J|A|C|S
A R T I C L E S

Interplay between Two-Electron and Four-Electron Donor Carbonyl Groups in Oxophilic Metal Systems: Highly Unsaturated Divanadocene Carbonyls

Qian-shu Li,*,† Xiuhui Zhang,† Yaoming Xie,‡ R. Bruce King,*,‡
and Henry F. Schaefer III‡

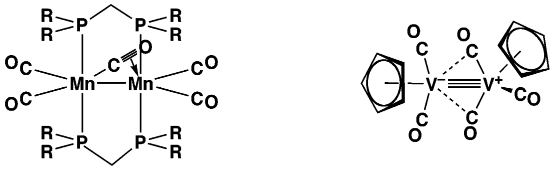
Contribution from the Institute of Chemical Physics, Beijing Institute of Technology, Beijing 100081, People's Republic of China, and Department of Chemistry and Center for Computational Chemistry, University of Georgia, Athens, Georgia 30602

Received November 10, 2006; E-mail: qsli@bit.edu.cn; rbking@chem.uga.edu

Abstract: The divanadocene carbonyls $Cp_2V_2(CO)_n$ (n = 5, 4, 3, 2, 1; Cp = η^5-C_5H_5) have been studied by density functional theory using the B3LYP and BP86 functionals. The global minimum for $Cp_2V_2(CO)_5$ with a $V\equiv V$ distance of 2.452 Å (BP86) is essentially the same as the structure of the known $Cp_2V_2(CO)_5$ determined by X-ray diffraction. The global minimum of $Cp_2V_2(CO)_4$ is a triplet electronic state with a $V\equiv V$ distance of 2.444 Å (BP86). However, slightly higher energy singlet $Cp_2V_2(CO)_4$ structures are found either with a $V\equiv V$ distance of 2.547 Å (BP86) and one four-electron donor bridging CO group or with a $V\overset{4}{-}V$ distance of 2.313 Å (BP86) and all two-electron donor bridging CO groups. Comparison is made between $Cp_2V_2(CO)_3$ and the recently synthesized quintuply bonded RCrCrR (R = bulky aryl group) complexes of Power and co-workers. Four-electron donor bridging carbonyl groups become more prevalent upon further decarbonylation, leading ultimately to three singlet $Cp_2V_2(\eta^2$-μ-$CO)_2$ isomers as well as triplet, quintet, and septet structures of $Cp_2V_2(CO)$ with extremely low ν(CO) frequencies around 1400 cm^{-1}. Our most remarkable structural finding is the extremely short vanadium−vanadium distance (1.80 Å, BP86) predicted for the singlet structure of $Cp_2V_2(CO)$.

1. Introduction

Until 1975 the carbonyl groups in diverse metal carbonyls, whether terminal or bridging, were always found bonded to transition metals only through the carbon atom and thus are clearly formal two-electron donors. The first exception to this general observation was the compound $(Ph_2PCH_2PPh_2)_2Mn_2(CO)_4(\eta^2$-$\mu$-CO) (Figure 1), which was prepared by Colton and Commons[1] by heating $Mn_2(CO)_{10}$ with 2 molar equivalents of the $Ph_2PCH_2PPh_2$ ligand in boiling decane. Determination of the structure of this manganese complex by X-ray diffraction[2] indicated a very unusual bridging CO group with an abnormally short Mn−O distance of 2.29 Å, suggesting some direct manganese−oxygen bonding as well as the usual manganese−carbon bonding to both manganese atoms expected for a bridging carbonyl group. The Mn−Mn distance of 2.934 Å in this complex suggested a single metal−metal bond so that the anomalous bridging CO group needed to be a formal four-electron donor for each manganese atom to have the favored eighteen-electron configuration. Such donation of four electrons can occur through one σ-bond and one π-bond. The π-bonding lowers the effective carbon−oxygen bond order, consistent with the very low bridging infrared ν(CO) frequency of 1645 cm^{-1} found experimentally for this metal complex.



$(Ph_2PCH_2PPh_2)_2Mn_2(CO)_4(\eta^2$-$\mu$-CO) **$(\eta^5$-$C_5H_5)_2V_2(CO)_5$**

Figure 1. Structures of $(Ph_2PCH_2PPh_2)Mn_2(CO)_4(\eta^2$-$\mu$-CO) and $Cp_2V_2(CO)_5$.

Our investigations of binuclear metal carbonyl structures predict a few additional examples of four-electron bridging η^2-μ-CO groups, of which $Mn_2(CO)_8(\eta^2$-μ-CO), as the lowest energy structure for $Mn_2(CO)_9$, is the most interesting[3] since it is closely related to the known $(Ph_2PCH_2PPh_2)_2Mn_2(CO)_4(\eta^2$-$\mu$-CO) discussed above (Figure 1). However, since four-electron bridging η^2-μ-CO groups require metal−oxygen as well as metal−carbon bonding, they are likely to be more prevalent in the chemistry of the relatively oxophilic early transition metals. For this reason we chose vanadium for this search for new types of compounds with four-electron donor bridging η^2-μ-CO groups. Binuclear cyclopentadienylvanadium carbonyls are of particular interest since $Cp_2V_2(CO)_5$ (Cp = η^5-C_5H_5, Figure 1) is known experimentally.[6] Structural studies on $Cp_2V_2(CO)_5$

---

† Beijing Institute of Technology.

‡ University of Georgia.

(1) Colton, R.; Commons, C. J. *Aust. J. Chem.* **1975**, *28*, 1673.

(2) Commons, C. J.; Hoskins, B. F. *Aust. J. Chem.* **1975**, *28*, 1663.

(3) Xie, Y.; Jang, J. H.; King, R. B.; Schaefer, H. F. *Inorg. Chem.* **2003**, *42*, 5219.

(4) Fischer, E. O.; Schneider, R. J. J. *Angew. Chem.* **1967**, *79*, 537.

10.1021/ja068058m CCC: $37.00 © 2007 American Chemical Society

indicate the absence of any four-electron donor bridging η^2-μ-CO groups, consistent with the absence of any abnormally low ν(CO) frequencies in its infrared spectrum. Furthermore, the short vanadium−vanadium distance of 2.459 Å in $Cp_2V_2(CO)_5$, determined by X-ray diffraction,[5,6] suggests the V≡V formal triple bond required to give both vanadium atoms the favored eighteen-electron rare gas configuration with all five CO groups functioning as the usual two-electron donors.

Decarbonylation of $Cp_2V_2(CO)_5$ (Figure 1) might be expected to give even more highly unsaturated binuclear cyclopentadienylvanadium carbonyls. Conversion of one or more normal two-electron terminal or bridging carbonyl groups to four-electron donor bridging carbonyl groups in such decarbonylation products might be considered as an alternative to vanadium−vanadium bond orders larger than 3 for maintaining the favored eighteen-electron vanadium configurations in decarbonylation products of $Cp_2V_2(CO)_5$. In this connection we have now used density functional theory (DFT) methods to investigate even more highly unsaturated binuclear cyclopentadienylvanadium carbonyls, which may be regarded as carbonylation products of a divanadocene analogous to the experimentally known permethylated dizincocene.[7] In this paper we report the optimized structures for both singlet and triplet isomers of the divanadocene carbonyls $Cp_2V_2(CO)_n$ ($n = 5, 4, 3, 2, 1$), which provide numerous examples of four-electron donor bridging carbonyl groups. Furthermore, the relatively low carbon−oxygen bond order of the η^2-μ-CO groups generated in this chemistry suggests a possible role of divanadocene carbonyl chemistry in novel catalytic systems for the reduction of carbon monoxide to methanol.

2. Theoretical Methods

Electron correlation effects were considered by employing DFT methods, which have evolved as a practical and effective computational tool, especially for organometallic compounds.[8−15] General discussions of the reliability of DFT methods for transition-metal-containing systems may be found in refs 8−15.

Two DFT methods were used in this study. The first functional is the B3LYP method, which is the hybrid HF/DFT method using the combination of the three-parameter Becke functional (B3) with the Lee−Yang−Parr (LYP) generalized gradient correlation functional.[16,17] The other DFT method used in the present paper is BP86, which combines Becke's 1988 exchange functional (B) with Perdew's 1986 gradient corrected correlation functional method (P86).[18,19] It has been noted elsewhere that the BP86 method may be somewhat more reliable than B3LYP for the type of organometallic systems considered in this paper.[20−22]

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[23,24] 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[25] augmented by two sets of p functions and a set of d functions, contracted following Hood, Pitzer, and Schaefer,[26] designated (14s11p6d/10s8p3d).

We have also tested the effects of adding f basis functions to the vanadium basis set. In this connection the changes in the V−V distances for the low-lying structures are very small (<0.01 Å) when the f functions are added.

The geometries of all of the structures were fully optimized using the DZP B3LYP and DZP BP86 methods. All of the computations were carried out with the Gaussian 03 program,[27] exercising the fine grid option (75 radial shells, 302 angular points) for evaluating integrals numerically, while the tight (10^{-8} hartree) designation is the default for the self-consistent field (SCF) convergence.

