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Organometallic Oxides: Preparation and Properties of the Clusters $[(\eta\text{-}C_5Me_5)V(\mu_3\text{-}O)]_4$ and $[(\eta\text{-}C_5Me_5)V]_4(\mu\text{-}O)_6$ by Reductive Aggregation of $(\eta\text{-}C_5Me_5)VCl_2(O)$

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Reduction of $Cp^*VCl_2(O)$ ($Cp^* = \eta\text{-}C_5Me_5$) by the powerful reductants sodium, potassium, magnesium, or calcium or the amalgams of these metals gave a mixture of the black cubane-like cluster $[Cp^*V(\mu_3\text{-}O)]_4$ and the black-green adamantane-like cluster $[Cp^*V]_4(\mu\text{-}O)_6$. A concurrent coproduct of the formation of $[Cp^*V]_4(\mu\text{-}O)_6$ was dark purple $[Cp^*V(\mu\text{-}Cl)_2]_3$. The formation of $[Cp^*V]_4(\mu\text{-}O)_6$ was favored in toluene, whereas $[Cp^*V(\mu_3\text{-}O)]_4$ was favored in tetrahydrofuran. The identity of the reductant did not influence the ratio of $[Cp^*V]_4(\mu\text{-}O)_6$ to $[Cp^*V(\mu_3\text{-}O)]_4$ produced. A scheme for the reduction is proposed; the key intermediate is $[Cp^*VClO]_2$. The cluster $[Cp^*V(\mu_3\text{-}O)]_4$ was paramagnetic ($\mu_{eff} = 2.35\ \mu_B$ at 300 K), and $[Cp^*V]_4(\mu\text{-}O)_6$ was diamagnetic. The syntheses of $[Cp^*VCl(O)]_2(\mu\text{-}O)$ by treatment of $Cp^*VCl_2(O)$ with Ag_2CO_3 and $[Cp^*VCl(\mu\text{-}O)]_4$ (which is paramagnetic, $\mu_{eff} = 4.51\ \mu_B$ at 300 K) by reduction of $Cp^*VCl_2(O)$ with mercury are reported.

Introduction

We have been preparing organometallic clusters that exhibit exchange interactions between the metal atoms.[1,2] Of particular interest were the cubanes of general formula $[Cp'M(\mu_3\text{-}A)]_4$ ($Cp' = \eta\text{-}C_5R_5$; M = d-block metal; A = p-block element, **1**)[2−20] and the adamantanes $[Cp'M]_4(\mu_2\text{-}O)_6$ (**2**)[21−23] containing tetrahedra of metal atoms. The many $[Cp'M(\mu_3\text{-}A)]_4$ (A = S, Se) cubanes either were diamagnetic or exhibited simple paramagnetic behavior with no evidence for significant exchange interactions.[3,5−19] However $[Cp'Cr(\mu_3\text{-}O)]_4$ ($Cp' = \eta\text{-}C_5H_5$ (Cp),[2] $\eta\text{-}C_5H_4Me$ (CpMe),[3] or $\eta\text{-}C_5Me_5$ (Cp*)[4]) were antiferromagnetic. The adamantane $[Cp^*Ti]_4(\mu\text{-}O)_6$ was diamagnetic,[21,22] and the magnetic behavior of $[Cp^*V]_4(\mu\text{-}O)_6$ was uncertain.[23,24]

Because of the antiferromagnetism of $[Cp'Cr(\mu_3\text{-}O)]_4$, we wished to investigate the magnetic behavior of the vanadium analogues $[Cp'V(\mu_3\text{-}O)]_4$ and of the previously reported $[Cp^*V]_4(\mu\text{-}O)_6$.[23] The neutral $[Cp'Cr(\mu_3\text{-}O)]_4$ clusters were prepared by mild oxidation of Cp'_2Cr.[2−4,25] Similar oxidations of Cp'_2V gave a wealth of clusters including $[Cp^*V]_4(\mu\text{-}O)_6$,[23−28] but the only indication of

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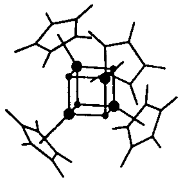
$[\mathrm{Cp'V}(\mu_3\text{-O})]_4$ was the observation of $[(\mathrm{C_5H_5})\mathrm{VO}]_4$ in the mass spectrum of the products of the oxidation of $\mathrm{Cp_2V}$ by $\mathrm{C_5H_5NO}$.[28] Recently we have been investigating the reductive aggregation of $\mathrm{Cp^*MCl}_n(\mathrm{A})$ complexes as a route to clusters containing the hard ligands nitrogen or oxygen as the A atom.[20,29,30] It appeared from their stoichiometries that reduction of $\mathrm{Cp^*VCl_2(O)}$[31−34] or $[\mathrm{Cp^*VCl}(\mu\text{-O})]_4$ (**3**)[31] would give $[\mathrm{Cp^*V}(\mu_3\text{-O})]_4$ and reduction of $[\mathrm{Cp^*VCl(O)}]_2(\mu\text{-O})$[32] would give $[\mathrm{Cp^*V}]_4(\mu\text{-O})_6$. An efficient synthesis of $\mathrm{Cp^*VCl_2(O)}$ has been described,[33,34] but none for $[\mathrm{Cp^*VCl}(\mu\text{-O})]_4$ or $[\mathrm{Cp^*VCl(O)}]_2(\mu\text{-O})$. Therefore we initially devised synthetic routes to these compounds, starting from $\mathrm{Cp^*VCl_2(O)}$. Reduction of $[\mathrm{Cp^*VCl}(\mu\text{-O})]_4$ or $[\mathrm{Cp^*VCl(O)}]_2(\mu\text{-O})$ did not give the desired clusters, but reduction of $\mathrm{Cp^*VCl_2(O)}$ gave $[\mathrm{Cp^*V}(\mu_3\text{-O})]_4$. The reductive aggregation was complicated by a concurrent redox disproportionation reaction, which gave $[\mathrm{Cp^*V}]_4(\mu\text{-O})_6$ and $[\mathrm{Cp^*V}(\mu\text{-Cl})_2]_3$ (**4**[33−35]). A scheme for the formation of the clusters is proposed, and the physical properties of $[\mathrm{Cp^*VCl}(\mu\text{-O})]_4$, $[\mathrm{Cp^*V}(\mu_3\text{-O})]_4$, and $[\mathrm{Cp^*V}]_4(\mu\text{-O})_6$ are discussed.



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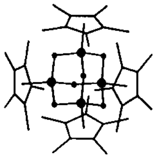

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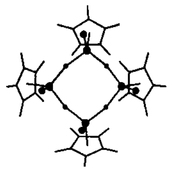

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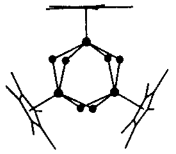

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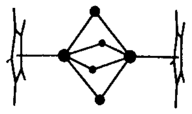

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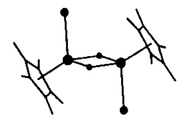

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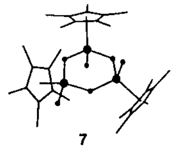

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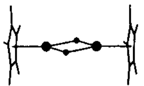

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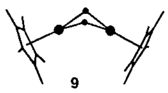

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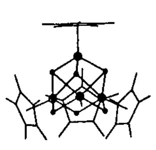

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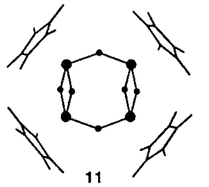

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Experimental Section

General Information. All manipulations were performed using a standard double-manifold vacuum/argon line. Solvents were predried, stored on the vacuum line over a drying agent, and distilled directly onto reagents. The starting material $\mathrm{Cp^*VCl_2(O)}$ was prepared by the literature method.[33,34] Metallic reducing agents were either freshly cut under argon (potassium, sodium) or flame dried under vacuum (magnesium, calcium). Metal amalgams were prepared by syringing mercury onto the predried metal under a counterflow of argon. The mercury was purified by first washing with dilute nitric acid, then with distilled water until the washings were neutral, then with acetone. It was heated at 100 °C under vacuum for 12 h before use.

Magnetic susceptibilities were measured on a Quantum Design (MPMS) SQUID magnetometer at UBC. The applied field was 10 000 G unless otherwise specified. All susceptibilities were corrected for the background signal of the magnetometer and sample holder, and for the diamagnetism of all atoms using Pascal's constants.[36] Other instruments were Varian XL200 or Unity 400 spectrometers for ^{1}H and ^{51}V NMR and a Kratos MS 50 instrument for mass spectra. Infrared spectra were measured as KBr pellets or Nujol mulls on a Perkin-Elmer 683 instrument. Microanalyses were by Galbraith Laboratories, Knoxville, TN. Extended Hückel molecular orbital calculations were performed using the CAChe system.

