Decarbonylation of Pentamethylcyclopentadienyl Tetracarbonylvанадиум,
Cp*V(CO)₄, in the Presence of Oxygen. The X-Ray Crystal Structure Analyses
of Cp*V(CO)₄ and [Cp*V(O)(μ-O)]₄

Max Herberhold, Anna-Maria Dietel, and Wolfgang Milius
Anorganisch-chemisches Laboratorium der Universität Bayreuth, Postfach 10 12 51,
D-95440 Bayreuth
Reprint requests to Prof. M. Herberhold. Fax: +49(0)921-55-2157.
E-mail: Max.Herberhold@uni.bayreuth.de

Dedicated to Professor Hartmut Bärnighausen on the occasion of his 70th birthday
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The reaction of Cp*V(CO)₄ (1) with molecular oxygen in diluted pentane solution leads to
a tetrameric dioxide, [Cp*V(O)(μ-O)]₄ (2), which is a precursor of the octanuclear aggregate
Cp*₆V₈O₁₇ (3). The molecular structures of 1 and 2 have been determined by X-ray crystal-
lography.

Key words: Vanadium, Organometallic Oxides, Crystal Structures

Introduction

Organometallic oxides containing the 10-elec-
tron fragment pentamethylcyclopentadienyl-vana-
dium (Cp*V) are well known [1–3]; prominent
examples are the pseudocubane cluster [Cp*V-
(μ₃-O)]₄ and the adamantane-type assembly
[Cp*V]₄(μ-O)₆ which contain vanadium(III) and
vanadium(IV), respectively. Both are conveniently
synthesized [2] by reductive aggregation of
Cp*V(O)Cl₂.

The vanadium[V] oxide, [Cp*VO₂], is not avail-
able in the monomeric form, but the trimer,
[Cp*V(O)(μ-O)]₃, has been obtained by the reac-
tion of Cp*V(O)Cl₂ with Ag₂CO₃ in THF solu-
tion [4].

As an alternative route to Cp* vanadium(V)
oxides, the oxidative decarbonylation of
Cp*V(CO)₄ (1) by molecular oxygen has been stud-
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 spec-
troscopic data (H, ¹³C, ¹⁷O and ⁵¹V) are consistent
with an oxo bridge between two tetraneuclear sub-
units, i.e. [Cp*V₄(O)(μ-O)]₄(μ-O). The same
product of composition Cp*₆V₈O₁₇ was also ob-
tained from analogous reactions of VCP*₂ [6],
oxygen gas in solution.

Results and Discussion

We have observed that a tetraneuclear interme-
diate, [Cp*VO₂]₄ (2), is formed during the early
stages of the oxidative decarbonylation of
Cp*V(CO)₄ (1) along the route to the octanuclear
aggregate, Cp*₆V₈O₁₇ (3).

Synthesis and reactivity of the tetramer
[Cp*V(O)(μ-O)]₄ (2)

If a slow stream of O₂ is bubbled through a satu-
rated solution of Cp*V(CO)₄ (1), e.g. 2 mmol of 1
in 100 ml of pentane, a quantitative conversion to
Cp*₆V₈O₁₇ (3) eventually takes place, and the
nearly colourless solvent can be decanted from the
insoluble black precipitate of 3. If, however, a di-
luted solution, e.g. 0.25 mmol of 1 in 100 ml of
pentane, is stirred in air (i.e., O₂ diluted by a four-
fold excess of N₂), a red-black pentane solution
is obtained from which some black precipitate of
compound 3 forms over night. The pentane solu-
tion contains the tetramer [Cp*V(O)(μ-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 (Cp*), 1261 m, 959 w and 927 w,
800 and 722 (broad) cm⁻¹, CsI pellet) indicates the
presence of both terminal and bridging oxo li-
gands. The ¹H NMR spectrum of 2 (in C₆D₆) con-
tains three signals at δ 2.21, 2.14 and 2.10 with
an integrated intensity ratio of 1:2:1, whereas two peaks are observed in the $^{51}$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 $^{51}$V NMR spectrum; it is accelerated in polar solvents such as CDCl$_3$. In line with this experience, a reliable $^{13}$C NMR spectrum of 2 was not obtained due to the formation of 3. The spectroscopic data of the red-black tetramer [Cp*$\nu$V(O)(μ-O)]$_4$ (2) are significantly different from those of the blue trimer [Cp*$\nu$V(O)(μ-O)]$_3$ ($\delta^{(1)}$H) 2.13 and 2.09, intensity ratio 1:2; $\delta(^{51}$V) – 530 and – 547, ratio 2:1, all values in CDCl$_3$; IR: 920 and 935 cm$^{-1}$ (V = O terminal) [4].