The vibrational frequencies were determined by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. The corresponding infrared intensities were also evaluated analytically.

For some stationary points (all gradients of the energy equal to zero), we find one or more imaginary vibrational frequencies. A single imaginary vibrational frequency implies that the stationary point in question is a transition state. In terms of the potential energy hypersurface a transition state has one negative force constant, that being along the reaction coordinate.

All computations for the singlet closed-shell systems were carried out with the spin-restricted method. The open-shell systems were done in a spin-unrestricted formalism. When a theoretical method yields an approximate wave function, the expectation value of the operator $\langle S^2 \rangle$ should be $S(S + 1)$. This provides a helpful test of the validity of unrestricted methods in quantum chemistry. For DFT as popularly applied (e.g., the BP86 and B3LYP methods used in this work) there is no wave function per se. However, construction of a single determinant wave function from the Kohn−Sham orbitals can provide an approximate test of spin conservation in DFT. This is the procedure followed to evaluate spin contamination in the present paper.

Most of the molecular systems described here have closed-shell singlet electronic ground states. However, several of these structures have small HOMO−LUMO gaps. In such cases, triplet or higher spin electronic states have been explicitly investigated, including full geometry optimizations.

3. Results

In the present study, the B3LYP and BP86 methods agree with each other fairly well in predicting the structural characteristics of $Cp_2V_2(CO)_n$. Although both the B3LYP and BP86 results are shown in the figures and tables, unless specifically noted, only the BP86 results (geometries, energies, and vibrational frequencies) are discussed in the text.

3.1. $Cp_2V_2(CO)_5$. Seven energetically low-lying structures were found for $Cp_2V_2(CO)_5$ (Figures 2 and 3 and Tables 1−3). The global minimum $Cp_2V_2(CO)_5$ (**5S-1** in Figure 2 and Table 1) is a C_s *trans* structure with two semibridging CO groups and is very close to the $(\eta^5\text{-}C_5H_5)_2V_2(CO)_5$ structure reported

---

(5) Cotton, F. A.; Kruczynski, L. *J. Organomet. Chem.* **1978**, *160*, 93.
(6) Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.
(7) Resa, I.; Carmona, E.; Gutierrez-Puebla, E.; Monge, A. *Science* **2004**, *305*, 1136.
(8) Ehlers, A. W.; Frenking, G. *J. Am. Chem. Soc.* **1994**, *116*, 1514.
(9) Delly, B.; Wrinn, M.; Lüthi, H. P. *J. Chem. Phys.* **1994**, *100*, 5785.
(10) Li, J.; Schreckenbach, G.; Ziegler, T. *J. Am. Chem. Soc.* **1995**, *117*, 486.
(11) Jonas, V.; Thiel, W. *J. Chem. Phys.* **1995**, *102*, 8474.
(12) Barckholtz, T. A.; Bursten, B. E. *J. Am. Chem. Soc.* **1998**, *120*, 1926.
(13) Niu, S.; Hall, M. B. *Chem. Rev.* **2000**, *100*, 353.
(14) Macchi, P.; Sironi, A. *Coord. Chem. Rev.* **2003**, *238*, 383.
(15) Carreon, J. -L.; Harvey, J. N. *Phys. Chem. Chem. Phys.* **2006**, *8*, 93.
(16) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
(17) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
(18) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
(19) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.
(20) See especially Furche, F.; Perdew, J. P. *J. Chem. Phys.* **2006**, *124*, 044103.
(21) Wang, H. Y.; Xie, Y.; King, R. B.; Schaefer, H. F. *J. Am. Chem. Soc.* **2005**, *127*, 11646.
(22) Wang, H. Y.; Xie, Y.; King, R. B.; Schaefer, H. F. *J. Am. Chem. Soc.* **2006**, *128*, 11376.
(23) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823.
(24) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.
(25) Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033.
(26) Hood, D. M.; Pitzer, R. M.; Schaefer, H. F. *J. Chem. Phys.* **1979**, *71*, 705.
(27) Frisch, M. J.; et. al. *Gaussian 03*, revision C 02; Gaussian, Inc.: Wallingford, CT, 2004 (see the Supporting Information for details).

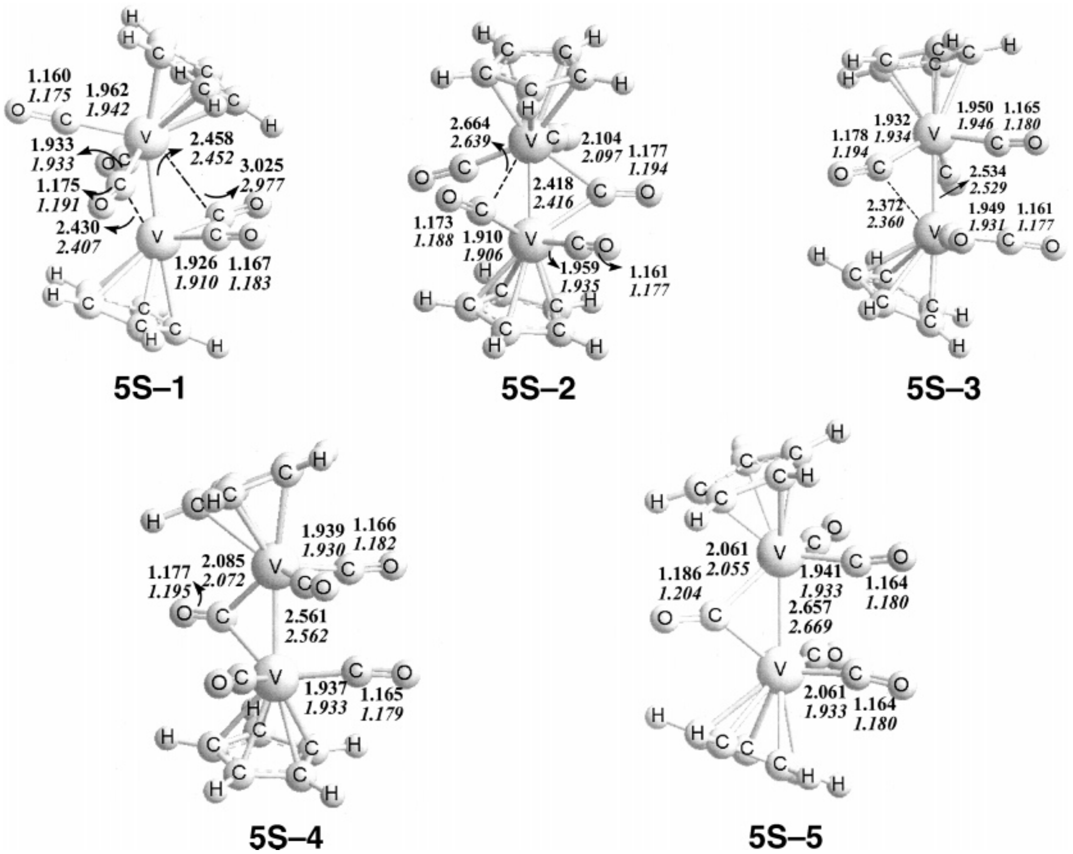


Figure 2. The five singlet stationary points of $Cp_2V_2(CO)_5$. The upper numbers (bold face) were obtained by the B3LYP method, while the lower numbers (italics) were obtained by BP86. The data in all of the other figures in the present paper have the same arrangement.

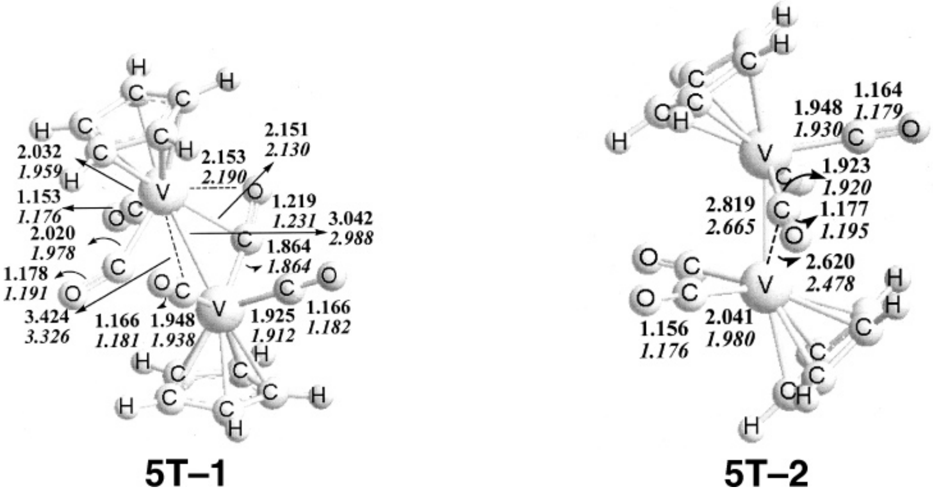


Figure 3. The two triplet stationary points of $Cp_2V_2(CO)_5$.

experimentally.[4−6] Thus, the V≡V distance in **5S-1** is predicted to be 2.452 Å. This is close to the experimentally determined value[6] of 2.459 Å at −150 °C and consistent with the formal V≡V triple bond required to give each vanadium atom the favored eighteen-electron configuration. For the semibridging carbonyls in **5S-1**, the shorter V−C distances are 1.933 Å and the longer ones are 2.407 Å in accord with the experimental values[6] of 1.94 and 2.41 ± 0.02 Å, respectively. The V−C−O bond angles are close to 180°, confirming the semibridging character of these two CO groups. The calculated ν(CO) frequencies for **5S-1** (Table 3) are close to the experimentally[5] reported ν(CO) frequencies for $(\eta^5\text{-}C_5H_5)_2V_2(CO)_5$ at 2009m, 1955s, 1910s, 1871m, and 1832m cm^{-1}.

