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ARTICLE TYPE

Trinuclear and tetranuclear cyclopentadienyl vanadium carbonyl clusters: unusual carbonyl groups in Herrmann's $(C_5H_5)_4V_4(CO)_4$ exhibiting low CO stretching frequencies

Lu Li [a,b], **Shida Gong**[a,c], **Xiuhui Zhang***[a,b], **Qian-shu Li**[b,c] and **R. Bruce King***[c,d]

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Abstract

The pyrolysis of $Cp_2V_2(CO)_5$ in tetrahydrofuran solution is reported by Herrmann and co-workers to give a tetranuclear $Cp_4V_4(CO)_4$ cluster as a major product and the trinuclear $Cp_3V_3(CO)_9$ as a minor product. Neither of these products has been characterized structurally. A theoretical study of the $Cp_4V_4(CO)_4$ system reveals a complicated energy surface having 10 structures within 25 kcal/mol of the global minimum encompassing singlet, triplet, and quintet spin states. The lowest energy $Cp_4V_4(CO)_4$ structures are nearly degenerate (within 1 kcal/mol) triplet and singlet structures with a central V_4 distorted tetrahedron with a μ_3-CO group bridging each face. Higher energy singlet and triplet $Cp_4V_4(CO)_4$ structures are also found with a central V_4 butterfly and an unusual η^2-μ_4-CO group bridging all four vanadium atoms through four V-C bonds and one V-O bond. None of the ten $Cp_4V_4(CO)_4$ structures has any terminal CO groups, which is totally different with the $Cp_4V_4(CO)_4$ structure with exclusively terminal CO groups suggested from the experimental work. The lowest energy $Cp_3V_3(CO)_9$ structure has a central equilateral V_3 triangle and all terminal CO groups. However, this $Cp_3V_3(CO)_9$ structure is disfavored by ~34 kcal/mol relative to fragmentation into the stable compounds $CpV(CO)_4$ + $Cp_2V_2(CO)_5$ consistent with its low yield in the $Cp_2V_2(CO)_5$ pyrolysis.

1. Introduction

Vanadium is of interest since it forms mononuclear, binuclear, trinuclear, and tetranuclear cyclopentadienylvanadium carbonyls. The orange mononuclear $CpV(CO)_4$ (Cp = η^5-C_5H_5) was synthesized by Fischer and Vigoureux[1] in the early days of cyclopentadienylmetal chemistry using the reaction of Cp_2V with CO under pressure. Its structure was subsequently determined experimentally in the solid state using X-ray crystallography[2] and in the gas phase using electron diffraction[3] (Fig. 1). Photolysis of $CpV(CO)_4$ gives the green binuclear $Cp_2V_2(CO)_5$ (refs. 4, 5, 6, 7), which is the first member of a series of stable binuclear first row transition metal derivatives containing formal M≡M triple bonds including also $Cp_2Cr_2(CO)_4$ (ref. 8) and $Cp_2Mn_2(CO)_5$ (ref. 9).

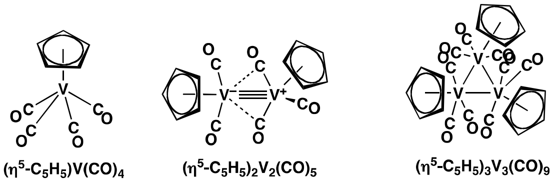


Fig. 1. The structures of $CpV(CO)_4$ and $Cp_2V_2(CO)_5$ established by X-ray crystallography and the presumed structure of $Cp_3V_3(CO)_9$ (refs. 2, 6, 10).

The trinuclear and tetranuclear cyclopentadienylvanadium carbonyls were obtained by Herrmann and coworkers from the pyrolysis of $Cp_2V_2(CO)_5$ in tetrahydrofuran with the mononuclear $CpV(CO)_4$ as a byproduct.[10] The deep black trinuclear $Cp_3V_3(CO)_9$ is obtained in only ~2% yield and has not been structurally characterized by X-ray crystallography. The presumed structure in Fig. 1 with a central V_3 triangle and exclusively terminal CO groups is in accord with the ν(CO) frequencies and obeys the 18-electron rule. The structure of the likewise black tetranuclear derivative $Cp_4V_4(CO)_4$ is somewhat a mystery since the only reported ν(CO) frequencies occur in the 1999 to 2029 cm^{-1} region associated with terminal CO groups. This would appear to exclude a structure analogous to that for the tetranuclear cyclopentadienyliron carbonyl cluster $Cp_4Fe_4(\mu_3$-$CO)_4$ in which each of the four faces of a central Fe_4 tetrahedron is bridged by a CO group.[11]

Possible $Cp_4V_4(CO)_4$ structures with the maximum six V-V bonds in a central V_4 tetrahedron and exclusively terminal CO groups require formal V=V double bonds for the six edges of the tetrahedron for each vanadium atom to have the favored 18-electron configuration. Such a bonding model requires 10 orbitals from each vanadium atom to form three V=V double bonds to the other vanadium atoms (total of six orbitals), the usual σ + 2π bond to the η^5-C_5H_5 ring (three more orbitals), and a σ bond to the terminal CO group (a tenth orbital). However, a vanadium atom clearly has only nine orbitals available in its sp^3d^5 bonding model so something is clearly wrong with this bonding model. In addition, if we assume six V-V single bonds for the edges of this tetrahedron, each vanadium atom will have an unfavorable configuration of only 15 electrons rather than 16 or 18 electrons. In an attempt to resolve this dilemma we have used density functional theory (DFT) to explore low-energy $Cp_4V_4(CO)_4$ structures. We have also used DFT to investigate probable structures for the trinuclear derivative $Cp_3V_3(CO)_9$, which has not been structurally characterized by X-ray crystallography. This paper reports the results of such studies.

