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Nonacarbonyldivanadium: Alternatives to Metal−Metal Quadruple Bonding

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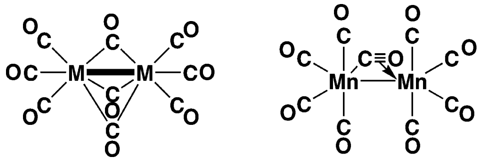
The first structural characterization of the highly unsaturated nonacarbonyldivanadium $V_2(CO)_9$ is reported using density functional theory (DFT) with the B3LYP and BP86 functionals. A complicated collection of minima with rather closely spaced energies was found. However, none of these many $V_2(CO)_9$ isomers was found to have a sufficiently short vanadium−vanadium distance for the $V\overset{4}{-}V$ quadruple bond required to give both metal atoms the favored 18-electron configuration. Triplet structures for $V_2(CO)_9$ were found to be competitive in energy with related singlet structures. Thus, the two lowest-energy isomers of $V_2(CO)_9$ are triplets. The four lowest-energy isomers of $V_2(CO)_9$ all have three very unsymmetrical bridging CO groups (typically "short" and "long" M−CO distances differing by 0.4−0.5 Å) rather than the symmetrical bridging CO groups found experimentally in $Fe_2(CO)_9$ and predicted for $M_2(CO)_9$ (M = Cr and Mn) from earlier studies. The $V{\equiv}V$ distances in each of these four isomers suggest a metal−metal triple bond. Next higher in energy for $V_2(CO)_9$ are three structures with single four-electron donor bridging CO groups identified by their computed ν(CO) frequencies and V−O distances. The V−V distances in these three isomers suggest metal−metal single bonds. This study of $V_2(CO)_9$ supports the following general points: (1) Metal−metal bonds of an order higher than three are not favorable in metal carbonyl chemistry. (2) The 18-electron rule for metal carbonyls begins to break down when the metal atom, i.e., vanadium in this case, has only five valence electrons.

1. Introduction

Homoleptic metal carbonyls with $M_2(CO)_9$ stoichiometry are of interest. Thus, $Fe_2(CO)_9$ has been known for approximately 100 years;[1] it is established by X-ray diffraction to have structure **I** (Figure 1a, M = Fe) with three symmetrical bridging CO groups.[2] The 18-electron rule predicts an iron−iron single bond in $Fe_2(CO)_9$, but the exact nature of this bond is not clear from electron density studies.[3,4]

The corresponding $M_2(CO)_9$ derivatives of manganese and chromium are required to have metal−metal double and triple bonds, respectively, for both transition metals to have the 18-electron noble gas electronic configuration. Neither $Mn_2(CO)_9$ nor $Cr_2(CO)_9$ has been isolated as stable molecules, but $Mn_2(CO)_9$ has been detected spectroscopically in low-temperature matrices.[5−7] However, the spectroscopic data for $Mn_2(CO)_9$ isolated in this matter do not correspond to a tribridged isomer **I** (Figure 1a, M = Mn) with an Mn═Mn double bond but instead to an alternative isomer **II** (Figure 1b) with a unique four-electron donor bridging CO group and an Mn−Mn single bond similar to that found in stable chelating bidentate small bite biphosphine derivatives $[R_2PCH_2PR_2]_2Mn_2(CO)_4(\eta^2\text{-}\mu\text{-}CO)$.[8,9] This $Mn_2(CO)_9$ isomer **II** is also found in density functional theory (DFT) studies[10] to be the lowest-energy isomer. However, a triplet $Mn_2(CO)_9$ isomer **I** (Figure 1, M = Mn) with three bridging CO groups similar to the known structure of $Fe_2(CO)_9$ is found by DFT[10] to be a stable structure (no imaginary vibrational frequencies) 16.0 kcal/mol (B3LYP) or 12.2 kcal/mol (BP86) above the global minimum **II** (M = Mn). The metal−metal distance in this isomer of $Mn_2(CO)_9$ is found to be suitably short, namely, 2.43 Å (B3LYP) or 2.41 Å (BP86), to correspond to the Mn═Mn double bond required for an 18-electron configuration for both manganese atoms. The Mn═Mn double bond in this isomer of $Mn_2(CO)_9$ is analogous to the O═O double bond in triplet dioxygen. For $Cr_2(CO)_9$, the lowest-energy isomer is predicted by DFT to have structure **I** (Figure 1a, M = Cr) with a metal−metal distance (2.31 Å by B3LYP or 2.28 Å by BP86) indicative of the Cr≡Cr triple bond required for an 18-electron configuration for both metal atoms.[11]



$M_2(CO)_6(\mu\text{-}CO)_3$ (I) $Mn_2(CO)_8(\eta^2\text{-}\mu\text{-}CO)$ (II)

Figure 1. Alternative structures for $M_2(CO)_9$ derivatives. (a) Structure of $M_2(CO)_6(\mu\text{-}CO)_3$ with six terminal CO groups and three bridging CO groups with a thick line to indicate metal−metal bonds with orders ranging from one to four. (b) Structure of $Mn_2(CO)_8(\eta^2\text{-}\mu\text{-}CO)$ with eight terminal CO groups and one four-electron donor bridging CO group.

Moving from chromium one atom to the left of the periodic table leads to vanadium. The corresponding $M_2(CO)_9$ derivative (M = V) requires a metal−metal quadruple bond in structure **I** (Figure 1a) for each metal to have the favored 18-electron rare gas electronic configuration. Metal−metal quadruple bonding

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is unknown experimentally in homoleptic metal carbonyl chemistry, although metal−metal quadruple bonding is well-known to occur in carbon-free binuclear derivatives of d^4 transition metals such as Re(III) in $Re_2Cl_8^{2-}$ and Cr(II) in $Cr_2(OCOCH_3)_4{\cdot}2H_2O$.[12] Furthermore, there are insufficient metal orbitals for a $V_2(CO)_9$ structure **I** with three bridging CO groups [i.e., $V_2(CO)_6(\mu\text{-}CO)_3$] and a vanadium−vanadium quadruple bond. Thus, in structure **I**, six metal orbitals are required for bonds to six CO groups (three terminal and three bridging), leaving only three orbitals from the nine-orbital sp^3d^5 manifold for metal−metal bonding. This implies that the metal−metal bond order in a $V_2(CO)_6(\mu\text{-}CO)_3$ structure (**I**) can be no higher than three. This paper describes alternative $V_2(CO)_9$ structures that we have found by density functional theory (DFT) methods.

2. Theoretical Methods

DFT methods, including to some degree electron correlation effects, are acknowledged to be practical and effective for organometallic compounds.[13] Two density functional methods are used in this paper. The first one is the hybrid Hartree−Fock (HF)/DFT method known as B3LYP, which is often thought to be a reliable approximation. It is the combination of Becke's three-parameter functional[14] with the Lee−Yang−Parr correlation functional.[15] Another DFT method is the BP86 method, which combines Becke's 1988 exchange functional[16] with Perdew's 1986 correlation functional.[17,18] These methods have been proven to be effective,[19] especially for molecules containing transition metals. In our case, the B3LYP and BP86 methods agree with each other fairly well for predicting the structural characteristics of $V_2(CO)_9$.