The $Cp_2V_2(CO)_5$ stationary point **5S-2** (Figure 2 and Table 1) at only 2.6 kcal/mol above **5S-1** is a C_2 structure with one normal bridging CO group and two semibridging CO groups. However, **5S-2** is a transition state with a significant imaginary vibrational frequency at 133i cm^{-1}. Following the corresponding normal mode leads to the global minimum **5S-1**. The equivalent V−C distances in the normal bridging CO group are 2.097 Å. The V−C distances to the semibridging CO groups are 1.906 and 2.639 Å. The V−C distances to the

Table 1. Total Energies (*E*, hartrees), Relative Energies (Δ*E*, kcal/mol), Number of Imaginary Vibrational Frequencies (Nimg), and V−V Distances (Å) for Singlet Stationary Points of $Cp_2V_2(CO)_5$

		5S-1 (C_s)	**5S-2** (C_2)	**5S-3** (C_s)	**5S-4** (C_2)	**5S-5** (C_{2v})
B3LYP	E	−2842.038611	−2842.033979	−2842.027507	−2842.005584	−2841.997699
	ΔE	0.0	2.9	7.0	20.7	25.7
	Nimg	0	1 (173i cm^{-1})	1 (13i cm^{-1})	1 (199i cm^{-1})	2 (70i and 37i cm^{-1})
	V−V	2.458	2.418	2.534	2.561	2.657
BP86	E	−2842.387986	−2842.383803	−2842.379263	−2842.3581666	−2842.351047
	ΔE	0.0	2.6	5.5	18.7	23.2
	Nimg	0	1 (133i cm^{-1})	0	1 (201i cm^{-1})	2 (60i and 36i cm^{-1})
	V−V	2.452	2.416	2.529	2.562	2.659

Table 2. Total Energies (*E*, hartrees), Energies Relative to That of **5S-1** (Δ*E*, kcal/mol), Number of Imaginary Vibrational Frequencies (Nimg), and V−V Distances (Å) for Low-lying Triplet Stationary Points of $Cp_2V_2(CO)_5$

		5T-1 (C_1)	**5T-2** (C_s)
B3LYP	E	−2842.030381	−2842.018171
	ΔE	5.2	12.8
	Nimg	0	2 (37i and 16i cm^{-1})
	V−V	3.042	2.819
BP86	E	−2842.367059	−2842.352210
	ΔE	13.1	22.4
	Nimg	0	1 (72i cm^{-1})
	V−V	2.988	2.665

terminal CO groups are 1.935 Å. The V≡V distance in **5S-2** is 2.416 Å, which is very close to that in **5S-1**.

Another stable singlet $Cp_2V_2(CO)_5$ isomer, **5S-3** (Figure 2 and Table 1), is also a semibridged structure with C_s symmetry and lies 5.5 kcal/mol above the global minimum **5S-1**. It has all real harmonic vibrational frequencies by BP86. The B3LYP method predicts a very small and perhaps artifactual imaginary harmonic vibrational frequency (13i cm^{-1}, Table 1), which can be removed with a finer integration grid (120, 974). The V−C distances to the semibridging carbonyl in **5S-3** are 1.934 and 2.360 Å, and the V−C−O bond angle is close to 180°. The V≡V distance in **5S-3** is 2.529 Å, which is longer than that in **5S-1** by ∼0.1 Å but still reasonable for a V≡V triple bond.

The other two singlet $Cp_2V_2(CO)_5$ stationary points, **5S-4** (C_2) and **5S-5** (C_{2v}), both exhibit singly bridged $Cp_2V_2(CO)_4(\mu\text{-}CO)$ structures (Figure 2), lying about or more than 20 kcal/mol above **5S-1**. Both of these structures have one or two significant imaginary vibrational frequencies (Table 1). By following the corresponding normal modes, structure **5S-4** goes to **5S-3**, and structure **5S-5** goes to **5S-4**.

The lowest triplet $Cp_2V_2(CO)_5$ isomer **5T-1** is a semibridged structure with C_1 symmetry (Figure 3), lying 13.1 kcal/mol above **5S-1**. It is a genuine minimum and has small spin contamination ($\langle S^2 \rangle = 2.02$). The V−C distances to the semibridging carbonyl are 1.864 and 2.130 Å, and this V−C−O bond angle is almost linear. The V−O distance is very short, namely, 2.190 Å, indicating this CO group to be a four-electron donor (two σ electrons and two π electrons). The low vibrational frequency of 1641 cm^{-1} found in **5T-1** (Table 3) can be assigned to this η^2-μ-CO group. The V−V distance in **5T-1** is 2.988 Å, which is much longer than that of **5S-1** by 0.5 Å. This suggests a V−V single bond, giving each vanadium atom the seventeen-electron configuration consistent with the triplet structure and the single four-electron donor η^2-μ-CO group.

A second triplet $Cp_2V_2(CO)_5$ stationary point, **5T-2** with C_s symmetry (Figure 3), is geometrically similar to **5S-1**, but has a small imaginary vibrational frequency (72i cm^{-1}). Following the corresponding normal mode leads to **5T-1**. Structure **5T-2**, like **5T-1**, has a small spin contamination ($\langle S^2 \rangle = 2.1$). Isomer **5T-2** lies about 22.4 kcal/mol above **5S-1**. The V−C distances for the two semibridging carbonyls are 1.920 and 2.478 Å. The V−C distances for the three terminal carbonyls are in the range of 1.93−1.98 Å (Figure 3). The V═V distance of 2.665 Å is consistent with the double bond required to give seventeen-electron configurations to both vanadium atoms in a binuclear triplet structure with all five CO groups functioning as two-electron donors.

3.2. $Cp_2V_2(CO)_4$. Six low-lying structures (three triplet and three singlet) were found for $Cp_2V_2(CO)_4$ (Figures 4 and 5 and Tables 4−6). The global minimum is predicted to be a triplet C_s doubly semibridged structure, **4T-1** (Figure 5 and Table 5). There is relatively small spin contamination, i.e., $\langle S^2 \rangle = 2.06$. The V−C distances for the two semibridging carbonyls are 1.935 and 2.304 Å, and the V−C−O bond angle is close to 180°. The V−C distance for one terminal carbonyl is 1.951 Å, and that for the other is 1.933 Å. The V≡V distance is 2.444 Å (BP86) in accord with the triple bond required to give each vanadium atom a seventeen-electron configuration consistent with the triplet electronic state.

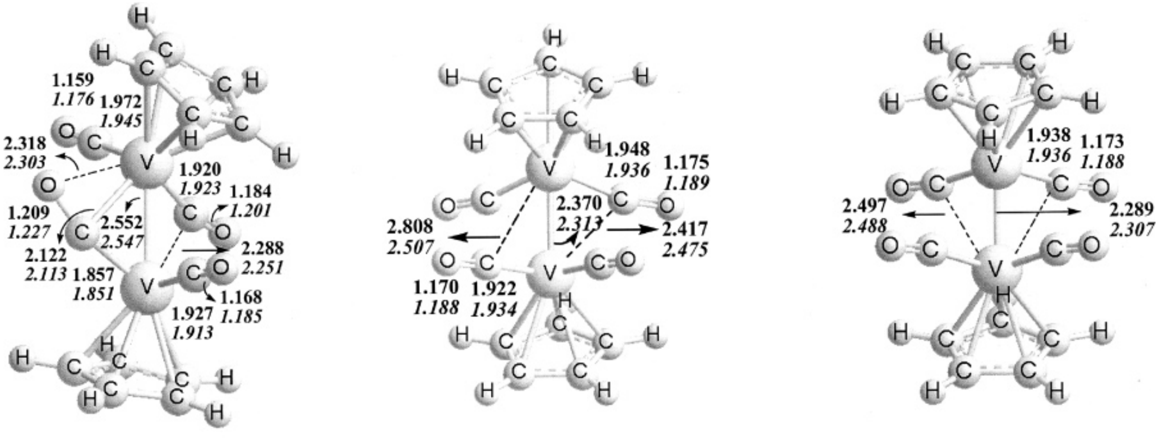
The next energetically low-lying $Cp_2V_2(CO)_4$ isomer has a doubly semibridged C_1 singlet structure, **4S-1** (Figure 4 and Table 4), which lies above **4T-1** by only 1.2 kcal/mol. It has all real harmonic vibrational frequencies (Table 4). The V−C distances for one of the semibridging carbonyls are 1.851 and 2.113 Å. The related V−O distance to this semibridging carbonyl group is very short (2.303 Å), indicating a four-electron donor η^2-μ-CO group consistent with its very low ν(CO) frequency of 1654 cm^{-1} (Table 6). The V−C distances for the other semibridging carbonyl are 1.923 and 2.251 Å, which are somewhat longer than those for the four-electron donor η^2-μ-CO group. The V−C distance is 1.913 Å for the inward pointing terminal CO group and 1.945 Å for the outward pointing terminal carbonyl group. The V−V distance in **4S-1** is 2.547 Å, which is longer than that in **4T-1** by ∼0.10 Å but still consistent with the V≡V triple bond required to give each vanadium atom the eighteen-electron configuration with one of the four CO groups a four-electron donor η^2-μ-CO group.