Synthesis of $[\mathrm{Cp^*V(O)Cl}]_2(\mu\text{-O})$. To a solution of $\mathrm{Cp^*VCl_2(O)}$ (0.75 g, 2.75 mmol) in tetrahydrofuran (100 cm^3), contained in a 250 cm^3 sidearm flask, was added freshly prepared $\mathrm{Ag_2CO_3}$[37] (0.75 g, 2.72 mmol). The mixture was stirred for 24 h, with the sidearm open to a mercury pressure-release valve at atmospheric pressure, to allow for release of $\mathrm{CO_2}$. The flask was evacuated, the sidearm closed, and the mixture stirred for a further 24 h. The mixture was then filtered through Celite to remove the off-white precipitate (presumed to be silver chloride) which had formed. The filtrate was reduced in volume to 10 cm^3 under vacuum, then frozen in a liquid nitrogen bath, and hexane 50 cm^3 was layered on to it. On warming to room temperature, dark green $[\mathrm{Cp^*V(O)Cl}]_2(\mu\text{-O})$ precipitated. It was collected by filtration, washed with hexane, and dried under vacuum. Yield: 0.43 g, 0.88 mmol, 64%. Anal. Found: C, 49.2; H, 6.0. Calcd for $\mathrm{C_{20}H_{30}Cl_2O_3V_2}$: C, 48.9; H, 6.2. Mass spectrum (EI, 70 eV, *m/z*, % abundance, assignment): 474, 2.1, $\mathrm{C_{20}H_{30}{}^{35}Cl_2O_2V_2}$ $(((\mathrm{C_5Me_5})\mathrm{VClO})_2)$; 455, 16.9, $\mathrm{C_{20}H_{30}{}^{35}ClO_3V_2}$ $(((\mathrm{C_5Me_5})\mathrm{VClO})((\mathrm{C_5Me_5})\mathrm{VO})\mathrm{O})$; 420, 14.1, $\mathrm{C_{20}H_{30}O_3V_2}$ $(((\mathrm{C_5Me_5})\mathrm{VO})_2\mathrm{O})$; 355, 6.9, $\mathrm{C_{10}H_{15}{}^{35}Cl_2O_3V_2}$ $(((\mathrm{C_5Me_5})\mathrm{VClO})(\mathrm{VClO})\mathrm{O})$; 320, 32.3, $\mathrm{C_{10}H_{15}{}^{35}ClO_3V_2}$ $(((\mathrm{C_5Me_5})\mathrm{VClO})(\mathrm{VO})\mathrm{O})$; 285, 14.6, $\mathrm{C_{10}H_{15}O_3V_2}$ $(((\mathrm{C_5Me_5})\mathrm{VO})(\mathrm{VO})\mathrm{O})$. ^{1}H NMR ($\mathrm{C_6{}^2H_6}$ solution): 2.04 ppm ($\Delta\nu_{1/2}$ 0.85 Hz). ^{1}H NMR ($\mathrm{C^2HCl_3}$ solution): 2.22 ppm ($\Delta\nu_{1/2}$ 2.9 Hz); lit. ($\mathrm{C^2HCl_3}$ solution) 2.22 ppm.[32] ^{51}V NMR ($\mathrm{C^2HCl_3}$ solution, 105 MHz, $\mathrm{VOCl_3}$ in $\mathrm{CCl_4}$ solution as external standard): −362 ppm; lit. ($\mathrm{C^2HCl_3}$ solution) −360 ppm.[32] Infrared spectrum: 945 cm^{-1} (w, sh), 965 cm^{-1} (s) (ν(V═O)); 725 cm^{-1} (s, br) (ν(V−O−V)); lit. 944 cm^{-1} (sh), 963 cm^{-1} (vs) (ν(V═O)); 730 cm^{-1} (br) (ν(V−O−V)).[32]

Synthesis of $[\mathrm{Cp^*VCl}(\mu\text{-O})]_4$. A solution of $\mathrm{Cp^*VCl_2(O)}$ (1.04 g, 3.81 mmol) in toluene (100 cm^3) was stirred with mercury (10 cm^3, 675 mmol) for 12 h, during which time the color changed from blue-green to brown and a white precipitate formed. The solution was decanted from the mercury, reduced in volume to 75 cm^3 under vacuum, then filtered through Celite. The resultant brown solution was frozen in liquid nitrogen and layered with hexane (75 cm^3). On warming to room temperature and setting aside for 12 h, fine brown needles of $[\mathrm{Cp^*VCl}(\mu\text{-O})]_4$ were deposited. These were collected by filtration, washed with hexane, and dried under vacuum. Yield: 0.59 g, 65%.

Reduction of $\mathrm{Cp^*VCl_2(O)}$ by Strong Reductants. Three types of experiment were performed: reduction of $\mathrm{Cp^*VCl_2}$-

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(O) in toluene or tetrahydrofuran with the amalgam of a strong metallic reductant; reduction of $Cp^*VCl_2(O)$ in toluene or tetrahydrofuran with the amalgam of a weak metallic reductant; and reduction of $Cp^*VCl_2(O)$ in tetrahydrofuran with a metallic or nonmetallic reductant. A representative example of each type of reduction is described.

1. Reduction of a Solution of $Cp^*VCl_2(O)$ in Toluene with Sodium Amalgam: Formation of $[Cp^*V]_4(\mu\text{-}O)_6$ and $[Cp^*V(\mu_3\text{-}O)]_4$. A solution of $Cp^*VCl_2(O)$ (1.33 g, 4.87 mmol) in toluene (100 cm^3) was added to sodium amalgam (0.92 g (40 mmol) sodium in 20 cm^3 mercury). The mixture was stirred vigorously for 12 h, during which time the solution changed color from blue-green to dark brown and a white precipitate (presumed to be sodium chloride) formed. The solution was decanted from the mercury and set aside for 24 h to allow the suspended solids to settle. The mixture was then filtered twice through acid-free Celite, giving a black residue and a green-black filtrate. CAUTION: the black residue was extremely pyrophoric when exposed to air; it was insoluble in nonpolar organic solvents, but reacted vigorously with protonic solvents. The toluene solvent was removed from the filtrate under vacuum, the resultant black residue extracted with hexane (100 cm^3), and the mixture filtered, giving a brown-black residue and a dark olive-green filtrate. After reducing the volume to 20 cm^3 under vacuum, the filtrate was set aside at −25 °C for 7 days, over which time black-green $[Cp^*V]_4(\mu\text{-}O)_6$ precipitated. It was collected by filtration and dried under vacuum. Yield: 0.40 g, 40%. The brown-black residue was extracted three times with toluene (100 cm^3 portions). The volume of the combined extracts was reduced to 20 cm^3 under vacuum and hexane (80 cm^3) added. On setting the solution aside at −25 °C for 4 days, black $[Cp^*V(\mu_3\text{-}O)]_4$ precipitated. It was collected by filtration and dried under vacuum. Yield: 0.15 g, 15%. Crystals suitable for X-ray diffraction were obtained by setting aside a saturated chloroform solution at room temperature for several days.

2. Reduction of a Solution of $Cp^*VCl_2(O)$ in Toluene with Magnesium Amalgam: Formation of $[Cp^*V]_4(\mu\text{-}O)_6$, $[Cp^*V(\mu_3\text{-}O)]_4$, and $[Cp^*V(\mu\text{-}Cl)_2]_3$. A solution of $Cp^*VCl_2(O)$ (1.80 g, 6.59 mmol) in toluene (100 cm^3) was added to magnesium amalgam (0.49 g (40 mmol) magnesium in 20 cm^3 mercury). The mixture was stirred vigorously for 12 h, during which time the solution changed color from blue-green to dark brown and a white precipitate formed. The solution was decanted from the mercury and set aside for 24 h to allow the suspended solids to settle. The mixture was then filtered twice through acid-free Celite, giving a gray, air-stable, residue (presumed to be magnesium dichloride) and a green-black filtrate. The toluene solvent was removed from the filtrate under vacuum and the resultant black residue extracted with hexane (100 cm^3) for 30 min. The mixture was then filtered, giving a brown-black residue and a dark olive-green filtrate. After reducing the volume to 20 cm^3 under vacuum, the filtrate was set aside at −25 °C for 7 days, over which time black-green $[Cp^*V]_4(\mu\text{-}O)_6$ precipitated. It was collected by filtration and dried under vacuum. Yield: 0.28 g, 20%. The brown-black residue was extracted three times with toluene (100 cm^3 portions). The volume of the combined extracts was reduced to 40 cm^3 under vacuum and hexane (60 cm^3) added. On setting the solution aside at −25 °C for 4 days, a black precipitate formed. Filtration of the mixture gave black $[Cp^*V(\mu_3\text{-}O)]_4$ (yield 0.33 g, 25%) and a dark filtrate. The hexane/toluene solvent mixture was removed from the filtrate under vacuum, giving an oily brown residue. This was extracted with tetrahydrofuran (30 cm^3), producing a red-brown solution which was layered with diethyl ether (40 cm^3). On setting aside at 4 °C for 18 days, the solution deposited dark purple crystals of $[Cp^*V(\mu\text{-}Cl)_2]_3$, which were suitable for X-ray diffraction. Yield: 0.15 g, 9%.

3. Reduction of a Solution of $Cp^*VCl_2(O)$ in Tetrahydrofuran with Magnesium: Formation of $[Cp^*V]_4(\mu\text{-}O)_6$, $[Cp^*V(\mu_3\text{-}O)]_4$, and $[Cp^*V(\mu\text{-}Cl)_2]_3$. A solution of $Cp^*VCl_2(O)$ (1.86 g, 6.81 mmol) in tetrahydrofuran (150 cm^3) was added to magnesium turnings (0.55 g, 22.6 mmol). The mixture was stirred for 48 h, during which time the solution changed color from blue-green to dark brown and a white precipitate (presumed to be magnesium dichloride) formed. The mixture was filtered through acid-free Celite and the tetrahydrofuran solvent removed from the filtrate under vacuum, leaving an oily brown residue. This was warmed (50 °C) under dynamic vacuum for 1 h to remove residual ethers. The resultant solid was extracted with hexane and worked up as described for the reduction of a solution of $Cp^*VCl_2(O)$ in toluene with magnesium amalgam above. Yield of $[Cp^*V]_4(\mu\text{-}O)_6$: 0.14 g, 10%. Yield of $[Cp^*V(\mu_3\text{-}O)]_4$: 0.48 g, 35%. Yield of $[Cp^*V(\mu\text{-}Cl)_2]_3$: 0.08 g, 5%.

