ELSEVIER

The oxophilicity of vanadium in unsaturated homoleptic binuclear vanadium carbonyl structures ☆

R. Bruce King [a,d,*], H.F. Schaefer [a], Zhaohui Liu [b,c], Qian-Shu Li [c,d,*], Yaoming Xie [a]

[a] Department of Chemistry and Center for Computational Chemistry, University of Georgia, Athens, Georgia 30602, USA
[b] Architecture Department, Chongqing Logistics Engineering University, Chongqing 400041, PR China
[c] Institute of Chemical Physics, Beijing Institute of Technology, Beijing 100081, PR China
[d] School of Chemistry and Environment, South China Normal University, Guangzhou 510631, PR China

Abstract

Density functional theory has been used to explore molecular structures of possible homoleptic binuclear vanadium carbonyls $V_2(CO)_n$ ($n = 12, 11, 10, 9,$ and 8) with the pure DFT method BP86. Octahedral or nearly octahedral $V(CO)_6$ units, similar to the known monomeric $V(CO)_6$, are found to be fundamental building blocks in the lowest energy structures of the homoleptic binuclear vanadium carbonyls $V_2(CO)_n$ ($n = 12, 11, 10,$ and 9). A $V(CO)_6$ unit often links to a second $V(CO)_n$ unit to form the binuclear vanadium carbonyl through one or two four-electron donor bridging CO groups as a consequence of the oxophilicity of vanadium. Single and triple vanadium–vanadium bonds are predicted to be favored whiledouble and quadruple vanadium–vanadium bonds are avoided. An interesting structure is found for $V_2(CO)_8$ consisting of two $V(CO)_4$ units linked by a vanadium–vanadium bond short enough to be the quintuple bond required by the 18-electron rule.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Vanadium metal carbonyls; Oxophilicity; Density functional theory

1. Introduction

Filling each of the nine orbitals in the transition metal sp^3d^5 manifold leads to the 18-electron rule [1,2], which applies to the homoleptic carbonyls of the central transition metals from chromium to nickel, inclusive. Thus the stable carbonyls of these metals are the mononuclear derivatives $Cr(CO)_6$, $Fe(CO)_5$, and $Ni(CO)_4$ as well as the binuclear $Mn_2(CO)_{10}$, $Fe_2(CO)_9$, and $Co_2(CO)_8$. The latter are all assumed to have metal–metal single bonds for the purposes of electron counting.

☆ This paper is dedicated to the memory of F.A. Cotton (1930–2007) in recognition of his contributions to many areas of inorganic and organometallic chemistry including metal–metal multiple bonding in coordination compounds.

* Corresponding authors.

E-mail addresses: rbking@chem.uga.edu (R.B. King), qsli@bit.edu.cn (Q.-S. Li).

Extension of the 18-electron rule for neutral metal carbonyls to the left of chromium runs into difficulty because of the relatively high coordination numbers required for enough CO groups for the relatively electron-poor early transition metals to attain the 18-electron configuration. Thus the most stable homoleptic vanadium carbonyl compound is not $V_2(CO)_{12}$, which would be formally seven-coordinate with six CO groups and one V–V single bond. Instead the only homoleptic vanadium carbonyl isolable as a stable compound is $V(CO)_6$ with octahedral coordination but only a 17-electron vanadium configuration [3].

Several years ago we initiated a study of probable homoleptic binuclear carbonyls $M_2(CO)_y$ of the first row transition metals using density functional theory (DFT). Our initial studies [4–9] focused on the central transition metals from chromium to nickel where the 18-electron rule is known to apply in simple metal carbonyl chemistry. Our subsequent studies on homoleptic binuclear vanadium

carbonyls were motivated by the following specific inter-connected questions:

(1) Would the higher affinity of the early transition metal vanadium for oxygen, i.e., its oxophilicity, be a factor in determining the most stable structures for homoleptic binuclear metal carbonyls by favoring low energy structures containing four-electron donor bridging η^2-μ-CO groups with a short bonding V–O distance?

(2) Is the dimer of the known 17-electron complex $V(CO)_6$, namely $V_2(CO)_{12}$, likely to be a stable, or at least detectable transient, species? In this connection Ozin et al. [10] claimed to have found $V_2(CO)_{12}$ in rare gas matrices at low temperatures from the cocondensation of vanadium atoms with carbon monoxide. Their identification of $V_2(CO)_{12}$ was based solely on their interpretation of the ν(CO) frequencies observed in these low temperature matrices.