There are two additional (almost degenerate) triplet isomers of $Cp_2V_2(CO)_4$, namely, **4T-2** and **4T-3** (Figure 5), both with all four CO groups in semibridging positions. The C_2 structure **4T-3** lies above **4T-1** by 11.1 kcal/mol (Table 4) and has a substantial imaginary vibrational frequency of 198i cm^{-1}. Following the corresponding normal mode leads to **4T-1**. The C_i isomer **4T-2** lies above **4T-1** by 11.6 kcal/mol with all real vibrational frequencies. There is a very small degree of spin

Table 3. Infrared Active ν(CO) Vibrational Frequencies (cm^{-1}) Predicted for the Seven Lowest Energy Isomers of $Cp_2V_2(CO)_5$[a]

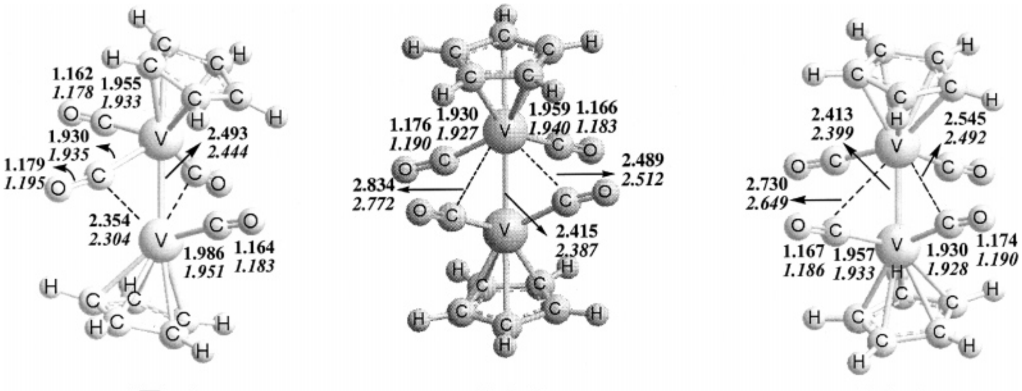
	B3LYP	BP86
5S-1 (C_s)	1908 (773), 1942 (247), 1977 (1090), 2008 (1463), 2051 (370)	1836 (551), 1865 (176), 1891 (927), 1926 (1129), 1966 (383)
5S-2 (C_2)	1899 (741), 1932 (390), 1970 (1008), 2023 (1640), 2050 (135)	1812 (516), 1861 (273), 1891 (886), 1938 (1400), 1963 (96)
5T-1 (C_1)	**1682 (391)**, 1893 (565), 1981 (757), 2011 (1802), 2072 (611)	**1641 (291)**, 1834 (366), 1900 (640), 1913 (2422), 1950 (1)
5S-3 (C_s)	1882 (953), 1922 (613), 1983 (352), 2014 (941), 2066 (1024)	1812 (684), 1846 (477), 1902 (280), 1925 (826), 1977 (811)
5T-2 (C_s)	1885 (1122), 1922 (66), 2009 (1748), 2034 (799), 2062 (384)	1806 (763), 1831 (42), 1920 (619), 1927 (1576), 1955 (30)
5S-4 (C_2)	**1881 (858)**, 1968 (294), 1971 (406), 1997 (1607), 2054 (749)	**1789 (701)**, 1883 (170), 1893 (476), 1913 (1147), 1966 (681)
5S-5 (C_{2v})	**1833 (955)**, 1966 (0), 1983 (619), 2013 (1512), 2059 (967)	**1747 (729)**, 1882 (0), 1903 (483), 1926 (1224), 1969 (817)

[a] Infrared intensities in parentheses are in km/mol; bridging ν(CO) frequencies are in bold.



4S–1 **4S–2** **4S–3**

Figure 4. The three singlet stationary points for $Cp_2V_2(CO)_4$.



4T–1 **4T–2** **4T–3**

Figure 5. The three triplet stationary points for $Cp_2V_2(CO)_4$.

Table 4. Total Energies (E, hartrees), Energies Relative to That of **4T-1** (ΔE, kcal/mol), Number of Imaginary Vibrational Frequencies (Nimg), and V−V Distances (Å) for the Three Singlet Stationary Points of $Cp_2V_2(CO)_4$

		4S-1 (C_1)	**4S-2** (C_s)	**4S-3** (C_{2h})
B3LYP	E	−2728.662891	−2728.654229	−2728.653416
	ΔE	11.4	16.8	17.3
	Nimg	0	1 (4i cm^{-1})	0
	V−V	2.552	2.370	2.289
BP86	E	−2729.005377	−2729.000597	−2729.000939
	ΔE	1.2	4.2	3.9
	Nimg	0	0	0
	V−V	2.547	2.313	2.307

Table 5. Total Energies (E, hartrees), Relative Energies (ΔE, kcal/mol), Number of Imaginary Vibrational Frequencies (Nimg), and V−V Distances (Å) for the Three Triplet Structures of $Cp_2V_2(CO)_4$

		4T-1 (C_s)	**4T-2** (C_i)	**4T-3** (C_2)
B3LYP	E	−2728.681008	−2728.655808	−2728.655746
	ΔE	0.0	15.8	15.9
	Nimg	0	1 (49i cm^{-1})	1 (109i cm^{-1})
	V−V	2.493	2.415	2.413
BP86	E	−2729.007233	−2728. 988763	−2728.989586
	ΔE	0.0	11.6	11.1
	Nimg	0	0	1 (199i cm^{-1})
	V−V	2.444	2.387	2.399

contamination in these triplet isomers ($\langle S^2 \rangle = 2.01$ for **4T-2**, and $\langle S^2 \rangle = 2.02$ for **4T-3**). The V−V distances are 2.387 Å for **4T-2** and 2.399 Å for **4T-3**, consistent with V≡V triple bonds required to give both vanadium atoms the seventeen-electron configurations for a binuclear triplet structure.

The other two singlet structures of $Cp_2V_2(CO)_4$ (**4S-2** and **4S-3** in Figure 4) have geometries similar to those of **4T-2** and **4T-3**. Stationary point **4S-3** has C_{2h} symmetry, whereas **4S-2** has C_s symmetry (Figure 4). Isomer **4S-3** lies above **4T-1** by 3.9 kcal/ mol and has all real vibrational frequencies (Table 4).

Table 6. Infrared Active ν(CO) Vibrational Frequencies (cm^{-1}) Predicted for the Seven Lowest Energy Stationary Points of $Cp_2V_2(CO)_4$[a]

	B3LYP	BP86
4T-1 (C_s)	1888 (1418), 1919 (110), 1997 (1464), 2035 (346)	1813 (1081), 1836 (110), 1898 (970), 1949 (494)
4S-1 (C_1)	**1727 (356),** 1866 (592), 1982 (1174), 2046 (773)	**1654 (282)**, 1785 (407), 1896 (971), 1949 (661)
4T-2 (C_i)	1915 (1744), 1917 (0), 1969 (1849), 2015 (0)	1840 (0), 1845 (1468), 1883 (1278), 1920 (0)
4T-3 (C_2)	1902 (910), 1943 (1459), 1957 (768), 2010 (219)	1823 (487), 1845 (1261), 1861 (973), 1910 (118)
4S-2 (C_s)	1906 (478), 1938 (1169), 1957 (1280), 2004 (252)	1844 (2), 1865 (1237), 1868 (1275), 1916 (1)
4S-3 (C_{2h})	1915 (0), 1935 (1746), 1946 (1608), 2001 (0)	1845 (0), 1866 (1250), 1869 (1259), 1917 (0)

[a] Infrared intensities in parentheses are in km/mol; bridging ν(CO) frequencies are in bold.