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 (Cl$_2$, SOCl$_2$, Me$_3$SiCl) leads to Cp*$\nu$V(O)Cl$_2$ (4) (cf. [6]). The reaction of 2 or 3 with trimethylsilyl azide, Me$_3$Si-N$_3$, was used to prepare Cp*$\nu$V azido complexes [7, 8].

Trimethylsilyl azide is able to abstract oxo ligands and to introduce azido ligands (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, Me$_3$Si-NCS, which leads to monomeric Cp*$\nu$V(O)(NCS)$_2$ and Cp*$\nu$V(NCS)$_3$ or (in the presence of air) to the dinuclear oxo-bridged product [Cp*$\nu$V(O)(NCS)]$_2$(μ-O), analogous to 7.

X-ray crystal structures of 1 and 2

The molecular structures of the tetracarbonyl-metal halfsandwich complexes Cp*$\nu$M(CO)$_4$ (M = V (1), Nb and Ta) have not been reported so far (cf. [10]). After many attempts we obtained suitable crystals of Cp*$\nu$V(CO)$_4$ (1) from pentane solution (monoclinic, space group $C2/c$, $Z = 8$). 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 Cp* ring (Table 1). The methyl substituents (C(5) – C(10)) are bent outwards, away from the metal by 6.7° (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°). The vanadium-ring center distance (V-Cp*Z) 191.1 pm in 1 is identical with that in the unsubstituted cyclopentadienyl complex CpV(CO)$_4$ in which the cyclopentadienyl ring is disordered (V-Cp(Z) 191.3 pm [11]). The angles between the (linear) carbonyl ligands in Cp*$\nu$V(CO)$_4$ (1) are 122.9 ± 0.9° for the trans- and 76.8 ± 0.4 for the cis-arrangement, whereas consistently small angles were registered for the two unsubstituted tetracarbonylmetal complexes CpV(CO)$_4$ (82.6(3), 78.4(3) and 75.7(1)° [11]) and CpNb(CO)$_4$ (75.0(4), 74.7(3) and 74.4(3)° [10]) which possess a mirror-symmetrical structure in the centrosymmetric space group $Pnma$.

Suitable crystals for an X-ray crystallographic structure analysis of the tetramer [Cp*$\nu$V(O)(μ-O)]$_4$ (2) were isolated during attempts to recrystallize Cp*$\nu$V(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 $P\bar{1}$, $Z = 4$) contains two pairs of molecules, i.e. A (Fig. 2) and B, with slightly differing distances and angles. The eight-membered ring of alternating [Cp*$\nu$V(O)] fragments and oxo bridges is nearly planar, with only one [Cp*$\nu$V(O)] corner protruding from the
plane of the remaining 7 atoms, V₃(μ-O)₄. In the case of molecule A (which contains V(1)–V(4) and O(1)–O(8)), a dihedral angle of 103.1°

It is interesting to note that the related eight-membered ring of the antiferromagnetic chloro-oxo vanadium(IV) complex, [Cp*V(Cl)(μ-O)]₄, is essentially planar [12]; the four oxo bridges occupy sites on a crystallographic plane, with the vanadium atoms alternating by ± 4.7 pm above and below the O₄ plane, and Cp* or Cl also alternating above and below this plane.