2. Theoretical Methods

Electron-correlation effects were considered by using density functional theory (DFT) methods, which have evolved as a practical and effective computational tool, especially for organometallic compounds.[12-18] In the present study, all of the computations were carried out by two selected DFT methods implemented in the Gaussian 09 program package.[19] The first functional is the pure DFT method known as BP86, which combines Becke's 1988 exchange functional (B)[20] with Perdew's 1986 gradient corrected correlation functional (P86).[21] The second method is the PBE method, which is a pure generalized gradient proposed by Perdew, Burke and Ernzerhof.[22] The results predicted by the two functionals are generally in agreement with each other. The BP86 and PBE methods have proven to be reliable for the transition metal organometallic systems[23,24], However, it has been noted elsewhere that the BP86 method usually provides more reliable vibrational frequencies[25,26] for the type of organometallic systems considered in this paper.

All calculations were performed using the double-ζ plus polarization (DZP) basis sets. The DZP basis sets used for carbon and oxygen add one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(C) = 0.75$ and $\alpha_d\ (O) = 0.85$ to the standard Huzinaga-Dunning contracted DZ sets[27,28] and are designated (9s5p1d/4s2p1d). For hydrogen, a set of p polarization functions with $\alpha_p\ (H) = 0.75$ is added to the Huzinaga-Dunning DZ set. The loosely contracted DZP basis set for vanadium is the Wachters primitive set[29] augmented by two sets of p functions and a set of d functions, contracted following Hood, Pitzer, and Schaefer,[30] designated (14s11p6d/10s8p3d).

In order to test the computational accuracy of the two selected DFT methods, we optimized the experimental determined compound $Cp_2V_2(CO)_5$[7] at the BP86/DZP and PBE/DZP levels of theory. The results are listed in Tables S1 and S2 (Supporting Information). As shown in Tables S1 and S2, the V-V bond lengths and the ν(CO) frequencies calculated by both BP86 and PBE methods are close to the experimental values, indicating that these two methods are reliable for this system. Thus, in the present study, the geometries of all structures were fully optimized using the DZP BP86 and DZP PBE methods. The fine grid (75 radial shells, 302 angular points) was the default for evaluating integrals numerically, and the tight (10^{-8} hartree) designation is the default for the self-consistent field (SCF) energy convergence. The finer (120, 974) integration grid was used to check small imaginary vibrational frequencies.

In the present study, the BP86 and PBE methods agree with each other fairly well in predicting the geometries and ν(CO) frequencies of $Cp_3V_3(CO)_9$ and $Cp_4V_4(CO)_4$. Therefore, only the BP86 results are discussed in the text. Both the results of PBE and BP86 methods are presented in the Supporting Information.

In addition, TZP basis set has been used to ascertain the DZP basis set minima at BP86/TZP level. The results calculated at BP86/DZP and BP86/TZP levels for our system are consistent with each other very well. Meanwhile, the hybrid functional PBE0 has been used to calculate the lowest energy structure of triplet and quintet state for $Cp_4V_4(CO)_4$. However, the spin contamination calculated at PBE0/DZP level is serious, with $\langle S^2\rangle = 3.5$ and 7.3 for **4T-1** and **4Q-1**, respectively, which are much larger than the corresponding ideal value of 2.0 and 6.0. Thus the PBE0 method has not been selected to calculate this system. The corresponding results have been presented in the Supporting Information (Tables S12 to S16).

3. Results and Discussion

3.1 The tetranuclear derivative $Cp_4V_4(CO)_4$

The $Cp_4V_4(CO)_4$ energy surface is a complicated one with five singlet, three triplet and two quintet stationary points within 25 kcal/mol of the global minimum (Figs. 2 to 4 and Table 1). All of these structures are predicted to be genuine minima with no imaginary vibrational frequencies. Eight of the ten $Cp_4V_4(CO)_4$ structures have central V_4 tetrahedra with all six V–V distances less than 3.0 Å corresponding to direct metal-metal interactions. The remaining two $Cp_4V_4(CO)_4$ structures **4T-2** and **4S-2** have central V_4 butterflies with five V–V bonding distances and a sixth V···V non-bonding distance of ~3.8 Å between the wingtips of the V_4 butterfly.

Table 1. The ten $Cp_4V_4(CO)_4$ stationary points within 25 kcal/mol of energy relative to **4T-1** indicating the geometry of the central V_4 unit and the V–V distances. Non-bonding V···V distances between the wingtips of the butterfly structures are indicated in parentheses.