(3) Could highly unsaturated homoleptic binuclear vanadium carbonyls, such as $V_2(CO)_9$ and $V_2(CO)_8$, have formal metal–metal bond orders higher than three similar to the recently discovered [11] chromium–chromium quintuple bond in the binuclear chromium(I) aryl R_2Cr_2 (R = C_6H_3-2,6-($C_6H_3$2,6-Pr^i_2)$_2$)?

(4) Would triplet structures with 17-electron vanadium configurations, similar to the 17-electron vanadium configuration in the known doublet $V(CO)_6$, be energetically competitive with singlet structures having 18-electron vanadium configurations? Singlet structures with formally coordinately unsaturated 16-electron configurations also appear reasonable for early transition metal derivatives as indicated by the stability of the 16-electron complexes (η^5-C_5H_5)(η^7-C_7H_7)Ti [12], (η^5-C_5H_5)$_2$Ti(CH$_3$)$_2$ [13], and (η^6-CH$_3C_6H_5$)$_2$Ti [14].

Our detailed computational results on the relevant binuclear vanadium carbonyls are presented in several papers [15–17]. These papers present full details on the numerous optimized structures that we found for various homoleptic binuclear vanadium carbonyls including their energies and vibrational frequencies. However, many of these binuclear vanadium carbonyl structures exhibit relatively small imaginary vibrational frequencies ($<100i$ cm^{-1}) indicating that they are close to the real minimum. Frequently such imaginary vibrational frequencies are ignored for this reason [6]. However, we have found that following the normal modes corresponding to these small imaginary vibrational frequencies in different binuclear vanadium carbonyl structures often leads to the same lower energy isomer. This suggests that the relevant structures for understanding binuclear vanadium carbonyl chemistry are only a small subset of the structures presented in our previous detailed papers [15–17]. This paper presents an overview of the chemistry of the homoleptic binuclear vanadium carbonyls

$V_2(CO)_n$ (n = 12, 11, 10, 9, and 8) based on these key structures arising from such exhaustive optimization procedures.

2. Theoretical methods

The DZP basis set for C and O atoms begins with Dunning's standard double-σ contraction [18] of Huzinaga's primitive sets [19] 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 vanadium is the Wachters primitive set [20] augmented by two sets of p functions and a set of d functions, contracted following Hood, Pitzer and Schaefer [21], designated (14s11p6d/10s8p3d). Thus for $V_2(CO)_{12}$, there are 458 contracted Gaussian functions in the present flexible DZP basis sets.

Electron correlation effects were considered by employing density functional theory (DFT) methods, which have evolved as a practical and effective computational tool, especially for organometallic compounds [22–30]. Thus two DFT methods were used in this study. The first functional is the B3LYP method, which is the hybrid HF/DFT method using the combination of the three-parameter Becke functional (B3) with the Lee–Yang–Parr (LYP) generalized gradient correlation functional [31,32]. The other DFT method used in the present paper is BP86, which combines Becke's 1988 exchange functional (B) with Perdew's 1986 gradient corrected correlation functional method (P86) [33,34]. It has been noted elsewhere that the BP86 method may be somewhat more reliable than B3LYP for the type of organometallic systems considered in this paper [35–37]. In the present study, the B3LYP and BP86 methods agree with each other fairly well in predicting the structural characteristics of the vanadium carbonyl derivatives of interest. Although both the B3LYP and BP86 results are shown in the figures only the BP86 results are discussed in the text.

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 infrared intensities were also evaluated analytically. The ν(CO) frequencies are of particular interest and are listed in Table 1 for the vanadium carbonyls discussed in this paper. All of the computations were carried out with the GAUSSIAN 03 program [38], exercising the fine grid option (75 radial shells, 302 angular points) for evaluating integrals numerically, while the tight (10^{-8} hartree) designation is the default for the self-consistent field (SCF) convergence.

