

# Decarbonylation of Pentamethylcyclopentadienyl Tetracarbonylvanadium, $\text{Cp}^*\text{V}(\text{CO})_4$ , in the Presence of Oxygen. The X-Ray Crystal Structure Analyses of $\text{Cp}^*\text{V}(\text{CO})_4$ and $[\text{Cp}^*\text{V}(\text{O})(\mu\text{-O})]_4$

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*Dedicated to Professor Hartmut Bärnighausen on the occasion of his 70th birthday*

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The reaction of  $\text{Cp}^*\text{V}(\text{CO})_4$  (**1**) with molecular oxygen in diluted pentane solution leads to a tetrameric dioxide,  $[\text{Cp}^*\text{V}(\text{O})(\mu\text{-O})]_4$  (**2**), which is a precursor of the octanuclear aggregate  $\text{Cp}^*_6\text{V}_8\text{O}_{17}$  (**3**). The molecular structures of **1** and **2** have been determined by X-ray crystallography.

**Key words:** Vanadium, Organometallic Oxides, Crystal Structures

## Introduction

Organometallic oxides containing the 10-electron fragment pentamethylcyclopentadienyl-vanadium ( $\text{Cp}^*\text{V}$ ) are well known [1–3]; prominent examples are the pseudocubane cluster  $[\text{Cp}^*\text{V}(\mu_3\text{-O})]_4$  and the adamantane-type assembly  $[\text{Cp}^*\text{V}]_4(\mu\text{-O})_6$  which contain vanadium(III) and vanadium(IV), respectively. Both are conveniently synthesized [2] by reductive aggregation of  $\text{Cp}^*\text{V}(\text{O})\text{Cl}_2$ .

The vanadium[V] oxide,  $[\text{Cp}^*\text{VO}_2]$ , is not available in the monomeric form, but the trimer,  $[\text{Cp}^*\text{V}(\text{O})(\mu\text{-O})]_3$ , has been obtained by the reaction of  $\text{Cp}^*\text{V}(\text{O})\text{Cl}_2$  with  $\text{Ag}_2\text{CO}_3$  in THF solution [4].

As an alternative route to  $\text{Cp}^*$  vanadium(V) oxides, the oxidative decarbonylation of  $\text{Cp}^*\text{V}(\text{CO})_4$  (**1**) by molecular oxygen has been studied [5] in hexane, toluene and THF solution. The black product which is isolated after solvent evaporation from the dark-red toluene solutions is an octanuclear aggregate. According to Bottomley and coworkers [6], the infrared and NMR spectroscopic data ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{17}\text{O}$  and  $^{51}\text{V}$ ) are consistent with an oxo bridge between two tetranuclear subunits, *i.e.*  $[\text{Cp}^*_3\text{V}_4(\text{O})_4(\mu\text{-O})_4]_2(\mu\text{-O})$ . The same product of composition  $\text{Cp}^*_6\text{V}_8\text{O}_{17}$  was also obtained from analogous reactions of  $\text{VCp}^*_2$  [6],  $[\text{Cp}^*\text{V}(\mu\text{-O})]_4$  [2] and  $[\text{Cp}^*\text{V}]_4(\mu\text{-O})_6$  [6] with oxygen gas in solution.

## Results and Discussion

We have observed that a tetranuclear intermediate,  $[\text{Cp}^*\text{VO}_2]_4$  (**2**), is formed during the early stages of the oxidative decarbonylation of  $\text{Cp}^*\text{V}(\text{CO})_4$  (**1**) along the route to the octanuclear aggregate,  $\text{Cp}^*_6\text{V}_8\text{O}_{17}$  (**3**).