Structure (Symmetry)	ΔE kcal/mol	Central V_4 unit geometry	V–V distances, Å
Triplet structures			
4T-1 (C_1)	0.0	Tetrahedron	2.527, 2.592, 2.909, 2.933, 2.965, 2.982
4T-2 (C_1)	11.0	Butterfly	2.433, 2.561, 2.599, 2.669, 2.993, (3.874)
4T-3 (C_2)	12.9	Tetrahedron	2.678, 2.910×2, 2.951×2, 3.016
Singlet structures			
4S-1 (S_4)	1.0	Tetrahedron	2.687×2, 2.891×4
4S-2 (C_1)	7.6	Butterfly	2.385, 2.591, 2.617, 2.658, 2.890, (3.845)
4S-3 (C_1)	9.2	Tetrahedron	2.430, 2.452, 2.510, 2.545, 2.871, 3.079
4S-4 (D_{2d})	13.7	Tetrahedron	2.441×2, 2.706×4
4S-5 (C_2)	14.5	Tetrahedron	2.448×2, 2.697, 2.703, 2.711×2
Quintet structures			
4Q-1 (C_1)	5.5	Tetrahedron	2.572, 2.727, 2.907, 2.975, 2.932, 2.964
4Q-2 (C_1)	13.5	Tetrahedron	2.435, 2.439, 2.526, 2.676, 2.949, 2.997

All of the eight $Cp_4V_4(CO)_4$ structures with central V_4 tetrahedra are highly distorted from ideal tetrahedral symmetry with six equal V-V distances. The most symmetrical such structures are the singlet structures **4S-1** and **4S-4** with S_4 and D_{2d} point group symmetry, respectively. The patterns of the six V-V distances in these tetrahedral structures vary widely from structure to structure with no clear pattern. However, in the two butterfly $Cp_4V_4(CO)_4$ structures the V-V distances follow a pattern with one V-V distance of ~2.4 Å, three V-V distances of ~2.6 Å, and one V-V distance of ~2.9 Å as well as a ~3.8 Å non-bonding distance between the butterfly wingtips. Attempts to assign simple formal bond orders for each V-V edge of these

$Cp_4V_4(CO)_4$ structures based on distance appear to be unrewarding, presumably because of extensive delocalization in the V_4 tetrahedra and butterflies.

None of the ten low-energy $Cp_4V_4(CO)_4$ structures have terminal CO groups (Table 2). All four CO groups in each of these structures bridge either a V-V edge, a V_3 triangular face, or all four vanadium atoms in the two butterfly structures. The single unusual η^2-μ_4-CO group bridging all four vanadium atoms in the two butterfly structures **4T-2** and **4S-2** is an unprecedented type of carbonyl group forming four V-C bonds of lengths ~1.9, ~2.1, ~2.1, and ~2.3 Å and one V-O bond of length ~1.95 Å. Such carbonyl groups exhibit unusually low ν(CO) frequencies, namely 1303 and 1318 cm^{-1} for **4T-2** and **4S-2**, respectively. They differ from the simple μ_4-CO groups found experimentally in $(\eta^5\text{-}C_5H_5)_4Mo_2Ni_2S_2(\mu_4\text{-}CO)$ (ref. 31) and $Rh_4(CO)_4(\mu\text{-}CO)_4(\mu_4\text{-}CO)(PBu^t_3)_2[Pt(PBu^t_3)]$ (ref. 32) and predicted to occur in the lowest energy $Co_4(CO)_{11}$ structure.[33] These latter μ_4-CO groups do not have metal-oxygen bonds to the μ_4-CO groups and exhibit higher ν(CO) frequencies of 1654, 1704, and 1636 cm^{-1}, respectively.

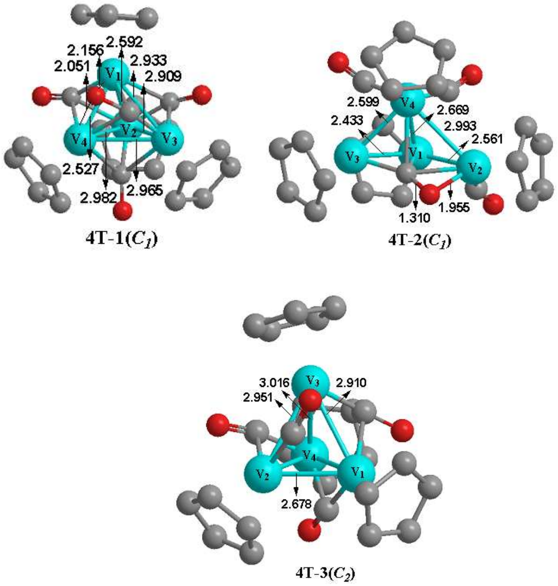


Fig. 2. The three triplet stationary points for $Cp_4V_4(CO)_4$. The numbers in bold face were obtained by the BP86 method. In all of the structure figures blue circles (●) represent vanadium atoms; red circles (●) represent oxygen atoms; and gray circles (●) represent carbon atoms; hydrogen atoms are omitted for clarity. The data in all of the other figures in the present paper have the same arrangement.

The lowest energy $Cp_4V_4(CO)_4$ structure **4T-1** has two short V-V bonds, namely, 2.592 Å (V_1-V_2) and 2.527 (V_1-V_4) Å, which can be interpreted as V=V double bonds[34]. Meanwhile, there are four long V-V bonds in **4T-1**, i.e., 2.909 (V_2-V_3), 2.933 (V_1-V_3), 2.965 (V_3-V_4) and 2.982 (V_2-V_4) Å, which are consistent with four V-V single bonds. In order to investigate the nature of the V-V bonds in **4T-1**, the related molecular orbital diagrams are illustrated in Fig. 5. The HOMO-7 and HOMO-4 orbitals can be assigned as the π-bonding orbital and σ-bonding orbital of V_1-V_2 double bond, respectively. The HOMO-8 and HOMO-16 orbitals are consistent with the π-bonding orbital and σ-bonding orbital of V_1-V_4 double bond, respectively. The HOMO-3, HOMO-5, HOMO-6 and HOMO-13 orbitals are corresponding to the σ-bonding orbitals of V_2-V_3, V_1-V_3, V_3-V_4 and V_2-V_4 single bonds, respectively. The MOs and related comments for the other structures have been put in the Supporting Information (Figures S6 to S15).