Characterization of $[Cp^*VCl(\mu\text{-}O)]_4$. The needle-like crystals of $[Cp^*VCl(\mu\text{-}O)]_4$ had the unit cell dimensions $a = b = 16.53$ Å, $c = 8.99$ Å and showed tetragonal symmetry. The literature values are $a = b = 16.568$ Å, $c = 9.005$ Å, space group $I\bar{4}2m$.[31] Anal. Found: C, 50.9; H, 6.2. Calcd for $C_{40}H_{60}Cl_4O_4V_4$: C, 50.5; H, 6.4. Mass spectrum (FAB in a NOBA matrix; m/z, % abundance, assignment): 948, 0.3, $C_{40}H_{60}{}^{35}Cl_4O_4V_4$ $(((C_5Me_5)VClO)_4)$; 913, 0.1, $C_{40}H_{60}{}^{35}Cl_3O_4V_4$ $((C_5Me_5)_4V_4Cl_3O_4)$; 813, 0.3, $C_{30}H_{45}{}^{35}Cl_4O_4V_4$ $((C_5Me_5)_3V_4Cl_4O_4)$; 778, 0.2, $C_{30}H_{45}{}^{35}Cl_3O_4V_4$ $((C_5Me_5)_3V_4Cl_3O_4)$; 678, 6.3, $C_{20}H_{30}{}^{35}Cl_4O_4V_4$ $((C_5Me_5)_2V_4Cl_4O_4)$; 643, 0.9, $C_{20}H_{30}{}^{35}Cl_3O_4V_4$ $((C_5Me_5)_2V_4Cl_3O_4)$; 543, 5.8, $C_{10}H_{15}{}^{35}Cl_4O_4V_4$ $((C_5Me_5)V_4Cl_4O_4)$; 508, 0.4, $C_{10}H_{15}{}^{35}Cl_3O_4V_4$ $((C_5Me_5)V_4Cl_3O_4)$; 404, 4.5, $C_{20}H_{30}O_2V_2$ $((C_5Me_5)_2V_2O_2)$. ^1H NMR (C^2HCl_3 solution): −6.5 ppm ($\Delta\nu_{1/2} = 2590$ Hz). Infrared spectrum (Nujol mull): 1020 cm^{-1}, m; 805 cm^{-1}, w; 440 cm^{-1}, m, assigned to vibrations of the η-C_5Me_5 ligand; 720 cm^{-1}, m; and 610 cm^{-1}, w, assigned to vibrations of the $[VCl(\mu_2\text{-}O)]_4$ unit. The cluster was paramagnetic, with $\mu_{eff} = 4.51$ μ_B at 300 K.

Characterization of $[Cp^*V(\mu_3\text{-}O)]_4$. ^1H NMR ($C_6{}^2H_6$ solution): 0.86 ppm ($\Delta\nu_{1/2} = 14.7$ Hz); ^1H NMR (C^2HCl_3 solution): 0.75 ppm ($\Delta\nu_{1/2}$ 18.8 Hz). The cluster was paramagnetic with $\mu_{eff} = 2.35$ μ_B at 300 K. High-resolution mass spectrum: found $m/z = 808.22093$; calcd for $\{^{12}C_{40}{}^1H_{60}{}^{51}V_4{}^{16}O_4\}^+$ $(\{[(C_5Me_5)VO]_4\}^+)$ 808.22504. Low-resolution mass spectrum (EI, 70 eV): $m/z = 808$, 100% relative abundance, assigned to $\{C_{40}H_{60}V_4O_4\}^+$ $(\{[(C_5Me_5)VO]_4\}^+)$; 673, 13, $\{C_{30}H_{45}V_4O_4\}^+$ $(\{(C_5Me_5)_3V_4O_4\}^+)$; 538, 12, $\{C_{20}H_{30}V_4O_4\}^+$ $(\{(C_5Me_5)_2V_4O_4\}^+)$; 404, 58, $\{C_{20}H_{30}V_2O_2\}^+$ $(\{[(C_5Me_5)VO]_2\}^+)$. Peak envelopes centered at m/z 437, 1; 237, 0.6, and 202, 0.6 were assigned to $\{Hg_2Cl\}^+$, $\{HgCl\}^+$, and $\{Hg\}^+$, respectively, on the basis of the isotope patterns. Infrared spectrum: 2980 cm^{-1}, m; 2920 cm^{-1}, s; 2865 cm^{-1}, m; 1445 cm^{-1}, m; 1425 cm^{-1}, m; 1375 cm^{-1}, s; 1080 cm^{-1}, m; 1020 cm^{-1}, m; 860 cm^{-1}, m, assigned to vibrations of the η-C_5Me_5 ligand; 450 cm^{-1}, m, assigned to a vibration of the $[V(\mu_3\text{-}O)]_4$ core. Anal. (after two recrystallizations from toluene/hexane). Found: C, 53.35, 53.41; H, 6.8, 6.8; Cl 1.5, 2.1. Calcd for $C_{40}H_{60}Cl_{0.4}Hg_{0.4}O_4V_4$ $([(C_5(CH_3)_5)V_4O_4]\cdot 0.2(Hg_2Cl_2))$: C, 53.2; H, 6.7; Cl 1.6 (see Results and Discussion).

The cluster $[Cp^*V(\mu_3\text{-}O)]_4$ was also characterized by a partial determination of the crystal structure by X-ray diffraction. The intensities of 27 618 reflections (to $2\theta = 53°$) were measured on a Siemens P4 diffractometer equipped with a rotating anode (Mo Kα, $\lambda = 0.710\ 73$ Å) and a CCD detector, from a crystal of dimensions 0.30 × 0.30 × 0.30 mm, obtained by recrystallization of the cluster from chloroform. A full sphere of data was collected. The dimensions of a tetragonal cell were $a = 17.043(2)$ Å, $c = 12.009(2)$ Å. The cell volume (3488.18(1) Å^3) combined with M_r for $C_{40}H_{60}V_4O_4$ (808.76) gave $D_c = 1.54$ Mg m^{-3} for $Z = 4$. This calculated density may be compared to those of $[Cp^*V(\mu_3\text{-}N)]_4$, 1.35 Mg m^{-3};[20] $[Cp^*Cr(\mu_3\text{-}O)]_4$, 1.38 Mg m^{-3};[4] $[Cp^*V]_4(\mu\text{-}O)_6$, 1.35 Mg m^{-3};[23] $[Cp^*Ti]_4(\mu\text{-}O)_6$, 1.27 Mg m^{-3}.[21] The systematic absences and equivalent intensities indicated that the space group was $P4/n$, which reduced the 27 618 measured intensities to 3545 unique reflections, all of

Table 1. Distances (Å) and Angles (deg) in the $V_4(\mu\text{-}O)_6$ Core of $[Cp^*V]_4(\mu\text{-}O)_6$

V(1)−V(2)[a]	3.008 (3)	V(1)−V(3)	3.008 (3)[d]	V(1)−V(4)	2.999 (3)
V(2)−V(3)	3.006 (3)	V(2)−V(4)	3.003 (3)	V(3)−V(4)	3.002 (3)
V(1)−O(4)	1.812 (8)	V(1)−O(5)	1.803 (7)	V(1)−O(6)	1.799 (9)
V(2)−O(1)	1.818 (7)	V(2)−O(2)	1.806 (8)	V(2)−O(4)	1.801 (7)
V(3)−O(1)	1.807 (7)	V(3)−O(3)	1.804 (8)	V(3)−O(5)	1.815 (7)
V(4)−O(2)	1.816 (8)	V(4)−O(3)	1.812 (8)	V(4)−O(6)	1.818 (7)
V(1)−Cp*(1)[b]	2.00 (1)	V(2)−Cp*(2)[a]	2.01 (1)	V(3)−Cp*(3)[a]	2.03 (2)
V(2)−O(1)−V(3)	112.0 (4)	V(2)−O(2)−V(4)	112.0 (4)	V(3)−O(3)−V(4)	112.2 (4)
V(1)−O(4)−V(2)	112.7 (4)	V(1)−O(5)−V(3)	112.5 (4)	V(1)−O(6)−V(4)	112.0 (4)
O(4)−V(1)−O(5)	107.7 (4)	O(4)−V(1)−O(6)	107.8 (4)	O(5)−V(1)−O(6)	108.6 (4)
O(1)−V(2)−O(2)	107.7 (4)	O(1)−V(2)−O(4)	108.3 (3)	O(2)−V(2)−O(4)	108.1 (4)
O(1)−V(3)−O(3)	107.8 (4)	O(1)−V(3)−O(5)	108.2 (3)	O(3)−V(3)−O(5)	108.2 (4)
O(2)−V(4)−O(3)	107.8 (4)	O(2)−V(4)−O(6)	107.9 (4)	O(3)−V(4)−O(6)	108.5 (4)

[a] The numbering scheme is shown in Figure 4. [b] Cp* is the centroid of the C_5 ring of the η-C_5Me_5 ligand; the disordered Cp*(4) is excluded.

which were used in the structure determination and refinement. The multiplicity of the general position in space group $P4/n$ is eight. Thus there must be two independent $[Cp^*V(\mu_3\text{-}O)]_4$ units in the unit cell. Direct methods[38,39] readily gave the position of the $[V(\mu_3\text{-}O)]_4$ unit of one of the independent molecules, and subsequent difference Fourier syntheses revealed the carbon atoms of the η-C_5Me_5 ligands attached to the vanadium atoms of the same cluster. This molecule could be refined successfully, but no second cluster could be found. A single peak, surrounded by a halo of apparently lighter atoms at a distance of approximately 3.0 Å, occupied the remaining space in the unit cell. None of these peaks could be refined as atoms. The same result was obtained when the structure was refined with the unaveraged data (27 618 reflections) in space group $P\bar{1}$ or in the monoclinic space group $P2/n$. This phenomenon is similar to that observed previously for a crystal exhibiting merohedral twinning.[40,41] Attempts to solve this problem are continuing; the present results confirm the cubane-like geometry of $[Cp^*V(\mu_3\text{-}O)]_4$.