### *Synthesis and reactivity of the tetramer $[\text{Cp}^*\text{V}(\text{O})(\mu\text{-O})]_4$ (**2**)*

If a slow stream of  $\text{O}_2$  is bubbled through a saturated solution of  $\text{Cp}^*\text{V}(\text{CO})_4$  (**1**), *e.g.* 2 mmol of **1** in 100 ml of pentane, a quantitative conversion to  $\text{Cp}^*_6\text{V}_8\text{O}_{17}$  (**3**) eventually takes place, and the nearly colourless solvent can be decanted from the insoluble black precipitate of **3**. If, however, a diluted solution, *e.g.* 0.25 mmol of **1** in 100 ml of pentane, is stirred in air (*i.e.*,  $\text{O}_2$  diluted by a four-fold excess of  $\text{N}_2$ ), a red-black pentane solution is obtained from which some black precipitate of compound **3** forms over night. The pentane solution contains the tetramer  $[\text{Cp}^*\text{V}(\text{O})(\mu\text{-O})]_4$  (**2**).

The molecular structure assigned to **2** on the basis of a crystal structure determination (Fig. 2) agrees with the spectroscopic data. The IR spectrum (1376 ( $\text{Cp}^*$ ), 1261 m, 959 w and 927 w, 800 and 722 (broad)  $\text{cm}^{-1}$ , CsI pellet) indicates the presence of both terminal and bridging oxo ligands. The  $^1\text{H}$  NMR spectrum of **2** (in  $\text{C}_6\text{D}_6$ ) contains three signals at  $\delta$  2.21, 2.14 and 2.10 with

an integrated intensity ratio of 1:2:1, whereas two peaks are observed in the  $^{51}\text{V}$  NMR spectrum ( $\text{C}_6\text{D}_6$ ) at  $\delta$  – 628 and – 649 with an approximate ratio of 3:1. The slow conversion of **2** to **3** can be noticed in the  $^{51}\text{V}$  NMR spectrum; it is accelerated in polar solvents such as  $\text{CDCl}_3$ . In line with this experience, a reliable  $^{13}\text{C}$  NMR spectrum of **2** was not obtained due to the formation of **3**. The spectroscopic data of the red-black tetramer  $[\text{Cp}^*\text{V}(\text{O})(\mu\text{-O})]_4$  (**2**) are significantly different from those of the blue trimer  $[\text{Cp}^*\text{V}(\text{O})(\mu\text{-O})]_3$  ( $\delta(^1\text{H})$  2.13 and 2.09, intensity ratio 1:2;  $\delta(^{51}\text{V})$  – 530 and – 547, ratio 2:1, all values in  $\text{CDCl}_3$ ; IR: 920 and  $935\text{ cm}^{-1}$  (V = O terminal) [4]. They also differ from those of the octanuclear aggregate,  $\text{Cp}^*_6\text{V}_8\text{O}_{17}$  (**3**), ( $\delta(^1\text{H})$  2.11 ( $\text{C}_6\text{D}_6$ ), only one type of  $\text{Cp}^*$  ligands,  $\delta(^{51}\text{V})$  – 472 and – 573 (1:3) in  $\text{CDCl}_3$ ; IR: 975, 957, 943, 797 (broad) and  $660\text{ cm}^{-1}$ ) [5].

The chemistry of **2** and **3** is comparable, although the more soluble tetramer **2** reacts faster than **3**. The presence of sources for chloro ligands ( $\text{Cl}_2$ ,  $\text{SOCl}_2$ ,  $\text{Me}_3\text{SiCl}$ ) leads to  $\text{Cp}^*\text{V}(\text{O})\text{Cl}_2$  (**4**) (*cf.* [6]). The reaction of **2** or **3** with trimethylsilyl azide,  $\text{Me}_3\text{Si-N}_3$ , was used to prepare  $\text{Cp}^*\text{V}$  azido complexes [7, 8].

Trimethylsilyl azide is able to abstract oxo ligands and to introduce azido ligands ( $\text{N}_3$ ) into the coordination sphere [7]. Whereas **5** and **8** were characterized on the basis of their IR and NMR spectra [7], the molecular structures of **6** and **7** were determined by X-ray crystallography [7,8].

