

Binuclear Vanadium Carbonyls: The Limits of the 18-Electron Rule

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The fact that the stable mononuclear vanadium carbonyl $V(CO)_6$ fails to satisfy the 18-electron rule has led to an investigation of the binuclear vanadium carbonyls $V_2(CO)_n$ ($n = 10-12$) using methods from density functional theory. There are several important experimental studies of these homoleptic binuclear vanadium carbonyls. The global minimum for $V_2(CO)_{12}$ is a singlet structure having two $V(CO)_6$ units linked by a long V–V single bond (3.48 Å by B3LYP or 3.33 Å by BP86) without any bridging CO groups. For $V_2(CO)_{11}$ the global minimum is a singlet structure $V_2(CO)_{10}(\eta^2-\mu-CO)$ with a four-electron π -donor bridging CO group. For $V_2(CO)_{10}$ the global minimum is an unsymmetrical singlet $(OC)_4V\equiv V(CO)_6$ structure with three semibridging CO groups and a V–V distance of 2.54 Å (B3LYP) or 2.51 Å (BP86), suggesting a $V\equiv V$ triple bond. The theoretical $\nu(CO)$ frequencies of this $V_2(CO)_{10}$ isomer agree approximately with those assigned by Ishikawa et al. (*J. Am. Chem. Soc.* **1987**, *109*, 6644) to a $V_2(CO)_{10}$ isomer produced in the photolysis of gas-phase $V(CO)_6$. In contrast, the laboratory bridging $\nu(CO)$ frequency assigned to $V_2(CO)_{12}$ by Ford et al. (*Inorg. Chem.* **1976**, *15*, 1666) seems more likely to arise from the lowest-lying triplet isomer of $V_2(CO)_{11}$.

1. Introduction

One of the key principles governing the structure and bonding in metal carbonyls is the so-called 18-electron rule, which is a consequence of filling each of the nine orbitals of the transition-metal sp^3d^5 manifold with electron pairs so that the metal atom has the electronic configuration of the next noble gas.^{1,2} All of the stable binary metal carbonyls that had been isolated up to 1959 obeyed this 18-electron rule. For the first-row transition metals, these include the mononuclear metal carbonyls $Cr(CO)_6$, $Fe(CO)_5$, and $Ni(CO)_4$ and the binuclear metal carbonyls $Mn_2(CO)_{10}$, $Fe_2(CO)_9$, and $Co_2(CO)_8$. All five of these binary metal carbonyls are key starting materials in synthetic transition-metal organometallic chemistry and are available commercially.

Applying the 18-electron rule to V predicts a formula $V_2(CO)_{12}$ for the stable binary vanadium carbonyl. Therefore, it was most surprising that when the first neutral binary vanadium carbonyl was isolated in 1959,³ it was found not to be the dimer $V_2(CO)_{12}$. Instead, the observed species was the monomer $V(CO)_6$ with only a 17-electron configuration for the V atom and thus a paramagnetic molecule with a single unpaired electron. Initially, the dimer $V_2(CO)_{12}$ was postulated to be in equilibrium with the monomer $V(CO)_6$ on the basis of the temperature dependence of its paramagnetism.⁴ However, this anomalous magnetic behavior of $V(CO)_6$ was subsequently reinterpreted in terms of the vibronic coupling model of Van Vleck–Kotani and exchange magnetic interaction between two magnetic centers.⁵ Despite the fact that $V(CO)_6$ has only a 17-electron V configuration, the significance of the 18-electron rule is indicated by the fact that $V(CO)_6$ is pyrophoric and decomposes only a little above room temperature whereas the essentially isostructural 18-electron $Cr(CO)_6$ is so chemically and thermally stable that it can even be steam-distilled in air.

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- (1) (a) Lukehart, C. M. *Fundamental Transition Metal Organometallic Chemistry*; Brooks-Cole/Wadsworth: Belmont, CA, 1985; Chapters 1 and 2. (b) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 4th ed.; Wiley: New York, 2005; Chapter 2.
- (2) (a) Jonas, V.; Thiel, W. *J. Chem. Phys.* **1996**, *105*, 3636. (b) Jonas, V.; Thiel, W. *J. Phys. Chem.* **1999**, *103*, 1381.

(3) Natta, G.; Ercoli, R.; Calderazzo, F.; Alberola, A.; Corradini, P.; Allegra, G. *Rend. Accad. Naz. Lincei* **1959**, *27*, 107.

(4) Keller, H. J.; Laubereau, P.; Nöthe, D. *Z. Naturforsch.* **1969**, *24B*, 257.

(5) Bernier, J. C.; Kahn, O. *Chem. Phys. Lett.* **1973**, *19*, 414.

Subsequent to the refutation of the original claim of the binuclear $V_2(CO)_{12}$ in equilibrium with $V(CO)_6$, experimental evidence was obtained by two research groups for the existence of binuclear binary vanadium carbonyls based on the observation of bridging as well as terminal IR $\nu(CO)$ frequencies. Thus, Ozin et al.⁶ found that cocondensation of CO with V atoms in rare gas matrices at relatively high V concentrations led to a species having $\nu(CO)$ frequencies at 2050, 2014, and 1852 cm^{-1} , which they assigned to an isomer of $V_2(CO)_{12}$ with two bridging CO groups. Subsequently, Ishikawa et al.⁷ found that excimer laser photolysis of $V(CO)_6$ vapor at 308 nm in the absence of added CO gave a species exhibiting $\nu(CO)$ frequencies at 2025, 1965, and 1890 cm^{-1} , which they assigned to $V_2(CO)_{10}$ formed by the combination of $V(CO)_4$ and $V(CO)_6$ fragments.

The research discussed in this paper uses density functional theory (DFT) methods to examine possible structures for the homoleptic binuclear vanadium carbonyls $V_2(CO)_n$ ($n = 10-12$) predicted by the 18-electron rule to have V–V triple, double, and single bonds, respectively. However, the existence of the stable 17-electron $V(CO)_6$, as noted above, suggests that the 18-electron rule might no longer be a major factor in governing the structures of such binuclear vanadium carbonyl derivatives. For example, triplet structures for $V_2(CO)_n$ ($n = 10-12$) could be generated by combining two 17-electron mononuclear vanadium carbonyl fragments with a formal metal–metal bond order 1 less than that required by the 18-electron rule. In addition, the ability to predict $\nu(CO)$ frequencies by these DFT methods provides a basis to assess the reported experimental evidence^{6,7} for binuclear vanadium carbonyls. The DFT methods used for transition-metal carbonyls including homoleptic binuclear carbonyls have been tested in previous works.⁸⁻¹¹

2. Theoretical Methods

The DZP basis set for C and O atoms begins with Dunning's standard double- ζ contraction¹² of Huzinaga's primitive sets¹³ plus a set of pure spherical harmonic d polarization functions with orbital exponents $\alpha_d(C) = 0.75$ and $\alpha_d(O) = 0.85$, designated as 9s5p1d/4s2p1d. The loosely contracted DZP basis set for V is the Wachters primitive set¹⁴ augmented by two sets of p functions and a set of d functions, contracted following Hood et al.,¹⁵ designated as 14s11p6d/10s8p3d. Thus, for $V_2(CO)_{12}$, there are 458 contracted Gaussian functions in the present flexible DZP basis sets.

DFT methods, which are acknowledged to be a practical and effective computational tool for organometallic compounds,¹⁶ are employed here. Among DFT procedures, the hybrid Hartree–Fock (HF)/DFT method known as B3LYP is a combination of Becke's three-parameter functional¹⁷ and the Lee–Yang–Parr correlation functional.¹⁸ Another DFT method, which combines Becke's 1988 exchange functional¹⁹ with Perdew's 1986 correlation functional²⁰ known as the BP86 method, has also proven effective and is used in this research.

The geometries of all structures were fully optimized using the DZP B3LYP and DZP BP86 methods, and the vibrational frequencies were determined by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. The corresponding IR intensities were also evaluated analytically. All of the computations were carried out with the *Gaussian03* program,²¹ exercising the fine-grid option (75 radial shells and 302 angular points) for evaluating integrals numerically, while the tight (10^{-8} hartree) designation is the default for the self-consistent-field convergence.

In the search for minima using all currently implemented DFT methods, low-magnitude imaginary vibrational frequencies are suspect because of significant limitations in the numerical integration procedures used in the DFT computations. Jacobsen and Ziegler have concluded that all imaginary vibrational frequencies with a magnitude of less than 100 cm^{-1} are considered relatively unimportant and are neglected in the analysis.²² Martin et al. also discussed the similar integration accuracy in their DFT calculations.²³ Therefore, we do not follow such low imaginary vibrational frequencies, unless they appear to be meaningful, such as the internal rotation modes.

A total of 37 structures for $V_2(CO)_n$ ($n = 10-12$) were found in this study. All 37 structures are depicted in the Supporting Information along with their computed harmonic vibrational frequencies. This paper discusses in detail only the 25 structures among the 37 that are energetically competitive with the global minima and have only insignificant imaginary vibrational frequencies. In the present case, the B3LYP and BP86 methods agree with each other fairly well in predicting the structural characteristics of $V_2(CO)_n$. 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. Results

3.1. $V_2(CO)_{12}$. A total of 10 structures were found for $V_2(CO)_{12}$. However, only four of these structures (Figure 1 and

(6) Ford, T. A.; Huber, H.; Klotzbücher, W.; Moskovits, M.; Ozin, G. A. *Inorg. Chem.* **1976**, *15*, 1666.
 (7) Ishikawa, Y.; Hackett, P. A.; Rayner, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 6644.
 (8) Schaefer, H. F.; King, R. B. *Pure Appl. Chem.* **2001**, *73*, 1059.
 (9) Xie, Y.; Jang, J. H.; King, R. B.; Schaefer, H. F. *Inorg. Chem.* **2003**, *42*, 5219.
 (10) Delley, B.; Wrinn, M.; Luthi, H. P. *J. Chem. Phys.* **1994**, *100*, 5785.
 (11) Ruis-Moraales, Y.; Schreckenbach, G.; Ziegler, T. *J. Phys. Chem.* **1996**, *100*, 3359.
 (12) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823.
 (13) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.
 (14) Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033.
 (15) Hood, D. M.; Pitzer, R. M.; Schaefer, H. F. *J. Chem. Phys.* **1979**, *71*, 705.

(16) Ziegler, T. *Can. J. Chem.* **1995**, *73*, 743.
 (17) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
 (18) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
 (19) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
 (20) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8842. Perdew, J. P. *Phys. Rev. B* **1986**, *34*, 7046.
 (21) Frisch, M. J.; et al. *Gaussian03*, Revision C 02; Gaussian, Inc.: Wallingford, CT, 2004. (See the Supporting Information for details.)
 (22) Jacobsen, H.; Ziegler, T. *J. Am. Chem. Soc.* **1996**, *118*, 4631.
 (23) Martin, J. M. L.; Bauschlicher, C. W.; Ricca, A. *Comput. Phys. Commun.* **2001**, *133*, 189.