Characterization of $[Cp^*V]_4(\mu\text{-}O)_6$. The cluster $[Cp^*V]_4(\mu\text{-}O)_6$ was characterized by comparison of the spectroscopic properties with those reported previously.[23,24] ^1H NMR ($C_6{}^2H_6$ or C^2HCl_3 solution): 2.00 ppm ($\Delta\nu_{1/2} = 5.9$ Hz); lit.[23] 2.00 ppm ($\Delta\nu_{1/2}$ not specified). The cluster was diamagnetic. Mass spectrum (EI, 70 eV): $m/z = 840$, 17% relative abundance, assigned to $\{C_{40}H_{60}V_4O_6\}^+$ ($\{[(C_5Me_5)V]_4O_6\}^+$); 706, 6, $\{C_{30}H_{46}V_4O_6\}^+$ ($\{(C_5Me_5)_3V_4O_6 + H\}^+$); 622, 11, $\{C_{30}H_{45}V_3O_4\}^+$ ($\{(C_5Me_5)_3V_3O_3\}^+$); 554, 5, $\{C_{20}H_{30}V_4O_5\}^+$ ($\{(C_5Me_5)_2V_4O_5\}^+$); 504, 10, $\{C_{20}H_{31}V_3O_5\}^+$ ($\{(C_5Me_5)_2V_3O_5 + H\}^+$); 419, 10, $\{C_{10}H_{15}V_4O_5\}^+$ ($\{(C_5Me_5)V_4O_5\}^+$). Infrared spectrum: 2980 cm^{-1}, m; 2915, s; 2865, m; 1435, m; 1380, s; 1070, m; 1030, m, assigned to vibrations of the η-C_5Me_5 ligand; 740 cm^{-1}, s, br; 610, m; 390, m; assigned to vibrations of the V_4O_6 core.

The X-ray diffraction diffraction data for $[Cp^*V]_4(\mu\text{-}O)_6$, obtained by oxidation of $Cp^*{}_2V$,[24] were as follows: $C_{40}H_{60}O_6V_4$; M_r, 840.7; triclinic, $P\bar{1}$; $a = 11.077(5)$ Å, $b = 11.113(4)$ Å, $c = 18.394(10)$ Å, $\alpha = 83.59(4)°$, $\beta = 83.73(4)°$, $\gamma = 66.62(4)°$; $Z = 2$; crystal dimensions $0.60 \times 0.30 \times 0.20$ mm; 2θ limits 2−49.9°; 16 554 reflections collected by $\theta-2\theta$ scan on Enraf-Nonius CAD4 at 293 K; 7198 unique, 3873 observed ($I > 2.5\sigma(I)$) reflections; $R(F') = 0.085$, $R_w(F') = 0.13$; GoF = 1.53; max. Δ/σ 0.59; max., min. Δe 0.82, −0.57 e Å^{-3}. A thermal ellipsoid plot is shown in Figure 1. Table 1 lists the important distances and angles. Other details of the refinement are given in the Supporting Information.

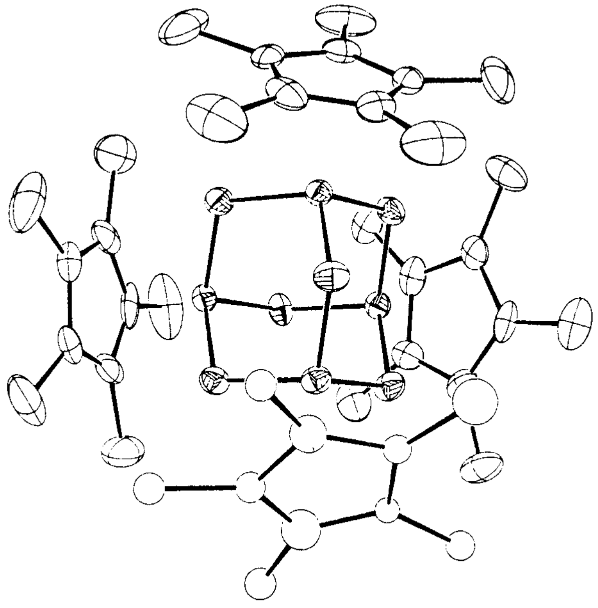

Figure 1. Thermal ellipsoid plot for $[Cp^*V]_4(\mu\text{-}O)_6$.

Characterization of $[Cp^*V(\mu\text{-}Cl)_2]_3$. ^1H NMR ($C_6{}^2H_6$ solution): −7.9 ppm ($\Delta\nu_{1/2}$ 52 Hz). Mass spectrum (EI, 70 eV): $m/z = 257$, 44% relative abundance, assigned to $\{C_{10}H_{16}V^{35}Cl_2\}^+$ ($\{(C_5Me_5)VCl_2 + H\}^+$); 221, 100, $\{C_{10}H_{16}V^{35}Cl\}^+$ ($\{(C_5Me_5)VCl + H\}^+$); 185, 18, $\{C_{10}H_{14}V\}^+$ ($\{(C_5Me_5)V - H\}^+$). The ^1H NMR and mass spectral results were identical to those found previously.[34] A crystalline product was obtained from the reaction between $Cp^*VCl_2(O)$ and magnesium amalgam in toluene. The crystals had the cell dimensions $a = 11.74$ Å, $b = 11.78$ Å, $c = 15.76$ Å, $\alpha = 68.53°$, $\beta = 88.02°$, $\gamma = 60.26°$, $V = 1733$ Å^3. The literature values for form II of $[Cp^*V(\mu\text{-}Cl)_2]_3$ were $a = 11.780(4)$ Å, $b = 11.802(3)$ Å, $c = 15.957(6)$ Å, $\alpha = 68.31(2)°$, $\beta = 87.84(3)°$, $\gamma = 60.21(2)°$, $V = 1788$ Å^3.[1]

Results and Discussion

Synthesis and Properties of $[Cp^*V(O)Cl]_2(\mu\text{-}O)$. The dark-green vanadium(V) compound $[Cp^*VCl(O)]_2(\mu\text{-}O)$ was previously prepared by Herberhold and coworkers from the reaction between "$Cp^*{}_3V_4O_9$" (obtained by oxidation of $Cp^*V(CO)_4$ with O_2) and Cp^*VCl_3.[32] These reactants are not readily accessible, and the overall yield from available starting materials was low. We found that the reaction between equimolar quantities of $Cp^*VCl_2(O)$ and Ag_2CO_3 rapidly gave $[Cp^*VCl(O)]_2(\mu\text{-}O)$ in 65% yield, according to eq 1. We showed previously that excess Ag_2CO_3 converted $Cp^*VCl_2(O)$

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Table 2. Products of the Reduction of $Cp^*VCl_2(O)$[a]

reductant	solvent	$[Cp^*V(\mu_3\text{-}O)]_4$	$[Cp^*V]_4(\mu\text{-}O)_6$	$[Cp^*V(\mu\text{-}Cl)_2]_3$	black material
Na/Hg	toluene	15	40		present
K/Hg	toluene	8	36		present
Ca/Hg	toluene	12	40		present
Mg/Hg	toluene	25	20	9	absent
Na/Hg	thf	15	trace		present
K/Hg	thf	11	trace		present
Ca/Hg	thf	17	trace		present
Mg/Hg	thf	32	12	5	absent
Mg (turnings)	thf	35	10	5	absent
Ca (shot)	thf	41	8		absent
Li_3N	thf	18	7	4	absent

[a] As % yield of purified product.

into $[Cp^*V(O)(\mu\text{-}O)]_3$,[42] presumably via the intermediacy of $[Cp^*VCl(O)]_2(\mu\text{-}O)$ (eq 2).

$$2Cp^*VCl_2(O) + Ag_2CO_3 \rightarrow [Cp^*VCl(O)]_2(\mu\text{-}O) + 2AgCl + CO_2 \quad (1)$$

$$3[Cp^*VCl(O)]_2(\mu\text{-}O) + 3Ag_2CO_3 \rightarrow 2[Cp^*V(O)(\mu\text{-}O)]_3 + 6AgCl + 3CO_2 \quad (2)$$

It appeared probable that reduction of $[Cp^*VCl(O)]_2(\mu\text{-}O)$ would give $[Cp^*V]_4(\mu\text{-}O)_6$. Although there was a color change from dark green through brown to olive-green when a solution of $[Cp^*VCl(O)]_2(\mu\text{-}O)$ in toluene was reacted with sodium amalgam, only a small quantity of product could be obtained after workup. The mass spectrum (EI) of this material showed only organic fragments of low mass, and the ^1H NMR spectrum ($C_6{}^2H_6$ solution) showed three signals, at 2.10, 2.14, and 2.21 ppm with a relative intensity of 1:2:1. There was no signal for $[Cp^*V]_4(\mu\text{-}O)_6$ at 2.00 ppm.[23]

Synthesis and Properties of $[Cp^*VCl(\mu\text{-}O)]_4$. The cluster $[Cp^*VCl(\mu\text{-}O)]_4$ (**3**) was obtained previously as a minor byproduct of the oxidation of Cp^*VCl_2 by dioxygen.[31] We have now found that $[Cp^*VCl(\mu\text{-}O)]_4$ was obtained essentially quantitatively when $Cp^*VCl_2(O)$ was treated with mercury (eq 3). This remarkably specific reaction of mercury is probably a function of its redox potential in toluene and of the clean surface presented by mercury.

$$4Cp^*VCl_2(O) + 4Hg \rightarrow [Cp^*VCl(\mu\text{-}O)]_4 + 2Hg_2Cl_2 \quad (3)$$

Treatment of $Cp^*VCl_2(O)$ with other mild reductants gave mixtures of products. In the cases of zinc and aluminum, some $[Cp^*VCl(\mu\text{-}O)]_4$ was produced, but $[Cp^*V(\mu_3\text{-}O)]_4$, $[Cp^*V]_4(\mu\text{-}O)_6$, and $[Cp^*V(\mu\text{-}Cl)_2]_3$ were also present. This indicated that these reductants acted like the strong reductants discussed below. Tin amalgam produced some $[Cp^*VCl(\mu\text{-}O)]_4$, but spectroscopy showed that other products (which were not $[Cp^*V(\mu_3\text{-}O)]_4$, $[Cp^*V]_4(\mu\text{-}O)_6$, or $[Cp^*V(\mu\text{-}Cl)_2]_3$) were also present.