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. Thus for an imaginary vibrational frequency with a magnitude less than 100 cm^{-1},
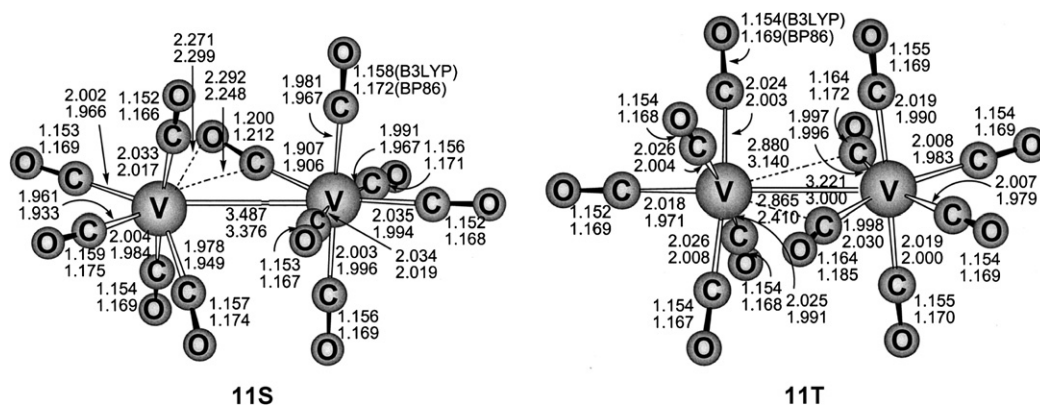
Table 1
Infrared active ν(CO) vibrational frequencies (cm^{-1}) predicted for the V$_2$(CO)$_n$ derivatives discussed in this paper (infrared intensities in parentheses are in km/mol; bridging CO frequencies are in bold)

Compound	ν(CO) frequencies, cm^{-1} (relative intensities in parentheses)
V$_2$(CO)$_{12}$ (**12S**)	2008 (1630), 1970 (366), 1953 (740)
V$_2$(CO)$_{11}$ (**11S**)	2060 (44), 2016 (1680), 1990 (630), 1983 (1660), 1978 (605), 1974 (1140), 1971 (870), 1953 (367), 1949 (535), 1974 (86), **1728 (390)**
V$_2$(CO)$_{11}$ (**11T**)	1996 (3520), 1980 (488), 1979 (515), 1976 (2403), 1972 (138), 1966 (1458), 1965 (491), 1943 (53), 1936 (11), **1848 (295)**
V$_2$(CO)$_{10}$ (**10S**)	2052 (202), 2006 (2010), 1993 (650), 1992 (630), 1954 (1520), 1954 (1540), 1922 (159), 1906 (374), 1906 (410)
V$_2$(CO)$_{10}$ (**10S′**)	2051 (152), 2012 (1860), 1999 (640), 1981 (135), 1970 (2600), 1950 (551), 1946 (526), 1937 (138), **1781 (378), 1759 (579)**
V$_2$(CO)$_{10}$ (**10T**)	2050 (38), 1996 (3620), 1990 (805), 1974 (2770), 1973 (1250), 1963 (441), 1955 (107), 1936 (830), **1699 (20), 1674 (508)**
V$_2$(CO)$_9$ (**9T**)	2046 (291), 1988 (633), 1988 (638), 1988 (2290), 1932 (976), 1932 (974), 1915 (150), 1901 (7650), 1901 (767)
V$_2$(CO)$_9$ (**9S**)	2047 (336), 1992 (723), 1990 (635), 1985 (2360), 1936 (620), 1935 (1550), 1895 (362), 1894 (36), 1873 (864)
V$_2$(CO)$_9$ (**9S′**)	2037 (26), 1996 (2000), 1969 (478), 1960 (1000), 1958 (1200), 1953 (1580), 1935 (9), 1929 (61), **1627 (239)**
V$_2$(CO)$_9$ (**9T′**)	2043 (235), 1992 (1280), 1978 (288), 1975 (2480), 1971 (1800), 1950 (572), 1922 (528), 1835 (312), **1668 (328)**
V$_2$(CO)$_8$ (**8S**)	2021 (0), 1988 (2830), 1958 (0), 1956 (604), 1939 (2260), 1931 (0), **1670 (0), 1665 (541)**
V$_2$(CO)$_8$ (**8S′**)	2041 (0), 1985 (1420), 1978 (2710), 1955 (0), 1947 (0), 1946 (1510), **1818 (974), 1812 (0)**
V$_2$(CO)$_8$ (**8S″**)	2059 (0), 1997 (1300), 1980 (2490), 1971 (0), 1951 (0)

there is an energy minimum identical or very close to the structure of the stationary point in question [39]. Therefore, we do not always follow the normal modes corresponding to such low imaginary vibrational frequencies.