The DZP basis sets for C and O are constructed by augmenting the Huzinaga−Dunning's standard double-ς set[20,21] with 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 set[22] augmented by two sets of p functions and a set of d functions, contracted following Hood, Pitzer, and Schaefer's Scheme[23] and designated (14s11p6d/10s8p3d). For $V_2(CO)_9$, there are 368 contracted Gaussian functions with these DZP basis sets.

The geometries of all $V_2(CO)_9$ structures were fully optimized using the DZP B3LYP and DZP BP86 methods. The vibrational frequencies were computed by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. The corresponding infrared intensities are evaluated analytically as well. All of the computations were carried out with the Gaussian 03 program[24] in Beijing, exercising the default grid (75 radial shells, 302 angular points) option for evaluating integrals numerically. The tight (10^{-8} hartree) designation is the default for the self-consistent field (SCF) convergence.

Both singlet and triplet structures for $V_2(CO)_9$ were investigated. A total of 11 singlet and 14 triplet structures were found. Only the 12 structures within 25 kcal/mol of the global minimum structure are discussed in this paper (Figures 2−4 and Tables 1, 3, and 5). These 12 structures can be divided into the following three categories: (1) the four lowest-energy structures, all with three semibridging CO groups but with different distributions of the terminal CO groups; (2) the next three structures in terms of energy, all of which have one four-electron donor CO group; and (3) the remaining five structures within 25 kcal/mol of the global minimum. The structures discussed in this paper are numbered in order of increasing energy with the singlet and triplet structures being designated as S and T, respectively. Thus, the global minimum structure, which is a triplet, is designated as **1T**.

3. Results

3.1. Four Lowest-Energy Isomers of $V_2(CO)_9$ (1T, 2T, 3S, and 4S; Figure 2 and Tables 1 and 2). The two lowest-energy isomers for $V_2(CO)_9$ are both triplets. The C_s global minimum structure **1T** has all real harmonic vibrational frequencies using both the B3LYP and BP86 methods. This structure has six CO groups connected to one vanadium atom and three CO groups to the other (Figure 2). However, three of the six CO groups bonded to the left vanadium atom are close enough to the right vanadium atom to be considered as semibridging CO groups. In these three semibridging carbonyls, the shorter V−C distances are 1.996 Å (B3LYP) or 2.002 Å (BP86), while the longer V−C distances are 2.460 Å (B3LYP) or 2.407 Å (BP86). The V−C distances for the "left" terminal carbonyls are 2.007 Å (B3LYP) or 1.987 Å (BP86), while those for the "right" terminal carbonyls are similar, e.g., 2.003 Å (B3LYP) or 1.966 Å (BP86). The vanadium−vanadium distance is 2.538 Å (B3LYP) or 2.482 Å (BP86), close to the vanadium−vanadium distance of 2.462 Å found by X-ray crystallography[25] for $(\eta^5\text{-}C_5H_5)_2V_2(CO)_5$, where a V≡V triple bond is required to give each vanadium atom the 18-electron configuration. All terminal C−O distances are in the range of 1.154−1.155 Å (B3LYP) or 1.168−1.172 Å (BP86), while the C−O distances for the semibridging carbonyls are slightly longer, i.e., 1.166 Å (B3LYP) or 1.179 Å (BP86). The V−C−O angles for the three semibridging CO groups show significant deviation from linearity, and they are 166.5° (B3LYP) or 165.0° (BP86); the V−C−O angles of all the terminal carbonyls are nearly linear (>178.5°). For the three semibridging carbonyls, the V−V−C angles are 64.5° (B3LYP) or 63.9° (BP86).

The next higher-lying structure for $V_2(CO)_9$, namely, **2T** which is 8.0 kcal/mol (B3LYP) or 2.8 kcal/mol (BP86) above the global minimum **1T**, is also a triplet structure with three semibridging CO groups. However, structure **2T** has five CO groups connected to one vanadium atom and four CO groups to the other (Figure 2). Structure **2T** is predicted to be a genuine minimum by both the B3LYP and BP86 methods. With the BP86 method, it has C_2 symmetry, while with the B3LYP method, it has C_1 symmetry, very slightly distorted from a C_2 structure. If the structure is constrained to C_2 symmetry, B3LYP predicts almost the same energy but with a small imaginary vibrational frequency ($44i$ cm^{-1}). The predicted vanadium−vanadium distance of 2.448 Å (B3LYP) or 2.418 Å (BP86) in **2T** is slightly shorter than that of structure **1T**. For the three bridging carbonyls, the shorter V−C distances are 1.977, 1.995, and 2.088 Å (B3LYP) or 1.979, 1.979, and 2.155 Å (BP86), while the longer ones are 2.280, 2.428, and 2.467 Å (B3LYP) or 2.155, 2.403, and 2.403 Å (BP86). The V−C distances of the terminal CO groups fall in the range of 1.985−2.030 Å (B3LYP) or 1.958−2.005 Å (BP86). The C−O distances fall in the range of 1.152−1.167 Å (B3LYP) and 1.167−1.181 Å (BP86). The V−C−O angles for the three bridging carbonyls deviate significantly from linearity, i.e., 168−170° (B3LYP) or 168−169° (BP86), but the V−C−O angles for the terminal carbonyls (>176°) are almost linear. For the three bridging carbonyls, the V−V−C angles are 59.7°, 65.3°, and 66.8° (B3LYP) or 55.9°, 65.4°, and 65.4° (BP86).

These two triplet structures (**1T** and **2T**) can be considered to have a 17-electron configuration on each vanadium atom analogous to the 17-electron configuration in the simple mononuclear $V(CO)_6$ radical, which has been isolated and