The cluster $[Cp^*VCl(\mu\text{-}O)]_4$ was paramagnetic with $\mu_{eff} = 4.51\ \mu_B$ at 300 K. Measurements at 10 000 and 20 000 G revealed the moment to be field independent over this range. The moment remained essentially constant from 300 K to about 30 K, below which it decreased to a minimum value of 3.67 μ_B at 2 K. The behavior could be modeled to a paramagnet with $S = 2$, $g = 1.85$ (an unusually low value), and a zero-field splitting of 3.8 cm^{-1}.[43] An extended Hückel calculation using the distances and angles determined by X-ray diffraction (D_{2d} symmetry[31]) showed that the cluster orbitals of lowest energy were b_1 at −7.829 eV, e at −7.808 eV, a_1 at −7.775 eV, and b_2 at −7.765 eV. Each of these orbitals had equal contributions from the equivalent d-orbitals of each of the four vanadium atoms and no contribution from ligand orbitals. At 0 K, an $S = 1$ ($b_1{}^2e^2$) ground state was therefore predicted. The $S = 2$ state, which was observed from the magnetic properties, could be achieved by promotion of an electron from the b_1 to the a_1 level, for which the energy separation was calculated as 0.054 eV (435 cm^{-1}). The magnetic behavior indicated that the $b_1{-}a_1$ energy separation was in fact much smaller than calculated (<30 K, 21 cm^{-1}, 0.0026 eV).

It was expected that reduction of $[Cp^*VCl(\mu\text{-}O)]_4$ would give $[Cp^*V(\mu_3\text{-}O)]_4$. However, there was no reaction between $[Cp^*VCl(\mu\text{-}O)]_4$ and magnesium turnings. When a solution of $[Cp^*VCl(\mu\text{-}O)]_4$ was reacted with magnesium amalgam in toluene, a gray precipitate formed, but there was no change in the color of the solution. The ^1H NMR spectrum (C^2HCl_3 solution) of the product showed several broad signals in the region between −10 and 0 ppm, as well as multiple resonances centered at 2.24 ppm. There was no signal for $[Cp^*V(\mu_3\text{-}O)]_4$ at 0.75 ppm ($\Delta\nu_{1/2} = 18.8$ Hz, see below).

Reaction of $Cp^*VCl_2(O)$ with Powerful Reductants. It was expected that reaction of $Cp^*VCl_2(O)$ with powerful reductants would produce $[Cp^*V(\mu_3\text{-}O)]_4$. In fact three products were formed: $[Cp^*V(\mu_3\text{-}O)]_4$, $[Cp^*V]_4(\mu\text{-}O)_6$, and either $[Cp^*V(\mu\text{-}Cl)_2]_3$ or a black, pyrophoric, insoluble material. The cluster $[Cp^*V(\mu\text{-}Cl)_2]_3$ was characterized by comparison of its ^1H NMR spectrum, mass spectrum, and crystallographic unit cell dimensions with those reported previously.[1,34,35] The cluster $[Cp^*V]_4(\mu\text{-}O)_6$ was characterized by comparison of its ^1H NMR spectrum to that reported previously[23,24] and by a detailed investigation of the mass and infrared spectra. The characterization and physical properties of $[Cp^*V(\mu_3\text{-}O)]_4$ are discussed below. The results are summarized in Table 2.

In all experiments, a toluene solution of $Cp^*VCl_2(O)$ was added to a 10-fold molar excess of a metal amalgam at room temperature. There was a change in color from the blue-green of the starting complex to dark brown within 1 h, and during this time a fine white precipitate of the metal chloride appeared. The reaction was allowed to proceed for 12 h, over which time the color of

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the solution darkened to black and further precipitation of metal chloride occurred. The same sequence of events occurred in tetrahydrofuran solution, except that the initial color change was essentially instantaneous. When magnesium turnings or calcium shot were added to Cp*VCl$_2$(O) in tetrahydrofuran, the blue-green to dark brown color change required 24 h, and complete reaction required 48 h. There was no reaction of Cp*VCl$_2$(O) with sodium in tetrahydrofuran, nor with magnesium, calcium, or sodium in toluene. Except in these cases, all of the reactions produced black [Cp*V(μ_3-O)]$_4$ and black-green [Cp*V]$_4$(μ-O)$_6$ on workup. Magnesium amalgam in toluene produced dark purple [Cp*V(μ-Cl)$_2$]$_3$, in addition to the two oxide clusters. The reductants magnesium amalgam and magnesium turnings in tetrahydrofuran also produced [Cp*V(μ-Cl)$_2$]$_3$, as determined by spectroscopy. The other reductants produced a black, pyrophoric, insoluble material, but no [Cp*V(μ-Cl)$_2$]$_3$ (see Table 2). The only nonmetal reductant that was investigated, lithium nitride, gave [Cp*V(μ_3-O)]$_4$, [Cp*V]$_4$(μ-O)$_6$, and [Cp*V(μ-Cl)$_2$]$_3$.

It is seen from Table 2 that powerful reductants gave the black, pyrophoric, insoluble material, whereas weaker reductants gave [Cp*V(μ-Cl)$_2$]$_3$, but none of the black material. In independent experiments, it was established that sodium amalgam reacted with [Cp*V(μ-Cl)$_2$]$_3$ to form a pyrophoric, black, insoluble material, similar to that obtained in the reductions of Cp*VCl$_2$(O). From its properties, this material is assumed to contain vanadium in a lower oxidation state than III, but it could not be further characterized. It was found also that magnesium amalgam did not react with [Cp*V(μ-Cl)$_2$]$_3$. It was concluded that [Cp*V(μ-Cl)$_2$]$_3$ was produced in all the reactions between Cp*VCl$_2$(O) and metals or metal amalgams, but that it was further reduced to the black material by powerful reductants.

The formation of an oxide cluster of vanadium(IV) containing no chloride ([Cp*V]$_4$(μ-O)$_6$) and a chloride cluster of vanadium(III) containing no oxide ([Cp*V(μ-Cl)$_2$]$_3$) on reduction of Cp*VCl$_2$(O) was very surprising. Great care was taken to ensure that there were no extraneous sources of oxygen or chlorine. Thus these clusters must have been formed concurrently, by a disproportionation.

We previously synthesized [Cp*V]$_4$(μ-O)$_6$ by deoxygenation of [Cp*V(O)(μ-O)]$_3$ (eq 4) or by oxidizing Cp*$_2$V with N$_2$O (eq 5).[23,24] Andersen and co-workers showed that the initial product of the reaction between Cp*$_2$V and N$_2$O was Cp*$_2$V(O) and proposed that this decomposed to [Cp*V]$_4$(μ-O)$_6$ via [Cp*VO]$_4$ (eqs 6 and 7).[44]

$$4[\mathrm{Cp^*V(O)}(\mu\text{-O})]_3 + 6\mathrm{PhMe_2P} \rightarrow 3[\mathrm{Cp^*V}]_4(\mu\text{-O})_6 + 6\mathrm{PhMe_2P(O)} \quad (4)$$

$$4\mathrm{Cp^*}_2\mathrm{V} + 6\mathrm{N_2O} \rightarrow [\mathrm{Cp^*V}]_4(\mu\text{-O})_6 + 6\mathrm{N_2} + 2(\mathrm{C_5Me_5})_2 \quad (5)$$

$$4\mathrm{Cp^*}_2\mathrm{V(O)} \rightarrow [\mathrm{Cp^*VO}]_4 + 2(\mathrm{C_5Me_5})_2 \quad (6)$$

$$[\mathrm{Cp^*VO}]_4 + 2\mathrm{Cp^*}_2\mathrm{V(O)} \rightarrow [\mathrm{Cp^*V}]_4(\mu\text{-O})_6 + 2\mathrm{Cp^*}_2\mathrm{V} \quad (7)$$

It was also suggested that any source of oxygen might oxidize [Cp*V(μ_3-O)]$_4$ to [Cp*V]$_4$(μ-O)$_6$.[44] In independent experiments, we found that slow hydrolysis of [Cp*V(μ_3-O)]$_4$ at room temperature gave a black intractable material. There was a rapid reaction between [Cp*V(μ_3-O)]$_4$ and an equimolar amount of O$_2$ to produce a material with properties similar to those of Cp*$_6$V$_8$O$_{17}$, which was previously obtained by oxidation of [Cp*V]$_4$(μ-O)$_6$ or Cp*$_2$V by O$_2$.[24] It was also established independently that [Cp*V]$_4$(μ-O)$_6$ was not reduced to [Cp*V(μ_3-O)]$_4$ by any of the reductants.

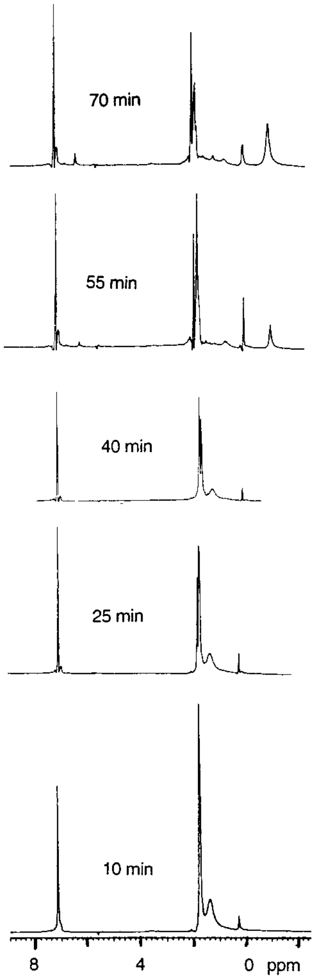

Figure 2. ^{1}H NMR spectra of the initial stages of the reduction of Cp*VCl$_2$(O) by sodium amalgam in C$_6{}^2$H$_6$ solution.