3. V$_2$(CO)$_{12}$: the saturated binuclear vanadium carbonyl

Before the discovery [3] of V(CO)$_6$ the stable homoleptic vanadium carbonyl was assumed to be the binuclear V$_2$(CO)$_{12}$ with a vanadium–vanadium single bond leading to 18-electron configurations for both vanadium atoms analogous to the stable Mn$_2$(CO)$_{10}$ and Co$_2$(CO)$_8$. Even after the discovery of the mononuclear V(CO)$_6$ as an isolable compound [3], it was assumed to be in equilibrium with V$_2$(CO)$_{12}$ as follows:

$$2V(CO)_6 \rightleftarrows V_2(CO)_{12} \tag{1}$$

The temperature dependence of the paramagnetism of V(CO)$_6$ solutions was initially interpreted [40] as evidence for the existence of V$_2$(CO)$_{12}$. Later, however, this anomalous magnetic behavior was reinterpreted in terms of the vibronic coupling model of Van Vleck-Kotani and exchange magnetic interaction between two magnetic centers [41].

Our DFT studies [15] on V$_2$(CO)$_{12}$ suggest instability with respect to dissociation into mononuclear V(CO)$_6$ fragments in contrast to the behavior of Mn$_2$(CO)$_{10}$ and Co$_2$(CO)$_8$. The lowest energy structure for V$_2$(CO)$_{12}$ (**12S** in Fig. 1) consists of two V(CO)$_6$ fragments joined by an unusually long V–V bond (3.334 Å) suggesting easy dissociation into mononuclear fragments by breaking this weak metal–metal bond. The weakness of the V–V bond in this V$_2$(CO)$_{12}$ structure is also supported by our calculated heat of dissociation [15] of only 5.7 kcal/mol (BP86) for the dissociation of V$_2$(CO)$_{12}$ into two V(CO)$_6$ fragments.

The stability of V(CO)$_6$, despite only a 17-electron configuration, compared with the instability of V$_2$(CO)$_{12}$ can be related to the favorable octahedral coordination of the vanadium atom. Dimerization of V(CO)$_6$ to give V$_2$(CO)$_{12}$ requires increasing the vanadium coordination

Fig. 1. The structure **12S** predicted for V$_2$(CO)$_{12}$.

number from six to seven by forming a V–V bond, which is an unfavorable process. Also no stable isomers of V$_2$(CO)$_{12}$ with bridging CO groups were found in our studies. A V$_2$(CO)$_{12}$ structure with one or more bridging CO groups requires even higher vanadium coordination numbers since conversion of a terminal CO to a bridging CO adds a new metal–carbon bond. For this reason the species with ν(CO) frequencies at 2050, 2014, and 1852 cm^{-1} formed from cocondensation of vanadium atoms with CO is very unlikely to be a V$_2$(CO)$_{12}$ isomer as suggested more than 30 years ago by Ozin and coworkers [10].

4. V$_2$(CO)$_{11}$: avoidance of a V═V double bond

The 18-electron rule suggests a structure for V$_2$(CO)$_{11}$ with a V═V double bond. Instead the lowest energy structure predicted [15] for V$_2$(CO)$_{11}$ (**11S** in Fig. 2) has a geometry consistent with a V–V single bond and a four-electron donor bridging CO group. Thus the V–V distance in **11S** is 3.376 Å, which is very close to the V–V single bond distance of 3.334 Å in V$_2$(CO)$_{12}$ (**12S**). The four-electron donor CO group in **11S** is indicated by a short V–O distance of 2.299 Å and very low ν(CO) frequency of

Fig. 2. The singlet (**11S**) and triplet (**11T**) isomers of $V_2(CO)_{11}$.

1728 cm^{-1} (Table 1). An analogous $Mn_2(CO)_9$ structure with a Mn–Mn single bond and a four-electron bridging CO group is found to be the global minimum [5]. The metal atoms have the favored 18-electron configurations in these structures.

A triplet isomer for $V_2(CO)_{11}$ (**11T** in Fig. 2) is also found lying 10.6 kcal/mol above the singlet isomer **11S**.[15] This triplet isomer has a V–V distance of 3.000 Å indicating a single bond to give each vanadium atom a 17-electron configuration similar to that in monomeric $V(CO)_6$ and leading to a triplet spin state. Nine of the 11 carbonyl groups in **11T** are terminal CO groups. The remaining two carbonyl groups are semibridging CO groups with V–C distances of 2.030 and 2.410 Å and V–C–O angles deviating significantly from linearity (152.9°).