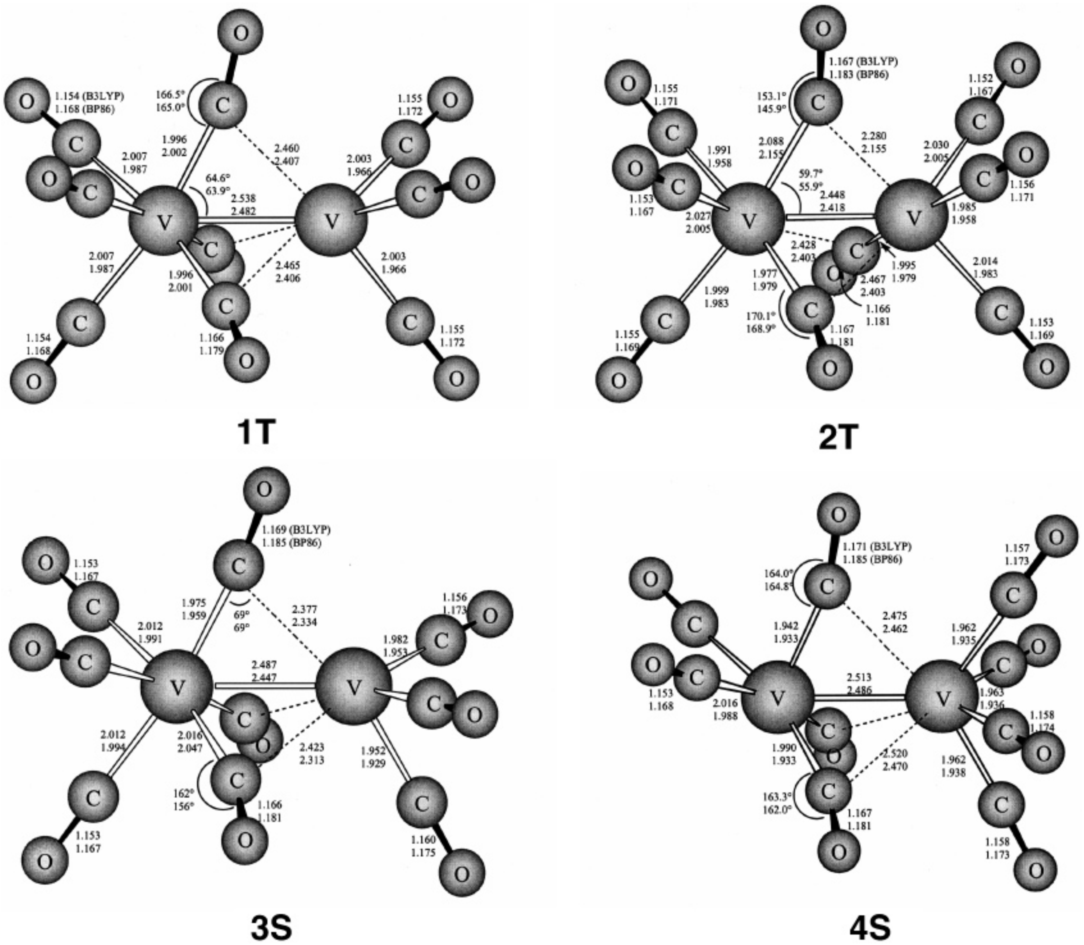

Figure 2. Four lowest-lying structures for $V_2(CO)_9$ (**1T**, **2T**, **3S**, and **4S**). All of these structures have three semibridging CO groups.

TABLE 1: Total Energies (*E*, in hartrees), Relative Energies (Δ*E*, in kilocalories per mole), and Vanadium−Vanadium Distances (in angstroms) for the Four Lowest-Energy Isomers of $V_2(CO)_9$

		C_s (**1T**)	C_1 or C_2 (**2T**)	C_s (**3S**)	C_s (**4S**)
B3LYP	*E*	−2908.32122	−2908.30843	−2908.30791	−2908.30316
	Δ*E*	0.0	8.0	8.4	11.3
	V−V	2.538	2.448	2.487	2.513
BP86	*E*	−2908.67290	−2908.66849	−2908.67026	−2908.67056
	Δ*E*	0.0	2.8	1.7	1.5
	V−V	2.482	2.418	2.447	2.486

TABLE 2: Metal Carbonyl *ν*(CO) Vibrational Frequencies Computed for the Four Lowest-Energy Isomers of $V_2(CO)_9$ (infrared intensities in parentheses in kilometers per mole)

	B3LYP	BP86
1T	2136 (78), 2089 (2340), 2070 (761), 2070 (762), 2025 (1160), 2025 (1150), 1996 (529), 1970 (1130), 1970 (1140)	2046 (291), 1988 (633), 1988 (638), 1988 (2290), 1932 (976), 1932 (974), 1915 (150), 1901 (7654), 1901 (767)
2T	2137 (19), 2078 (3040), 2061 (1490), 2052 (935), 2047 (1760), 2044 (500), 1974 (442), 1961 (687), 1958 (530)	2044 (7), 1990 (2820), 1971 (1190), 1965 (974), 1963 (562), 1958 (918), 1893 (273), 1890 (740), 1877 (391)
3S	2137 (224), 2077 (773), 2076 (952), 2075 (2500), 2030 (1870), 2021 (864), 1987 (93), 1976 (643), 1956 (1250)	2047 (336), 1992 (723), 1990 (635), 1985 (2360), 1936 (620), 1935 (1550), 1895 (362), 1894 (36), 1873 (864)
4S	2129 (57), 2082 (2400), 2070 (865), 2048 (53), 2036 (1690), 2035 (1720), 1984 (325), 1962 (688), 1942 (652)	2037 (36), 1997 (2090), 1979 (720), 1957 (44), 1950 (1410), 1950 (1410), 1902 (259), 1888 (498), 1874 (449)

characterized structurally.[26] In fact, the left vanadium atom in structure **1T** is bonded to six CO groups as in $V(CO)_6$. The corresponding singlet structures **3S** and **4S** (Figure 2) have also been found as genuine minima with no imaginary vibrational frequencies (Table 1 and Figure 2). In these singlet structures, one vanadium atom may be considered to have an 18-electron configuration, whereas the other vanadium has a 16-electron configuration. All of these suggested metal electron configurations for $V_2(CO)_9$ isomers **1T**, **2T**, **3S**, and **4S** assume a V≡V triple bond consistent with the computed vanadium−vanadium distances in the range of 2.41−2.53 Å (Table 1).

The lowest-lying of the singlet structures for $V_2(CO)_9$ is **3S** which is 8.4 kcal/mol (B3LYP) or 1.7 kcal/mol (BP86) above the global minimum **1T**. Structure **3S** is closely related to structure **1T** again with six CO groups on the left vanadium atom and three terminal CO groups on the right vanadium atom. The right vanadium atom in **3S** can be considered to be the vanadium atom with the 16-electron configuration and has