^{1}H NMR Study of the Reduction of Cp*VCl$_2$(O) by Sodium Amalgam. The initial stages of the reduction of Cp*VCl$_2$(O) by sodium amalgam in C$_6{}^2$H$_6$ solution were followed by monitoring the ^{1}H NMR spectra of aliquots removed from the reaction solution at intervals of time. A continuous study was impossible because of the presence of the sodium amalgam reductant. A study of the later stages of the reaction was prevented by the buildup of colloidal sodium chloride and the black material (see the Experimental Section). The spectra are shown in Figure 2.

Before adding the reductant, the spectrum of the solution showed a signal at 1.79 ppm ($\Delta\nu_{1/2}$ = 1.7 Hz), assigned to the starting material Cp*VCl$_2$(O) (lit.:[31] 1.81 ppm in C$_6{}^2$H$_5$C^{2}H$_3$). After 10 min, the bright blue-green of color of the Cp*VCl$_2$(O) solution had become duller,

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[44] Smith, M. R.; Matsunaga, P. T.; Andersen, R. A. *J. Am. Chem. Soc.* **1993**, *115*, 7049.

and a fine white suspension, presumed to be sodium chloride, was observed. At this time the NMR spectrum showed the signal at 1.79 ppm ($\Delta\nu_{1/2} = 7.2$ Hz) and a broad signal at 1.40 ppm ($\Delta\nu_{1/2} = 134$ Hz) After 25 min, the solution was green-brown, more white precipitate had formed, and the NMR spectrum now showed three signals: 1.78 ppm ($\Delta\nu_{1/2} = 5.4$ Hz); 1.40 ppm ($\Delta\nu_{1/2} = 140$ Hz); and 1.86 ppm ($\Delta\nu_{1/2} = 4.6$ Hz). The intensity of the signal at 1.78 ppm was slightly greater than that at 1.86 ppm, and the broad signal at 1.40 ppm was less intense than in the spectrum taken after 10 min. After 40 min, the color of the solution had not further altered, and the same three signals as after 25 min were observed. However, the signal at 1.40 ppm was now much less intense than previously, and the signal at 1.79 ppm was now much broader ($\Delta\nu_{1/2} = 20$ Hz) and less intense than that at 1.86 ppm ($\Delta\nu_{1/2} = 8.2$ Hz). After 55 min, the signals at 1.79 and 1.40 ppm had disappeared into the background and been replaced by a peak centered at 1.93 ppm with a shoulder at approximately 1.86 ppm (combined $\Delta\nu_{1/2} = 35$ Hz). In addition, two new signals had appeared, one at 2.05 ppm ($\Delta\nu_{1/2} = 8.0$ Hz) and one at -0.80 ppm ($\Delta\nu_{1/2} = 45$ Hz). After 70 min, the same signals were observed (2.04 ppm ($\Delta\nu_{1/2} = 6.5$ Hz), 1.93 ppm with a shoulder at 1.86 ppm (combined $\Delta\nu_{1/2} = 40$ Hz) and -0.79 ($\Delta\nu_{1/2} = 70$ Hz)); the intensity of the signals at 2.04 and -0.79 ppm had increased with respect to that at 1.93 ppm, compared to the spectrum taken after 55 min.

Scheme for the Reduction of $Cp^*VCl_2(O)$ to $[Cp^*V(\mu_3\text{-}O)]_4$, $[Cp^*V]_4(\mu\text{-}O)_6$, and $[Cp^*V(\mu\text{-}Cl)_2]_3$. The ^1H NMR study showed that reduction of $Cp^*VCl_2(O)$ (to which was assigned the signal at 1.79 ppm ($\Delta\nu_{1/2} = 1.70$ Hz)) with sodium amalgam rapidly produced a single species with a signal at 1.40 ppm ($\Delta\nu_{1/2} = 134$ Hz). Reduction of $Cp^*VCl_2(O)$ must first give Cp^*VClO (eq 8), but since the reductant was in large excess, this would be rapidly reduced to Cp^*VO (eq 9). Thus the broad signal at 1.40 ppm ($\Delta\nu_{1/2} = 134$ Hz) was assigned to paramagnetic Cp^*VO. In the initial stages of the reaction, when the concentration of Cp^*VO was low and that of $Cp^*VCl_2(O)$ high, it would not oligomerize, but would react with excess $Cp^*VCl_2(O)$ to form $[Cp^*VClO]_2$ (eq 10). It is proposed that $[Cp^*VClO]_2$ has a structure

$$Cp^*V^{V}Cl_2(O) + 1/n[Red] \rightarrow Cp^*V^{IV}ClO + 1/n[Red]Cl_n \quad (8)$$

$$Cp^*V^{IV}ClO + 1/n[Red] \rightarrow Cp^*V^{III}O + 1/n[Red]Cl_n \quad (9)$$

$$Cp^*V^{III}O + Cp^*V^{V}Cl_2(O) \rightarrow [Cp^*V^{IV}ClO]_2 \quad (10)$$

similar to $[Cp'M(\mu\text{-}Cl)(\mu\text{-}O)]_2$ (**5**[34,35,45–48]) or $[Cp'MCl(\mu\text{-}O)]_2$ (**6**[34,45–48]), which have been characterized. Extended Hückel molecular orbital calculations showed that the two d-electrons of $[Cp^*VClO]_2$ with either structure **5** or **6** would be paired in an orbital that represented a V–V σ-bond.[46] Thus $[Cp^*VClO]_2$ would be diamagnetic, and the narrow signal at 1.86 ppm ($\Delta\nu_{1/2} = 4.6$ Hz), which was first observed after 25 min reaction time, was assigned to it. Further oligomerization of the intermediate $[Cp^*VClO]_2$ to $[Cp^*VCl(\mu\text{-}O)]_4$ was unlikely, because of the low initial concentration and the presence of excess reductant. Also, $[Cp^*VCl(\mu\text{-}O)]_4$ was not reduced to $[Cp^*V(\mu_3\text{-}O)]_4$ (see above).

If $[Cp^*VClO]_2$ adopted the $[Cp^*V(\mu\text{-}Cl)(\mu\text{-}O)]_2$ structure **5**, an oxygen–chlorine ligand exchange accompanied by a redox disproportionation of vanadium could occur (eq 11). A symmetrical interchange of ligands

$$[Cp^*V^{IV}(\mu\text{-}Cl)(\mu\text{-}O)]_2 \rightarrow Cp^*V^{V}O_2 + Cp^*V^{III}Cl_2 \quad (11)$$

would regenerate Cp^*VClO. The signal at 2.05 ppm ($\Delta\nu_{1/2} = 8.0$ Hz), which first appeared after 55 min, was assigned to diamagnetic Cp^*VO_2 produced by reaction 11. This assignment is supported by the values for the trimer $[Cp^*V(O)(\mu\text{-}O)]_3$ with structure **7** (2.09 and 2.13 ppm[42]). The broad signal at -0.80 ppm ($\Delta\nu_{1/2} = 70$ Hz), which also first appeared after 55 min, was assigned to Cp^*VCl_2. This compound would be reduced by powerful reductants (see above), but would otherwise aggregate to $[Cp^*V(\mu\text{-}Cl)_2]_3$ with structure **4**. This cluster showed a signal in the ^1H NMR spectrum at -7.0 ppm ($\Delta\nu_{1/2} = 52$ Hz).[34] The trimer $[Cp^*V(\mu\text{-}Cl)_2]_3$ would not be observed in the present experiment, since aggregation would only occur in the later stages of the reaction. It was identified conclusively by X-ray diffraction as a product of the reduction of $Cp^*VCl_2(O)$ by magnesium amalgam in toluene after a 12 h reaction time.

If $[Cp^*VClO]_2$ adopted the $[Cp^*VCl(\mu\text{-}O)]_2$ structure **6**, reduction would be preferred to disproportionation (eq 12). The structure $[Cp^*V(\mu\text{-}O)]_2$ (**8**) is proposed for the divanadium compound $[Cp^*VO]_2$.

$$[Cp^*V^{IV}Cl(\mu\text{-}O)]_2 + 2/n[Red] \rightarrow [Cp^*V^{III}O]_2 + 2/n[Red]Cl_n \quad (12)$$

Extended Hückel calculations predicted that **8**, with a planar $V(\mu\text{-}O)_2V$ unit, would have no unpaired electrons although the HOMO–LUMO gap would be only 0.11 eV. On the other hand, with a butterfly (tetrahedral) geometry for the $V(\mu\text{-}O)_2V$ unit (**9**), two unpaired electrons were predicted. The signal at 1.93 ppm (for which $\Delta\nu_{1/2}$ = cannot be determined, see Figure 2) was assigned to $[Cp^*V(\mu\text{-}O)]_2$. Note that $[Cp^*V(\mu\text{-}O)]_2$ may also be formed by direct dimerization of Cp^*VO, although this is unlikely in the early stages of the reaction when excess $Cp^*VCl_2(O)$ will still be present.

The proposed scheme is in agreement with the observed changes in the ^1H NMR spectrum with time (see Figure 2). The intensity of the signal at 1.79 ppm assigned to the starting material $Cp^*VCl_2(O)$ decreased through 40 min reaction time, due to the consumption of this compound. The signal also broadened, from $\Delta\nu_{1/2} = 1.70$ Hz to $\Delta\nu_{1/2} = 20$ Hz, due to the concurrent formation of paramagnetic compounds. The signal assigned to the intermediate Cp^*VO (1.40 ppm ($\Delta\nu_{1/2} = 134$ Hz)) also decreased through 40 min reaction time, due to the consumption of this compound in the formation of $[Cp^*VClO]_2$. The signals assigned to Cp^*VCl_2-

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(O) and Cp*VO had disappeared after 55 min reaction time, when the signals assigned to Cp^*VO_2 (2.04 ppm ($\Delta\nu_{1/2} = 6.5$ Hz)), Cp^*VCl_2 (−0.80 ppm ($\Delta\nu_{1/2} = 45$ Hz)), and $[Cp^*V(\mu\text{-O})]_2$ (1.93 ppm) first appeared. The signal assigned to $[Cp^*VClO]_2$ (1.86 ppm ($\Delta\nu_{1/2} = 8.2$ Hz)) diminished in intensity over the time period 40−70 min, as the signals assigned to Cp^*VO_2, Cp^*VCl_2, and $[Cp^*V(\mu\text{-O})]_2$ increased.