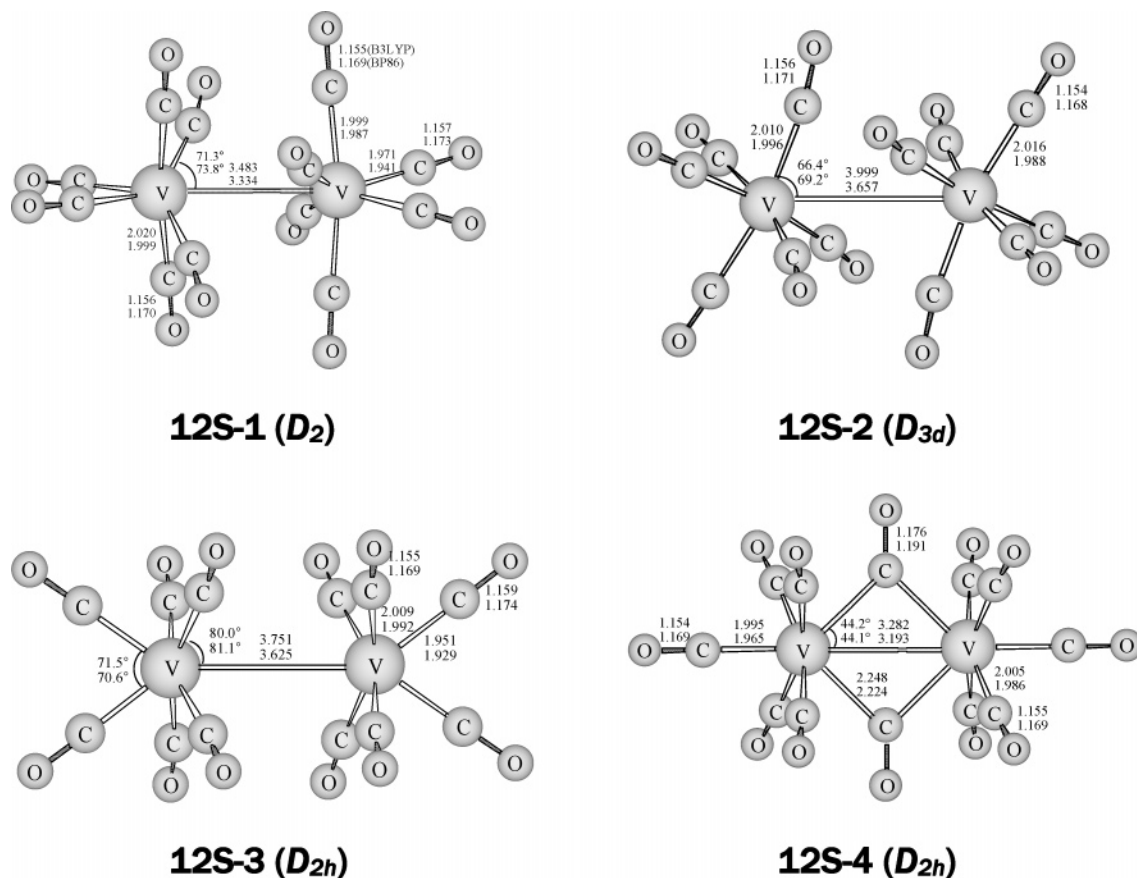


Figure 1. Structures of $V_2(CO)_{12}$.

Table 1. Total Energies (E in hartrees), Relative Energies (ΔE in kcal/mol), and V–V Distances (in Å) for the Four Lowest-Energy Isomers of $V_2(CO)_{12}$

		12S-1 (D_2)	12S-2 (D_{3d})	12S-3 (D_{2h})	12S-4 (D_{2h})
B3LYP	E	–3248.37823	–3248.37482	–3248.36376	–3248.34208
	ΔE	0.0	2.1	9.1	22.7
	Nimg	0	0	2 (46i, 21i)	1 (190i)
	V–V	3.483	3.999	3.751	3.282
BP86	E	–3248.76364	–3248.75340	–3248.75048	–3248.73581
	ΔE	0.0	6.4	8.3	17.4
	Nimg	0	2 (14i, 14i)	2 (32i, 20i)	1 (138i)
	V–V	3.334	3.657	3.625	3.193

Table 2. IR-Active $\nu(CO)$ Vibrational Frequencies (cm^{-1}) Predicted for the Four Lowest-Energy Isomers of $V_2(CO)_{12}$ (IR Intensities in Parentheses Are in km/mol)

	B3LYP	BP86
12S-1 (D_2)	2083 (2140), 2067 (2942), 2063 (1681), 2049 (1450), 2047 (21), 2044 (1644), 2029 (211), 2027 (33), 2026 (4)	2008 (1630), 1986 (2455), 1982 (1706), 1970 (366), 1962 (31), 1960 (997), 1953 (740), 1948 (25), 1947 (18)
12S-2 (D_{3d})	2079 (5870), 2062 (1200), 2054 (2250), 2018 (37)	2011 (3500), 1978 (1260), 1970 (1620), 1949 (370)
12S-3 (D_{2h})	2081 (2700), 2073 (1870), 2065 (3660), 2029 (446), 2028 (1470)	1999 (2220), 1995 (2360), 1987 (1685), 1952 (740), 1950 (1070)
12S-4 (D_{2h})	2093 (2700), 2064 (1390), 2058 (2600), 2052 (3700), 1879 (646)	2014 (2260), 1980 (1050), 1974 (2160), 1971 (3110), 1807 (435)

Table 1) were within 20 kcal/mol of the global minimum **12S-1** and are discussed in detail in this paper. All four of these structures are singlets; the lowest-lying triplet structure for $V_2(CO)_{12}$ was found to lie 52.5 kcal/mol (BP86) above the global minimum **12S-1**.

The global minimum found for $V_2(CO)_{12}$ (**12S-1**) is an unbridged structure $(CO)_6VV(CO)_6$ of D_2 symmetry having all real harmonic vibrational frequencies by both the B3LYP

and BP86 methods (Table 3). Its V–V distance is predicted to be 3.334 Å (BP86). This might be a standard V–V single bond, consistent with the favored 18-electron configuration for each V atom. However, there are no experimentally known examples of low-oxidation-state V complexes with V–V single bonds to provide a basis for estimating V–V single bond distances. In any case, the V–V distance in **12S-1** is very long, suggesting a weak interaction between

Table 3. Total Energies (E in hartrees), Relative Energies (ΔE in kcal/mol), and V–V Distances (in Å) for the Two Lowest-Energy Isomers of $V_2(CO)_{11}$ (**11S-1** and **11S-2** in Figure 2)

		11S-1 (C_1)	11S-2 (C_s)
B3LYP	E	–3135.03192	–3135.02242
	ΔE	0.0	6.0
	Nimg	0	2 (65i, 29i)
	V–V	3.487	3.692
BP86	E	–3135.40656	–3135.39247
	ΔE	0.0	8.8
	Nimg	0	3 (87i, 47i, 17i)
	V–V	3.376	3.558

the two $V(CO)_6$ units and facile dissociation into two $V(CO)_6$ molecules. The V–C distances are in the range of 1.941–1.999 Å. For the eight inward CO groups, the V–V–C angles are 73.8° and 85.5°, while the V–C–O angles are 171.7° and 177.4°. However, for the four outward CO groups, the relevant V–C–O angles are 178.0°. In fact, most terminal V–C–O angles for other structures in the present study are nearly linear, and thus we will not discuss them.

The next-lowest-energy structure (**12S-2**) at 6.4 kcal/mol (BP86) above the global minimum **12S-1** is also an unbridged $(CO)_6VV(CO)_6$ structure of D_{3d} symmetry (Figure 1). The BP86 method predicts a negligible doubly degenerate imaginary vibrational frequency at 14i cm^{-1} . The V–V distance in **12S-2** is 3.657 Å, which is longer than that in **12S-1** by 0.3 Å, suggesting at most a very weak V–V single bond. For the six inward CO groups, the V–C distances are 1.996 Å and the corresponding V–V–C angles are at 69.3°. For the six outward CO groups, the V–C distances are 1.988 Å and the relevant V–V–C angles are 126.7°. The V–C–O angles for the six inward CO groups are 170.9°.

The third structure for $V_2(CO)_{12}$ in terms of energy (**12S-3**) (D_{2h}) is also an unbridged structure $(CO)_6VV(CO)_6$ (Figure 1) lying above **12S-1** by 8.3 kcal/mol (BP86). Structure **12S-3** has two small-magnitude imaginary harmonic vibrational frequencies at 32i and 20i cm^{-1} . Following the normal modes corresponding to these imaginary vibrational frequencies leads to **12S-1**. The V–V distance in **12S-3** is 3.625 Å, which is even longer than that of **12S-1** by ~0.3 Å, again suggesting a weak interaction between the two $V(CO)_6$ halves. For the eight inward CO groups, the V–C distances are 1.992 Å, the V–V–C angles are 81.1°, and the V–C–O angles are 173.1°. For the four outward CO groups, the V–C distances are 1.929 Å and the corresponding C–O distances are 1.174 Å.

The structure of $V_2(CO)_{12}$ that is next higher in energy is **12S-4**, which is a D_{2h} dibridged structure $(CO)_5V(\mu-CO)_2V(CO)_5$ (Figure 1) lying 17.4 kcal/mol (BP86) above **12S-1**. However, **12S-4** is a transition state with a significant imaginary vibrational frequency at 138i cm^{-1} . By following the appropriate normal mode, this D_{2h} structure eventually collapses to the global minimum **12S-1**. The V–V distance in **12S-4** is 3.193 Å, shorter than that of **12S-1** by ~0.2 Å but still very long for even a single bond. The V–C distances are 2.224 Å for the two bridging CO groups. The V–C distances for the eight equatorial groups are 1.986 Å. The corresponding V–V–C angles are 98.6°. The V–C distances are 1.965 Å for the two axial CO groups.

Table 2 lists the IR-active $\nu(CO)$ frequencies for the four isomers of $V_2(CO)_{12}$ discussed above and depicted in Figure 1. Isomers **12S-1**, **12S-2**, and **12S-3** exhibit only terminal $\nu(CO)$ frequencies in the range of 1947–2011 cm^{-1} (BP86) in accordance with the presence of only terminal CO groups. However, the IR spectrum of **12S-4** exhibits not only similar terminal $\nu(CO)$ frequencies but also a single bridging $\nu(CO)$ frequency at 1807 cm^{-1} in accordance with the single symmetrical bridging CO group in its structure.

The stable homoleptic vanadium carbonyl under normal conditions is the 17-electron monomer $V(CO)_6$ rather than the dimer $V_2(CO)_{12}$. In this connection, the dissociation of the lowest-energy isomer of $V_2(CO)_{12}$ (**12S-1**) into $2V(CO)_6$ is calculated to be exothermic by 12.4 kcal/mol using the B3LYP functional but endothermic by 5.7 kcal/mol using the BP86 functional. Thus, the two functionals do not agree on the energetics of this reaction although the energy difference between $V_2(CO)_{12}$ and $2V(CO)_6$ is obviously rather small. In previous work from our laboratory on binuclear cobalt carbonyls,²⁴ similar disagreement between calculations using the B3LYP and BP86 functionals was found for the relative energies of the lowest-energy singlet isomer of $Co_2(CO)_8$ with only terminal CO groups and the singlet $Co_2(CO)_6(\mu-CO)_2$ isomer with two bridging CO groups. From a variety of earlier comparisons, we favor the BP86 energy predictions.²⁵

3.2. $V_2(CO)_{11}$. A total of 10 structures were found for $V_2(CO)_{11}$. Eight of these structures (Figures 2–4) were within 30 kcal/mol of the global minimum **11S-1** and are discussed in detail in this paper.