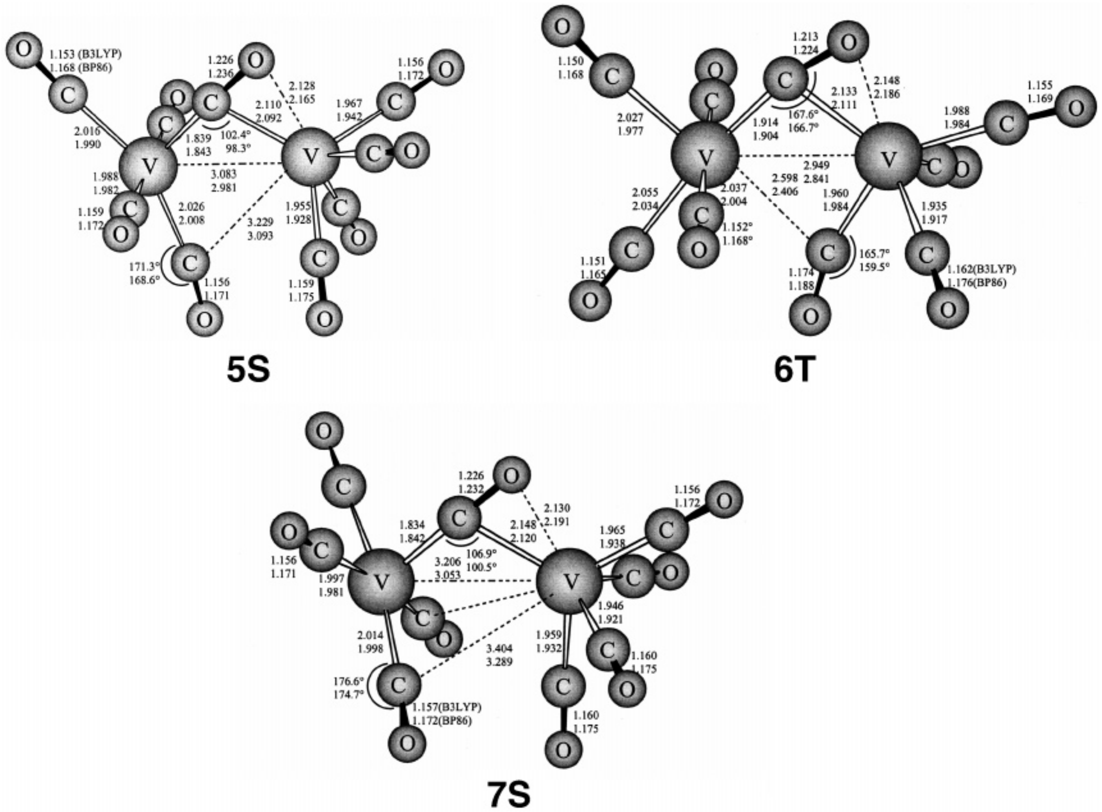

Figure 3. Three structures for $V_2(CO)_9$ with four-electron donor bridging η^2-μ-CO groups (**5S**, **6T**, and **7S**).

distinctly different angles between the V−CO bonds, reflecting the empty orbital of the sp^3d^5 manifold implied by the 16-electron configuration. Similarly, the next lowest-lying singlet $V_2(CO)_9$ structure **4S** (Figure 2) is closely related to the triplet structure **2T** since both structures have five CO groups on one vanadium atom (the left vanadium atom in Figure 2) and four CO groups on the other vanadium atom (the right vanadium atom in Figure 2). In the case of structure **4S**, the left vanadium atom with five CO groups can be considered to be the vanadium with the 16-electron configuration since there is an obvious “open space” in the structure to accommodate the “empty” vanadium orbital in its sp^3d^5 manifold.

All four of these isomers of $V_2(CO)_9$ (**1T**, **2T**, **3S**, and **4S**) have three semibridging CO groups with very different V−C distances to the two vanadium atoms. The structures are depicted in Figure 2 so that the V−C distances of these semibridging CO groups to the left vanadium atom are 2.0 ± 0.1 Å and those to the right vanadium atom are 2.4 ± 0.1 Å. The asymmetry of these semibridging CO groups is sufficient that their computed ν(CO) frequencies (Table 2) fall in the typical terminal ν(CO) region around 2000 cm^{-1} without any ν(CO) frequencies below 1850 cm^{-1} characteristic of symmetrical bridging CO groups. In general, the computed infrared ν(CO) spectra for these four isomers of $V_2(CO)_9$ (**1T**, **2T**, **3S**, and **4S**) are very similar to each other (Table 2). None of these four $V_2(CO)_9$ structures has any imaginary vibrational frequencies, indicating that they are genuine minima at these levels of theory.

3.2. The Next Three Structures of $V_2(CO)_9$ in Terms of Energy (5S, 6T, and 7S; Figure 3 and Tables 3 and 4). The next three structures of $V_2(CO)_9$ in terms of energy, namely, **5S**, **6T**, and **7S** (Figure 3 and Table 2), all have four terminal CO groups bonded to each vanadium atom. The ninth CO group is a bridging CO group, which is oriented so that it forms a normal σ-bond to the left vanadium atom in Figure 3 using only its carbon atom and a π-bond to the right vanadium atom using both its carbon and oxygen atoms. A bridging CO group of a similar type is found in $[\mu\text{-}CH_2(PPh_2)_2]_2Mn_2(CO)_4(\eta^2\text{-}\mu\text{-}CO)$, which is a stable isolable compound.[8,9] The involvement of the oxygen atom of this bridging CO group in its bonding to the right vanadium atom is indicated by the relatively short V−O distances in the range of 2.1−2.2 Å. The vanadium−vanadium distances in these isomers are around 3.0 Å, suggestive of a weak vanadium−vanadium single bond.

TABLE 3: Total Energies (E, in hartrees), Relative Energies (ΔE, in kilocalories per mole), Vanadium−Vanadium Distances (in angstroms), and Number of Imaginary Vibrational Frequencies (N_{imag}) for the Three Isomers of $V_2(CO)_9$ with an η^2-μ-CO Group (5S, 6T, and 7S)

		C_s (**5S**)	C_s (**6T**)	C_s (**7S**)
B3LYP	E	−2908.30306	−2908.30164	−2908.30015
	ΔE	11.4	12.9	13.2
	V−V	3.083	2.949	3.206
	N_{imag}	0	0	1 (24i cm^{-1})
BP86	E	−2908.66680	−2908.66158	−2908.66378
	ΔE	3.8	7.1	5.7
	V−V	2.981	2.841	3.053
	N_{imag}	0	0	1 (27i cm^{-1})

The energetically lowest-lying of these three $V_2(CO)_9$ isomers is the C_s singlet isomer **5S** (Figure 3), which lies 12.9 kcal/mol (B3LYP) or 7.1 kcal/mol (BP86) above the global minimum **1T**. The orientation of the single bridging CO group in **5S** is consistent with it acting as a donor of a total of four electrons with an electron pair to the left vanadium atom through a V−C σ-bond and a second electron pair to the right vanadium atom through a π-interaction from the C═O bond. Thus, the shorter V−C distance to this bridging CO group is 1.839 Å (B3LYP) or 1.834 Å (BP86), while the longer V−C distance is 2.110 Å (B3LYP) or 2.092 Å (BP86). The V−O distance to this bridging CO group is 2.128 Å (B3LYP) or 2.165 Å (BP86), consistent

TABLE 4: Metal Carbonyl ν(CO) Frequencies Computed for the Three Lowest-Energy Isomers of $V_2(CO)_9$ with Four-Electron Donor Bridging η^2-μ-CO Groups (5S, 6T, and 7S)[a]

	B3LYP	BP86
5S	2129 (21), 2084 (2180), 2056 (1410), 2052 (486), 2047 (570), 2036 (2510), 2017 (149), 2013 (174), **1659** (**381**)	2037 (26), 1996 (2000), 1969 (478), 1960 (1000), 1958 (1200), 1953 (1580), 1935 (9), 1929 (61), **1627** (**239**)
6T	2138 (302), 2084 (735), 2081 (1090), 2069 (1900), 2061 (2700), 2028 (894), 1995 (924), 1921 (419), **1714** (**381**)	2043 (235), 1992 (1280), 1978 (288), 1975 (2480), 1971 (1800), 1950 (572), 1922 (528), 1835 (312), **1668** (**328**)
7S	2126 (28), 2082 (1836), 2049 (2), 2047 (1880), 2040 (309), 2038 (3170), 2015 (213), 2011 (183), **1656** (**403**)	2036 (29), 1996 (1660), 1963 (83), 1959 (1580), 1953 (2510), 1950 (141), 1931 (201), 1927 (106), **1636** (**278**)

[a] Infrared intensities in parentheses are in kilometers per mols. The frequencies arising from the η^2-μ-CO groups are in bold type.

