, spin-flip transitions in all of the visible spectra is also evidence for strong antiferromagnetic interaction between pairs of $S = {}^3/_2$ V^{II} ions.

The magnetic moment of 3.73 μ_B for $[V_2Cl_3(PMe_3)_6][AlCl_2Et_2]$ at 303 K indicates that here again there is significant antiferromagnetic coupling, but less than in the $[V_2Cl_3(THF)_6]^+$ ion. This may be due in part to the greater V···V distance: 3.103 Å vs. ca. 2.98 Å in the THF-containing complex.

In view of the reformulation[1] of "VCl$_2$(THF)$_2$" as $[V_2Cl_3$-$(THF)_6]_2Zn_2Cl_6$, the question of whether "VCl$_2$(PEt$_3$)$_2$", reportedly obtained from "VCl$_2$(THF)$_2$" by reaction with PEt$_3$ in benzene[13] ought to be reformulated as $[V_2Cl_3(PEt_3)_6]_2Zn_2Cl_6$

naturally arises, and our characterization of $[V_2Cl_3(PMe_3)_6]$-$AlEt_2Cl_2$, obtained from $[V_2Cl_3(THF)_6]AlEt_2Cl_2$, encourages such a speculation. From the gram susceptibility of 3.78×10^{-6} emu at 308 K reported for "VCl$_2$(PEt$_3$)$_2$", we can calculate a magnetic moment of ca. 3.3 μ_B per $[V_2Cl_3(PEt_3)_6][Zn_2Cl_6]_{1/2}$, which is in adequate agreement with the values of 3.73 and 3.38 μ_B that we have measured for the $[V_2Cl_3(PMe_3)_6]^+$ and $[V_2Cl_3(THF)_6]^+$ ions, respectively. However, this line of inferential reasoning may be too simplistic. We note first that "VCl$_2$(PEt$_3$)$_2$" is reported to be green, whereas our compound **4** is red-purple. Second, in preliminary experiments we find that the colors of compounds of the $[V_2Cl_3(PR_3)_6]AlR_2Cl_2$ type are strongly influenced by the solvents used to prepare them or to redissolve them. We believe that more work is required to determine the nature of "VCl$_2$-(PEt$_3$)$_2$" as well as to clarify the behavior of the $[V_2Cl_3(PR_3)_6]^+$ ions in solution.

We would emphasize that the new synthetic procedures reported here are very efficient and afford a very practical entry into nonaqueous vanadium(II) chemistry. The smooth conversion of the $[V_2Cl_3(THF)_6][AlCl_2R_2]$ compounds to $[V(MeOH)_6]Cl_2$ and $V(MeOH)_4Cl_2$, which are in turn convenient, soluble compounds not containing any other metallic element, is notable.

Supplementary Material Available: Tables of anisotropic thermal parameters, all bond distances and angles, and observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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Structure and Redox Properties of the Water-Oxidation Catalyst [(bpy)₂(OH₂)RuORu(OH₂)(bpy)₂]⁴⁺

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Abstract: The crystal and molecular structure of the water-oxidation catalyst μ-oxobis[aquabis(2,2′-bipyridine)ruthenium(III)] perchlorate dihydrate, [(bpy)$_2$(OH)$_2$RuORu(OH$_2$)(bpy)$_2$](ClO$_4$)$_4$·2H$_2$O [where bpy is C$_{10}$H$_8$N$_2$], has been determined from three-dimensional X-ray counter data. The complex crystallizes in the monoclinic space group $C2/c$ with four molecules in a cell of dimensions $a = 22.712$ (9) Å, $b = 13.189$ (4) Å, $c = 20.084$ (5) Å, $\beta = 122.08$ (3)°. The structure has been refined to a value of the weighted R factor of 0.052 based on 2887 independent intensities with $I \geq 3\sigma(I)$. The structure shows that the bridging Ru–O–Ru angle is 165.4°, the Ru–O bond lengths being 1.869 (1) Å. Electrochemical studies show that the Ru^{III}–Ru^{III} dimer undergoes an initial one-electron oxidation to Ru^{III}–Ru^{IV} and that the potential of the couple has a complex pH dependence because of the acid–base properties of the two redox states. Above pH 2.2, oxidation to Ru^{III}–Ru^{IV} is followed by a two-electron oxidation to [(bpy)$_2$(O)Ru^{IV}ORu^V(O)(bpy)$_2$]$^{3+}$ followed by a pH-independent, one-electron oxidation to [(bpy)$_2$(O)Ru^{V}ORu^V(O)(bpy)$_2$]$^{4+}$. In solutions more acidic than 2.2, Ru^{IV}–Ru^V is unstable with respect to disproportionation, and oxidation of the Ru^{III}–Ru^{IV} dimer to [(bpy)$_2$(O)Ru^{V}ORu^V(O)(bpy)$_2$]$^{4+}$ occurs via a three-electron step.

There is an emerging, diverse redox chemistry associated with the higher oxidation states of polypyridyl complexes of ruthenium and osmium containing aqua ligands. Depending on the pH,

oxidation can be accompanied by loss of protons to give hydroxo or oxo complexes which in the higher oxidation states are stabilized by p $\rightarrow$ dπ electronic donation,[1] e.g.,