A similar reaction sequence can be established [9] for the reaction of **2** or **3** with trimethylsilyl isothiocyanate,  $\text{Me}_3\text{Si-NCS}$ , which leads to mono-

meric  $\text{Cp}^*\text{V}(\text{O})(\text{NCS})_2$  and  $\text{Cp}^*\text{V}(\text{NCS})_3$  or (in the presence of air) to the dinuclear oxo-bridged product  $[\text{Cp}^*\text{V}(\text{O})(\text{NCS})]_2(\mu\text{-O})$ , analogous to **7**.

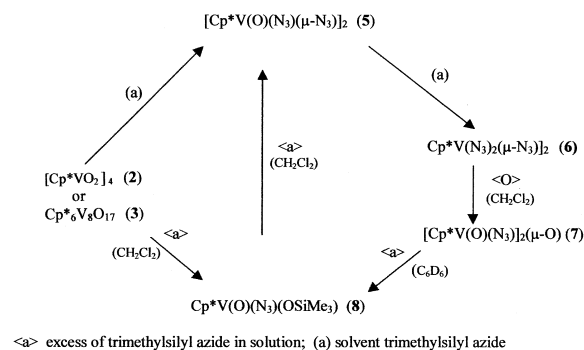
### X-ray crystal structures of **1** and **2**

The molecular structures of the tetracarbonyl-metal halfsandwich complexes  $\text{Cp}^*\text{M}(\text{CO})_4$  ( $\text{M} = \text{V}$  (**1**), Nb and Ta) have not been reported so far (*cf.* [10]). After many attempts we obtained suitable crystals of  $\text{Cp}^*\text{V}(\text{CO})_4$  (**1**) from pentane solution (monoclinic, space group  $\text{C}2/c$ ,  $Z = 8$ ). The square-pyramidal, tetra-legged piano-stool geometry is presented in Figs. 1a and 1b; the bond lengths and selected angles are compiled in Table 1.

The vanadium atom is not exactly centered above the  $\text{Cp}^*$  ring (Table 1). The methyl substituents (C(5)–C(10)) are bent outwards, away from the metal by  $6.7^\circ$  (av.). The planes defined by C(1)–C(5) (cyclopentadienyl ring) and C(11)–C(14) (carbonyl carbon atoms) are essentially parallel (dihedral angle  $1.3^\circ$ ). The vanadium-ring center distance (V– $\text{Cp}^*(Z)$  191.1 pm in **1**) is identical with that in the unsubstituted cyclopentadienyl complex  $\text{CpV}(\text{CO})_4$  in which the cyclopentadienyl ring is disordered (V– $\text{Cp}(Z)$  191.3 pm [11]). The angles between the (linear) carbonyl ligands in  $\text{Cp}^*\text{V}(\text{CO})_4$  (**1**) are  $122.9 \pm 0.9^\circ$  for the *trans*- and  $76.8 \pm 0.4$  for the *cis*-arrangement, whereas consistently small angles were registered for the two unsubstituted tetracarbonylmetal complexes  $\text{CpV}(\text{CO})_4$  ( $82.6(3)$ ,  $78.4(3)$  and  $75.7(1)^\circ$  [11]) and  $\text{CpNb}(\text{CO})_4$  ( $75.0(4)$ ,  $74.7(3)$  and  $74.4(3)^\circ$  [10]) which possess a mirror-symmetrical structure in the centrosymmetric space group  $\text{Pnma}$ .

Suitable crystals for an X-ray crystallographic structure analysis of the tetramer  $[\text{Cp}^*\text{V}(\text{O})(\mu\text{-O})]_4$  (**2**) were isolated during attempts to recrystallize  $\text{Cp}^*\text{V}(\text{CO})_4$  (**1**) from diethyl ether under an atmosphere of argon which inadvertently contained traces of air. The molecular structure of **2** is shown in Fig. 2, essential bond lengths and bond angles are given in Tables 2 and 3, respectively.