with a π-bond from the CO group to the vanadium atom. Furthermore, the C−O distance in the bridging CO group is 1.226 Å (B3LYP) or 1.236 Å (BP86), which is much longer than that in the terminal CO groups [1.153−1.159 Å (B3LYP) or 1.171−1.175 Å (BP86)], consistent with the lowering of the C−O bond order by π-donation to the right vanadium atom. The four-electron donor bridging CO group in the $V_2(CO)_9$ isomer **5S** is computed to exhibit a very low ν(CO) frequency (Table 4) of 1659 cm^{-1} (B3LYP) or 1627 cm^{-1} (BP86), consistent with reduction of the formal C−O bond order by π-donation to the right vanadium atom. A similar low ν(CO) frequency (1645 cm^{-1}) was found in the stable manganese carbonyl complex [μ-$CH_2(PPh_2)_2$]$_2Mn_2(CO)_4$(η^2-μ-CO), which has been characterized by X-ray diffraction.[8,9]

The V−C distances to the terminal CO groups in **5S** fall in the range of 1.955−2.026 Å (B3LYP) or 1.928−2.008 Å (BP86), and the terminal C−O distances fall in the range of 1.153−1.159 Å (B3LYP) or 1.171−1.175 Å (BP86). The V−C−O angle for the bridging CO in **5S** shows little deviation from linearity at 176° (B3LYP) or 175° (BP86). The corresponding V−C−V angle for this bridging CO is 102° (B3LYP) or 98° (BP86). For the eight terminal carbonyls, one of the V−C−O angles deviates significantly from linearity, namely, 171° (B3LYP) or 169° (BP86), consistent with weak interaction with the second vanadium atom. However, the other seven V−C−O angles exhibit small deviations from linearity in the range of 177−179°.

The vanadium−vanadium distance in **5S**, namely, 3.083 Å (B3LYP) or 2.981 Å (BP86), is much longer than that in the four lowest-energy structures (**1T**, **2T**, **3S**, and **4S**) discussed in the previous section. This suggests a relatively weak vanadium−vanadium interaction, possibly at most a V−V single bond. A formal V−V single bond is required to give each vanadium atom a 16-electron configuration since each vanadium atom receives 10 electrons from the total of five CO groups bonded to the vanadium in question.

The next higher-energy structure predicted for $V_2(CO)_9$ after **5S** is the triplet structure **6T** (Figure 3) at 16.7 kcal/mol (B3LYP) or 19.7 kcal/mol (BP86). The V−V distance in **6T** is 2.949 Å (B3LYP) or 2.841 Å (BP86), which is ∼0.14 Å shorter than that in the singlet **5S** and suggestive of a V−V single bond.

This $V_2(CO)_9$ isomer **6T** has two distinctly different bridging CO groups. One of these bridging CO groups is a two-electron donor similar to the three semibridging CO groups found in the four lowest-energy $V_2(CO)_9$ structures (**1T**, **2T**, **3S**, and **4S** in Figure 2) discussed above. The computed ν(CO) frequency of 1921 cm^{-1} (B3LYP) or 1835 cm^{-1} (BP86) can be assigned to this bridging CO group (Table 4). The second bridging CO group in **6T** is a four-electron donor similar to the bridging CO group in **5S** (Figure 3 and Table 3). The ν(CO) frequency assigned to this four-electron donor η^2-μ-CO group in **6T** is computed (Table 4) to be 1714 cm^{-1} (B3LYP) or 1668 cm^{-1} (BP86). The shorter V−C distance for the four-electron donor CO group in **6T** is 1.914 Å (B3LYP) or 1.904 Å (BP86), whereas the longer V−C distance in **6T** is 2.133 Å (B3LYP) or 2.111 Å (BP86). For the terminal CO groups of **6T**, the V−C distances for the left (in Figure 3) vanadium atom are in the range of 2.027−2.055 Å (B3LYP) or 1.977−2.034 Å (BP86), while the V−C distances for the right vanadium atom are slightly shorter, in the range of 1.935−1.988 Å (B3LYP) or 1.917−1.984 Å (BP86). This suggests slightly stronger π-back-bonding of the terminal CO groups to the right vanadium atom than to the left vanadium atom, consistent with the fact that the right vanadium atom has only three terminal CO groups but the left vanadium atom has four terminal CO groups. The V−C−O angle for the four-electron donor CO group in **6T** is 168° (B3LYP) or 167° (BP86) bent toward the right V atom, consistent with π-electron donation to the right vanadium atom. The V−C−O angle for the two-electron donor bridging CO group in **6T** is 166° (B3LYP) or 160° (BP86) away from the V atom, indicating σ-electron donation only. The V−C−O angles for the seven terminal carbonyls in **6T** deviate only slightly from linearity (>175°).

The other $V_2(CO)_9$ isomer with an apparent four-electron donor CO group is **7S** (Figure 3). The geometry and relative energy of **7S** are similar to those of **5S**. However, isomer **7S** is a transition state with a small imaginary vibrational frequency (24*i* cm^{-1} with B3LYP or 27*i* cm^{-1} with BP86). The mode of this imaginary vibrational frequency corresponds to internal rotation around the V−V bond leading to structure **5S**. The V−V distance in **7S** [3.206 Å (B3LYP) or 3.053 Å (BP86)] is longer than that of structure **5S** by 0.12 Å (B3LYP) or 0.07 Å (BP86). This suggests a weak vanadium−vanadium interaction, possibly a V−V single bond, with a similar electronic structure for **7S** and **5S**. In this connection, the bond distances and bond angles in **7S** are similar to those in **5S**. Thus, the shorter V−C distance to the bridging CO group in **7S** is 1.834 Å (B3LYP) or 1.842 Å (BP86), while the longer V−C distance is 2.148 Å (B3LYP) or 2.120 Å (BP86). The corresponding C−O distance is 1.226 Å (B3LYP) or 1.232 Å (BP86). The V−C−O angle for the bridging carbonyl remains almost linear (>177°). The other eight V−C−O angles also exhibit small deviations from linearity (>175°).

3.3. The Remaining Five Structures of $V_2(CO)_9$ within 25 kcal/mol of the Global Minimum 1T (Figure 4 and Tables 5 and 6). In addition to the seven $V_2(CO)_9$ isomers discussed in the previous sections, there are five other isomers of $V_2(CO)_9$ within 25 kcal/mol of the global minimum **1T** (Figure 4 and Table 5).