In both **4T-1** and **4S-1** all four CO groups are μ_3-CO groups bridging the four faces of the central V_4 tetrahedron. However, in **4T-1** one of these face-bridging CO groups is an unusual six-electron donor η^2-μ_3-CO group bonded to the V_3 face through both the carbon and oxygen atoms with three bonding V-C distances of 1.831, 2.101, and 2.142 Å and two bonding V-O distances of 2.051 and 2.156 Å (Fig. 2). This leads to 17-electron configuration for two vanadium atoms, 16-electron and 18-electron configurations for another two vanadium atoms. The η^2-μ_3-CO group in **4T-1** is predicted to exhibit an unusually low ν(CO) frequency of 1371 cm^{-1} (Table 2). Such a η^2-μ_3-CO group is found experimentally in the cyclopentadienylniobium carbonyl derivative $Cp_3Nb_3(CO)_6(\eta^2\text{-}\mu_3\text{-}CO)$, which likewise exhibits an unusually low ν(CO) frequency of 1330 cm^{-1} for its η^2-μ_3-CO group.[35] The three remaining CO groups in **4T-1** and all four CO groups in **4S-1** are the usual face-bridging μ_3-CO groups bonded to the V_3 face only through the carbon atoms. Such μ_3-CO groups are predicted to exhibit significantly higher ν(CO) frequencies than the η^2-μ-CO groups ranging from 1518 to 1656 cm^{-1}.

Table 2. Infrared active ν(CO) vibrational frequencies (cm^{-1}) predicted for the ten lowest energy stationary points of $Cp_4V_4(CO)_4$ (infrared intensities in parentheses are in km/mol). The abnormally low ν(CO) frequencies for μ_4-CO and η^2-μ_3-CO groups are listed in **bold** type.

Structure	CO groups	ν(CO) frequencies
4T-1 (C_1)	η^2-μ_3-CO + 3μ_3-CO	**1371(39)**,1518(188),1626(358),1656(314)
4T-2 (C_1)	η^2-μ_4-CO + 3μ-CO	**1303(54)**,1731(431),1749(636),1803(567)
4T-3 (C_2)	4η^2-μ-CO	1517(25),1517(282),1540(358),1568(19)
4S-1 (S_4)	4 μ_3-CO	1538(24),1540(261),1540(261),1546(0)
4S-2 (C_1)	η^2-μ_4-CO + 3μ-CO	**1318(65)**,1712(305),1742(775),1780(514)
4S-3 (C_1)	4 μ_3-CO	1670(607),1687(229),1705(465),1716(244)
4S-4(D_{2d})	4 μ_3-CO	1618(671),1618(671),1631(212),1647(0)
4S-5 (C_2)	4 μ_3-CO	1615(672),1615(662),1628(219),1645(0)
4Q-1(C_1)	2μ_3-CO + 2μ-CO	1360(52),1498(192),1616(361),1639(195)
4Q-2(C_1)	2μ_3-CO + 2μ-CO	1638(373),1656(334),1685(667),1699(136)

The prediction of a lowest energy $Cp_4V_4(CO)_4$ structure with only face-bridging CO groups (either **4T-1** or **4S-1**) is in disagreement with the previously proposed $Cp_4V_4(CO)_4$ structure with exclusively terminal CO groups.[10] Thus our prediction of ν(CO) frequencies of 1518, 1626, 1656 and 1371 cm^{-1} for the lowest energy $Cp_4V_4(CO)_4$ structure **4T-1** disagrees with the experimentally determined ν(CO) frequencies of 2029, 2001, 1999 cm^{-1} for $Cp_4V_4(CO)_4$ (KBr pellet) in the typical range of terminal ν(CO) frequencies. We therefore optimized alternative $Cp_4V_4(CO)_4$ structures with all terminal CO groups. However, $Cp_4V_4(CO)_4$ structures with all terminal CO groups, designated in the Supporting Information as **4T-4** and **4Q-3**, were predicted to have such high energies (>100 kcal/mol in some cases) to be chemically irrelevant (Tables S3 to S5 and Fig. S1 in the Supporting Information). This was confirmed by performing single-point calculations with the larger basis sets BP86/6-311+G(2d,2p) and PBE/6-311+G(2d,2p) on the optimized geometries of **4T-1**, **4T-4** and **4Q-3** to obtain more accurate energies. Furthermore, IOP (3/124=3) was used to make the Grimme dispersion corrections.[36 - 38] These more accurate calculations showed that that **4T-4** and **4Q-3** with all terminal CO groups still lie more than 100 kcal/mol above **4T-1**. We conclude that the experimentally observed terminal ν(CO) frequencies for $Cp_4V_4(CO)_4$ must arise from a decomposition product. Such decomposition of $Cp_4V_4(CO)_4$ during the process of preparing a sample for infrared spectroscopy is not unlikely since $Cp_4V_4(CO)_4$ is reported to be very air-sensitive. Furthermore, the infrared spectra of $Cp_4V_4(CO)_4$ were taken either in chlorinated solvents such as dichloromethane or carbon tetrachloride or in KBr pellets, which are conditions likely to lead to decomposition of air-sensitive compounds.[10]