The triclinic unit cell (space group  $\text{P}\bar{1}$ ,  $Z = 4$ ) contains two pairs of molecules, *i. e.* **A** (Fig. 2) and **B**, with slightly differing distances and angles. The eight-membered ring of alternating  $[\text{Cp}^*\text{V}(\text{O})]$  fragments and oxo bridges is nearly planar, with only one  $[\text{Cp}^*\text{V}(\text{O})]$  corner protruding from the



Scheme 1. Reactions of **2** and **3** with trimethylsilyl azide,  $\text{Me}_3\text{Si-N}_3$  (a).

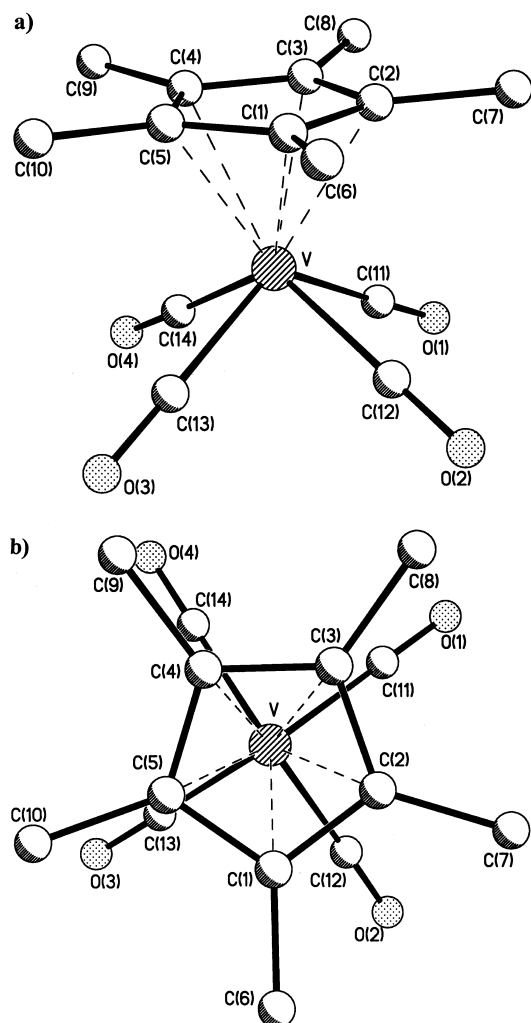


Fig. 1. Molecular structure of  $\text{Cp}^*\text{V}(\text{CO})_4$  (**1**) in the crystal. 1a: Piano-stool model; 1b: View along the  $\text{V}-\text{Cp}^*(\text{Z})$  axis.

plane of the remaining 7 atoms,  $\text{V}_3(\mu\text{-O})_4$ . In the case of molecule **A** (which contains  $\text{V}(1)-\text{V}(4)$  and  $\text{O}(1)-\text{O}(8)$ ), a dihedral angle of  $103.1^\circ$  is found between plane  $\text{O}(5)-\text{V}(1)-\text{O}(8)$  and the main plane  $\text{O}(5)\text{V}(2)\text{O}(6)\text{V}(3)\text{O}(7)\text{V}(4)\text{O}(8)$  (mean deviations 4.1 pm, *cf.* Fig. 3).

It is interesting to note that the related eight-membered ring of the antiferromagnetic chloro-oxo vanadium(IV) complex,  $[\text{Cp}^*\text{V}(\text{Cl})(\mu\text{-O})]_4$ , is essentially planar [12]; the four oxo bridges occupy sites on a crystallographic plane, with the vanadium atoms alternating by  $\pm 4.7$  pm above and be-

Table 1. Bond lengths [pm] and selected bond angles [ $^\circ$ ] in pentamethylcyclopentadienyl tetracarbonylvanadium,  $\text{Cp}^*\text{V}(\text{CO})_4$  (**1**).