The two lowest-lying structures for $V_2(CO)_{11}$ (**11S-1** and **11S-2**; Figure 2 and Table 3) are characterized by a single four-electron donor bridging CO group. The global minimum **11S-1** is a singly bridged structure $(CO)_5V(\mu-CO)V(CO)_5$ with C_1 symmetry (Figure 2), and all real harmonic vibrational frequencies are predicted by both the B3LYP and BP86 methods. The V–V distance is quite long, 3.376 Å (BP86), even for a single bond. The bridging CO group acts as π donor to the left-hand V atom through the C=O bond, thereby becoming a four-electron donor to the pair of V atoms. Thus, a V–V single bond is required for each V atom to satisfy the favored 18-electron configuration. For the bridging carbonyl, the shorter V–C distance is 1.906 Å, while the longer V–C distance is 2.248 Å. For the 10 terminal carbonyls, the V–C distances are in the range of 1.933–2.019 Å. The four-electron donor bridging CO group in **11S-1** is indicated by a very low $\nu(CO)$ frequency (Table 4) at 1728 cm^{-1} .

Structure **11S-2** for $V_2(CO)_{11}$ is also a singly bridged structure but with C_s symmetry (Figure 2). This structure lies energetically above **11S-1** by 8.8 kcal/mol (BP86), and it has three small imaginary vibrational frequencies (<100i cm^{-1}). Following the normal modes of these imaginary vibrational frequencies carries structure **11S-2** to **11S-1**. The V–V distance in **11S-2** is 3.558 Å, which is slightly longer

(24) Kenny, J.; King, R. B.; Schaefer, H. F. *Inorg. Chem.* **2001**, *40*, 900.
 (25) Furche, F.; Perdew, J. P. *J. Chem. Phys.* **2006**, *124*, 044103.

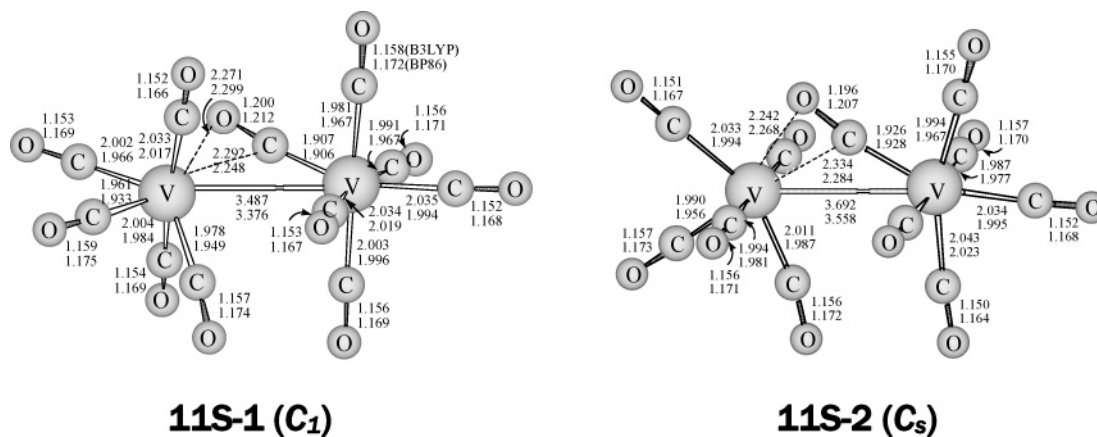


Figure 2. Two lowest-energy isomers of $V_2(CO)_{11}$.

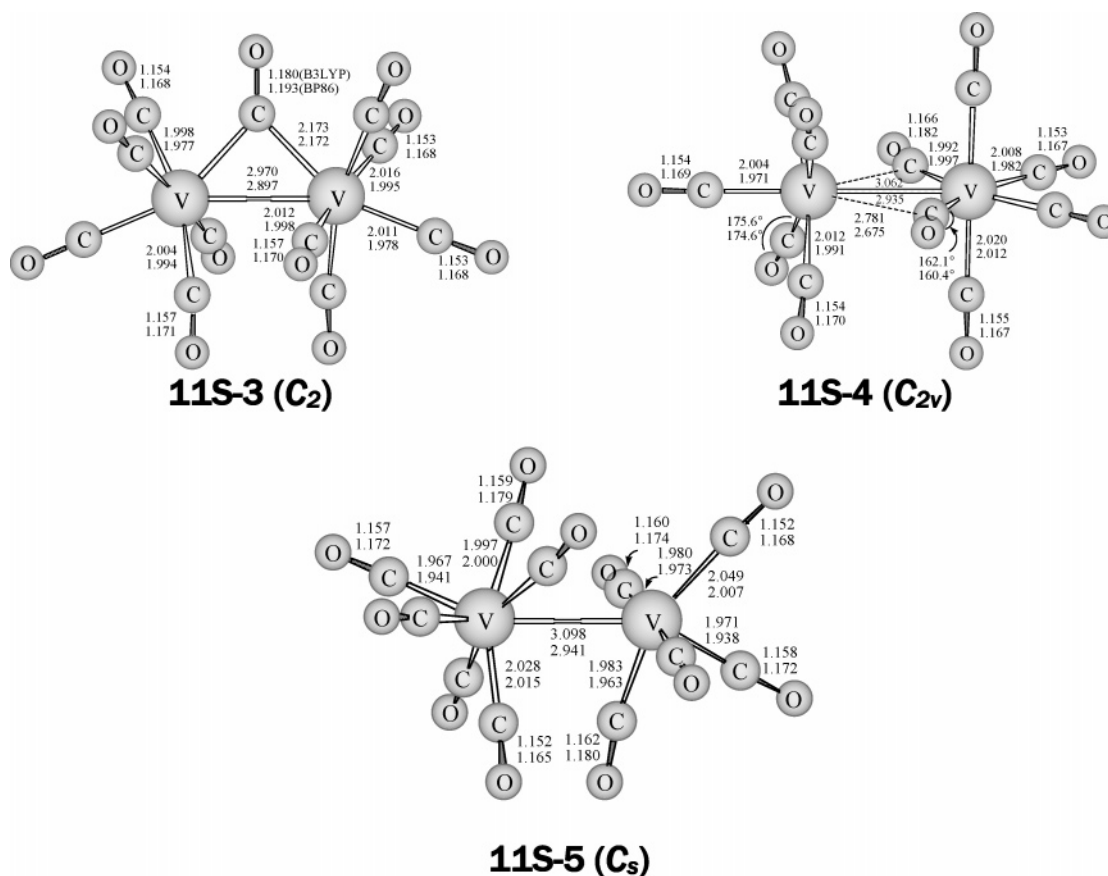


Figure 3. Three additional singlet isomers of $V_2(CO)_{11}$.

than that in **11S-1**, suggesting a very weak V–V single bond. In the single bridging CO group in **11S-2**, the shorter V–C distance is 1.928 Å, while the longer V–C distance is 2.284 Å. For the 10 terminal CO groups, the V–C distances are in the range of 1.956–1.995 Å. The four-electron donor bridging CO group in **11S-2** is indicated by a very low $\nu(CO)$ frequency (Table 4) at 1742 cm^{-1} .

The next higher energy singlet structure for $V_2(CO)_{11}$ (**11S-3** in Table 5) is a singly bridged C_2 structure (Figure 3) lying higher in energy above the global minimum **11S-1** by 12.3 kcal/mol (BP86). Structure **11S-3** has a small imaginary vibrational frequency at 18i cm^{-1} . Following the normal mode of this imaginary frequency leads to structure **11S-1**. The V–V bond distance in **11S-3** is 2.897 Å, which

is ~ 0.5 Å shorter than that of **11S-1**. This illustrates the fact that shorter metal–metal bond distances are not always indicative of greater stability. The V–C distances to the bridging CO group in **11S-3** are 2.172 Å, while those to the 10 terminal CO groups are 1.977–1.998 Å. The V–C–O angles for the bridging CO group in **11S-3** are $\sim 138^\circ$. The bridging CO group in **11S-3** is predicted to exhibit a $\nu(CO)$ frequency (Table 4) of 1809 cm^{-1} .

The next $V_2(CO)_{11}$ singlet structure in terms of energy, namely, **11S-4**, is a structure with C_{2v} symmetry and two highly unsymmetrical bridging CO groups (Figure 3). This structure lies higher in energy than **11S-1** by 13.9 kcal/mol (BP86). Structure **11S-4** has two small imaginary vibrational frequencies at 47i and 17i cm^{-1} . Following the modes of

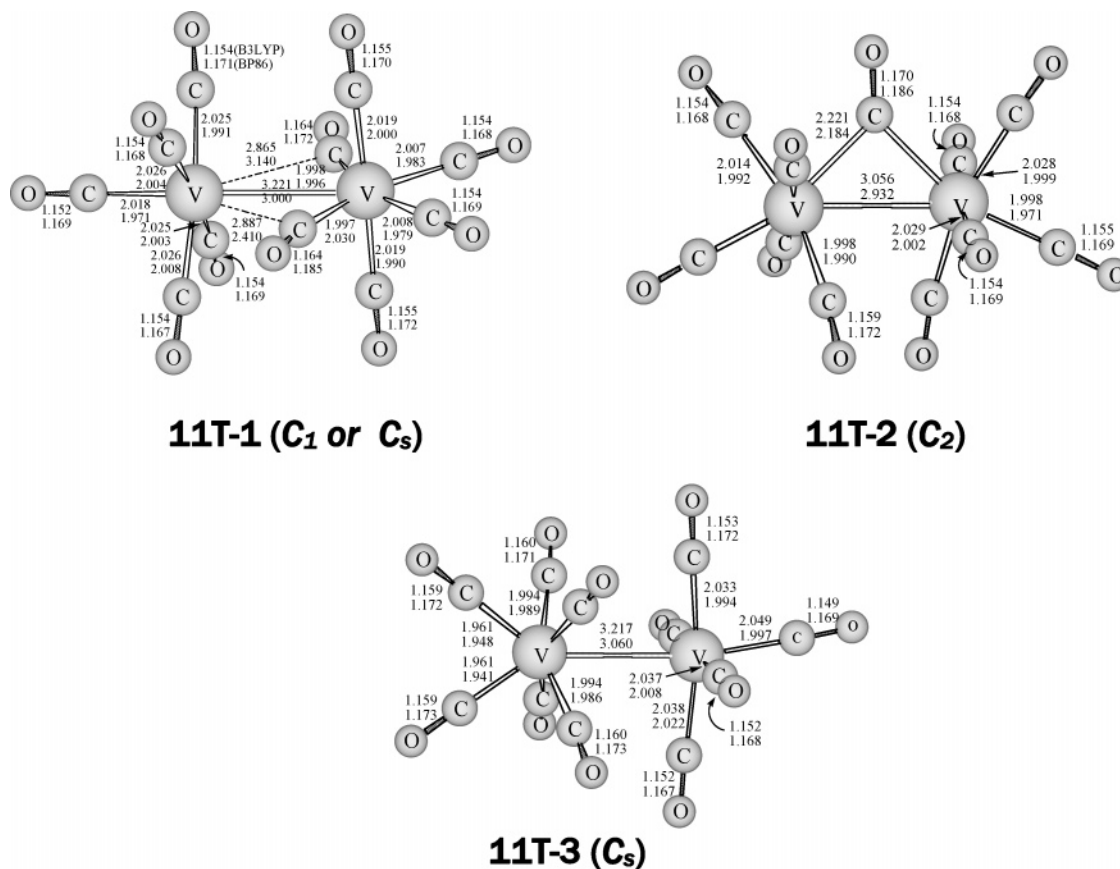


Figure 4. Three lowest-lying triplet isomers of $V_2(CO)_{11}$.