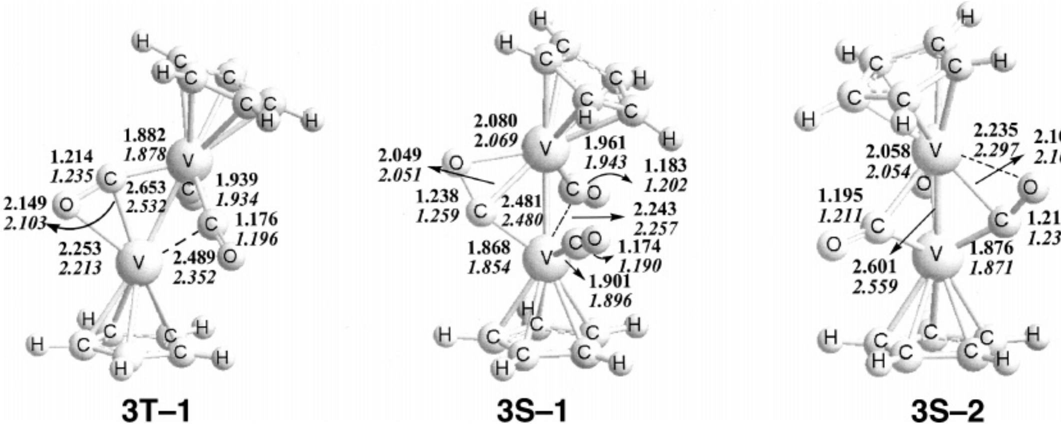


Figure 6. The three stationary points of $Cp_2V_2(CO)_3$.

Table 7. Total Energies (E, hartrees), Relative Energies (ΔE, kcal/mol), Number of Imaginary Vibrational Frequencies (Nimg), and V−V Distances (Å) for the Three Isomers of $Cp_2V_2(CO)_3$

		3T-1 (C_s)	**3S-1** (C_1)	**3S-2** (C_2)
B3LYP	E	−2615.314302	−2615.284401	−2615.275621
	ΔE	0.0	18.8	24.3
	Nimg	1 (11i cm^{-1})	0	0
	V−V	2.653	2.481	2.601
BP86	E	−2615.630904	−2615.615171	−2615.615300
	ΔE	0.0	9.9	9.8
	Nimg	0	0	0
	V−V	2.532	2.480	2.559

All four CO groups in **4S-3** are semibridging with V−C distances of 1.936 and 2.488 Å. Isomer **4S-2** has geometry (except for the orientation of the Cp rings) and energy similar to those of **4S-3** (Table 4). There is a very small imaginary vibrational frequency (4i cm^{-1}) in **4S-2** by B3LYP, which becomes real when a finer integration grid (99, 590) is used. The V−V distance is 2.307 Å in **4S-3** and 2.313 Å in **4S-2**. This V−V distance is shorter than that in **4T-1** by ~0.1 Å and consistent with the $\mathrm{V}\overset{4}{-}\mathrm{V}$ quadruple bond required to give both vanadium atoms the favored eighteen-electron configuration.

3.3. $Cp_2V_2(CO)_3$. Three energetically low-lying structures were found for $Cp_2V_2(CO)_3$ (Figure 6 and Tables 7 and 8). The global minimum **3T-1** is a triplet C_s structure with three semibridging CO groups. It has all real vibrational frequencies by BP86 but a very small imaginary vibrational frequency (11i cm^{-1}) by B3LYP. However, this tiny imaginary frequency was shown to arise from numerical error, since it becomes real when a finer grid (99, 590) is used. The spin contamination is not serious with $\langle S^2 \rangle = 2.14$. The V−C distances for one of the semibridging carbonyls are 1.878 and 2.103 Å. The short V−O distance (to another V atom) of 2.213 Å for one of these semibridging carbonyls indicates a four-electron donor η^2-μ-CO group. The ν(CO) frequency of this η^2-μ-CO group (Table 8) is predicted to be 1608 cm^{-1}. The V−V distance in **3T-1** is 2.532 Å, which can correspond to the V≡V triple bond required to give each vanadium atom a seventeen-electron configuration in a structure with one four-electron donor carbonyl group.

The next isomer of $Cp_2V_2(CO)_3$ (**3S-1**) is a C_1 singlet with two semibridging carbonyl groups lying 9.9 kcal/mol above **3T-1** (Figure 6). The V−C distances to one of the semibridging CO groups are 1.854 and 2.051 Å. The short V−O distance (to another V atom) of 2.069 Å from this semibridging carbonyl group indicates a four-electron donor η^2-μ-CO group. A very low ν(CO) frequency of 1503 cm^{-1} is predicted for this η^2-μ-CO group (Table 8). For the other semibridging CO group the V−C distances are 1.943 and 2.257 Å. This second semibridging CO group is a normal two-electron donor as indicated by the relatively long V−O distance and corresponds to the predicted ν(CO) frequency of 1786 cm^{-1} (Table 8). The V−V distance 2.480 Å, which is shorter than that in **3T-1** by only 0.05 Å (BP86), corresponds to a V≡V triple bond in **3S-1**.

The isomer next higher in energy for $Cp_2V_2(CO)_3$, namely, the C_2 isomer **3S-2** (Figure 6), is predicted to lie 9.8 kcal/mol above the global minimum **3T-1** and has all real vibrational frequencies. This isomer has one symmetrical bridging carbonyl and two semibridging carbonyls. The V−C distances for the normal bridging carbonyl are 2.054 Å. The V−C distances for the two semibridging carbonyls are 1.871 and 2.105 Å. The V−O distances (to another V atom) are very short, namely, 2.297 Å, indicating that the two semibridging carbonyls are four-electron donor η^2-μ-CO groups. The ν(CO) frequencies of 1617 and 1656 cm^{-1} correspond to the two η^2-μ-CO groups, whereas the significantly higher ν(CO) frequency of 1746 cm^{-1} (still in the bridging carbonyl region) corresponds to the symmetrical two-electron donor bridging CO group. The V−V distance is 2.559 Å, similar to that of **3T-1**, and can correspond to the V≡V triple bond required to give both metal atoms eighteen-

Table 8. Infrared Active ν(CO) Vibrational Frequencies (cm^{-1}) Predicted for the Three Lowest Energy Isomers of $Cp_2V_2(CO)_3$[a]

	B3LYP	BP86
3T-1 (C_s)	**1693 (592)**, 1903 (1338),1952 (150)	**1608 (397)**, 1804 (1038), 1845 (108)
3S-1 (C_1)	**1581 (390)**, **1877 (939)**, 1953 (561)	**1503 (311)**, **1786 (629)**, 1876 (520)
3S-2 (C_2)	**1654 (571)**, **1701 (341)**, **1821 (508)**	**1617 (478), 1656 (358), 1746 (355)**

[a] Infrared intensities in parentheses Aare in km/mol; bridging ν(CO) frequencies are in bold.

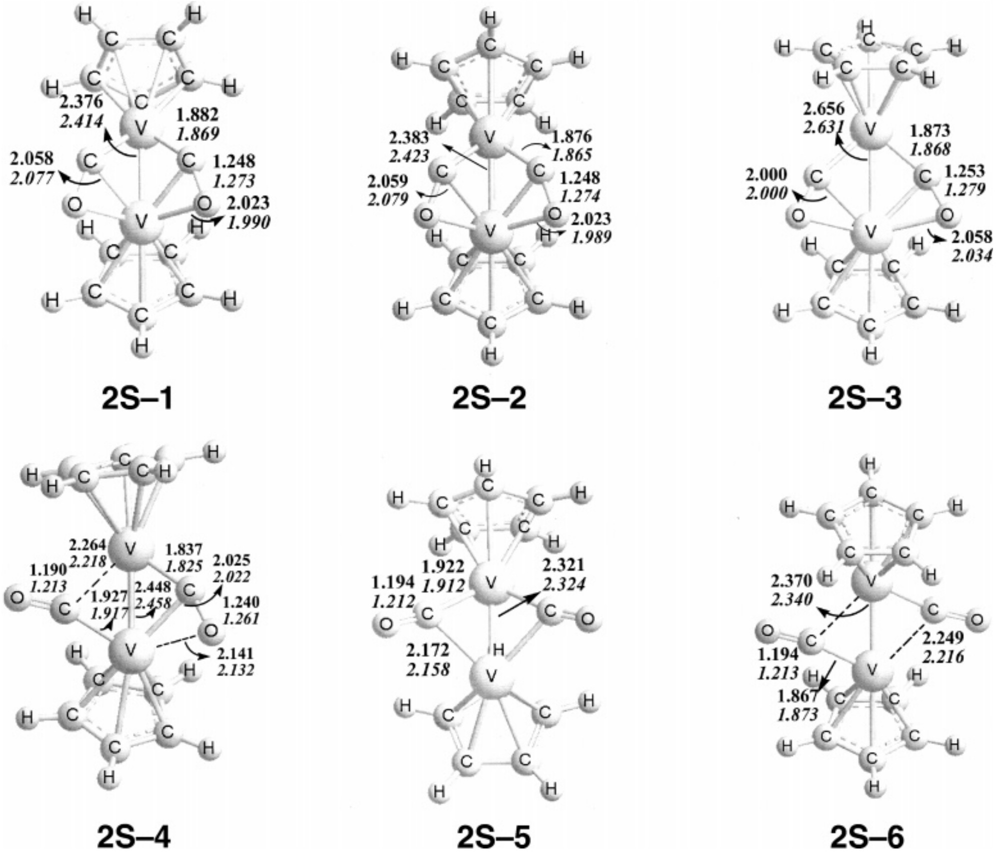


Figure 7. The six singlet stationary points of $Cp_2V_2(CO)_2$.