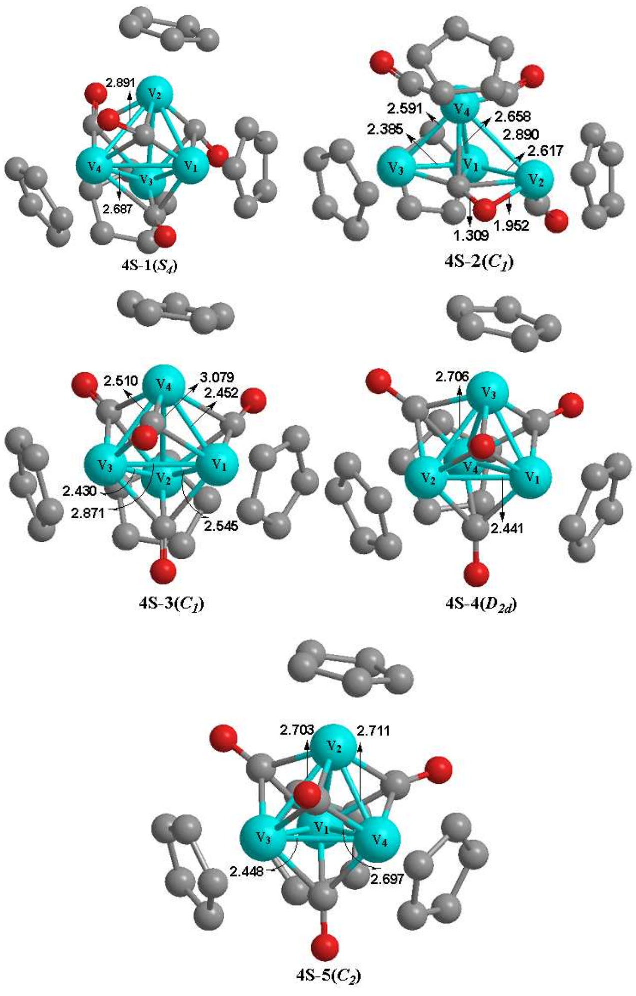


Fig. 3. The five singlet stationary points for $Cp_4V_4(CO)_4$.

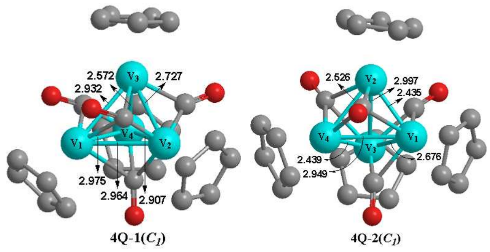
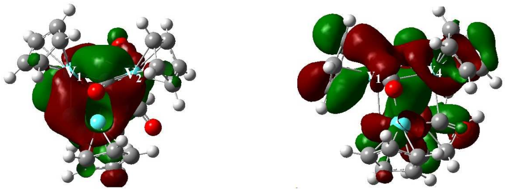
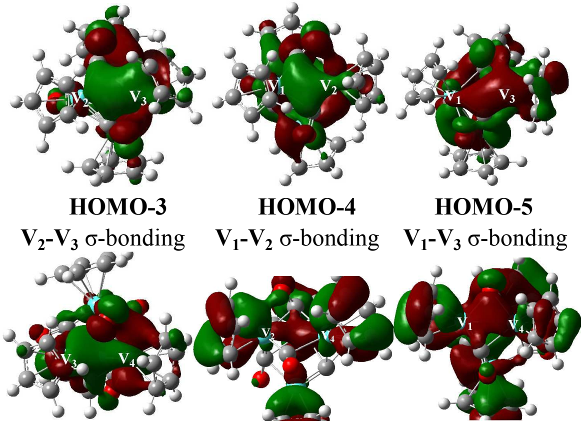


Fig. 4. The two quintet stationary points for $Cp_4V_4(CO)_4$.



HOMO-7 **HOMO-8**
V_1-V_2 π-bonding **V_1-V_4** π-bonding

(a) The molecular orbital diagrams related to the V-V π-bonding of **4T-1**.



HOMO-3 **HOMO-4** **HOMO-5**
V_2-V_3 σ-bonding **V_1-V_2** σ-bonding **V_1-V_3** σ-bonding

HOMO-6 **HOMO-13** **HOMO-16**
V_3-V_4 σ-bonding **V_2-V_4** σ-bonding **V_1-V_4** σ-bonding

(b) The molecular orbital diagrams related to the V-V σ-bonding of **4T-1.**

Fig.5 The molecular orbital diagrams related to the V-V π-bonding orbitals (a) and V-V σ-bonding orbitals (b) of **4T-1**.

3.2 $Cp_3V_3(CO)_9$

The potential energy surface of $Cp_3V_3(CO)_9$ is considerably simpler than that of $Cp_4V_4(CO)_4$ since only three structures were found within 16 kcal/mol of the global minimum (Fig. 6). All three structures are predicted to be genuine minima with no imaginary vibrational frequencies. In all three $Cp_3V_3(CO)_9$ structures the V–V distances range from ~3.0 to ~3.6 Å corresponding to the formal single bonds required to give each vanadium atom the favored 18-electron configuration.