Conspicuously absent from the isomers of $V_2(CO)_{11}$ found in our DFT studies are structures with V=V double bonds. Thus the vanadium atoms in the singlet structure **11S** attain the favored 18-electron configuration by a four-electron donor bridging CO group rather than a V=V double bond. This energetic preference is a demonstration of the oxophilicity of the early transition metal vanadium. Also the triplet isomer of $V_2(CO)_{11}$ (**11T**), with 17-electron vanadium configurations and a V–V single bond, lies only 10.6 kcal/mol above the **11S** global minimum.

5. $V_2(CO)_{10}$: VV triple bonds and four-electron bridging CO groups

The 18-electron rule suggests a V≡V triple bond in $V_2(CO)_{10}$ in the absence of four-electron donor bridging CO groups. Furthermore, CpCr and $V(CO)_3$ units are isoelectronic and isolobal so that $V_2(CO)_{10}$ corresponds to $Cp_2Cr_2(CO)_4$ (Fig. 3), which was among the first stable metal carbonyl derivatives with a metal–metal triple bond to be synthesized [42].

In view of these considerations it is not surprising that the global minimum for $V_2(CO)_{10}$, namely **10S** (Fig. 4) [15], is such a structure with a V≡V distance of 2.510 Å indicative of a triple bond by comparison with the V–V sin-
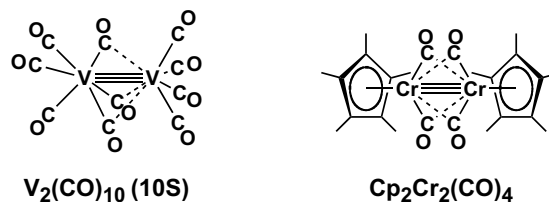
Fig. 3. Analogy between $V_2(CO)_{10}$ and $Cp_2Cr_2(CO)_4$.

gle bond distances of ∼3.3 Å found in the singlets **12S** and **11S**. Structure **10S** has seven terminal CO groups and three semibridging CO groups. The semibridging CO groups in **10S** are similar to those in **11T** with V–C distances of 1.99 and 2.48 Å. Note that the arrangement of the semibridging CO groups in $V_2(CO)_{10}$ (**10S**) is different from that in $Cp_2Cr_2(CO)_4$ (Fig. 3). Thus $V_2(CO)_{10}$ (**10S**) has three semibridging CO groups, all with the "short" M–C bonds to the same vanadium atom leading to a quasioctahedral $V(CO)_6$ building block in this structure, namely the "left" vanadium atom in Fig. 4. However, in $Cp_2Cr_2(CO)_4$ all four CO groups are semibridging CO groups with two "short" Cr–C bonds to each chromium atom (Fig. 3) [42].