Table 4. IR-Active $\nu(CO)$ Vibrational Frequencies (cm^{-1}) Predicted for the Eight Lowest-Energy Isomers of $V_2(CO)_{11}$ (IR Intensities in Parentheses Are in km/mol ; Bridging CO Frequencies Are in Boldface Font)

	B3LYP	BP86
11S-1 (C_1)	2149 (29), 2096 (2750), 2080 (134), 2071 (1000), 2068 (1850), 2059 (1220), 2053 (930), 2034 (560), 2031 (750), 2021 (135), 1773 (444)	2060 (44), 2016 (1680), 1990 (630), 1983 (1660), 1978 (605), 1974 (1140), 1971 (870), 1953 (367), 1949 (535), 1974 (86), 1728 (390)
11S-2 (C_s)	2151 (26), 2100 (2765), 2090 (890), 2076 (301), 2070 (1250), 2054 (370), 2053 (3230), 2043 (352), 2037 (900), 1783 (340)	2061 (49), 2017 (1880), 2003 (706), 1986 (290), 1984 (950), 1972 (411), 1972 (2650), 1955 (550), 1974 (470), 1742 (322)
11S-3 (C_2)	2079 (4700), 2072 (480), 2069 (278), 2063 (760), 2056 (2790), 2056 (1660), 2052 (133), 2025 (28), 2017 (3), 1868 (339)	2004 (3150), 1981 (420), 1979 (300), 1977 (1100), 1974 (2410), 1972 (900), 1967 (106), 1946 (36), 1938 (41), 1809 (238)
11S-4 (C_{2v})	2152 (3), 2080 (3420), 2070 (1180), 2064 (2900), 2063 (7), 2062 (1650), 2053 (1630), 2038 (17), 1962 (450)	2064 (23), 2005 (2850), 1991 (8), 1986 (2030), 1984 (1070), 1974 (620), 1963 (1300), 1954 (415), 1882 (293)
11S-5 (C_s)	2144 (25), 2084 (2760), 2078 (710), 2064 (1440), 2059 (1090), 2043 (670), 2033 (1790), 2032 (620), 2024 (406), 2001 (483), 1996 (115)	2055 (72), 2002 (2300), 1999 (550), 1981 (1460), 1972 (480), 1961 (880), 1950 (443), 1943 (1260), 1930 (504), 1912 (19), 1906 (197)
11T-1 (C_s or C_1)	2073 (202), 2068 (2560), 2063 (3170), 2061 (2020), 2056 (589), 2045 (2), 2033 (5), 2030 (4810), 1980 (1360), 1973 (617)	1996 (3520), 1980 (488), 1979 (515), 1976 (2403), 1972 (138), 1966 (1458), 1965 (491), 1943 (53), 1936 (11), 1848 (295)
11T-2 (C_2)	2070 (3550), 2063 (4350), 2062 (610), 2055 (1890), 2054 (271), 2047 (13), 2045 (250), 2025 (363), 1988 (63), 1920 (278)	1992 (3810), 1979 (840), 1977 (2400), 1972 (313), 1972 (237), 1970 (194), 1967 (1090), 1943 (61), 1934 (9), 1833 (231)
11T-3 (C_s)	2151 (170), 2088 (1290), 2075 (2360), 2074 (905), 2069 (1530), 2060 (1420), 2031 (265), 2024 (321), 2022 (3), 2016 (390), 2008 (660)	2056 (24), 1989 (2400), 1982 (2270), 1978 (855), 1970 (1130), 1964 (780), 1958 (2), 1957 (545), 1948 (400), 1939 (68), 1933 (29)

these imaginary vibrational frequencies again leads to **11S-1**. The V–V bond distance is quite long, namely, 2.935 Å. The bridging CO groups are highly unsymmetrical with shorter V–C distances of 1.997 Å and longer V–C distances of 2.675 Å. The V–C–O angles for the bridging CO groups in **11S-4** deviate significantly from linearity (160.4°). The $\nu(CO)$ frequency predicted for the bridging CO groups in

11S-4 is 1882 cm^{-1} . The highly unsymmetrical bridging CO groups in **11S-4** exhibit $\nu(CO)$ frequencies 73–74 cm^{-1} higher than the symmetrical bridging CO groups in **11S-3**. This indicates that the order of the CO multiple bond in the unsymmetrical bridging CO groups in **11S-4** is closer to that for terminal CO groups than to that for the symmetrical bridging CO groups in **11S-3**.

Table 5. Total Energies (E in hartrees), Energies Relative to **11S-1** (ΔE in kcal/mol), and V–V Distances (in Å) for the Other Three Singlet Isomers of $V_2(CO)_{11}$ at Accessible Energies (Figure 3)

		11S-3 (C_2)	11S-4 (C_{2v})	11S-5 (C_s)
B3LYP	E	-3135.00688	-3135.00588	-3135.00044
	ΔE	15.7	16.3	19.8
	Nimg	1 (31 <i>i</i>)	2 (37 <i>i</i> , 16 <i>i</i>)	2 (49 <i>i</i> , 38 <i>i</i>)
	V–V	2.970	3.062	3.098
BP86	E	-3135.38706	-3135.38433	-3135.37997
	ΔE	12.3	13.9	16.7
	Nimg	1 (18 <i>i</i>)	2 (47 <i>i</i> , 17 <i>i</i>)	2 (48 <i>i</i> , 39 <i>i</i>)
	V–V	2.897	2.935	2.941

Table 6. Total Energies (E in hartrees), Energies Relative to **11S-1** (ΔE in kcal/mol), and V–V Distances (in Å) for the Three Triplet Isomers of $V_2(CO)_{11}$ within 30 kcal/mol of the Global Minimum **11S-1**

		11T-1 (C_1 or C_s)	11T-2 (C_2)	11T-3 (C_s)
B3LYP	E	-3135.02178	-3135.01467	-3135.01186
	ΔE	6.4	10.8	12.6
	Nimg	0	1 (339 <i>i</i>)	1 (64 <i>i</i>)
	V–V	3.221	3.056	3.217
BP86	E	-3135.38970	-3135.38839	-3135.37811
	ΔE	10.6	11.4	17.9
	Nimg	0	1 (189 <i>i</i>)	1 (64 <i>i</i>)
	V–V	3.000	2.932	3.060

The remaining singlet structure for $V_2(CO)_{11}$ within 20 kcal/mol of the global minimum **11S-1** is an unbridged C_s structure $(CO)_6VV(CO)_5$ (**11S-5** in Figure 3), lying higher in energy than **11S-1** by 16.7 kcal/mol (BP86). Structure **11S-5** has two small imaginary vibrational frequencies at 48*i* and 39*i* cm^{-1} . Following the modes of the imaginary vibrational frequencies leads from **11S-5** to **11S-1**. The V–V bond distance in **11S-5** is 2.941 Å. The V–C distances to all 11 of the CO groups in **11S-5** are in the range of 1.938–2.015 Å. The V–C–O angles for the central CO groups deviate somewhat from linearity (167–171°).

Five energetically low-lying triplet structures for $V_2(CO)_{11}$ have been found. Three of these structures lie within 30 kcal/mol of the $V_2(CO)_{11}$ global minimum **11S-1** and are discussed in this paper (Table 6 and Figure 4).

The triplet structure of lowest energy is **11T-1** with C_s or C_1 symmetry (Figure 4). This structure lies 10.6 kcal/mol (BP86) above the global minimum **11S-1** for $V_2(CO)_{11}$. With the B3LYP method, structure **11T-1** is a doubly bridged structure $(OC)_5V(\mu-CO)_2V(CO)_4$ with C_s symmetry (Figure 4). However, with the BP86 method, the corresponding structure is singly bridged with C_1 symmetry. The V–V distance is 3.000 Å, and the shorter V–C distance to the bridging CO group is 2.030 Å, while the longer one is 2.410 Å. The V(left)–V(right)–C angle to the bridging CO group is 53.2°. The V–C–O angle of this bridging CO group deviates significantly from linearity (152.9°). The V–C distances for the terminal carbonyls in **11T-1** fall in the range of 1.971–2.008 Å.

The $V_2(CO)_{11}$ triplet structure of next higher energy is the C_2 symmetrically singly bridged structure **11T-2** (Figure 4), which is geometrically similar to the singlet structure **11S-3**. The energy of structure **11T-2** is higher than that of the lowest-lying $V_2(CO)_{11}$ triplet **11T-1** by 0.8 kcal/mol (BP86). However, structure **11T-2** is a transition state with a significant imaginary vibrational frequency at 189*i* cm^{-1} . Following this vibrational mode leads to **11T-1**. The V–V

distance in **11T-2** is 2.932 Å, which is slightly shorter than that of **11T-1**. The V–C distances to the bridging CO group in **11T-2** are 2.184 Å, whereas the V–C distances to the 10 terminal CO groups fall in the range of 1.971–2.002 Å. The V–C–O angles for the bridging CO group are $\sim 138^\circ$.

The other energetically accessible triplet structure for $V_2(CO)_{11}$ is the unbridged C_s structure **11T-3** (Figure 4), lying energetically above **11T-1** by 7.3 kcal/mol (BP86). Structure **11T-3** has one small imaginary vibrational frequency ($\sim 60i$ cm^{-1}). Following the corresponding vibrational mode leads to **11T-1**. The V–V bond distance in **11T-3** is 3.060 Å, which is longer than that in **11T-2** by ~ 0.15 Å and close to that of **11T-1**. The V–C distances to the five terminal carbonyls attached to the “right” V atom (Figure 4) fall in the range of 1.994–2.022 Å. However, the V–C distances to the six terminal carbonyls attached to the “left” V atom are shorter, namely, 1.941–1.989 Å.

3.3. $V_2(CO)_{10}$. A total of 17 stationary points were found for $V_2(CO)_{10}$, namely, nine singlet structures and eight triplet structures. Among these structures, seven of the singlet structures and six of the triplet structures were within 30 kcal/mol of the global minimum; only those 13 structures will be considered in this paper. These 13 structures can be classified into the following three general types: (a) structures with a V–V distance of around 2.5 Å, suggesting a $V\equiv V$ triple bond (these include only five singlet structures within reasonable energies relative to the global minimum **10S-1**, which is a structure of this type); (b) three in which a $V(CO)_6$ unit appears to function as a bidentate ligand toward a $V(CO)_4$ unit through two of its CO groups acting as four-electron π donors (these include both singlet and triplet structures); (c) five other types of triplet $V_2(CO)_{10}$ structures within 25 kcal/mol of the global minimum.

3.3.1. Structures with a V–V Distance Suggesting a $V\equiv V$ Triple Bond. Five singlet structures of this type were found (Tables 7 and 8 and Figure 5) including the global minimum **10S-1**. The predicted V–V distances of around 2.5 Å for these $V_2(CO)_{10}$ structures are inferred to imply $V\equiv V$ triple bonds consistent with the $V\equiv V$ distance of 2.462 Å determined by X-ray crystallography²⁶ in $(\eta^5-C_5H_5)_2V_2(CO)_5$, required for both V atoms to have the favored 18-electron rare gas configuration. A $V\equiv V$ triple bond in these $V_2(CO)_{10}$ structures also gives both V atoms the favored 18-electron rare gas configuration.

The C_s structure **10S-1** with six CO groups bonded to the “left” V atom and four CO groups bonded to the “right” V atom (Figure 5) is the global minimum for $V_2(CO)_{10}$. However, three of the six CO groups bonded to the “left” V atom are close enough to the right V atom to be considered as semibridging CO groups. The V–V distance is 2.510 Å, suggesting a $V\equiv V$ triple bond as noted above. In the three semibridging carbonyls, the shorter V–C distances are 1.994 and 1.997 Å while the longer V–C distances are 2.474 and 2.486 Å. The bridging C–O distances are 1.179 Å. For the “left” terminal carbonyls, the V–C distances are 1.986 and

(26) Cotton, F. A.; Kruczynski, L.; Frenz, B. A. *J. Organomet. Chem.* **1978**, *160*, 93.