$\text{V}-\text{C}(1)$	225.2(4)	$\text{C}(1)-\text{C}(2)$	142.0(6)
$\text{V}-\text{C}(2)$	224.6(4)	$\text{C}(1)-\text{C}(5)$	142.1(6)
$\text{V}-\text{C}(3)$	226.8(4)	$\text{C}(2)-\text{C}(3)$	142.9(6)
$\text{V}-\text{C}(4)$	228.3(4)	$\text{C}(3)-\text{C}(4)$	140.3(6)
$\text{V}-\text{C}(5)$	226.7(4)	$\text{C}(4)-\text{C}(5)$	141.7(7)
$\text{V}-\text{C}(11)$	194.0(5)	$\text{C}(1)-\text{C}(6)$	149.5(7)
$\text{V}-\text{C}(12)$	193.8(5)	$\text{C}(2)-\text{C}(7)$	150.6(6)
$\text{V}-\text{C}(13)$	192.3(5)	$\text{C}(3)-\text{C}(8)$	150.5(6)
$\text{V}-\text{C}(14)$	194.0(5)	$\text{C}(4)-\text{C}(9)$	150.5(6)
		$\text{C}(5)-\text{C}(10)$	151.7(6)
$\text{C}(11)-\text{O}(1)$	114.2(5)	$\text{V}-\text{Cp}^*(\text{Z})$	191.5
$\text{C}(12)-\text{O}(2)$	113.7(5)		
$\text{C}(13)-\text{O}(3)$	116.2(5)		
$\text{C}(14)-\text{O}(4)$	113.8(5)		
$\text{C}(11)-\text{V}-\text{C}(12)$	77.2(2)	$\text{V}-\text{C}(11)-\text{O}(1)$	179.0(5)
$\text{C}(11)-\text{V}-\text{C}(13)$	122.0(2)	$\text{V}-\text{C}(12)-\text{O}(2)$	178.5(5)
$\text{C}(11)-\text{V}-\text{C}(14)$	76.4(2)	$\text{V}-\text{C}(13)-\text{O}(3)$	178.6(5)
$\text{C}(12)-\text{V}-\text{C}(13)$	76.5(2)	$\text{V}-\text{C}(14)-\text{O}(4)$	178.7(5)
$\text{C}(12)-\text{V}-\text{C}(14)$	123.8(2)		
$\text{C}(13)-\text{V}-\text{C}(14)$	77.1(2)		

$\text{Cp}^*(\text{Z})$  is the center of the pentamethylcyclopentadienyl ring,  $\text{Cp}^*$ .

low the  $\text{O}_4$  plane, and  $\text{Cp}^*$  or Cl also alternating above and below this plane.

It is tempting to assume that the particular  $[\text{Cp}^*\text{V}(\text{O})]$  corner of **2** loses its  $\text{Cp}^*$  ring ligand and combines with a second  $\text{Cp}^*$ -deficient fragment  $[\text{Cp}^*_3\text{V}_4\text{O}_8]$  via an additional oxo bridge to give  $[\text{Cp}^*_3\text{V}_4(\text{O})_4(\mu\text{-O})_4](\mu\text{-O})$  (**3**). Single oxo

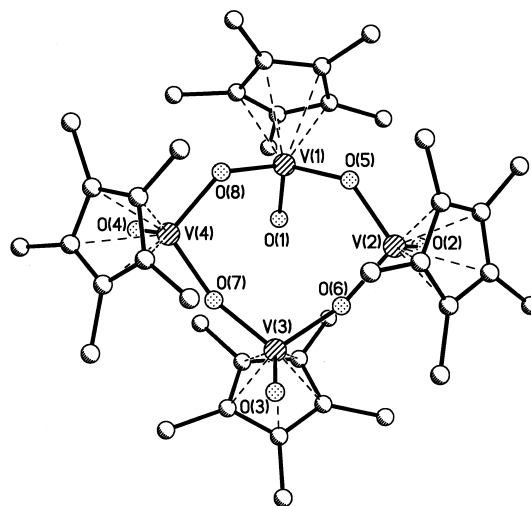


Fig. 2. Molecular structure of  $[\text{Cp}^*\text{V}(\text{O})(\mu\text{-O})]_4$  (**2**), molecule **A**.