The global minimum structure **9S-1** found for $Cp_3V_3(CO)_9$ has C_3 symmetry with all terminal CO groups and a central equilateral V_3 triangle (Fig. 6). All nine CO groups in $Cp_3V_3(CO)_9$ are terminal CO groups and exhibit ν(CO) frequencies ranging from 1833 to 1984 cm^{-1} (Table 3). The lowest energy structure of the analogous $Cp_3Nb_3(CO)_9$ also has all terminal CO groups with ν(CO) vibrational frequencies ranging from 1813 to 1986 cm^{-1} at the BP86/SDD level.[35]

The predicted ν(CO) frequencies ranging from 1833 to 1984 cm^{-1} for the unbridged $Cp_3V_3(CO)_9$ structure **9S-1** (Table 3) are significantly lower than the reported experimental ν(CO) frequencies of 2000 and 2036 cm^{-1} in KBr or 2014 and 2041 cm^{-1} in CCl_4 for $Cp_3V_3(CO)_9$. This apparent disagreement of the theoretical and experimental ν(CO) frequencies for $Cp_3V_3(CO)_9$ could be a consequence of halogenation or halogen substitution under the experimental conditions of preparing the sample for infrared spectroscopy in KBr and CCl_4 media. Thus the reported experimental ν(CO) frequencies might actually be those of some halogen derivative. Again decomposition of $Cp_3V_3(CO)_9$ during the process of taking the infrared spectrum in halogenated media is consistent with the reported air-sensitivity of this species.

The $Cp_3V_3(CO)_9$ isomer next higher in energy is the C_1 structure **9S-2**, lying 6.5 kcal/mol above **9S-1** (Fig. 6). Structure **9S-2** has two bridging and seven terminal CO groups. The edge lengths of the central scalene V_3 triangle in **9S-2** are 3.045, 3.443, and 3.614 Å, all of which can correspond to formal single bonds. The shortest V–V edge of this V_3 triangle is the one bridged by two CO groups in accord with expectation. These bridging CO groups are predicted to exhibit ν(CO) frequencies of 1755 and 1784 cm^{-1} whereas the seven terminal CO groups exhibit ν(CO) frequencies ranging from 1865 to 1989 cm^{-1} (Table 3).

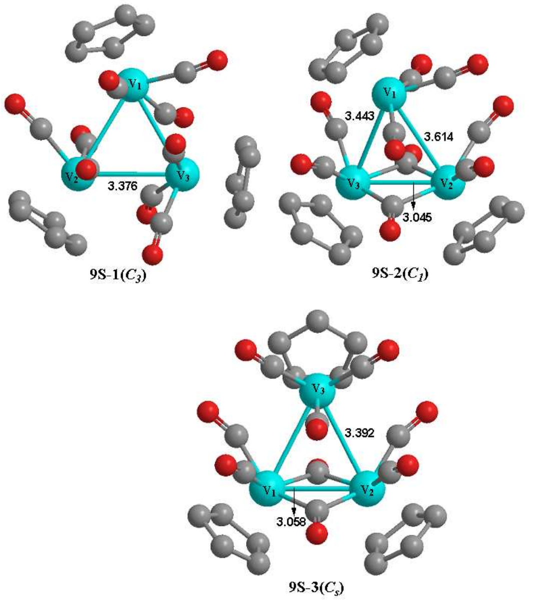


Fig. 6. The three singlet stationary points for $Cp_3V_3(CO)_9$.

Table 3. Infrared active ν(CO) vibrational frequencies (cm^{-1}) predicted for the three singlet stationary points of $Cp_3V_3(CO)_9$ (infrared intensities in parentheses are in km/mol).

	BP86
9S-1 (C_3)	1833(37)1833(37),1873(996),1895(646),1895(646), 1906(304),1922(451),1922(451),1984(877)
9S-2 (C_1)	**1755(327),1784(146)**,1865(308),1892(560),1903(29), 1912(168),1933(637),1951(1487),1989(651)
9S-3 (C_s)	**1714(338),1794(247)**,1858(406),1861(352),1871(109), 1919(27),1939(1437),1940(457),1983(1392)

The third $Cp_3V_3(CO)_9$ structure **9S-3**, lying 15.8 kcal/mol in energy above **9S-1**, has a central isosceles V_3 triangle with two bridging and seven terminal CO groups (Fig. 6). The two equivalent V–V distances are 3.392 Å and the third unique V–V distance is 3.058 Å. The latter V–V edge is bridged by two CO groups exhibiting ν(CO) frequencies at 1714 and 1794 cm^{-1}. Structures **9S-2** and **9S-3** have the same numbers of terminal and bridging CO groups but differ in the orientations of the Cp rings.

3.3 Thermochemistry

Several years ago we reported a comprehensive DFT study on the structures of the binuclear cyclopentadienylvanadium carbonyl derivatives $Cp_2V_2(CO)_n$ (n = 7, 6, 5, 4, 3, 2, 1).[39] However, this study did not include any thermochemistry. In order to provide insight into thermochemistry relevant to the formation of $Cp_4V_4(CO)_4$ and $Cp_3V_3(CO)_9$ from $Cp_2V_2(CO)_5$ we first studied the thermochemistry of the binuclear $Cp_2V_2(CO)_n$ derivatives. We find the experimentally known $Cp_2V_2(CO)_5$ as well as the unknown $Cp_2V_2(CO)_3$ to be viable towards disproportionation into $Cp_2V_2(CO)_{n+1}$ + $Cp_2V_2(CO)_{n-1}$ (n = 5, 3) (Table 4). However, a similar disproportionation of $Cp_2V_2(CO)_4$ into $Cp_2V_2(CO)_5$ + $Cp_2V_2(CO)_3$ is mildly exothermic at ~3 kcal/mol suggesting that $Cp_2V_2(CO)_4$ is not a viable species.