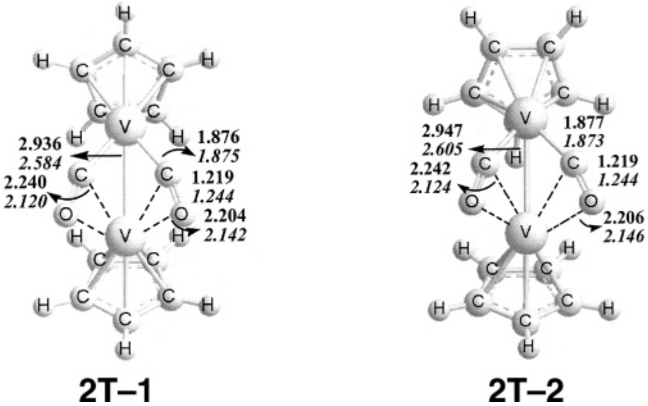


Figure 8. The two triplet stationary points of $Cp_2V_2(CO)_2$.

electron configurations in the presence of two four-electron donor carbonyl groups.

3.4. $Cp_2V_2(CO)_2$. Eight low-lying stationary points were found for $Cp_2V_2(CO)_2$ (Figures 7 and 8 and Tables 9−11). The global minimum can be either a triplet structure, **2T-1**, or a singlet structure, **2S-1**, depending on the DFT method (Tables 9 and 10). Thus, B3LYP predicts two triplet structures to lie below the singlet structure **2S-1** by about 18 kcal/mol, whereas BP86 predicts the singlet isomer **2S-1** to lie below the two triplet isomers by about 3 kcal/mol.

The two lowest lying singlet isomers of $Cp_2V_2(CO)_2$ (**2S-1** and **2S-2** in Figure 7) exhibit C_s doubly semibridged structures. The difference between **2S-1** and **2S-2** is the orientation of the two Cp rings, staggered for **2S-1** and eclipsed for **2S-2**. The V−C distances for the two semibridging carbonyls in **2S−1** are 1.869 and 2.077 Å. The V−O distances (to another V atom) are very short, namely, 1.990 Å, indicating that both semibridging carbonyls are four-electron donor η^2-μ-CO groups. This is consistent with their extremely low ν(CO) frequencies of 1392 and 1456 cm^{-1} (Table 11) and relatively long C−O distances (1.27 Å), indicating very low C−O bond orders for the carbonyl groups. The V−V distance is 2.414 Å. Structure **2S-2** is essentially similar to **2S-1** with respect to the CO groups and the V−V distance.

The two triplet stationary points of $Cp_2V_2(CO)_2$ (**2T-1** and **2T-2** in Figure 8), like the singlet isomers **2S−1** and **2S−2**, also exhibit C_s symmetry and are geometrically and energetically similar to each other, except for the orientation of the two Cp rings, eclipsed in **2T-1** and staggered in **2T-2**. The spin contamination $\langle S^2 \rangle$ for **2T-1** is ∼2.2. The two CO groups in **2T-1** and **2T-2** are both semibridging with V−C distances of

Table 9. Total Energies (*E*, hartrees), Energies Relative to That of **2T-1** for B3LYP (Δ*E*, kcal/mol), Number of Imaginary Vibrational Frequencies (Nimg), and V−V Distances (Å) for the Six Singlet Stationary Points of $Cp_2V_2(CO)_2$

		2S-1 (C_s)	**2S-2** (C_s)	**2S-3** (C_s)	**2S-4** (C_1)	**2S-5** (C_s)	**2S-6** (C_i)
B3LYP	*E*	−2501.89460	−2501.89357	−2501.89075	−2501.87959	−2501.87288	−2501.86746
	Δ*E*	17.8	18.4	20.2	27.2	31.4	34.8
	Nimg	0	1 (11*i* cm^{-1})	0	0	0	1 (30*i* cm^{-1})
	V−V	2.376	2.383	2.656	2.448	2.321	2.370
BP86	*E*	−2502.22341	−2502.22251	−2502.21366	−2502.20235	−2502.20013	−2502.19556
	Δ*E*	0.0	0.6	6.1	13.2	14.6	17.5
	Nimg	1 (16*i* cm^{-1})	1 (20*i* cm^{-1})	0	0	0	0
	V−V	2.414	2.423	2.631	2.458	2.324	2.340

Table 10. Total Energies (*E*, hartrees), Energies Relative to That of **2S-1** for BP86 (Δ*E*, kcal/mol), Number of Imaginary Vibrational Frequencies (Nimg), and V−V Distances (Å) for the Two Triplet Isomers of $Cp_2V_2(CO)_2$

		2T-1 (C_s)	**2T-2** (C_s)
B3LYP	*E*	−2501.92276	−2501.92290
	Δ*E*	0.1	0.0
	Nimg	1 (4*i* cm^{-1})	1 (15*i* cm^{-1})
	V−V	2.936	2.947
BP86	*E*	−2502.21941	−2502.21880
	Δ*E*	2.5	2.9
	Nimg	1 (11*i* cm^{-1})	1 (42*i* cm^{-1})
	V−V	2.584	2.605

Table 11. Infrared Active *ν*(CO) Vibrational Frequencies (cm^{-1}) Predicted for the Eight Lowest Energy Stationary Points of $Cp_2V_2(CO)_2$[a]

	B3LYP	BP86
2T-1 (C_s)	**1629 (555), 1714 (519)**	**1541 (315), 1592 (350)**
2T-2 (C_s)	**1630 (562), 1716 (525)**	**1540 (331), 1593 (357)**
2S-1 (C_s)	**1500 (316), 1549 (313)**	**1392 (227), 1456 (217)**
2S-2 (C_s)	**1496 (312), 1548 (296)**	**1391 (228), 1456 (208)**
2S-3 (C_s)	**1513 (365), 1536 (147)**	**1412 (113), 1444 (129)**
2S-4 (C_1)	**1583 (401)**, 1846 (661)	**1511 (282)**, 1737 (457)
2S-5 (C_s)	1810 (1272), 1850 (622)	1730 (930), 1773 (500)
2S-6 (C_i)	1807 (1549), 1836 (0)	1740 (1095), 1755 (0)

[a] Infrared intensities in parentheses are in km/mol; η^2-*μ*-CO four-electron donor bridging *ν*(CO) frequencies are in bold.

∼1.87 and ∼2.12 Å. The V−O distances are ∼2.14 Å, indicating that both bridging CO groups are four-electron donors consistent with the very low *ν*(CO) frequencies of 1541 and 1592 cm^{-1} in **2T-1** (Table 11). For **2T-1** and **2T-2**, the B3LYP and BP86 methods predict quite different V−V distances, namely, 2.936 Å (B3LYP) or 2.584 Å (BP86) for **2T-1** and 2.947 Å (B3LYP) or 2.605 Å (BP86) for **2T-2**. The V−V distance in **2T-1** or **2T-2** is longer than that in **2S-1** or **2S-2** by 0.6 Å (B3LYP) or 0.2 Å (BP86). As we pointed out in Section 2, the BP86 V−V distances would appear to be the more reliable.[20]

The isomer **2S-3** (Figure 7**)** also has a C_s structure with two equivalent semibridging carbonyl groups and lies above **2S-1** by 6.1 kcal/mol. The V−C distances for the two semibridging carbonyls are 1.868 and 2.000 Å. Similar to **2S-1** and **2S-2**, the V−O distances (to another V atom) in **2S-3** for both semibridging carbonyls are very short, namely, 2.034 Å, indicating that both semibridging carbonyls are four-electron donor η^2-*μ*-CO groups. Again this is consistent with the very low *ν*(CO) frequencies at 1444 and 1412 cm^{-1} (Table 11). The V−V distance in **2S-3** is 2.631 Å.

Isomer **2S-4** (Figure 7) at 13.2 kcal/mol above **2S-1** is also a C_1 doubly semibridged structure. The two semibridging carbonyls are not equivalent. One appears to be a four-electron donor η^2-*μ*-CO group with a short V−O distance of 2.132 Å, while the other has a V···O distance too long to be a similar four-electron donor. The V−C distances for the four-electron donor CO group are 1.825 and 2.022 Å. The V−C distances for the other semibridging carbonyl are 1.917 and 2.218 Å. In **2S-4** the four-electron donor semibridging CO group is predicted to exhibit a *ν*(CO) frequency of 1511 cm^{-1}, whereas the two-electron donor semibridging CO group is predicted to exhibit a much higher *ν*(CO) frequency of 1737 cm^{-1} (Table 11). The V−V distance is 2.458 Å.