The lowest-lying of these $V_2(CO)_9$ structures is the singlet structure **8S** with two bridging carbonyl groups, i.e., $(CO)_4V(\mu\text{-}CO)_2V(CO)_3$ (Figure 4). This structure lies 13.5 kcal/mol (B3LYP) or 5.6 kcal/mol (BP86) above the global minimum **1T** and is a genuine minimum with all real harmonic vibrational frequencies predicted by both DFT methods. The vanadium−vanadium distance in structure **8S** (Figure 4) is 2.479 Å (B3LYP) or 2.478 Å (BP86), consistent with a V≡V triple bond. The shorter V−C distances to the bridging CO groups in **8S**

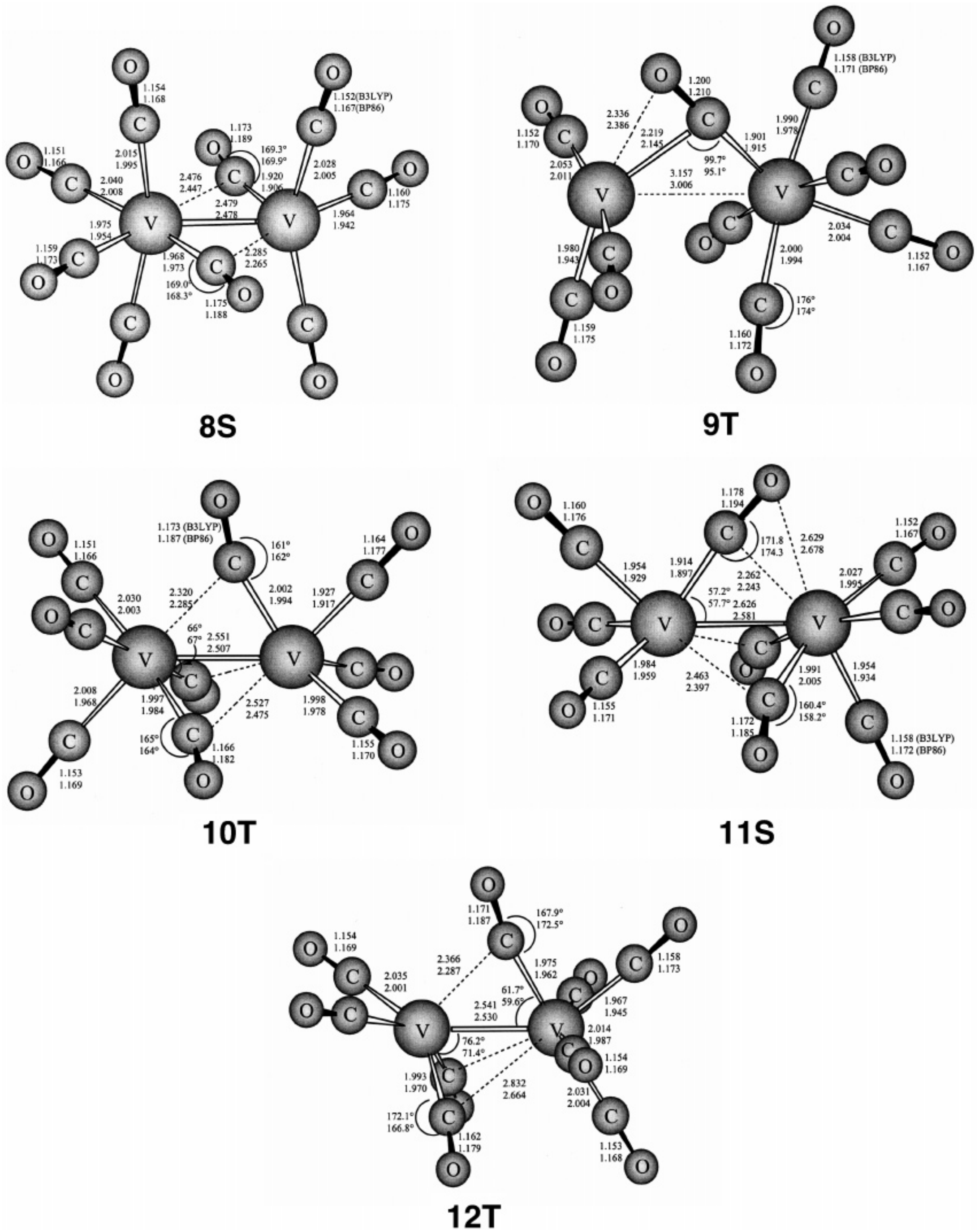

Figure 4. Five remaining structures of $V_2(CO)_9$ within 25 kcal/mol of the global minimum **1T**.

TABLE 5: Total Energies (*E*, in hartrees), Relative Energies (Δ*E*, in kilocalories per mole), Vanadium−Vanadium Distances (in angstroms), and Number of Imaginary Vibrational Frequencies (N_{imag}) for the Five Remaining Isomers of $V_2(CO)_9$ within 25 kcal/mol of the Global Minimum 1T

		C_s (**8S**)	C_s (**9T**)	C_s (**10T**)	C_s (**11S**)	C_s (**12T**)
B3LYP	E	−2908.29972	−2908.29458	−2908.29276	−2908.29068	−2908.28539
	ΔE	13.5	16.7	17.8	19.2	22.5
	V−V	2.479	3.157	2.551	2.626	2.541
	N_{imag}	0	1 (11*i*)	1 (35*i*)	0	1 (61*i*)
BP86	E	−2908.66390	−2908.64151	−2908.65507	−2908.66185	−2908.64575
	ΔE	5.6	19.7	11.2	6.9	17.0
	V−V	2.478	3.006	2.507	2.581	2.530
	N_{imag}	0	0	1 (29*i*)	0	1 (56*i*)

are 1.920 and 1.968 Å (B3LYP) or 1.906 and 1.973 Å (BP86), while the longer ones are 2.476 and 2.285 Å (B3LYP) or 2.447 and 2.265 Å (BP86, Figure 4). The corresponding C−O distances are 1.173 and 1.175 Å (B3LYP) or 1.189 and 1.188 Å (BP86). The V−O distances in **8S** are 3.271 and 3.049 Å (B3LYP) or 3.238 and 3.047 Å (BP86), indicating that these bridging CO groups are two-electron rather than four-electron donors. This is consistent with the computed ν(CO) frequencies

TABLE 6: Metal Carbonyl *ν*(CO) Frequencies Computed for the Five Remaining Lowest-Energy Isomers of $V_2(CO)_9$ within 25 kcal/mol of the Global Minimum 1T[a]

	B3LYP	BP86
8S	2145 (51), 2092 (1410), 2072 (3080), 2066 (793), 2045 (54), 2040 (727), 2034 (1660), **1939** (**1080**), **1923** (**223**)	2053 (67), 2001 (1510), 1985 (404), 1984 (2580), 1961 (50), 1957 (953), 1948 (735), **1865** (**950**), **1849** (**24**)
9T	2135 (307), 2086 (1540), 2074 (973), 2067 (987), 2064 (2060), 2037 (308), 2005 (962), 1996 (454), **1670** (**352**)	2038 (194), 1991 (2090), 1983 (288), 1975 (1720), 1974 (687), 1948 (300), 1927 (634), 1919 (251), **1636** (**314**)
10T	2140 (52), 2094 (1780), 2069 (198), 2061 (2820), 2041 (354), 2034 (1940), 2015 (225), 2010 (345), **1784** (**881**)	2048 (203), 1994 (1620), 1982 (537), 1967 (350), 1962 (2440), 1955 (1330), 1928 (170), 1928 (125), **1745** (**546**)
11S	2133 (198), 2081 (871), 2078 (2974), 2046 (1460), 2040 (1740), 2032 (411), **1949** (**241**), **1939** (**664**), **1887** (**450**)	2039 (33), 1988 (2580), 1986 (784), 1962 (1180), 1953 (1200), 1947 (360), **1875** (**188**), **1868** (**454**), **1814 (360)**
12T	2136 (195), 2078 (1844), 2073 (1200), 2067 (2140), 2046 (1090), 2010 (1150), 1979 (371), 1963 (535), **1919** (**481**)	2041 (183), 1988 (2230), 1984 (871), 1971 (1320), 1956 (1010), 1937 (883), 1893 (280), 1884 (465), **1841** (**389**)

[a] Infrared intensities in parentheses are in kilometers per mole. The frequencies assigned to the bridging CO groups are in bold type.

of 1939 and 1923 cm^{-1} (B3LYP) or 1865 and 1849 cm^{-1} (BP86) for these two bridging carbonyls (Table 6).