Table 4. Energies for reactions of cyclopentadienylvanadium carbonyls (BP86).

	BP86
$2Cp_2V_2(CO)_5 \rightarrow Cp_2V_2(CO)_6 + Cp_2V_2(CO)_4$	22.8
$2Cp_2V_2(CO)_4 \rightarrow Cp_2V_2(CO)_5 + Cp_2V_2(CO)_3$	–2.8
$2Cp_2V_2(CO)_3 \rightarrow Cp_2V_2(CO)_4 + Cp_2V_2(CO)_2$	19.6
$2Cp_2V_2(CO)_2 \rightarrow Cp_2V_2(CO)_3 + Cp_2V_2(CO)$	7.3
$Cp_3V_3(CO)_9 \rightarrow Cp_2V_2(CO)_5 + CpV(CO)_4$	–34.0
$2Cp_2V_2(CO)_2 \rightarrow Cp_4V_4(CO)_4$	–74.7
$4Cp_2V_2(CO)_5 \rightarrow 4CpV(CO)_4 + Cp_4V_4(CO)_4$	4.0
$6\ Cp_2V_2(CO)_5 \rightarrow 2CpV(CO)_4 + Cp_4V_4(CO)_4 + 2\ Cp_3V_3(CO)_9$	49.0

The reported synthesis of $Cp_4V_4(CO)_4$ involves net disproportionation of $4Cp_2V_2(CO)_5$ into $4CpV(CO)_4$ + $Cp_4V_4(CO)_4$. This process in a solvent-free environment is predicted to be mildly endothermic at 4.0 kcal/mol (Table 4). However, the presence of the coordinating solvent tetrahydrofuran in the reported synthesis of $Cp_4V_4(CO)_4$ from $Cp_2V_2(CO)_5$ could facilitate this reaction by generation of a complex such as $CpV(CO)_3(THF)$ from the $CpV(CO)_4$ byproduct. Another key to the formation of $Cp_4V_4(CO)_4$ from $Cp_2V_2(CO)_5$ might be the highly exothermic dimerization of $Cp_2V_2(CO)_2$ at 75 kcal/mol.

The thermochemistry summarized in Table 4 also suggests why $Cp_4V_4(CO)_4$ rather than $Cp_3V_3(CO)_9$ is the major product from the pyrolysis of $Cp_2V_2(CO)_5$. In particular, the fragmentation of $Cp_3V_3(CO)_9$ into the stable compounds $CpV(CO)_4$ + $Cp_2V_2(CO)_5$ is predicted to be a strongly exothermic thereby account for the very low reported yield of ~1.7 % of $Cp_3V_3(CO)_9$ obtained from the pyrolysis of $Cp_2V_2(CO)_5$.

4. Summary

The very air-sensitive tetranuclear derivative $Cp_4V_4(CO)_4$ is reported by Herrmann and co-workers to be a major product from the pyrolysis of $Cp_2V_2(CO)_5$ in tetrahydrofuran solution.[10] However, $Cp_4V_4(CO)_4$ could not be characterized structurally by X-ray crystallography. Experimental observation of only terminal ν(CO) frequencies in $Cp_4V_4(CO)_4$ suggested a structure with exclusively terminal CO groups.

In order to gain some insight into the nature of $Cp_4V_4(CO)_4$ cluster, we undertook a DFT study on this system. This study revealed a complicated potential energy surface with 10 structures within 25 kcal/mol of the global minimum. These 10 structures encompass singlet, triplet, and quintet spin states. Eight of these 10 structures have central V_4 tetrahedra with six direct V-V interactions. However, the V_4 tetrahedra in all eight of these structures are distorted in contrast to the regular central Fe_4 tetrahedron in the structurally characterized[11] $Cp_4Fe_4(\mu_3\text{-}CO)_4$. The remaining two $Cp_4V_4(CO)_4$ structures have central V_4 butterflies with only five direct V-V interactions. Each of these two butterfly structures has an unprecedented η^2-μ_4-CO group bridging all four vanadium atoms by forming four V-C bonds and one V-O bond. Such η^2-μ_4-CO groups exhibit unusually low ν(CO) frequencies around 1310 ± 8 cm^{-1}. None of the ten $Cp_4V_4(CO)_4$ structures has any terminal CO groups thereby suggesting that the experimental observation of terminal ν(CO) frequencies in the infrared spectrum of $Cp_4V_4(CO)_4$ was an artifact arising from the decomposition of this air-sensitive compound.

The lowest energy $Cp_4V_4(CO)_4$ structures are singlet and triplet distorted tetrahedral V_4 clusters with each of four tetrahedral faces bridged by μ_3-CO groups. Such μ_3-CO groups are predicted to exhibit extremely low ν(CO) frequencies ranging from 1371 to 1656 cm^{-1} that might have been overlooked in the experimental work.[10]

A low-yield byproduct of the pyrolysis of $Cp_2V_2(CO)_5$ in tetrahydrofuran is the trinuclear $Cp_3V_3(CO)_9$. The lowest energy $Cp_3V_3(CO)_9$ structure is a symmetrical C_3 structure having a central equilateral V_3 triangle with all terminal CO groups. This structure is predicted to be disfavored relative to fragmentation into the stable compounds $CpV(CO)_4$ + $Cp_2V_2(CO)_5$. This may account for its low yield from the $Cp_2V_2(CO)_5$ pyrolysis.