Isomer **2S-5** (Figure 7), at about 14.6 kcal/mol above **2S-1**, is also a C_s doubly semibridged structure with all real vibrational frequencies (Table 9). The V−C distances for the two semibridging carbonyls are 1.912 and 2.158 Å. The predicted *ν*(CO) frequencies (Table 11) of **2S-5** are 1730 and 1773 cm^{-1}, consistent with two-electron donor bridging carbonyl groups. The V−V distance in **2S-5** is 2.324 Å, which is shorter than that in **2T-1** by 0.3 Å (BP86). Structure **2S-5** thus has the shortest V−V distance of all of the $Cp_2V_2(CO)_2$ stationary points.

The last isomer of $Cp_2V_2(CO)_2$ at reasonable energy levels, namely, **2S-6** (Figure 7) with C_i symmetry, is another doubly semibridged structure lying above **2S-1** by 17.5 kcal/mol. It has all real vibrational frequencies by BP86, but B3LYP again predicts a small imaginary frequency (30*i* cm^{-1}, Table 9). The V−C distances for the two equivalent semibridging carbonyls are 1.873 and 2.216 Å. The predicted *ν*(CO) frequencies (Table 11) of isomer **2S-6** are 1740 and 1755 cm^{-1}, consistent with two-electron donor bridging carbonyl groups. The V−V distance in **2S-6** is 2.340 Å.

3.5. $Cp_2V_2(CO)$. A total of four energetically low-lying $Cp_2V_2(CO)$ isomers were found (Figure 9 and Table 12). Each isomer has a different spin multiplicity. The global minimum for $Cp_2V_2(CO)$ (**1Q-1**) by the BP86 functional is a quintet structure with C_s symmetry and a semibridging CO group. The septet and singlet structures (**1H-1** and **1S-1**, respectively) of $Cp_2V_2(CO)$ lie above the quintet global minimum by about 11−13 kcal/mol (BP86). The triplet structure **1T-1** lies energetically only 2.5 kcal/mol above the quintet global minimum. Each state has various conformers with the five-membered rings in different orientations, but the geometries of these conformers are quite similar, and the energies are within 0.5 kcal/mol.

The short V−O distances around 2.0 Å in the quintet, triplet, and septet isomers of $Cp_2V_2(CO)$, namely, **1Q-1, 1T-1**, and **1H-1**, respectively (Figure 9), indicate that the bridging CO groups in these isomers are four-electron donors, consistent with their very low *ν*(CO) frequencies (Table 12) at 1412 cm^{-1} (**1Q-1**), 1363 cm^{-1} (**1T-1**), and 1495 cm^{-1} (**1H-1**). However, the configuration of the CO group in the singlet isomer **1S-1** of

$Cp_2V_2(CO)$ indicates it to be a normal two-electron donor bridging CO group, consistent with its ν(CO) frequency at 1790 cm^{-1}.

The bridging CO group in the global minimum (quintet state) of $Cp_2V_2(CO)$ (**1Q-1**) is only slightly unsymmetrical with a short V−C distance of 1.882 Å and a long V−C distance of 1.944 Å. The geometry of septet $Cp_2V_2(CO)$ (**1H-1**) is similar to that of the quintet state, but with slightly longer V−C bond distances. The singlet state **1S-1** of $Cp_2V_2(CO)$ has a less symmetrical bridging CO group with even longer V−C distances of 1.944 and 2.202 Å.

The V═V distance of 2.528 Å in the quintet structure **1Q-1** of $Cp_2V_2(CO)$ can be interpreted as a double bond with fourteen-electron configurations for the vanadium atoms. Similarly, the much longer V−V distance of 2.970 Å in the septet isomer **1H-1** of $Cp_2V_2(CO)$ can be interpreted as a single bond with thirteen-electron configurations for the vanadium atoms. Thus, these highly paramagnetic isomers have vanadium electronic configurations far less than the favored eighteen-electron configuration. The singlet isomer **1S-1** of $Cp_2V_2(CO)$ has a very short V−V distance of 1.803 Å, suggesting a very high formal metal−metal bond order.

4. Discussion

4.1. Relationships among Metal−Metal Bond Order, Four-Electron Donor Carbonyl Groups, and Metal Electronic Configurations upon Decarbonylation of $Cp_2V_2(CO)_5$. Photolysis of $CpV(CO)_4$ is reported[28] to give $Cp_2V_2(CO)_5$ directly without any evidence so far for isolable $Cp_2V_2(CO)_7$ or $Cp_2V_2(CO)_6$ intermediates. The experimental structure for $Cp_2V_2(CO)_5$ determined by X-ray crystallography[5] is very close to that computed for the global minimum of $Cp_2V_2(CO)_5$, namely, isomer **5S-1** (Figure 2 and Table 1). This structure has all two-electron donor CO groups and a V≡V distance of 2.452 Å, consistent with the formal triple bond giving both vanadium atoms the favored eighteen-electron noble gas configuration.

The two lowest energy triplet structures for $Cp_2V_2(CO)_5$ found in this work have lower formal vanadium−vanadium bond orders relating to the seventeen-electron configurations expected for the vanadium atoms in a binuclear triplet structure. Thus, structure **5T-2** (Figure 3 and Table 2) has all two-electron donor CO groups and a V═V distance of 2.665 Å, which is longer than that in **5S-1**, suggesting a double bond rather than the triple bond of **5S-1**. The triplet structure **5T-1** has an even longer V−V distance of 2.988 Å, suggesting a single bond. However, this is balanced out by one of the five CO groups in **5T-1** becoming a four-electron donor so that each vanadium atom retains the expected seventeen-electron configuration expected for a binuclear triplet structure.

Similar optimum vanadium electronic configurations (18 for singlets and 17 for triplets) are found for the lowest energy $Cp_2V_2(CO)_4$ isomers (Figures 4 and 5). The global minimum **4T-1** for $Cp_2V_2(CO)_4$ has a V≡V distance of 2.444 Å, suggesting a formal triple bond and all two-electron donor CO groups so that each vanadium atom has the seventeen-electron configuration for a binuclear triplet. The corresponding singlet structure **4S-2** for $Cp_2V_2(CO)_4$ has a shorter vanadium distance of 2.313 Å, which can be interpreted as a formal V−V quadruple bond, thereby giving each vanadium atom the favored eighteen-electron configuration for a singlet structure with all two-electron donor CO groups. The lower energy of the triplet isomer **4T-1** relative to the singlet isomer **4S-2** of $Cp_2V_2(CO)_4$ using either functional suggests resistance to metal−metal bond orders greater than 3, possibly owing to the weakness of the δ-bonding in an M−M quadruple bond. A lower energy singlet isomer, **4S-1**, of $Cp_2V_2(CO)_4$ (but still higher in energy than the triplet **4T-1**) avoids a vanadium−vanadium quadruple bond by having one four-electron bridging CO group, thereby giving both vanadium atoms the favored eighteen-electron configuration with only a formal V≡V triple bond.

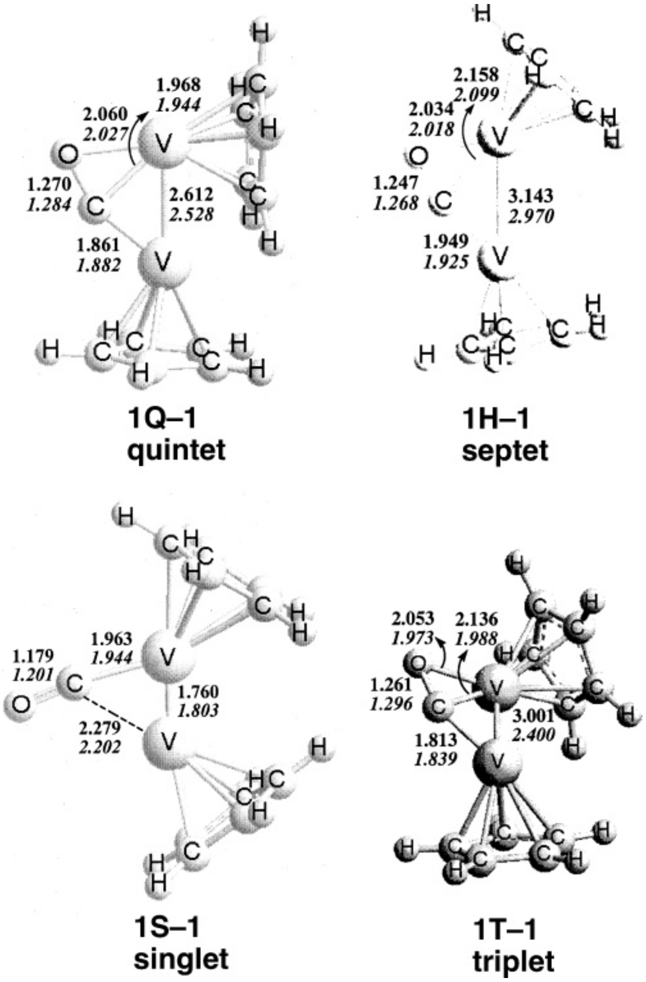


Figure 9. The four isomers of $Cp_2V_2(CO)$.