The final products $[Cp^*V(\mu_3\text{-O})]_4$ and $[Cp^*V]_4(\mu\text{-O})_6$ would be produced by dimerization of $[Cp^*V(\mu\text{-O})]_2$ or by the reaction between $[Cp^*V(\mu\text{-O})]_2$ and Cp^*VO_2, respectively. These reactions must be multistep processes, which would take place after the 70 min of the NMR experiment had elapsed.

The overall reaction for the formation of $[Cp^*V(\mu_3\text{-O})]_4$ is eq 13, and for $[Cp^*V]_4(\mu\text{-O})_6$, eq 14. The relative yields of $[Cp^*V]_4(\mu\text{-O})_6$ and $[Cp^*V(\mu\text{-Cl})_2]_3$ (Table 2) were in accord with eq 14.

$$4Cp^*VCl_2(O) + 8/n[Red] \rightarrow [Cp^*V(\mu_3\text{-O})]_4 + 8/n[Red]Cl_n \quad (13)$$

$$18Cp^*VCl_2(O) + 24/n[Red] \rightarrow 3[Cp^*V]_4(\mu\text{-O})_6 + 2[Cp^*V(\mu\text{-Cl})_2]_3 + 24/n[Red]Cl_n \quad (14)$$

It is seen from Table 2 that the formation of $[Cp^*V]_4(\mu\text{-O})_6$ was favored in toluene as solvent, whereas $[Cp^*V(\mu_3\text{-O})]_4$ was favored in tetrahydrofuran. This is explained by the effect of solvent on the structure of $[Cp^*VClO]_2$, and hence on reactions 11 and 12. In $[Cp^*V(\mu\text{-Cl})(\mu\text{-O})]_2$ (**5**) the vanadium is seven-coordinate, in $[Cp^*VCl(\mu\text{-O})]_2$ (**6**) only six. The coordinating solvent tetrahydrofuran would stabilize **6**, which would be reduced to $[Cp^*V(\mu\text{-O})]_2$ (reaction 12). Toluene would favor **5**, which would undergo the redox disproportionation reaction 11, producing the Cp^*VO_2 necessary for formation of $[Cp^*V]_4(\mu\text{-O})_6$. The reduction reactions 8, 9, and 12, are required for the formation of both $[Cp^*V(\mu_3\text{-O})]_4$ and $[Cp^*V]_4(\mu\text{-O})_6$. This explains why the ratio of $[Cp^*V(\mu_3\text{-O})]_4$ to $[Cp^*V]_4(\mu\text{-O})_6$ produced was not markedly dependent on the reductant.

Characterization and Physical Properties of $[Cp^*V(\mu_3\text{-O})]_4$. The cluster $[Cp^*V(\mu_3\text{-O})]_4$ was black and pyrophoric. It was soluble in chloroform and tetrahydrofuran, but only sparingly soluble in toluene and insoluble in hexane. It crystallized readily from chloroform. In this respect, $[Cp^*V(\mu_3\text{-O})]_4$ behaved like $[Cp^*Cr(\mu_3\text{-O})]_4$[4] and $[Cp^*Ti(\mu_3\text{-N})]_4$,[49] but unlike $[Cp^*V(\mu_3\text{-N})]_4$[20] and $[Cp^*V]_4(\mu\text{-O})_6$,[23] which were very soluble in hydrocarbon solvents. Since the exterior of all the clusters consisted of an essentially spherical array of the 20 methyl groups of the η-C_5Me_5 ligands, it is not clear why there is such a marked difference in solubilities.

Microanalysis of amorphous $[Cp^*V(\mu_3\text{-O})]_4$ gave the correct C/H ratio, but the absolute values for carbon and hydrogen were low and there was a small chlorine content. The ^{1}H NMR spectrum showed no signals in the region 0−10 ppm other than that at 0.75 ppm ($\Delta\nu_{1/2}$ = 18.8 Hz), indicating that no organic compound other than $C_5(CH_3)_5$ was present. The mass spectra showed very weak peak envelopes with an isotopic distribution which could be derived from fragments of Hg_2Cl_2. Since Hg_2Cl_2 is soluble in organic solvents and sublimes at 383 °C,[50] it would not be removed by filtration through Celite nor by recrystallization. We were unable to obtain sufficient quantities of crystalline $[Cp^*V(\mu_3\text{-O})]_4$ (which did not contain mercury in any form) for microanalysis. Analytically pure material could not be obtained from the reduction of $Cp^*VCl_2(O)$ with a nonamalgamated metal such as calcium. Such reductions had to be conducted in tetrahydrofuran and it was impossible to remove all traces of solvated $[Red]Cl_n$ (e.g., $Ca(thf)_4Cl_2$) from the product. The carbon, hydrogen, and chlorine analyses showed that the formulas of the amorphous material was $[Cp^*V(\mu_3\text{-O})]_4\cdot 0.2Hg_2Cl_2$. We observed a similar incorporation of Hg_2Cl_2 in $[Cp^*V(\mu_3\text{-N})]_4$ and $[Cp^*Mo]_4O_7$, obtained from reduction of $[Cp^*VCl(\mu\text{-N})]_2$ or $Cp^*MoCl_2(O)$ by sodium amalgam.[51,52] Poli and co-workers also found low carbon analyses for related molybdenum compounds.[53]

The X-ray crystallographic experiments showed that $[Cp^*V(\mu_3\text{-O})]_4$ was a cubane. The cluster was also characterized by ^{1}H NMR and infrared spectroscopies and by mass spectrometry. The ^{1}H NMR spectrum showed a signal at 0.75 ppm with $\Delta\nu_{1/2} = 18.8$ Hz (295 K), indicating a species with unpaired electrons. The infrared spectrum showed an absorption band of medium intensity at 450 cm^{-1}, assigned to the anti-translational vibration of the $[V(\mu_3\text{-O})]_4$ core. This frequency compares to 441 cm^{-1} for the intense band assigned to the $[V(\mu_3{-}N)]_4$ anti-translational vibration in $[Cp^*V(\mu_3\text{-N})]_4$[20] and 550 cm^{-1} for the intense band assigned to the $[Cr(\mu_3\text{-O})]_4$ anti-translational vibration in $[Cp^*Cr(\mu_3\text{-O})]_4$.[4] The high-resolution mass spectrum showed the parent ion with an error of 5 ppm. The low-resolution spectrum showed the parent ion and fragments corresponding to successive loss of two C_5Me_5 ligands.

The cluster $[Cp^*V(\mu_3\text{-O})]_4$ was paramagnetic with $\mu_{eff} = 2.35\ \mu_B$ at 300 K. A plot of T vs $1/\chi$ showed a slight curvature, and the magnetic moment was much lower than the spin-only value of 2.83 μ_B, indicating that the magnetic behavior was more complicated than that of a simple paramagnet. Rauchfuss and co-workers found that $[(CpMe)V(\mu_3\text{-S})]_4$ was paramagnetic with $\mu_{eff} = 2.68\ \mu_B$ at 300 K and a linear T vs $1/\chi$ plot.[7,11,12] The energy level ordering for the cluster orbitals of $[CpV(\mu_3\text{-O})]_4$ was calculated by the extended Hückel method to be $e < a_1 < 1t_2 < t_1 < 2t_2$, using a V−V distance of 2.65 Å and a V−O distance of 1.86 Å (Figure 3). For $[CpM(\mu_3\text{-S})]_4$ cubanes the order is $e < a_1 < 1t_2 < t_1 < 2t_2$ or $a_1 < e < 1t_2 < t_1 < 2t_2$.[2,6−8] Thus $[Cp'V(\mu_3\text{-A})]_4$ (A = O, S), with eight cluster electrons, would be predicted to have the configuration $e^4a_1^21t_2^2t_1^02t_2^0$ and be paramagnetic, with an $S = 1$ ground state and a spin-only magnetic moment of 2.83 μ_B. We are continuing with a detailed investigation of the magnetic behavior of these clusters.

Structure and Properties of $[Cp^*V]_4(\mu\text{-O})_6$. We reported previously that $[Cp^*V]_4(\mu\text{-O})_6$ had the adamantane-like structure **2** on the basis of X-ray diffraction

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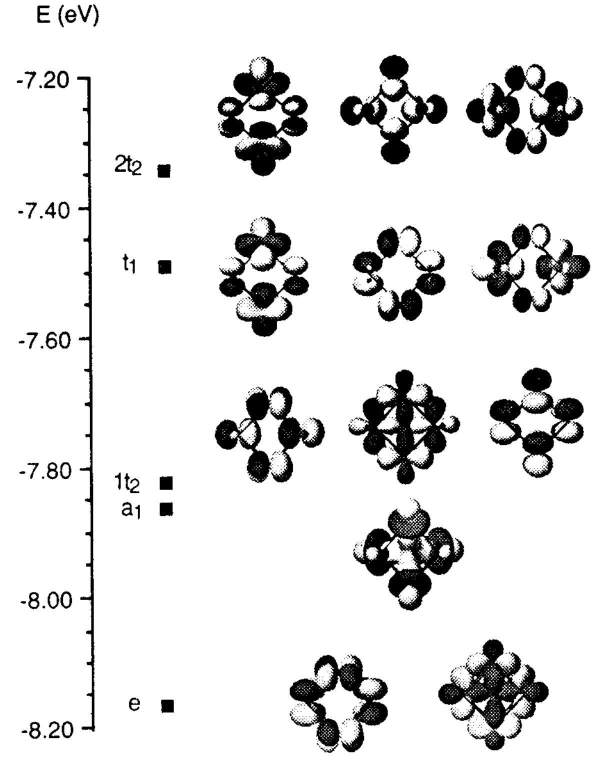

Figure 3. Energy level ordering for the cluster orbitals of $[CpV(\mu_3\text{-}O)]_4$.

on crystals obtained from both reactions 4 and 5.[23] This refinement used an X-ray data set which was a combination of intensities measured from three different crystals. All atoms were refined isotropically. We have now performed a more satisfactory anisotropic refinement using only the data from one crystal, which was a product of reaction 5. This confirmed the adamantane-like structure **2**. A thermal ellipsoid plot is shown in Figure 1, and important distances and angles are given in Table 1. Despite many attempts, we were not able to obtain crystals of $[Cp^*V]_4(\mu\text{-}O)_6$ from the reduction of $Cp^*VCl_2(O)$. With the exception of the magnetism, the physical and chemical properties of $[Cp^*V]_4(\mu\text{-}O)_6$ prepared by the reduction reaction 14 were the same as those of the cluster prepared by the oxidation reaction 5.