For the terminal CO groups in **8S**, the V−C distances are 1.964−2.040 Å (B3LYP) or 1.942−2.008 Å (BP86) and the C−O distances are 1.151−1.160 Å (B3LYP) or 1.166−1.175 Å (BP86). The V−C−O angles of the seven terminal carbonyls in **8S** deviate little from linearity, i.e., 176−179° (B3LYP) or 175−178° (BP86). These small deviations occur because of the interaction among the terminal CO groups. The V−C−O angles for the bridging CO groups in **8S** deviate significantly from linearity, i.e., 169.0° and 169.4° (B3LYP) or 168.3° (B3LYP) and 169.9° (BP86). The V−V−C angles for the two bridging CO groups are 67.1° and 60.5° (B3LYP) or 66.4° and 59.9° (BP86).

The next $V_2(CO)_9$ structure is a triplet structure **9T**, which lies 16.7 kcal/mol (B3LYP) or 19.7 kcal/mol (BP86) above the global minimum **1T**. This structure is a monobridged structure $(CO)_3V(\mu\text{-}CO)V(CO)_5$ with a four-electron donor bridging CO group (Figure 4). The B3LYP functional gives a very small (11*i* cm^{-1}) imaginary vibrational frequency for **9T**. The mode of this imaginary vibrational frequency corresponds to internal rotation around the V−V bond. However, the BP86 method finds structure **9T** to be a genuine minimum with all real harmonic vibrational frequencies, but its energy is higher by ∼12.6 kcal/mol relative to that of structure **6T**, which has a similar four-electron donor bridging CO group.

The V−V distance in $V_2(CO)_9$ isomer **9T** (3.157 Å with B3LYP or 3.006 Å with BP86) is the longest such distance in all of the triplet structures, suggesting a very weak metal−metal interaction. In structure **9T**, the shorter V−C distance to the bridging CO group is 1.901 (B3LYP) or 1.915 Å (BP86), whereas the longer one is 2.219 (B3LYP) or 2.145 Å (BP86). The V−O distance to the left vanadium atom in Figure 4 is only 2.336 (B3LYP) or 2.386 Å (B3LYP), consistent with a four-electron donor η^2-μ-CO bridging carbonyl group similar to that in **6T** (Figure 3). The almost linear (179°) V−C−O angle for the bridging carbonyl in **9T** is also consistent with π-electron donation to the left vanadium atom. The computed ν(CO) frequency for this bridging CO group in **9T** is 1670 cm^{-1} (B3LYP) or 1636 cm^{-1} (BP86), which is appreciably lower than the value of 1714 cm^{-1} (B3LYP) or 1668 cm^{-1} (BP86), respectively, computed for the closely related **6T** (Table 6). The V−C distances of the terminal carbonyls fall in the range of 1.980−2.052 Å (B3LYP) or 1.943−2.011 Å (BP86). The C−O distances fall in the range of 1.152−1.160 Å (B3LYP) or 1.167−1.175 Å (BP86).

The $V_2(CO)_9$ isomer **10T** which is 17.8 kcal/mol (B3LYP) or 11.2 kcal/mol (BP86) higher than the global minimum **1T** has a structure similar to that of **1T** with three semibridging CO groups but with a different distribution of the short and long V−C bonds from the vanadium atoms to the semibridging CO groups. This $V_2(CO)_9$ isomer (**10T**) has a small imaginary vibrational frequency, namely, 35*i* cm^{-1} (B3LYP) or 29*i* cm^{-1} (BP86). Following the vibrational mode of this imaginary frequency leads to structure **2T** by shifting the short and long V−C bonds of one of the semibridging CO groups. The V−V distance is 2.551 Å (B3LYP) or 2.507 Å (BP86), which is slightly longer than that of structure **2T** by ∼0.1 Å. The shorter V−C distances of the three semibridging CO groups in **10T** are 1.997 and 2.002 Å (B3LYP) or 1.984 and 1.994 Å (BP86), and the longer V−C distances are 2.320 and 2.527 Å (B3LYP) or 2.285 and 2.475 Å (BP86). The semibridging CO group in **10T** with V−C bonds of 2.002 Å (B3LYP) or 1.994 Å (BP86) and 2.320 Å (B3LYP) or 2.285 Å (BP86) is less “asymmetrical” than the other semibridging CO groups found in the other $V_2(CO)_9$ isomers and probably is the cause of the lowest ν(CO) frequency (Table 6) at 1784 cm^{-1} (B3LYP) or 1745 cm^{-1}, which is well into the bridging ν(CO) region. The V−C distances of the terminal CO groups in **10T** fall in the range of 1.927−2.030 Å (B3LYP) or 1.917−2.003 Å (BP86). The C−O distances fall in the range of 1.151−1.173 Å (B3LYP) or 1.166−1.187 Å (BP86). The V−C−O angles of the three semibridging CO groups in **10T** deviate significantly from linearity, i.e., 161−165° (B3LYP) or 162−164° (BP86). However, the V−C−O angles of the terminal CO groups deviate little from linearity (>177°). For the three semibridging CO groups, the V−V−C angles are 59.8° and 66.2° (B3LYP) or 59.7° and 65.6° (BP86).

The singlet $V_2(CO)_9$ isomer **11S** (Figure 4) which is 19.2 kcal/mol (B3LYP) or 6.9 kcal/mol (BP86) above the global minimum is a genuine minimum predicted by both DFT methods. The V−V distance in **11S**, namely, 2.626 Å (B3LYP) or 2.581 Å (BP86), suggests vanadium−vanadium multiple bonding. The shorter V−C distances to the semibridging CO groups are 1.991 and 1.914 Å (B3LYP) or 2.005 and 1.897 Å (BP86), while the longer ones are 2.463 and 2.262 Å (B3LYP) or 2.397 and 2.243 Å (BP86). These three semibridging CO groups are probably responsible for the three lowest computed ν(CO) frequencies (Table 6) at 1949, 1939, and 1887 cm^{-1} (B3LYP) or 1875, 1868, and 1814 cm^{-1} (BP86). The corresponding C−O distances are 1.172 and 1.178 Å (B3LYP) or 1.185 and 1.194 Å (BP86). The six V−C distances to the terminal CO groups are in the range of 1.954−2.027 Å (B3LYP) or 1.929−1.995 Å (BP86), and the C−O distances in the terminal CO groups are 1.152−1.160 Å (B3LYP) or 1.167−1.176 Å (BP86). The V−C−O angles for the bridging CO groups deviate significantly from linearity, namely, 160.4° and 171.8° (B3LYP) or 158.2° and 174.4° (BP86). However, the V−C−O angles of the six terminal CO groups are nearly linear, namely, 177.4−179.4° (B3LYP) or 176.6−179.6° (BP86). The

V−V−C angles for the three bridging CO groups are 62.7° and 57.2° (B3LYP) or 57.7° and 61.5° (BP86).