It is tempting to assume that the particular [Cp*V(O)] corner of 2 loses its Cp* ring ligand and combines with a second Cp*-deficient fragment [Cp*₃V₄O₈] via an additional oxo bridge to give [Cp*₃V₄(O)₄(μ-O)₄][μ-O] (3). Single oxo
bridges between cluster aggregates are known, e.g. \([\text{Cp}_5\text{V}_6(\mu_3\text{-O})_8]_2(\mu\text{-O})\) \[13\].

In complex 2 the bond distances between the vanadium atoms and the respective terminal oxo ligand (av. 161.3(8) ± 0.8 pm) indicate V=O double bonds, whereas the vanadium-oxygen bond lengths within the ring (av. 180.2 ± 0.9 pm) are compatible with single bonds. The angles O-V-O within the ring of molecule A (av. 105.6 ± 0.8°) 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(1.0°) at O(5) and O(8), but 164.5(0.7°) at O(6) and O(7) respectively, whereas all V-O-V angles are 165.1(5)° in the planar ring of \([\text{Cp*V(Cl)(\mu\text{-O})}]_4\) \[12\]. Generally, the distances and angles in 2 are similar to the corresponding parameters of related molecules such as \(\text{Cp*V(O)Cl}_2\) \[12\] and \([\text{Cp*V(Cl)(\mu\text{-O})}]_4\) \[12\] (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$_2$Cl$_2$ over P$_4$O$_10$) and saturated with argon.

The parent compound, \(\text{Cp*V(CO)}_4\) \(1\) \[14\], the octanuclear aggregate \(\text{Cp}_6\text{V}_8\text{O}_{17}\) \(3\) \[5\] and the azido complex \([\text{Cp*V(N}_3)_2(\mu\text{-N}_3)]_2\) \(6\) \[8\] were prepared according to the quoted literature procedures.

#### Synthesis of \(\text{Cp*V(O)(\mu\text{-O})}_4\) \(2\)

In a 250 ml round-bottomed flask, a solution of 75 mg (0.25 mmol) \(\text{Cp*V(CO)}_4\) \(1\) in 100 ml of pentane was stirred in air for 4 h. After standing overnight, 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 by giving 50 mg (91%) of 2 as a black powder, dec. above 300° without melting.

#### Synthesis of \(\text{Cp*V(N}_3)_2(\mu\text{-N}_3)]_2\) \(6\)

Starting from 150 mg (0.50 mmol) of \(\text{Cp*V(CO)}_4\) \(1\), 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$_3$Si-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
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-Kα radiation, λ = 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(O)Cl₂ (4)

Reflection intensities were measured on a four circle diffractometer Siemens P4. C₁₄H₁₅O₄V, 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, β = 101.840(9)°, V = 2926.4(6) · 10⁶ pm³, Z = 8, μ = 0.684 mm⁻¹; 2986 reflections collected in the range 3° ≤ 2θ ≤ 50°, 2245 reflections independent, 1520 assigned to be observed [I > 2σ(I)], full-matrix least squares refinement against F² with 173 parameters converged at R₁/wR₂-values of 0.051/0.121, the max./min. residual electron density was 0.362/0.259 · 10⁻⁶ e · pm⁻³.

Crystal structure of [Cp*V(O)(µ-O)]₄ (2)

Reflection intensities were measured on the STOE Image Plate Diffraction System I. C₄₀H₁₂₀O₈V₄, a plate with dimensions 0.14 × 0.12 × 0.08 mm, crystallizes in the triclinic space group P1 with the lattice parameters a = 1162.3(2), b = 2014.9(4), c = 2077.8(4) pm, α = 110.61(3)°, β = 102.76(3)°, γ = 97.47(3)°, V = 4325.5(15) · 10⁶ pm³, Z = 4, μ = 0.874 mm⁻¹; 36.709 reflections collected in the range 3° ≤ 2θ ≤ 56°, 19082 reflections independent, 2445 assigned to be observed [I > 2σ(I)], full-matrix least squares refinement against F² 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 · 10⁻⁶ e · pm⁻³.

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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)336-033; E-mail: deposit@chemcrys.cam.ac.uk