Higher energy structures are found for $V_2(CO)_{10}$ containing two four-electron donor bridging CO groups [15]. These structures arise by bonding a bidentate $V(CO)_6$ ligand to a $V(CO)_4$ unit through two four-electron bridging CO groups. This type of bonding is favorable because of the oxophilicity of vanadium. In the singlet structure **10S'** (Fig. 4), which lies 22.0 kcal/mol (BP86) in energy above the global minimum **10S**, each vanadium atom attains the favored 18-electron configuration by forming a V–V single bond as indicated by a distance of 3.296 Å very close to the V–V single bond distances in **12S** (Fig. 1) and **11S** (Fig. 2). In the triplet structure **10T** (Fig. 4), which lies 23.9 kcal/mol above the global minimum **10S**, there is no direct vanadium–vanadium bond as indicated by a non-bonding V⋯V distance of 4.338 Å. The 17-electron configurations for each vanadium atom, required for a triplet spin state, are thereby preserved.
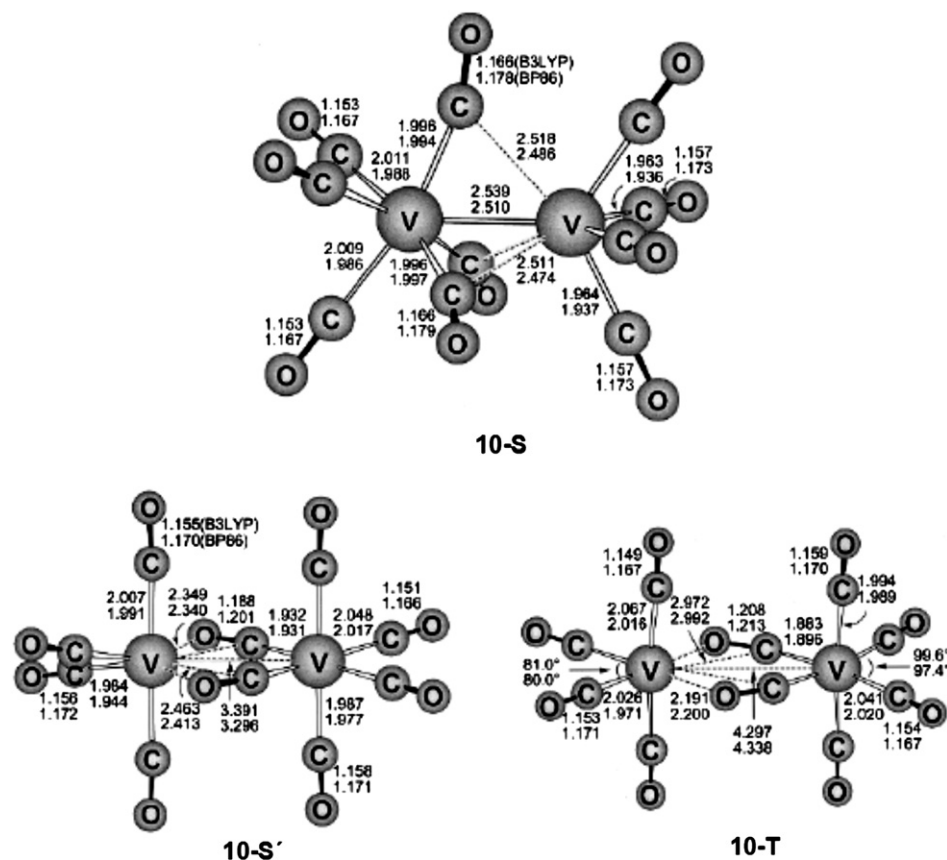
Fig. 4. Isomers of $V_2(CO)_{10}$.

## 6. $V_2(CO)_9$: avoidance of a metal–metal quadruple bond

The highly unsaturated $V_2(CO)_9$ requires a V≡V quadruple bond for each vanadium atom to have the favored 18-electron configuration. However, no low energy isomers were found for $V_2(CO)_9$ in which the vanadium–vanadium distance is short enough to suggest such a quadruple bond even though a total of 25 stationary states were found for $V_2(CO)_9$ suggesting a very complicated potential energy surface [16]. All of the structures found for $V_2(CO)_9$ instead have less than 18-electron configurations for at least one of the vanadium atoms. Four-electron donor bridging CO groups are also observed in some cases.

The lowest energy structures for $V_2(CO)_9$ all have V≡V distances around 2.5 Å suggesting metal–metal triple bonds and three semibridging CO groups. The global minimum for $V_2(CO)_9$ is the triplet **9T** (Fig. 5) with a structure similar to the singlet global minimum **10S** (Fig. 4) of $V_2(CO)_{10}$ except for one less carbonyl group (on the "right" vanadium atom in Figs. 4 and 5). The V≡V distance of 2.482 Å in **9T** is very similar to the V≡V distance of 2.510 Å in **10S** suggesting a similar metal–metal triple bond corresponding to 17-electron configurations for both vanadium atoms in accord with the triplet state.

Closely related low-lying singlet structures are also found for $V_2(CO)_9$. The lowest lying such structure **9S**,

which lies only 1.7 kcal/mol (BP86) above **9T**, has a similar arrangement of three semibridging CO groups and a similar V≡V distance of 2.447 Å, again suggesting a metal–metal triple bond [16]. In this case one of the metal atoms must have an 18-electron configuration and the other metal atom a 16-electron configuration. Structure **9S** (Fig. 5) may be derived from the $V_2(CO)_{10}$ global minimum **10S** by loss of the "top" CO group from the "right" vanadium atom. Thus in **9S** the "left" vanadium atom can be considered to have an 18-electron configuration, but the "right" vanadium atom has only a 16-electron configuration.