Table 7. Total Energies (E in hartrees), Relative Energies (ΔE in kcal/mol), and V–V Distances (in Å) for the Five Isomers of $V_2(CO)_{10}$ with V–V Distances Suggestive of $V\equiv V$ Triple Bonds

		10S-1 (C_s)	10S-2 (C_2)	10S-3 (C_{2h})	10S-4 (C_{2v})	10S-5 (D_{2h})
B3LYP	E	–3021.68589	–3021.67484	–3021.67365	–3021.67018	–3021.66858
	ΔE	0.0	6.9	7.7	10.9	10.9
	Nimg	0	1 (18 <i>i</i>)	1 (17 <i>i</i>)	2 (63 <i>i</i> , 3 <i>i</i>)	3 (315 <i>i</i> , 53 <i>i</i> , 47 <i>i</i>)
	V–V	2.539	2.493	2.522	2.586	2.476
BP86	E	–3022.05992	–3022.04738	–3022.04510	–3022.04399	–3022.04014
	ΔE	0.0	7.9	9.3	10.0	12.4
	Nimg	0	1 (41 <i>i</i>)	1 (24 <i>i</i>)	2 (70 <i>i</i> , 16 <i>i</i>)	3 (337 <i>i</i> , 62 <i>i</i> , 48 <i>i</i>)
	V–V	2.510	2.479	2.518	2.588	2.470

Table 8. IR-Active $\nu(CO)$ Vibrational Frequencies (cm^{-1}) Predicted for the Five Isomers of $V_2(CO)_{10}$ with V–V Distances Suggesting $V\equiv V$ Triple Bonds (IR Intensities in Parentheses Are in km/mol ; Bridging CO Frequencies Are Listed in Boldface Font)

		B3LYP	BP86
10S-1 (C_s)		2141 (140), 2088 (2430), 2078 (751), 2077 (730), 2041 (1745), 2040 (1770), 1999 (241), 1976 (680), 1975 (623)	2052 (202), 2006 (2010), 1993 (650), 1992 (630), 1954 (1520), 1954 (1540), 1922 (159), 1906 (374), 1906 (410)
10S-2 (C_2)		2089 (2910), 2077 (473), 2073 (77), 2068 (2410), 2050 (2520), 2049 (18), 2038 (222), 1968 (1030), 1952 (100)	2006 (2450), 1984 (218), 1983 (2165), 1982 (95), 1967 (2044), 1964 (4), 1959 (41), 1893 (716), 1880 (92)
10S-3 (C_{2h})		2091 (2770), 2073 (3010), 2065 (476), 2045 (2450), 1969 (1090)	2007 (2470), 1988 (2510), 1983 (199), 1962 (1850), 1891 (798)
10S-4 (C_{2v})		2142 (76), 2083 (2740), 2072 (715), 2066 (206), 2061 (3020), 2050 (44), 2037 (4), 2027 (1730), 1984 (162), 1970 (820)	2052 (174), 2003 (2110), 1988 (628), 1987 (2), 1978 (2127), 1956 (13), 1948 (378), 1944 (1370), 1899 (187), 1889 (589)
10S-5 (D_{2h})		2076 (3320), 2071 (3020), 2061 (91), 2046 (2280), 1982 (1090)	2001 (2410), 1986 (2514), 1977 (254), 1961 (1916), 1896 (750)

1.988 Å and the C–O distances are 1.167 Å. For the “right” terminal CO groups, the V–C distances are 1.936 and 1.937 Å and the C–O distances are 1.173 Å. The V–C–O angles for the three semibridging CO groups deviate significantly from linearity (163.3° and 163.5°). The V–V–C angles of the three semibridging CO groups are 65.5° and 65.8°. The other V–V–C angles are 118.0°, 122.2°, 126.0°, and 127.8°.

The next two structures for $V_2(CO)_{10}$ in terms of energy, namely, **10S-2** (C_2) and **10S-3** (C_{2h}), are both doubly bridged $(CO)_4V(\mu-CO)_2V(CO)_4$ structures (Figure 5), which are geometrically proximate to each other with similar energies. Structure **10S-2** lies higher in energy than structure **10S-1** by 7.9 kcal/mol (BP86), whereas structure **10S-3** lies above **10S-1** by 9.3 kcal/mol (Table 7). However, each of them has a small-magnitude imaginary vibrational frequency (Table 7). Following the normal modes of the imaginary vibrational frequencies for either **10S-2** or **10S-3** leads to **10S-1**. The V–V distance for structure **10S-2** is 2.479 Å, and that of structure **10S-3** is 2.518 Å in accordance with $V\equiv V$ triple bonds. Compared with structure **10S-1**, the $V\equiv V$ distances in structures **10S-2** and **10S-3** are slightly shorter.

For the bridging CO groups in structure **10S-2**, the shorter V–C distances are 2.013 Å whereas the longer V–C distances are 2.333 Å. The bridging C–O distances in **10S-2** are 1.182 Å. For the bridging CO groups in structure **10S-3**, the shorter V–C distances are 1.987 Å whereas the longer V–C distances are 2.350 Å. The bridging C–O distances are 1.183 Å.

For the terminal CO groups in structure **10S-2**, the V–C distances of the eight terminal carbonyls are 1.953, 1.985, 1.990, and 1.993 Å. The C–O distances of the eight terminal carbonyls in **10S-2** fall in the range of 1.167–1.170 Å. For the terminal CO groups in structure **10S-3**, the V–C

distances are 1.951, 1.997, and 2.001 Å. The C–O distances of the eight terminal carbonyls in **10S-3** are in the range of 1.167–1.172 Å. The bridging V–C–O angles for both structures **10S-2** and **10S-3** deviate significantly from linearity ($\sim 160^\circ$).

The C_{2v} structure **10S-4** is also a doubly bridged structure (Figure 5), but the same V atom has the short V–C distances to the two unsymmetrical bridging CO groups. The relative energy of **10S-4** is higher than that of structure **10S-1** by 10.0 kcal/mol, which is also higher than those of structures **10S-2** and **10S-3** (Table 7). Structure **10S-4** has two small insignificant imaginary vibrational frequencies ($< 100i\text{ cm}^{-1}$). Structure **10S-4** collapses to structure **10S-1** by following the normal modes corresponding to the larger imaginary vibrational frequency.

The V–V distance in structure **10S-4** is 2.588 Å, which is longer than that in structures **10S-1**, **10S-2**, and **10S-3** but still suggestive of the $V\equiv V$ triple bond required to give both V atoms the favored 18-electron configuration. The shorter V–C distances to the unsymmetrical bridging CO groups are 1.995 Å, whereas the longer V–C distances are 2.371 Å. The corresponding C–O distances are 1.181 Å. The V–C distances to the terminal carbonyls fall in the range of 1.935–1.993 Å. The bridging V–C–O angles show significant deviation from linearity at 160.7°.

The D_{2h} structure **10S-5** is a symmetrically doubly bridged structure (Figure 5), which lies in energy above structure **10S-1** by 12.4 kcal/mol (BP86). It has a large b_2 imaginary vibrational frequency at 337*i* cm^{-1} and two small imaginary vibrational frequencies at $< 100i\text{ cm}^{-1}$. By following the normal mode related to the largest imaginary vibrational frequency, the D_{2h} structure **10S-5** collapses to the C_s structure **10S-1**. The V–V distance in structure **10S-5** is predicted to be 2.470 Å, which is close to that of structure

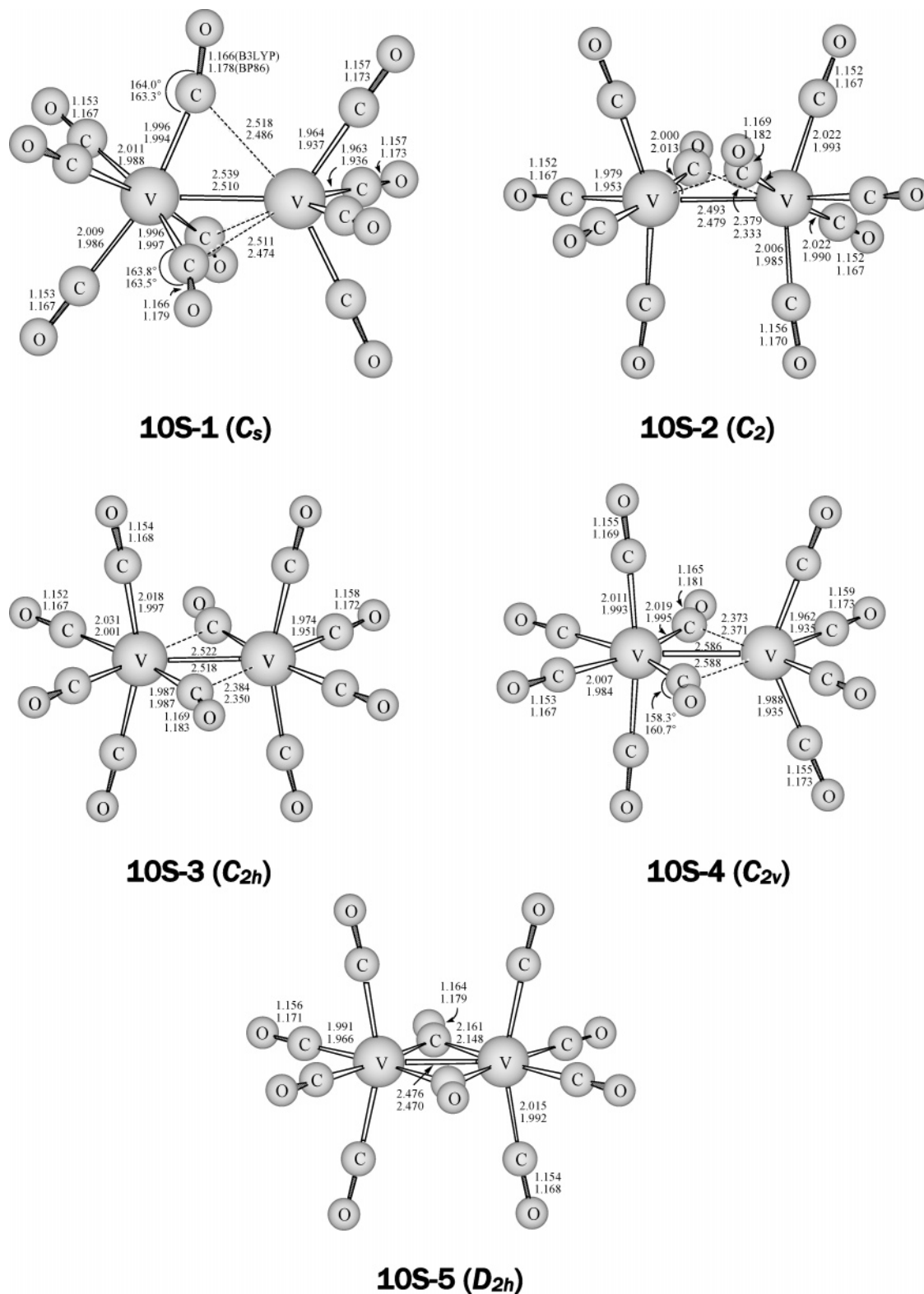


Figure 5. Five isomers of $V_2(CO)_{10}$ with $V\equiv V$ distances suggesting $V-V$ triple bonds.