An interesting aspect of the structure of $[Cp^*V]_4(\mu\text{-}O)_6$ was the apparent distortion of the cluster from T_d to C_3 symmetry. The four vanadium atoms form a perfect tetrahedron of side 3.004 (3) Å, but the $\eta\text{-}C_5Me_5$ ligand attached to V(4) was disordered and the other three $\eta\text{-}C_5Me_5$ ligands were arranged as though they were related by a 3-fold axis passing through V(4) and the centroid of the V(1)−V(3) triangle. The oxygen atom positions also conformed to this symmetry, there being four sets of V−O distances (see Figure 4 and Table 1). This apparent 3-fold symmetry is not required by the space group ($P\bar{1}$), nor is it found in the otherwise isomorphous $[Cp^*Ti]_4(\mu\text{-}O)_6$.[21] The distortion of the symmetry of the $V_4(\mu\text{-}O)_6$ core from the adamantane-like T_d to C_3 is small but consistent.

In addition to the adamantane structure **2**, two other structures are known or have been proposed for $[Cp'M]_4A_6$ clusters.[54−57] Structure **10** was found for

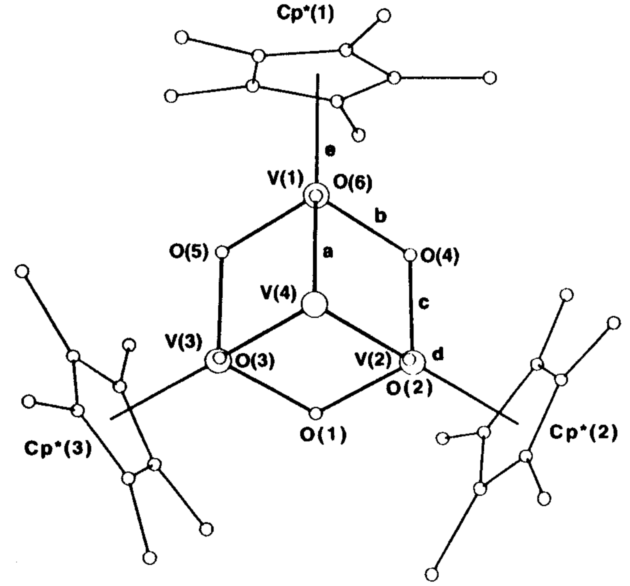

Figure 4. Structure of $[Cp^*V]_4(\mu\text{-}O)_6$ showing the apparent 3-fold symmetry. Footnote to Figure 4. The average distances are $a = 1.815$ (7, 3) Å, $b = 1.815$ (7, 3) Å, $c = 1.804$ (7, 3) Å, $d = 1.803$ (8, 4) Å, $e = 2.015$ (12, 13) Å.

$[Cp^*Ti]_4(\mu_2\text{−}Se)_3(\mu_3\text{−}Se)_3$.[54] Structure **11** was proposed for the cluster $[Cp^*Nb]_4O_6$ from spectroscopic evidence,[55] and Bénard and co-workers calculated by ab initio methods that structure **11**, with D_{2h} symmetry, was 26 kcal mol^{-1} more stable than the adamantane structure **2** for $[Cp^*V]_4(\mu\text{-}O)_6$.[57] However, apart from the small distortion to C_3 symmetry, we have found no evidence for any structure other than the adamantane-like **2** for $[Cp^*V]_4O_6$.

The cluster $[Cp^*V]_4(\mu\text{-}O)_6$ was diamagnetic at 300 K. Below 170 K a very small moment was observed, which may be due to paramagnetic impurities.[58] These impurities may also be responsible for the relative broadness of the ^1H NMR signal for the methyl protons of $[Cp^*V]_4(\mu\text{-}O)_6$, $\Delta\nu_{1/2} = 5.9$ Hz in benzene solution, compared to $[Cp^*V(\mu_3\text{-}N)]_4$, $\Delta\nu_{1/2} = 1.5$ Hz.[20]

Extended Hückel molecular orbital calculations on $[CpV]_4(\mu\text{-}O)_6$ with structure **2** and V−V and V−O distances of 3.000 and 1.810 Å, respectively, indicated that the energy level ordering of the 12 cluster orbitals was $a_1 < e < 1t_2 < t_1 < 2t_2$.[24,55,56] Thus $[CpV]_4(\mu\text{-}O)_6$, with four cluster electrons, would be predicted to have the configuration $a_1^2e^21t_2^0$ and be paramagnetic, with an $S = 1$ ground state and a spin-only magnetic moment of 2.83 μ_B. The $a_1 \rightarrow e$ energy gap was calculated to be 0.14 eV, and the $e \rightarrow 1t_2$ gap, 0.31 eV. Bénard and co-workers calculated, by ab initio methods, that $[CpV]_4(\mu\text{-}O)_6$ with structure **2** should be a quintet, with the electronic configuration $a_1^1b_2^1e^2$ (exact D_{2d} symmetry, correlating with $a_1^1t_2^3$ in T_d symmetry).[57] The computed V−V distances were 3.251 and 3.234 Å and the V−O

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[58] The magnetic moment of $[Cp^*V]_4(\mu\text{-}O)_6$ was previously reported as 2.90 μ_B by the Faraday method and 2.15 μ_B by the Evans NMR method, both at room temperature.[24] It is believed that impurities generated by the oxidation of Cp_2^*V were responsible for the observed magnetism.

distances 1.778 and 1.795 Å,[57] compared to the 3.004 and 1.799−1.818 Å found by X-ray diffraction. Extended Hückel calculations with V−V and V−O distances of 3.200 and 1.810 Å gave the ordering $e < a_1 < 1t_2 < t_1 < 2t_2$ and therefore predicted the observed singlet ground state. However, a V−V distance of 3.20 Å or greater cannot be reconciled with the observed 3.00 Å or with the Ti−Ti distance in $[CpTi]_4(\mu\text{-}O)_6$, 3.229 Å.[21] On the other hand, calculations with V−V and V−O distances of 3.000 and 1.760 Å also gave the ordering $e < a_1 < 1t_2 < t_1 < 2t_2$ and therefore predicted a singlet ground state. One explanation for the failure of theory to predict the molecular and electronic structure of $[Cp^*V]_4O_6$ is that the role of the metal is overemphasized compared to the role of the bridging oxygen.

Syntheses of $[Cp^*V(\mu_3\text{-}O)]_4$, $[Cp^*V]_4(\mu\text{-}O)_6$, and $[Cp^*V(\mu\text{-}Cl)_2]_3$ by Reduction of $Cp^*VCl_2(O)$. The reduction of $Cp^*VCl_2(O)$ by calcium in tetrahydrofuran to produce$[Cp^*V(\mu_3\text{-}O)]_4$ in 40% yield after purification represents the first synthesis of this cluster. Reduction of $Cp^*VCl_2(O)$ with sodium or calcium amalgam in toluene produced $[Cp^*V]_4(\mu\text{-}O)_6$ in 40% yield after recrystallization. The best previous synthesis, oxidation of Cp^*_2V with N_2O, gave an 85% yield, but purification was very difficult because of the oily $(C_5Me_5)_2$ which was a coproduct.[24] A very facile synthesis of pure $[Cp^*V(\mu\text{-}Cl)_2]_3$ in 70% yield was reported previously.[34,35] Thus the reduction of $Cp^*VCl_2(O)$ represents convenient syntheses of $[Cp^*V(\mu_3\text{-}O)]_4$ and $[Cp^*V]_4(\mu\text{-}O)_6$. The only drawback to the syntheses was the removal of colloidal $[Red]Cl_n$ and mercury chlorides.

Conclusion

Reduction of $Cp^*VCl_2(O)$ by metals or metal amalgams in toluene or tetrahydrofuran gave the cubane cluster $[Cp^*V(\mu_3\text{-}O)]_4$ and the adamantane cluster $[Cp^*V]_4(\mu\text{-}O)_6$; a coproduct of the latter was $[Cp^*V(\mu\text{-}Cl)_2]_3$. The formation of $[Cp^*V]_4(\mu\text{-}O)_6$ was favored in toluene, whereas $[Cp^*V(\mu_3\text{-}O)]_4$ was favored in tetrahydrofuran. The reductants did not influence the ratio of $[Cp^*V]_4(\mu\text{-}O)_6$ to $[Cp^*V(\mu_3\text{-}O)]_4$ produced. The cluster $[Cp^*V(\mu_3\text{-}O)]_4$ was paramagnetic; $[Cp^*V]_4(\mu\text{-}O)_6$ was diamagnetic.

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Supporting Information Available: Tables of crystal data, diffractometry conditions, refinement details, fractional coordinates, thermal parameters, and interatomic distances and angles for $[Cp^*V]_4(\mu\text{-}O)_6$. This material is available free of charge via the Internet at http://pubs.acs.org.

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