The next decarbonylation product is $Cp_2V_2(CO)_3$, which requires a vanadium−vanadium quintuple bond to give each vanadium atom the favored eighteen-electron configuration in a binuclear singlet structure in the absence of four-electron donor bridging carbonyl groups. No evidence is found in any of the $Cp_2V_2(CO)_3$ isomers for a structure with a sufficiently short vanadium−vanadium distance to suggest a quintuple bond, undoubtedly because the nine valence orbitals of the vanadium sp^3d^5 manifold are not sufficient to form a quintuple bond, three bonds to a η^5-C_5H_5 ring, and the bonds to the carbonyl groups. Such a metal−metal quintuple bond was recently discovered[29] in the binuclear chromium(I) aryl RCrCrR with an extremely

---

[28] Hermann, W. A.; Plank, J. *Chem. Ber.* **1979**, *112*, 392.

[29] Nguyen, T.; Sutton, A. D.; Brynda, M.; Fettinger, J. C.; Long, G. J.; Power, P. P. *Science* **2005**, *310*, 844.

Table 12. Total Energies (E, hartrees), Relative Energies (ΔE, kcal/mol), Number of Imaginary Vibrational Frequencies (Nimg), Infrared ν(CO) Frequencies (cm^{-1}; Intensities (km/mol) in Parentheses), and V−V Distances (Å) for the Four Isomers of $Cp_2V_2(CO)$

		1Q-1 (C_s)	**1T-1** (C_1)	**1H-1** (C_s)	**1S-1** (C_s)
B3LYP	E	−2388.51465	−2388.51731	−2388.52169	−2388.46309
	ΔE	0.0	−1.7	−4.4	32.4
	Nimg	0	0	0	0
	ν(CO)	1469 (416)	1509 (535)	1584 (356)	1909 (942)
	V−V	2.612	3.001	3.143	1.760
	$\langle S^2 \rangle$	6.30	3.26	12.09	0.00
BP86	E	−2388.80431	−2388.80031	−2388.78679	−2388.78348
	ΔE	0.0	2.5	11.0	13.1
	Nimg	1 ($3i$ cm^{-1})	0	0	0
	ν(CO)	1412 (330)	1363 (103)	1495 (231)	1790 (698)
	V−V	2.528	2.400	2.970	1.803
	$\langle S^2 \rangle$	6.05	2.14	12.06	0.00

bulky aryl group (R = C_6H_3-2,6-(C_6H_3-2,6-Pr^i_2)$_2$, Pr^i = isopropyl). However, in such RCrCrR derivatives, the chromium atoms need only to form one single bond each to an R group, leaving plenty of valence orbitals for the metal−metal quintuple bond.

The three $Cp_2V_2(CO)_3$ isomers (Figure 6) all have V≡V distances around 2.5 Å, suggesting formal triple bonds. Both vanadium atoms in the singlet isomer **3S-2** with a V≡V triple bond and two four-electron donor carbonyl groups have the favored eighteen-electron configurations. Similarly, both vanadium atoms in the triplet isomer **3T-1** with a V≡V triple bond and a single four-electron donor carbonyl group have the seventeen-electron configurations expected for a binuclear triplet. However, the eighteen-electron rule appears to break down in the singlet isomer **3S-1** with a V≡V distance, again suggesting a formal triple bond but only one four-electron donor CO group rather than the two four-electron donor CO groups of **3S-2**. Apparently one of the vanadium atoms in **3S-1** has only a sixteen-electron configuration.

The vanadium atoms in the even more unsaturated derivatives $Cp_2V_2(CO)_2$ (Figures 7 and 8) and $Cp_2V_2(CO)$ (Figure 9) clearly do not have the eighteen-electron configurations for singlets or seventeen-electron configurations for binuclear triplets. The two lowest lying singlet $Cp_2V_2(CO)_2$ structures (**2S-1** and **2S-2**) have two four-electron donor CO groups and V≡V distances in the range 2.41−2.42 Å (BP86), suggesting triple bonds corresponding to one sixteen-electron and one eighteen-electron vanadium atom. Since the vanadium atoms are very different in these structures with only one vanadium atom bonded to the carbonyl oxygen atoms, this is not surprising. The higher energy singlet $Cp_2V_2(CO)_2$ structures (**2S-5** and **2S-6**) have only normal two-electron donor bridging CO groups but shorter V≡V distances in the range 2.32−2.34 Å (BP86), suggesting a quadruple bond corresponding to sixteen-electron configurations for both vanadium atoms. This implies that the CO π-bonds characteristic of the four-electron donor CO groups are more favorable energetically than the δ-bonding component of a metal−metal quadruple bond.

The very short vanadium−vanadium distance of 1.803 Å in the singlet $Cp_2V(CO)$ isomer **1S-1** (Figure 9) is close to the experimentally determined 1.835 Å formal chromium−chromium quintuple bond in the chromium(I) aryl[29] RCrCrR, suggesting the possibility of a formal vanadium−vanadium quintuple bond. Since the bridging CO group in the singlet $Cp_2V_2(CO)$ isomer is clearly a two-electron donor, this would give each of the vanadium atoms sixteen-electron configurations. This is not unreasonable for an early-transition-metal derivative as indicated by the stability of Cp_2MX_2 complexes (M = Ti, Zr, Hf; X = halogen, alkyl, etc.).

4.2. Possible Involvement of Divanadocene Derivatives with Four-Electron Bridging Carbonyl Groups in Carbon Monoxide Hydrogenation. Our theoretical studies predict divanadocene carbonyl chemistry to be a prolific source of compounds containing four-electron donor η^2-μ-CO bridging carbonyl groups, probably owing to the oxophilicity of the early transition metal vanadium. Such four-electron donor bridging carbonyl groups were almost never found in our earlier studies on dimetallocene carbonyl derivatives of the middle to late transition metals iron,[30] cobalt, [21] and nickel.[31]

Our predicted data for these divanadocene carbonyl derivatives provide insight into the properties of four-electron donor η^2-μ-CO groups as the metal electron density is increased in the sequence $Cp_2V_2(CO)_3(\eta^2\text{-}\mu\text{-CO})$ (**4S-1** in Figure 4) < $Cp_2V_2(CO)_2(\eta^2\text{-}\mu\text{-CO})$ (**3T-1** in Figure 6) < $Cp_2V_2(\eta^2\text{-}\mu\text{-CO})_2$ (**2S-1** in Figure 7), where the number of electron-withdrawing two-electron donor CO groups (through strong π back-bonding) is reduced from three to two to zero, respectively. Thus, the C−O distances in this series are seen to increase and the ν(CO) frequencies are seen to decrease for the η^2-μ-CO groups with decreasing numbers of other CO groups. This indicates a reduction in the effective CO bond order as metal electrons become increasingly available for donation into the C−O antibonding orbitals.

There is a good chance that at least some of this novel divanadocene carbonyl chemistry predicted theoretically can be realized experimentally by a suitable choice of substituents on the cyclopentadienyl rings, leading to possible catalytic intermediates for CO hydrogenation. In this connection the substitution of a CO group in $Cp_2V_2(CO)_5$ with weak nucleophiles has been shown by CO exchange studies[32] to proceed by a dissociative mechanism involving a $Cp_2V_2(CO)_4$ intermediate. Furthermore, pyrolysis of $Cp_2V_2(CO)_5$ in boiling tetrahydrofuran gives a tetramer $Cp_4V_4(CO)_4$, which has not been characterized structurally but which has been shown by its infrared ν(CO) frequencies to contain terminal CO groups.[33] Formation of $Cp_4V_4(CO)_4$ could arise by dimerization of a $Cp_2V_2(CO)_2$

---

(30) Wang, H. Y.; Xie, Y.; King, R. B.; Schaefer, H. F. *Inorg. Chem.* **2006**, *45*, 3384.

(31) Wang, H. Y.; Xie, Y.; King, R. B.; Schaefer, H. F. *Inorg. Chem.* **2006**, *45*, 5621.

(32) Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 1840.

(33) Herrmann, W. A.; Plank, J.; Reiter, B. *J. Organomet. Chem.* **1979**, *164*, C25.

intermediate with concurrent bridging → terminal CO conversion during the dimerization process. Similar preparative methods using $Cp_2V_2(CO)_5$ derivatives with sterically demanding substituents on the cyclopentadienyl rings to inhibit further dimerization or polymerization might allow the isolation of stable highly unsaturated $Cp_2V_2(CO)_4$ or $Cp_2V_2(CO)_2$ derivatives having structures similar to those suggested in the present study. Such bulky substituents on the cyclopentadienyl rings should also inhibit disproportionation reactions to salts related to $Cp_2V^+V(CO)_6^-$.

Acknowledgment. We are indebted to the National Science Foundations of the United States (Grant CHE-0209857) and the 111 Project (B07012) in China for support of this work.

Supporting Information Available: Tables S1−S28, theoretical harmonic vibrational frequencies for the 28 structures using the BP86 method, Tables S29−S56, theoretical Cartesian coordinates for the 28 structures using the BP86 method, and the complete Gaussian reference (ref 27). This material is available free of charge via the Internet at http://pubs.acs.org.

JA068058M