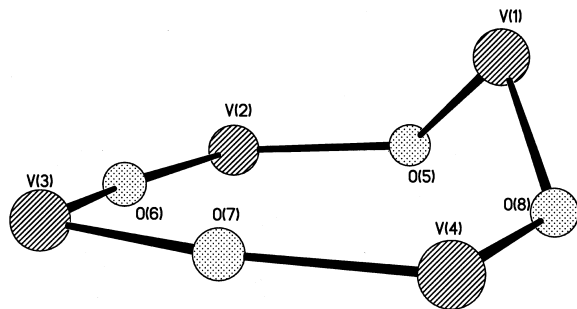


Fig. 3. Central eight-membered  $V_4O_4$  ring in  $[Cp^*V(O)(\mu-O)]_4$  (**2**), molecule **A**.

bridges between cluster aggregates are known, *e. g.*  $[Cp_5V_6(\mu_3-O)_8]_2(\mu-O)$  [13].

In complex **2** the bond distances between the vanadium atoms and the respective terminal oxo ligand (av.  $161.3(8) \pm 0.8$  pm) indicate  $V=O$  double bonds, whereas the vanadium-oxygen bond lengths within the ring (av.  $180.2 \pm 0.9$  pm) are compatible with single bonds. The angles  $O-V-O$  within the ring of molecule **A** (av.  $105.6 \pm 0.8^\circ$ ) are very similar. However, due to the non-planar geometry of the eight-membered ring, two types of  $V-O-V$  angles are found, *i. e.*  $128.3 \pm 1.0^\circ$  at  $O(5)$  and  $O(8)$ , but  $164.5 \pm 0.7^\circ$  at  $O(6)$  and  $O(7)$  respectively, whereas all  $V-O-V$  angles are  $165.1(5)^\circ$  in the planar ring of  $[Cp^*V(Cl)(\mu-O)]_4$  [12]. Generally, the distances and angles in **2**

Table 3. Angles  $[\circ]$  involving vanadium and oxygen in the tetramer  $[Cp^*V(O)(\mu-O)]_4$  (**2**), molecule **A**.

$O(1)-V(1)-O(5)$	103.9(4)	$O(2)-V(2)-O(5)$	104.5(4)
$O(1)-V(1)-O(8)$	104.5(4)	$O(2)-V(2)-O(6)$	104.9(5)
$O(5)-V(1)-O(8)$	106.1(3)	$O(5)-V(2)-O(6)$	104.8(4)
$Z^1-V(1)-O(1)$	115.6	$Z^2-V(2)-O(2)$	117.4
$Z^1-V(1)-O(5)$	113.6	$Z^2-V(2)-O(5)$	111.8
$Z^1-V(1)-O(8)$	112.3	$Z^2-V(2)-O(6)$	112.8
$O(3)-V(3)-O(6)$	103.3(4)	$O(4)-V(4)-O(7)$	105.5(4)
$O(3)-V(3)-O(7)$	103.8(4)	$O(4)-V(4)-O(8)$	105.4(4)
$O(6)-V(3)-O(7)$	105.9(4)	$O(7)-V(4)-O(8)$	105.6(3)
$Z^3-V(3)-O(3)$	116.2	$Z^4-V(4)-O(4)$	114.9
$Z^3-V(3)-O(6)$	111.5	$Z^4-V(4)-O(7)$	112.3
$Z^3-V(3)-O(7)$	114.9	$Z^4-V(4)-O(8)$	112.5
$V(1)-O(5)-V(2)$	129.3(5)	$V(2)-O(6)-V(3)$	165.2(5)
$V(3)-O(7)-V(4)$	163.9(5)	$V(4)-O(8)-V(1)$	127.3(5)

$Z^n$  is the center of the pentamethylcyclopentadienyl ring coordinated to  $V(n)$  ( $n = 1,2,3,4$ ).

are similar to the corresponding parameters of related molecules such as  $Cp^*V(O)Cl_2$  [12] and  $[Cp^*V(Cl)(\mu-O)]_4$  [12] (Table 4).