10S-2 and again suggestive of a $V\equiv V$ triple bond. The $V-C$ distances to the bridging CO groups are quite long, namely, 2.148 Å. The corresponding $C-O$ distances are 1.179 Å. The eight terminal $V-C$ bond distances are 1.966 and 1.992 Å. The corresponding $C-O$ distances are 1.168 and 1.171 Å. The $V-C-V$ angles for the bridging CO groups are $\sim 70^\circ$.

3.3.2. Structures with a $V(CO)_6$ Unit “Chelated” to a $V(CO)_4$ Unit. Such structures include the singlet structures **10S-6** and **10S-7** and the triplet structure **10T-1** (Table 9 and Figure 6). The $V(CO)_6$ ligand chelates to the $V(CO)_4$ unit through two four-electron π -donor bridging CO groups, which are characterized by very low $\nu(CO)$ frequencies (Table 10) in the range of 1674–1800 cm^{-1} . The $V-V$

Table 9. Total Energies (E in hartrees), Relative Energies (ΔE in kcal/mol), and V–V Distances (in Å) for the Three Isomers of $V_2(CO)_{10}$ with a $V(CO)_6$ Unit Chelated to a $V(CO)_4$ Unit

		10S-6 (C_2)	10S-7 (C_{2v})	10T-1 (C_{2v})
B3LYP	E	-3021.66230	-3021.66010	-3021.67344
	ΔE	14.8	16.2	7.8
	Nimg	0	1	0
	V–V	3.391	3.389	4.297
BP86	E	-3022.02463	-3022.01960	-3022.02184
	ΔE	22.0	25.3	23.9
	Nimg	0	2	0
	V–V	3.296	3.341	4.338

distances in the singlet structures **10S-6** and **10S-7** are ~ 3.3 Å, suggestive of the V–V single bond needed to give the V atoms the favored 18-electron configuration. However, in the corresponding triplet **10T-1**, the V–V distance is a nonbonding distance of ~ 4.3 Å corresponding to a 17-electron configuration for each V atom consistent with two unpaired electrons.

The C_2 $(CO)_4VV(CO)_6$ structure **10S-6** (Figure 6) has all real vibrational frequencies and thus is a genuine minimum. Structure **10S-7** has two a_2 ($113i$ and $17i$ cm^{-1}) imaginary vibrational frequencies (Table 9). By following the normal modes related to these imaginary vibrational frequencies, the C_{2v} structure **10S-7** collapses to the C_2 structure **10S-6** by twisting a small angle around the V–V axis. Structure **10S-6** lies energetically above structure **10S-1** by 22.0 kcal/mol, while structure **10S-7** lies higher than structure **10S-6** by 3.3 kcal/mol (Table 1).

The V–V distances in structures **10S-6** and **10S-7** are quite long (~ 3.3 Å) so that these two structures can be regarded as loose complexes of $V(CO)_4$ and $V(CO)_6$, with the $V\cdots V$ interaction occurring primarily through the middle two π -donating CO groups rather than through multiple bonding between the two V atoms. Thus, the $V(CO)_6$ unit can be regarded as a bidentate chelating ligand toward the $V(CO)_4$ unit using two four-electron π -donor CO groups. For the lower energy of the two structures, namely, **10S-6**, the shorter bridging V–C distances are 1.94 Å and the longer bridging $V\cdots C$ distances are 2.41 Å, implying that the two fragments have a weak connection. The V–C distances for the terminal CO groups are in the range of 1.94–2.02 Å. The V–C–O angles for the bridging CO groups are about 169° . The geometrical parameters for structure **10S-7** are very close to those for structure **10S-6**.

The related C_{2v} triplet structure **10T-1** for $V_2(CO)_{10}$ is a genuine minimum with an energy higher than that of the singlet global minimum (structure **10S-1**) by 23.9 kcal/mol. The V–V distance is very long (4.338 Å). There are two π -donor CO groups connecting the two V atoms. The shorter V–C distances are 1.896 Å, while the longer $V\cdots C$ distances are 2.992 Å. The corresponding C–O distances are 1.213 Å, and the V–C–O angles are bent by $\sim 163^\circ$ toward the center. The terminal V–C distances fall in the range of 1.97–2.02 Å.

3.3.3. Five Remaining $V_2(CO)_{10}$ Structures within 25 kcal/mol of the Global Minimum. Five triplet structures for $V_2(CO)_{10}$ (Table 11 and Figure 7) were found within 25 kcal/mol of the global minimum **10S-1** in addition to **10T-1**

discussed above. Structure **10T-2**, with V–V distances of 3.025 Å (BP86), is best formulated with a V–V single bond and one four-electron π -donor bridging CO group, thereby giving each V atom the 17-electron configuration required for a triplet structure. Using this model, the “left” V atom bonded to five CO groups (including the bridging CO group) has a formal negative charge whereas the “right” V atom bonded to six CO groups has a formal positive charge. The other triplet structures **10T-3**, **10T-4**, **10T-5**, and **10T-6** have V–V distances suggesting V=V double bonds, which lead again to 17-electron configurations for both V atoms assuming that all of the CO groups are the normal two-electron donors.

The V atoms in the C_s structure **10T-2** (Figure 7) are singly bridged by a four-electron π -donor CO group, which exhibits an IR $\nu(CO)$ frequency at 1756 cm^{-1} (Table 12). Structure **10T-2** is nearly degenerate with structure **10T-1**, being lower by only 4.6 kcal/mol (Table 11). The V–V distance of **10T-2** (3.025 Å) is much shorter than that of **10T-1**, indicative of a weak V–V single bond. For the bridging CO group, the shorter V–C distance is 1.923 Å, while the longer $V\cdots C$ distance is 2.174 Å. The B3LYP method predicts **10T-2** to be a genuine minimum, whereas the BP86 method gives a negligible imaginary vibrational frequency ($6i$ cm^{-1}), which can be regarded as a numerical noise.

The C_{2v} structure **10T-3** (Figure 7) is a doubly bridged structure with an energy close to that of structure **10T-1**, lower by only 3.0 kcal/mol. The B3LYP method predicts all real harmonic vibrational frequencies, but the BP86 method predicts two very small imaginary vibrational frequencies ($34i$ and $1i$ cm^{-1}), which can be considered to be insignificant. Structure **10T-3** is geometrically similar to structure **10T-1**, but **10T-3** has a much shorter V–V distance, namely, 2.903 Å. For the bridging CO groups, the shorter V–C distances are 1.973 Å, while the longer V–C distances are 2.472 Å. The corresponding C–O distances are 1.181 Å, and the V–C–O angles show significant deviation from linearity at 169.6° . For the terminal carbonyls, the V–C distances are in the range of 1.97–1.99 Å.

The C_{2h} structure **10T-4** is also a doubly bridged structure (Figure 7), but the two bridging CO groups come from different V atoms. The energy of **10T-4** is also close to that of structures **10T-1**, **10T-2**, and **10T-3** and lower than that of structure **10T-1** by 1.9 kcal/mol. Structure **10T-4** has one ($117i$ cm^{-1}) imaginary vibrational frequency (Table 11). Following the corresponding normal mode leads from **10T-4** to **10T-2**. The V–V distance of **10T-4** is even shorter, namely, 2.686 Å. For the bridging CO groups, the shorter V–C distances are 1.997 Å, while the longer V–C distances are 2.396 Å; the corresponding C–O distances are 1.184 Å. The V–C–O angles show significant deviation from linearity at 162° . The V–C distances for the terminal carbonyls are in the range of 1.95–2.02 Å, and the terminal C–O distances are about ~ 1.17 Å.

The C_s structure **10T-5** is a singly bridged structure (Figure 7). The shorter V–C distance is 1.967 Å, while the longer V–C distance is 2.443 Å. However, two other CO groups may also have weaker interactions with the opposite V atom,

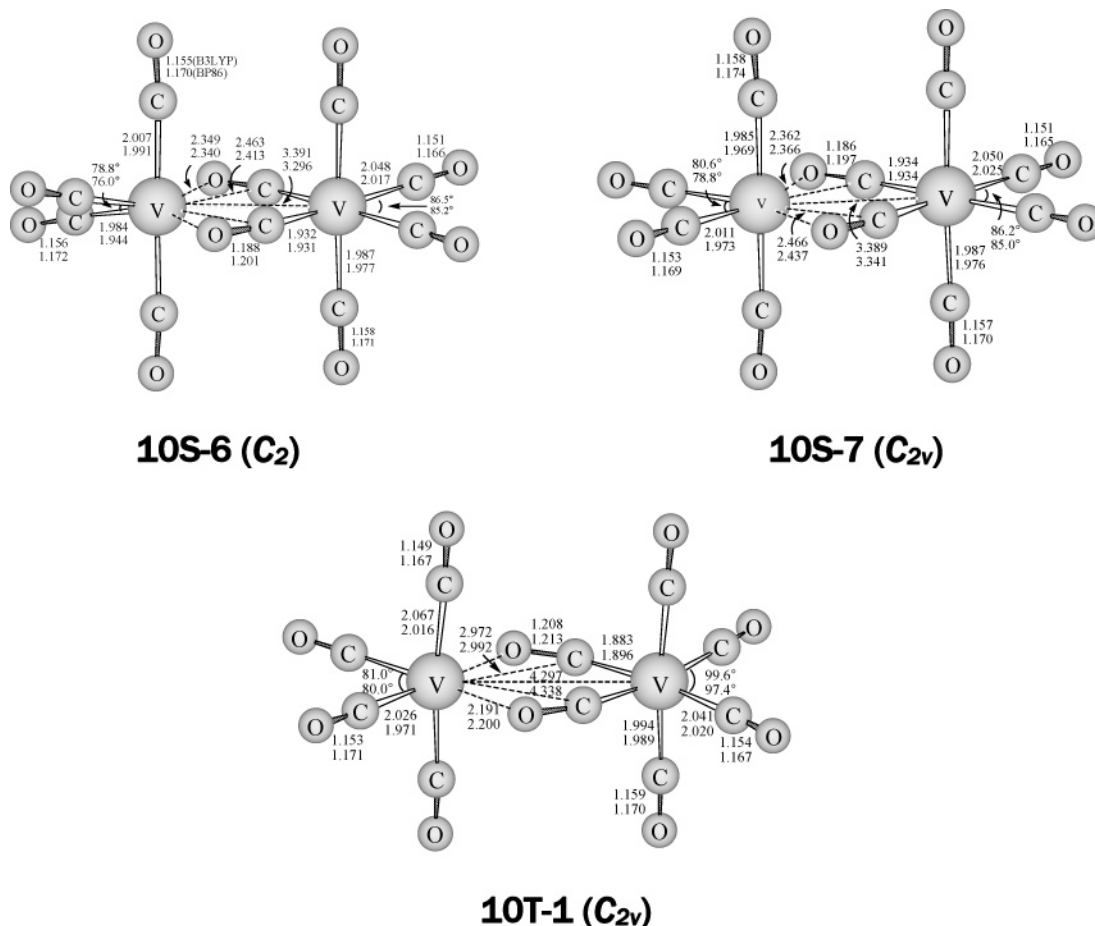


Figure 6. $V_2(CO)_{10}$ structures with a $V(CO)_6$ unit “chelated” to a $V(CO)_4$ unit.