The $V_2(CO)_9$ isomer **12T**, which is 22.5 kcal/mol (B3LYP) or 17.0 kcal/mol (BP86) above the global minimum, is another structure with three highly unsymmetrical semibridging CO groups. This structure exhibits a small imaginary frequency, namely, $61i$ cm^{-1} (B3LYP) or $56i$ cm^{-1} (BP86). The $V_2(CO)_9$ isomer **12T** collapses to structure **2T** by following the vibrational mode represented by this imaginary frequency, indicating the close relationships between these isomers. The V−V distance in **12T** of 2.541 Å (B3LYP) or 2.530 Å (BP86) is 0.10 Å (B3LYP) or 0.08 Å (BP86) longer than that in **2T** but shorter than that in **10T**. The shorter V−C distances in the three semibridging CO groups of **12T** are 1.975 and 1.993 Å (B3LYP) or 1.962 and 1.970 Å (BP86), and the longer ones are 2.366 and 2.832 Å (B3LYP) or 2.287 and 2.664 Å (BP86). For the six terminal CO groups, the V−C distances fall in the range of 1.967−2035 Å (B3LYP) or 1.945−2.001 Å (BP86). The V−C−O angles for the bridging CO groups in **12T** deviate significantly from linearity at 167.9° and 172.0° (B3LYP) or 166.8° and 172.5° (BP86). However, the V−C−O angles for the terminal CO groups deviate only slightly from linearity ($>175°$) by either the B3LYP or BP86 method.

4. Discussion

The metals to the immediate right of vanadium in the periodic table, namely, Cr, Mn, and Fe, are known either experimentally (M = Fe)[2] or by DFT methods (M = Cr[11] and Mn[10]) to form $M_2(CO)_9$ derivatives having three symmetrical or nearly symmetrical bridging CO groups and metal−metal distances corresponding to the formal metal−metal bond order required to give both metal atoms the favored 18-electron configuration (**I** in Figure 1). Thus, these $Cr_2(CO)_9$, $Mn_2(CO)_9$, and $Fe_2(CO)_9$ structures have metal−metal bond distances corresponding to triple, double, and single bonds, respectively. A related structure for $V_2(CO)_9$ would be required to have a vanadium−vanadium quadruple bond for each vanadium atom to yield the favored 18-electron noble gas configuration. None of the 12 computed structures for $V_2(CO)_9$ within 25 kcal/mol of the global minimum **1T** has a short vanadium−vanadium distance indicative of such a high metal−metal bond order.

Our inability to find any stable isomers (i.e., minima) for $V_2(CO)_9$ with vanadium−vanadium distances that are sufficiently short for a quadruple bond means that one or both vanadium atoms must have less than the favored 18-electron configurations in these structures unless there are sufficient numbers of four-electron donor bridging η^2-μ-CO groups. Such special bridging CO groups can be identified by unusually low ν(CO) vibrational frequencies, typically in the range of 1600−1750 cm^{-1} as well as V−O distances within bonding range (typically 2.1−2.2 Å). Four-electron donor η^2-μ-CO groups were identified in isomers **5S**, **6T**, **7S**, and **9T** using these criteria**.** However, all of these structures have V−V distances in the range of 2.95−3.21 Å (B3LYP) or 2.84−3.05 Å (BP86), suggesting V−V single bonds rather than the $V\equiv V$ triple bonds required to give the vanadium atoms the favored 18-electron rare gas configurations in these structures. For example, the vanadium atoms in the two singlet $V_2(CO)_8(\eta^2$-μ-CO) structures (**5S** and **7S**) can have only 16-electron metal configurations.

Another feature of the $V_2(CO)_9$ structures found in this work is the occurrence of numerous triplet structures that are energetically competitive with related singlet structures. This is not surprising since mononuclear $V(CO)_6$ is a doublet with a 17-electron configuration for its vanadium atom. Combining two such 17-electron vanadium units in a binuclear complex with one unpaired electron on each vanadium atom would necessarily lead to such a triplet.

No $V_2(CO)_9$ isomer was found having three symmetrically bridging CO groups analogous to structure **I** (Figure 1) found experimentally (M = Fe)[2] or computationally (M = Mn[10] and Cr[11]) for the metals following vanadium in the periodic table. In contrast, the four lowest-lying structures for $V_2(CO)_9$ in terms of their energies, namely, triplets **1T** and **2T** and singlets **3S** and **4S**, all have three highly unsymmetrical semibridging CO groups. These four structures differ from each other in terms of the multiplicity (singlet vs triplet) and the distribution of their terminal CO groups. The vanadium−vanadium distances in all four of these structures (**1T**, **2T**, **3S**, and **4S**) fall in the range of 2.44−2.54 Å (B3LYP) or 2.42−2.49 Å (BP86), consistent with a $V\equiv V$ triple bond. With such a V−V single bond, triplet isomers **1T** and **2T** have 17-electron configurations for each vanadium atom whereas singlet isomers **3S** and **4S** have one vanadium atom with an 18-electron configuration and the other vanadium atom with a 16-electron configuration.

5. Summary

Attempts to optimize the structure of the highly unsaturated $V_2(CO)_9$ led to a complicated collection of isomers having rather closely spaced energies. However, none of these many $V_2(CO)_9$ isomers was found to have a sufficiently short vanadium−vanadium distance for the $V\overset{4}{-}V$ quadruple bond required to give both metal atoms the favored 18-electron configuration. Furthermore, triplet structures for $V_2(CO)_9$ were found to be competitive in energy with related singlet structures. Thus, the two lowest-energy isomers of $V_2(CO)_9$ are triplets. The four isomers of $V_2(CO)_9$ with the lowest energy all have three very unsymmetrical bridging CO groups (typically short and long M−CO distances differing by 0.4−0.5 Å) rather than the symmetrical bridging CO groups found experimentally[2] in $Fe_2(CO)_9$ and predicted for $M_2(CO)_9$ (M = Cr and Mn) from earlier DFT studies.[10,11] The $V\equiv V$ distances in these four isomers suggest a metal−metal triple bond. Next higher in energy for $V_2(CO)_9$ are three structures with single four-electron donor bridging CO groups identified by single low ν(CO) frequencies and V−O bonding distances.

This study of $V_2(CO)_9$ supports the following general points: (1) Metal−metal bonds with an order larger than three are not usually favorable in metal carbonyl chemistry. (2) The 18-electron rule for metal carbonyls begins to break down when the metal atom, i.e., vanadium in this case, has only five valence electrons.

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Supporting Information Available: Complete tables of harmonic vibrational frequencies for 12 $V_2(CO)_9$ isomers (Tables S1−S12). This material is available free of charge via the Internet at http://pubs.acs.org.

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