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Notes and references

[a] *Key Laboratory of Cluster Science, Ministry of Education of China, School of Chemistry, Beijing Institute of Technology, Beijing 100081, P. R. China; E-mail:zhangxiuhui@bit.edu.cn*

[b] *State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081, PR China*

[c] *MOE Key Laboratory of Theoretical Chemistry of Environment, Center for Computational Quantum Chemistry, South China Normal University, Guangzhou 510006, PR China*

[d] *Department of Chemistry and Center for Computational Chemistry, University of Georgia, Athens, Georgia 30606, USA; E-mail:rbking@uga.edu*

†Electronic Supplementary Information (ESI) available: Table S1: The values of V-V bond (Å) for $Cp_2V_2(CO)_5$;Table S2: The ν(CO) vibrational frequencies (cm^{-1}) for $Cp_2V_2(CO)_5$;Tables S3 to S5: Total energies (E, in hartree) and relative energies (ΔE, in kcal/mol) for **4T-1**, **4T-4** and **4Q-3** of $Cp_4V_4(CO)_4$; Tables S6 to S8: Total energies (E, in hartree), relative energies (ΔE, in kcal/mol), spin square values $\langle S^2\rangle$, number of imaginary vibrational frequencies (Nimg) for the five singlet, three triplet and two quintet structures of $Cp_4V_4(CO)_4$; Table S9: Infrared active ν(CO) vibrational frequencies (cm^{-1}) predicted for the ten lowest energy stationary points of $Cp_4V_4(CO)_4$ using the PBE method; Table S10: Total energies (E, in hartree), relative energies (ΔE, in kcal/mol), number of imaginary vibrational frequencies (Nimg) for the three singlet structures of $Cp_3V_3(CO)_9$; Table S11: Infrared active ν(CO) vibrational frequencies (cm^{-1}) predicted for the three singlet stationary points of $Cp_3V_3(CO)_9$ using the PBE method; Tables S12 to S14: Total energies (E, in hartree), relative energies (ΔE, in kcal/mol), spin square values $\langle S^2\rangle$, number of imaginary vibrational frequencies (Nimg) at BP86/TZP level of the theory for the five singlet, three triplet and two quintet structures of $Cp_4V_4(CO)_4$; Table S15: Total energies (E, in hartree), relative energies (ΔE, in kcal/mol), number of imaginary vibrational frequencies (Nimg) at BP86/TZP level of the theory for the three singlet structures of $Cp_3V_3(CO)_9$; Table S16: Total energies (E, in hartree), relative energies (ΔE, in kcal/mol), spin square values $\langle S^2\rangle$, number of imaginary vibrational frequencies (Nimg) at PBE0/DZP level of the theory for the lowest energy structure and one quintet structure of $Cp_4V_4(CO)_4$; Table S17: Total energies (E, in hartree) and number of imaginary vibrational frequencies (Nimg) at BP86/DZP and PBE/DZP levels of the theory for $Cp_2V_2(CO)_n$ (n = 6, 5, 4, 3, 2, 1); Figure S1: Optimized structures for **4T-4** and **4Q-3** of $Cp_4V_4(CO)_4$ by BP86 and PBE methods; Figures S2 to S4: Optimized structures for the five singlet, three triplet and two quintet structures of $Cp_4V_4(CO)_4$ by BP86 and PBE methods; Figure S5: Optimized structures for the three singlet structures of $Cp_3V_3(CO)_9$ by BP86 and PBE methods; Figures S6 to S14: The comments and molecular orbital diagrams related to the V-V π-bonding orbitals (a) and V-V σ-bonding orbitals (b) for the five singlet, two triplet and two quintet structures of $Cp_4V_4(CO)_4$; Figure S15: The comments and molecular orbital diagrams related to the V-V σ-bonding orbitals for the lowest energy structure of $Cp_3V_3(CO)_9$; Tables S18 to S29: Theoretical cartesian coordinates (in Å) for the five singlet, four triplet and three quintet structures of $Cp_4V_4(CO)_4$ using the BP86 method; Tables S30 to S32: Theoretical cartesian coordinates (in Å) for the three singlet structures of $Cp_3V_3(CO)_9$ using the BP86 method; Tables S33 to S35: The theoretical harmonic vibrational frequencies for the twelve structures of $Cp_4V_4(CO)_4$ using the BP86 method; Table S36: The theoretical harmonic vibrational frequencies for the three structures of $Cp_3V_3(CO)_9$ using the BP86 method; Complete Gaussian 09 reference (Reference 19).

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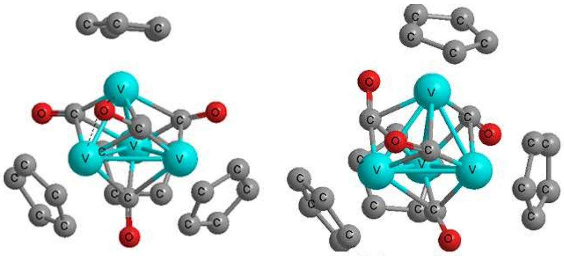

The lowest triplet structure The lowest singlet structure

The global minimum $Cp_4V_4(CO)_4$ structure with all μ_3-CO is in disagreement with the experimental supposed structure with exclusively terminal CO.