Table 10. IR-Active $\nu(CO)$ Vibrational Frequencies (cm^{-1}) Computed for the Three Isomers of $V_2(CO)_{10}$ with a $V(CO)_6$ Unit Chelated to a $V(CO)_4$ Unit (IR Intensities in Parentheses Are in km/mol ; Bridging CO Frequencies Are Listed in Boldface Font)

	B3LYP	BP86
10S-6 (C_2)	2143 (76), 2098 (2760), 2093 (710), 2064 (8), 2057 (2400), 2049 (1480), 2042 (594), 2019 (51), 1845 (423) , 1817 (800)	2051 (152), 2012 (1860), 1999 (640), 1981 (135), 1970 (2600), 1950 (551), 1946 (526), 1937 (138), 1781 (378) , 1759 (579)
10S-7 (C_{2v})	2144 (56), 2100 (3080), 2097 (708), 2075 (600), 2067 (5), 2048 (3240), 2046 (500), 2010 (101), 1857 (310) , 1833 (815)	2055 (162), 2014 (2180), 2010 (580), 1985 (105), 1986 (2390), 1982 (477), 1951 (476), 1923 (449), 1800 (299) , 1783 (640)
10T-1 (C_{2v})	2151 (112), 2102 (2170), 2091 (1990), 2077 (973), 2072 (1010), 2050 (7), 2027 (1110), 2024 (1290), 1758 (1730) , 1670 (780)	2050 (38), 1996 (3620), 1990 (805), 1974 (2770), 1973 (1250), 1963 (441), 1955 (107), 1936 (830), 1699 (20) , 1674 (508)

Table 11. Total Energies (E in hartrees), Relative Energies (ΔE in kcal/mol), and V–V Distances (in Å) for the Five Remaining Triplet Isomers of $V_2(CO)_{10}$ within 25 kcal/mol of the Global Minimum (Figure 7)

		10T-2 (C_s)	10T-3 (C_{2v})	10T-4 (C_{2h})	10T-5 (C_s)	10T-6 (C_{2h})
B3LYP	E	−3021.67246	−3021.66875	−3021.66072	−3021.65692	−3021.65457
	ΔE	8.4	10.8	15.8	18.2	19.7
	Nimg	0	0	2 (61i, 2i)	1 (33i)	2 (87i, 75i)
	V–V	3.321	2.979	2.771	2.785	2.781
BP86	E	−3022.02914	−3022.02667	−3022.02488	−3022.02193	−3022.02126
	ΔE	19.3	20.9	22.0	23.8	24.3
	Nimg	1 (6i)	2 (34i, 1i)	1 (117i)	1 (30i)	1 (76i)
	V–V	3.025	2.903	2.686	2.705	2.784

with the longer $V\cdots C$ distances 2.703 Å (Figure 7). Structure **10T-5** lies below structure **10T-1** by 0.1 kcal/mol. Structure **10T-5** has a small imaginary vibrational frequency at 30i cm^{-1} . The V–V distance is short, namely, 2.705 Å, and close to that of the structure **10T-4**. The V–C–O angles to the bridging CO groups show significant deviation from linearity ($<170.3^\circ$).

The C_{2h} structure **10T-6** is essentially a nonbridging structure $(CO)_5VV(CO)_5$ (Figure 7). However, two CO groups from each V atom interact weakly with the other V atom, displaying four highly unsymmetrical semibridging CO groups. The four shorter V–C distances to these CO groups are 1.981 Å, whereas the four longer $V\cdots C$ distances are 2.784 Å. The V–V distance is 2.784 Å, which is very close

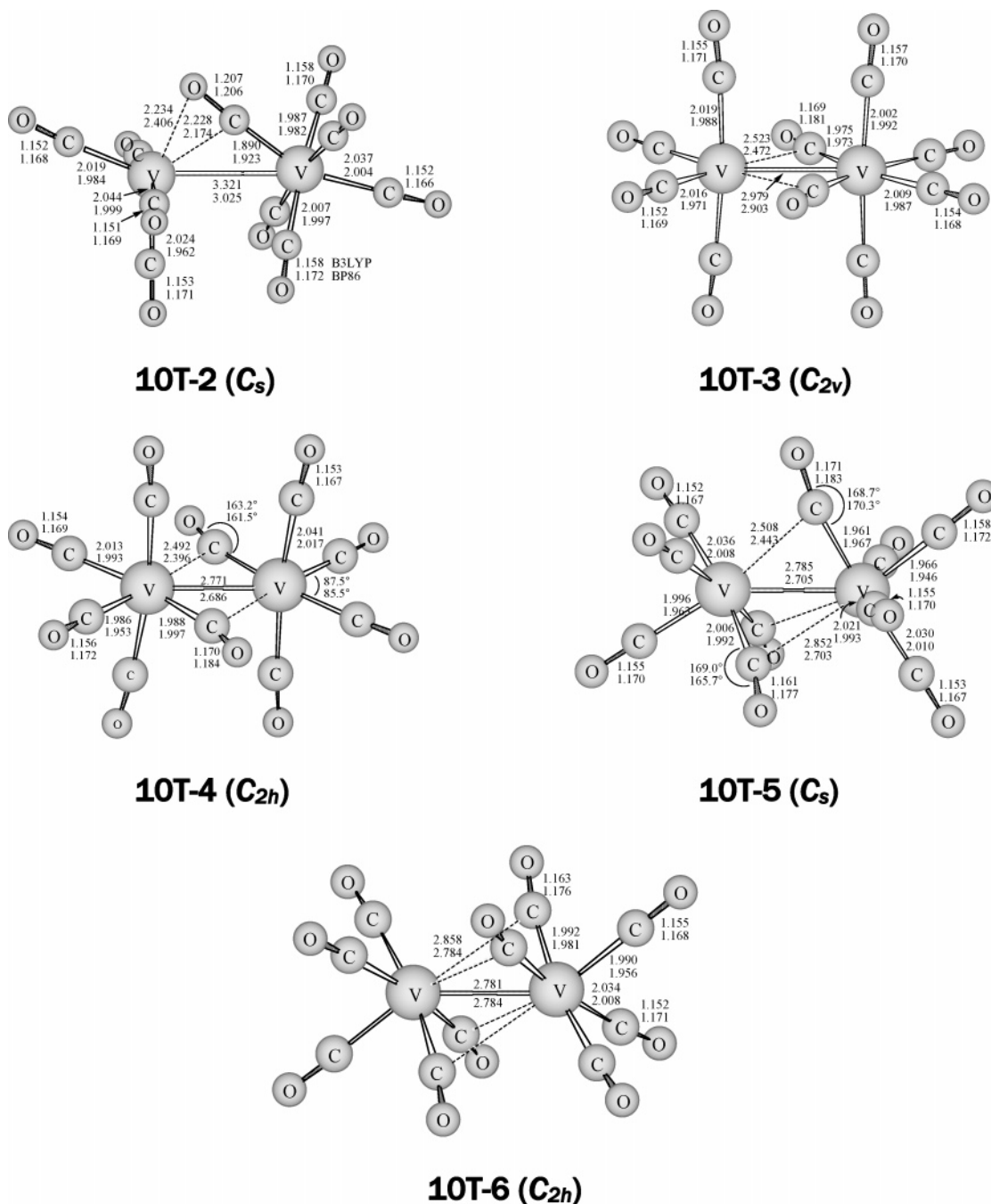


Figure 7. Other triplet structures of $V_2(CO)_{10}$.

to the V–V distances in structures **10T-4** and **10T-5**. Compared with **10T-1**, the relative energy of structure **10T-6** is 0.4 kcal/mol. Structure **10T-6** is a stationary point having a small imaginary vibrational frequency with BP86 ($76i\text{ cm}^{-1}$).

4. Discussion

4.1. $V_2(CO)_{12}$. Our calculations suggest that the only viable structure for $V_2(CO)_{12}$ is the unbridged structure **12S-1** (Figure 1) consisting of two $V(CO)_6$ units linked by a long V–V single bond. All of the other energetically accessible structures found for $V_2(CO)_{12}$, namely, **12S-2**, **12S-3**, and **12S-4**, collapse to **12S-1** when the normal modes corresponding to

their imaginary vibrational frequencies are followed. The relatively long V–V bond linking the two $V(CO)_6$ units in **12S-1** as well as the small energy difference (5.7 kcal/mol endothermic predicted by BP86) suggests easy dissociation into two 17-electron mononuclear $V(CO)_6$ fragments.³ However, the 17-electron $V(CO)_6$, although an isolable compound, is much more reactive than the essentially isostructural 18-electron $Cr(CO)_6$. Because none of the energetically accessible $V_2(CO)_{12}$ isomers have bridging CO groups, the IR bridging $\nu(CO)$ frequencies observed by Ozin et al.⁶ at 10–35 K in inert matrices and assigned by them to $V_2(CO)_{12}$ must arise from some other dinuclear or polynuclear vanadium carbonyl species. Structure **12S-1** is predicted to

Table 12. IR-Active $\nu(\text{CO})$ Vibrational Frequencies (cm^{-1}) Predicted for the Five Remaining Triplet Isomers of $\text{V}_2(\text{CO})_{10}$ within 25 kcal/mol of the Global Minimum (IR Intensities in Parentheses Are in km/mol ; Bridging CO Groups Are Listed in Boldface Font)

	B3LYP	BP86
10T-2 (C_s)	2149 (36), 2100 (2250), 2073 (471), 2072 (2320), 2071 (48), 2049 (2070), 2042 (225), 2021 (700), 2021 (398), 1741 (770)	2054 (70), 1999 (2910), 1984 (600), 1974 (810), 1967 (1877), 1966 (510), 1960 (1200), 1938 (37), 1937 (4), 1756 (381)
10T-3 (C_{2v})	2144 (1), 2076 (3872), 2067 (540), 2065 (135), 2057 (3130), 2054 (1510), 2033 (870), 2019 (44), 1957 (18), 1939 (1060)	2053 (68), 1995 (3050), 1985 (570), 1978 (144), 1972 (2470), 1956 (8), 1954 (1110), 1936 (176), 1891 (117), 1874 (725)
10T-4 (C_{2h})	2076 (2870), 2069 (3300), 2054 (1010), 2046 (2630), 1949 (1180)	1987 (3210), 1984 (2430), 1967 (620), 1962 (1570), 1881 (834)
10T-5 (C_s)	2064 (2160), 2050 (4), 2043 (800), 1993 (2990), 1983 (236), 1972 (238), 1965 (1300), 1957 (735), 1919 (457), 1872 (447)	2143 (8), 2079 (3210), 2058 (46), 2048 (1320), 2035 (1800), 2011 (540), 1975 (1305), 1953 (1130), 1943 (522), 1907 (176)
10T-6 (C_{2h})	2077 (3080), 2074 (1810), 2046 (3680), 2012 (1332), 1978 (3070)	1990 (3210), 1982 (1520), 1962 (2200), 1938 (1050), 1928 (1010)

lie below the dissociation limit $\text{V}_2(\text{CO})_{11} + \text{CO}$ by 10.9 kcal/mol (BP86).

4.2. $\text{V}_2(\text{CO})_{11}$. The global minimum for $\text{V}_2(\text{CO})_{11}$ was found to be a $\text{V}_2(\text{CO})_{10}(\eta^2\text{-}\mu\text{-CO})$ structure **11S-1** (Figure 2) with a single four-electron donor bridging CO group and a V–V distance suggesting a long single bond. Both metal atoms thus have the favored 18-electron configuration. An analogous $\text{Mn}_2(\text{CO})_8(\eta^2\text{-}\mu\text{-CO})$ structure⁹ was found to be the global minimum for $\text{Mn}_2(\text{CO})_9$, which would be expected to be related to $\text{V}_2(\text{CO})_{11}$ but with one less CO group on each metal atom. All of the other energetically accessible singlet structures for $\text{V}_2(\text{CO})_{11}$, namely, **11S-2**, **11S-3**, **11S-4**, and **11S-5** (Figures 2 and 3), have small imaginary vibrational frequencies corresponding to normal modes leading to **11S-1**, suggesting that **11S-1** is the only viable singlet structure for $\text{V}_2(\text{CO})_{11}$.