## Experimental Section

The reactions were routinely carried out under argon in Schlenk vessels; the solvents were dried (pentane over Na/K alloy,  $CH_2Cl_2$  over  $P_4O_{10}$ ) and saturated with argon.

The parent compound,  $Cp^*V(CO)_4$  (**1**) [14], the octanuclear aggregate  $Cp^*_6V_8O_{17}$  (**3**) [5] and the azido complex  $[Cp^*V(N_3)_2(\mu-N_3)]_2$  (**6**) [8] were prepared according to the quoted literature procedures.

### Synthesis of $[Cp^*V(O)(\mu-O)]_4$ (**2**)

In a 250 ml round-bottomed flask, a solution of 75 mg (0.25 mmol)  $Cp^*V(CO)_4$  (**1**) in 100 ml of pentane was stirred in air for 4 h. After standing over night, some insoluble black precipitate (up to 5 mg) had formed. The clear black pentane solution (which appears red in transparent light) was brought to dryness to give 50 mg (91%) of **2** as a black powder, dec. above  $300^\circ$  without melting.

### Synthesis of $[Cp^*V(N_3)_2(\mu-N_3)]_2$ (**6**)

Starting from 150 mg (0.50 mmol) of  $Cp^*V(CO)_4$  (**1**), the oxidative decarbonylation in the presence of  $O_2$  gas in pentane or toluene solution led to a mixture of **2** and **3**. The black residue was dissolved in 10 ml of neat trimethylsilyl azide,  $Me_3Si-N_3$ . After 3–4 weeks at ambient temperature the solvent was evaporated under reduced pressure and the dark-green residue dried in a high vacuum to give 90–95 mg (79–83%) of

Table 2. Bond lengths [pm] involving vanadium in the tetramer  $[Cp^*V(O)(\mu-O)]_4$  (**2**), molecule **A**.

$V(1)-O(1)$	162.1(8)	$V(2)-O(2)$	160.5(8)
$V(1)-O(5)$	179.9(7)	$V(2)-O(5)$	179.8(8)
$V(1)-O(8)$	180.9(7)	$V(2)-O(6)$	179.4(8)
$V(1)-C(1)$	242.1(16)	$V(2)-C(11)$	235.9(15)
$V(1)-C(2)$	241.8(16)	$V(2)-C(12)$	228.9(14)
$V(1)-C(3)$	229.4(14)	$V(2)-C(13)$	224.3(13)
$V(1)-C(4)$	225.9(13)	$V(2)-C(14)$	239.3(16)
$V(1)-C(5)$	226.3(13)	$V(2)-C(15)$	243.8(14)
$V(1)-Cp^*(Z^1)$	202.0	$V(2)-Cp^*(Z^2)$	202.9
$V(3)-O(3)$	160.8(8)	$V(4)-O(4)$	161.8(7)
$V(3)-O(6)$	179.8(8)	$V(4)-O(7)$	180.1(7)
$V(3)-O(7)$	179.4(7)	$V(4)-O(8)$	182.8(8)
$V(3)-C(21)$	244.7(15)	$V(4)-C(31)$	230.9(18)
$V(3)-C(22)$	227.7(15)	$V(4)-C(32)$	230.8(16)
$V(3)-C(23)$	227.3(15)	$V(4)-C(33)$	232.3(15)
$V(3)-C(24)$	236.6(14)	$V(4)-C(34)$	244.4(15)
$V(3)-C(25)$	245.3(15)	$V(4)-C(35)$	236.4(18)
$V(3)-Cp^*(Z^3)$	205.0	$V(4)-Cp^*(Z^4)$	205.6

$Cp^*(Z^n)$  is the center of the pentamethylcyclopentadienyl ring coordinated to  $V(n)$  ( $n = 1,2,3,4$ ).