Some triplet structures for $\text{V}_2(\text{CO})_{11}$ have energies within 11 kcal/mol of the singlet $\text{V}_2(\text{CO})_{11}$ global minimum **11S-1**. The lowest-lying triplet $\text{V}_2(\text{CO})_{11}$ structure **11T-1** can be formulated as a 17-electron $\text{V}(\text{CO})_6$ unit forming a V–V dative bond to a $\text{V}(\text{CO})_5$ unit so that the latter also has a V atom with a 17-electron configuration. The other energetically accessible triplet $\text{V}_2(\text{CO})_{11}$ structures **11T-2** and **11T-3** collapse to **11T-1** along the normal modes corresponding to their imaginary vibrational frequencies. Thus, structure **11T-1** appears to be the only viable triplet structure for $\text{V}_2(\text{CO})_{11}$. The relatively long V–V bond (≥ 3.0 Å) in **11T-1** suggests facile dissociation into mononuclear fragments, presumably $\text{V}(\text{CO})_6 + \text{V}(\text{CO})_5$, so that this isomer of $\text{V}_2(\text{CO})_{11}$ is not a promising synthetic objective. Structure **11S-1** lies below $\text{V}_2(\text{CO})_{10} + \text{CO}$ by 12.2 kcal/mol (BP86).

4.3. $\text{V}_2(\text{CO})_{10}$. The collection of energetically accessible structures for $\text{V}_2(\text{CO})_{10}$ is more complicated than those for the carbonyl-rich species $\text{V}_2(\text{CO})_{11}$ and $\text{V}_2(\text{CO})_{12}$. The most favorable structures for singlet $\text{V}_2(\text{CO})_{10}$ appear to have an unsymmetrical distribution of CO groups that can be considered as a $\text{V}(\text{CO})_6$ unit linked to a $\text{V}(\text{CO})_4$ unit. This can occur either with a $\text{V}\equiv\text{V}$ triple bond and all CO groups as two-electron donors (**10S-1** in Figure 5) or with a V–V single bond and two of the CO groups as four-electron π -donor bridging CO groups (**10S-6** in Figure 6). In either case, both V atoms have the favored 18-electron configurations. In the latter case, the $\text{V}(\text{CO})_6$ fragment can be considered as a bidentate ligand by using two of its six CO

groups as π -donor ligands to “chelate” to the $\text{V}(\text{CO})_4$ fragment to give the V atom in the latter fragment the same 18-electron configuration. Neither **10S-1** nor **10S-6** has any imaginary vibrational frequencies, and thus they are true minima for $\text{V}_2(\text{CO})_{10}$. The other energetically accessible singlet isomers for $\text{V}_2(\text{CO})_{10}$, namely, **10S-2**, **10S-3**, **10S-4**, **10S-5**, and **10S-7**, collapse to either **10S-1** or **10S-6** when following the normal modes corresponding to their imaginary vibrational frequencies; thus, **10S-1** and **10S-6** can be considered the only viable structures for singlet $\text{V}_2(\text{CO})_{10}$.

A number of energetically accessible triplet structures are also found for $\text{V}_2(\text{CO})_{10}$. Because such triplet structures are necessarily composed of linked 17-electron mononuclear vanadium carbonyl units, their V–V bond orders are 1 less than those in the corresponding singlet $\text{V}_2(\text{CO})_{10}$ structures composed of linked 18-electron mononuclear vanadium carbonyl units. This difference leads to longer V–V distances for the triplet structures compared with related singlet structures.

The lowest-lying triplet $\text{V}_2(\text{CO})_{10}$ structure **10T-1** (Figure 6) is a true minimum closely related to the singlet structure **10S-6** with a bidentate “chelating” $\text{V}(\text{CO})_6$ ligand coordinated to a $\text{V}(\text{CO})_4$ unit through two four-electron π -donor CO groups. However, because a V–V bond is not needed to give the metal atoms a 17-electron configuration, the $\text{V}\cdots\text{V}$ distance in **10T-1** is a clearly nonbonding separation of ~ 4.3 Å.

4.4. Comparison of Binuclear Vanadium Carbonyls and Binuclear Cyclopentadienylchromium Carbonyls. None of the binuclear vanadium carbonyls discussed in this paper has been isolated, although some evidence for their existence is found in the IR $\nu(\text{CO})$ spectra of vanadium carbonyl systems in low-temperature matrices.^{6,7} However, the cyclopentadienylchromium unit, $\eta^5\text{-CpCr}$, is isolobal and isoelectronic with a $\text{V}(\text{CO})_3$ unit, which can be considered to be a building block for the binuclear vanadium carbonyls discussed in this paper. In this connection, the known $\eta^5\text{-Cp}_2\text{Cr}_2(\text{CO})_6$ can be considered to be an analogue of $\text{V}_2(\text{CO})_{12}$ and the known $\eta^5\text{-Cp}_2\text{Cr}_2(\text{CO})_4$ as an analogue of $\text{V}_2(\text{CO})_{10}$. However, the Cr–Cr distances in binuclear cyclopentadienylchromium carbonyls are expected to be somewhat shorter than the V–V distances in the analogous binuclear vanadium carbonyls because the three CO ligands in a $\text{V}(\text{CO})_3$ unit are stronger electron π acceptors than the

single cyclopentadienyl ligand in a η^5 -CpCr unit. Nevertheless, it is instructive to compare our computed structures for binuclear vanadium carbonyls with the computed structures for the corresponding binuclear cyclopentadienylchromium carbonyls.

The structure of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_6$ is found by X-ray crystallography²⁷ to have exclusively terminal CO groups with a relatively long Cr–Cr single bond distance of 3.281 Å as compared with the V–V single bond distance of 3.334 Å (BP86) predicted for the lowest-energy isomer of $\text{V}_2(\text{CO})_{12}$, namely, **12S-1**. Similarly, the structure of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_4$ is found by X-ray crystallography²⁸ to have a Cr≡Cr distance of 2.21 ± 0.02 Å, which is even shorter than the ~ 2.5 Å V–V distance found here for the isomers of $\text{V}_2(\text{CO})_{10}$, e.g., **10S-1** and **10S-2**, postulated to have a V≡V triple bond. This difference may be a consequence of the stronger back-bonding and greater steric demands of three CO ligands relative to one η^5 -Cp ligand.

4.5. Comparison with Experimental Data. It is instructive to compare our calculated $\nu(\text{CO})$ frequencies for various binuclear vanadium carbonyls with those found experimentally for vanadium carbonyl systems at low temperatures in inert matrices. In this connection, we and others^{29–31} have observed that for first-row transition metals the $\nu(\text{CO})$ frequencies predicted using the BP86 functional are likely to be closer to the experimental values than the $\nu(\text{CO})$ frequencies calculated using the B3LYP functional. Of course, this close agreement between BP86 and experiment is somewhat fortuitous because the theoretical frequencies are harmonic while the experimental results are fundamentals.

Ishikawa et al.⁷ have studied the photolysis of gas-phase $\text{V}(\text{CO})_6$ at excimer laser wavelengths using time-resolved IR kinetic absorption spectroscopy. At long reaction times, they find a set of IR $\nu(\text{CO})$ frequencies at 1890, 1965, and 2025 cm^{-1} , which they assign to $\text{V}_2(\text{CO})_{10}$, formed by a combination of a $\text{V}(\text{CO})_4$ fragment and $\text{V}(\text{CO})_6$. Keeping in mind the limited resolution of their experiments, these three bands could correspond to the most intense $\nu(\text{CO})$ vibrations in the most stable isomer computed for $\text{V}_2(\text{CO})_{10}$, namely, **10S-1** (Table 8). In particular, their observed bridging $\nu(\text{CO})$ frequency of 1890 cm^{-1} is close to our computed bridging $\nu(\text{CO})$ frequency of 1906 cm^{-1} (BP86) for **10S-1**. Their two observed terminal CO frequencies of 2025 and

1965 cm^{-1} are close to the most intense terminal vibrations of 2006 and 1954 cm^{-1} calculated for **10S-1** using the BP86 functional. We therefore suspect that these workers generated the isomer **10S-1** of $\text{V}_2(\text{CO})_{10}$ in their photolysis experiments. Significant progress has occurred in matrix isolation spectroscopy since 1987, and we encourage new experiments on the vanadium carbonyl systems.

The other spectroscopic evidence for binuclear vanadium carbonyls in low-temperature matrixes was obtained by Ozin and co-workers,⁶ who claimed to have observed possible $\nu(\text{CO})$ frequencies for $\text{V}_2(\text{CO})_{12}$ from reactions of V atoms with CO at 10–35 K in low-temperature inert matrixes. However, our results suggest that these bands cannot be from a $\text{V}_2(\text{CO})_{12}$ isomer (as discussed above) because none of the stable $\text{V}_2(\text{CO})_{12}$ isomers have bridging CO groups. Nevertheless, the question remains as to which vanadium carbonyl derivative these workers really observed in their experiments. Comparison of the bridging $\nu(\text{CO})$ frequency of 1852 cm^{-1} found by Ozin and co-workers⁶ with our calculated bridging $\nu(\text{CO})$ frequencies for various binuclear vanadium carbonyls hints that the vanadium carbonyl that they observed might be the lowest-lying triplet isomer of $\text{V}_2(\text{CO})_{11}$, namely, **11T-1** (Figure 4), for which we compute a bridging $\nu(\text{CO})$ frequency of 1848 cm^{-1} (BP86 in Table 4). However, we observe that **11T-1** is predicted to lie 10.6 kcal/mol (Table 6) above the lowest singlet state of $\text{V}_2(\text{CO})_{11}$. Therefore, the energy difference ΔE between $\text{V}_2(\text{CO})_{12}$ (**12S-1**) and $\text{V}_2(\text{CO})_{11}$ (**11T-1**) + CO would be $10.6 + 10.9 = 21.5$ kcal/mol. At the low temperatures (10–35 K in Ozin's experiment), the free energy differences should be close to ΔE . Actually, when the theoretical entropies are considered, our theoretical free energy difference for this dissociation is reduced to 21.2 kcal/mol (10 K) or 19.9 kcal/mol (35 K). Note that Ozin and co-workers⁶ have no experimental evidence for the number of CO groups in the binuclear vanadium carbonyl derivative that they observed. Thus, their binuclear vanadium carbonyl could be $\text{V}_2(\text{CO})_{11}$ rather than $\text{V}_2(\text{CO})_{12}$.

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Supporting Information Available: Harmonic vibrational frequencies and IR intensities for 10 isomers of $\text{V}_2(\text{CO})_{12}$, 10 isomers of $\text{V}_2(\text{CO})_{11}$, and 17 isomers of $\text{V}_2(\text{CO})_{10}$, structures of the isomers, and the complete Gaussian reference (ref 21). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(27) Adams, R. D.; Collins, D. E.; Cotton, F. A. *J. Am. Chem. Soc.* **1974**, *96*, 749.

(28) Curtis, M. D.; Butler, W. M. *J. Organomet. Chem.* **1978**, *155*, 131.

(29) Xie, Y.; King, R. B.; Schaefer, H. F. *Spectrochim. Acta A* **2005**, *A61*, 1693.

(30) Barckholtz, T. A.; Bursten, B. E. *J. Am. Chem. Soc.* **1998**, *120*, 1926.

(31) Rosa, A.; Ricciarde, G.; Baerends, E. J.; Stufkens, D. J. *Inorg. Chem.* **1996**, *35*, 2886.