Complex	Cp*V(O)Cl <sub>2</sub> ( <b>4</b> ) [12]	[Cp*V(O)(μ-O)] <sub>4</sub> ( <b>2</b> ) (this work)	[Cp*V(Cl)(μ-O)] <sub>4</sub> [12]
V = O	157.6(8)	161.3(8) av. 180.2(8) av.	180.0(2)
V-Cp*(Z)	199.9	203.9 av.	198.4
Cp*(Z)-V-O (terminal O)	113.2	116.0 av.	–
Cp*(Z)-V-O (bridging O)	–	112.7 av.	135.4
O-V-O (bridges)	–	105.6 av.	104.8(2)
V-O-V (bridges)	–	164.5 av. 128.3 av.	165.1(5)

Table 4. Characteristic distances [pm] and angles [°] in oxovanadium complexes.

Cp\*(Z) is the center of the Cp\* ring.

green-black **6**. The azido complex may decompose explosively above 100 °C, and scratching with a metal spatula can also cause violent disintegration. The spectroscopic data of **6** agree with the literature values [8].

#### *X-ray structure determinations of 1 and 2 [15]*

The reflection intensities were collected with graphite-monochromated Mo-K<sub>α</sub> – radiation,  $\lambda = 71.073$  pm. Structure solution and refinement was carried out with the program package SHELXTL-PLUS V.5.1; the temperature for both structure determinations was 296 K.

All non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms were placed in calculated positions and refined applying the riding model with fixed isotropic temperature factors.

#### *Crystal structure of Cp\*V(CO)<sub>4</sub> (1)*

Reflection intensities were measured on a four circle diffractometer Siemens P4. C<sub>14</sub>H<sub>15</sub>O<sub>4</sub>V, orange platelet with dimensions 0.18 × 0.14 × 0.06 mm, crystallizes in the monoclinic space group C2/c with the lattice parameters  $a = 1514.61(18)$ ,  $b = 680.56(8)$ ,  $c = 2900.7(3)$  pm,  $\beta = 101.840(9)^\circ$ ,  $V = 2926.4(6) \cdot 10^6$  pm<sup>3</sup>,  $Z = 8$ ,  $\mu =$

0.684 mm<sup>−1</sup>; 2986 reflections collected in the range  $3^\circ \leq 2\theta \leq 50^\circ$ , 2245 reflections independent, 1520 assigned to be observed [ $I > 2\sigma(I)$ ], full-matrix least squares refinement against  $F^2$  with 173 parameters converged at  $R1/wR2$ -values of 0.051/0.121, the max./min. residual electron density was 0.362/− 0.259 · 10<sup>−6</sup> e · pm<sup>−3</sup>.

#### *Crystal structure of [Cp\*V(O)(μ-O)]<sub>4</sub> (2)*

Reflection intensities were measured on the STOE Image Plate Diffraction System I. C<sub>40</sub>H<sub>120</sub>O<sub>8</sub>V<sub>4</sub>, a plate with dimensions 0.14 × 0.12 × 0.08 mm, crystallizes in the triclinic space group  $P\bar{1}$  with the lattice parameters  $a = 1162.3(2)$ ,  $b = 2014.9(4)$ ,  $c = 2077.8(4)$  pm,  $\alpha = 110.61(3)^\circ$ ,  $\beta = 102.76(3)^\circ$ ,  $\gamma = 97.47(3)^\circ$ ,  $V = 4325.5(15) \cdot 10^6$  pm<sup>3</sup>,  $Z = 4$ ,  $\mu = 0.874$  mm<sup>−1</sup>; 36.709 reflections collected in the range  $3^\circ \leq 2\theta \leq 56^\circ$ , 19082 reflections independent, 2445 assigned to be observed [ $I > 2\sigma(I)$ ], full-matrix least squares refinement against  $F^2$  with 533 parameters converged at  $R1/wR2$  values of 0.092/0.207; numerical absorption correction, the max./min. residual electron density was 0.684/− 0.303 · 10<sup>−6</sup> e · pm<sup>−3</sup>.

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- [15] Crystallographic Data (excluding structure factors) for the structures **1** and **2** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-201885 (**2**) and CCDC-201886 (**1**). Copies of the data can be obtained free of charge from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: int. code +(1223)336-0333; E-mail: deposit@ chemcrys.cam.ac.uk