Both singlet and triplet structures with four-electron bridging CO groups were also found for $V_2(CO)_9$, namely **9S′** and **9T′** at 3.8 and 7.1 kcal/mol above **9T**, respectively [16]. The V–V distance in the singlet isomer **9S′** is 2.981 Å suggesting a V–V single bond and 16-electron configurations for both metal atoms. In the triplet isomer **9T′** the V=V distance of 2.841 Å is about 0.14 Å shorter than in **9S′** suggesting a double bond and the 17-electron configurations for both vanadium atoms required for a triplet. The four-electron bridging CO groups in **9S′** and **9T′** exhibit unusually short V–O distances of 2.165 and 2.186 Å as well as the expected unusually low $\nu(CO)$ frequencies of 1627 and 1668 cm^{-1}, respectively (Table 1).
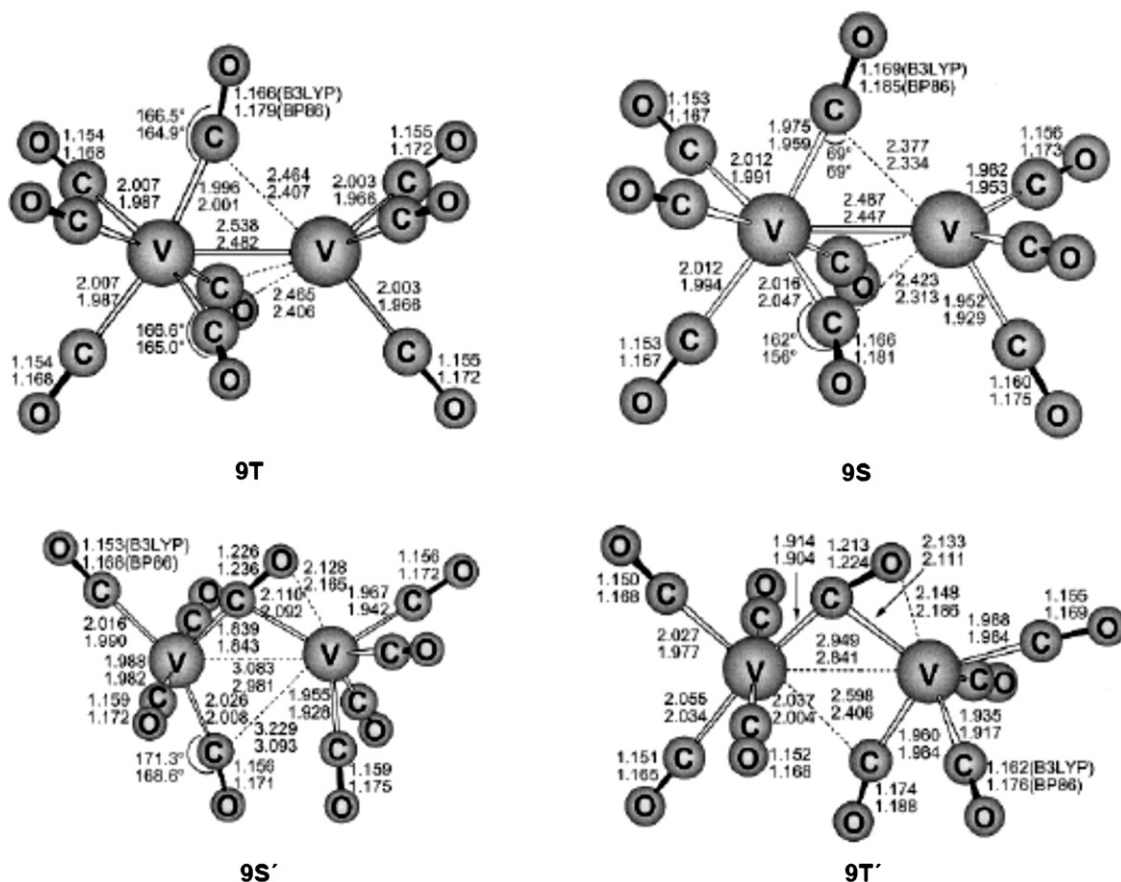
Fig. 5. Low energy structures for $V_2(CO)_9$.

7. $V_2(CO)_8$: a metal–metal quintuple bond?

The highly unsaturated $V_2(CO)_8$ requires a metal–metal bond order of five for both metal atoms to have the favored 18-electron configuration. The vanadium–vanadium distances in the two lowest lying isomers found for $V_2(CO)_8$ are inconsistent with such a high metal–metal bond order [17].

The global minimum for $V_2(CO)_8$ (8S in Fig. 6) is best formulated with a V–V single bond and two four-electron bridging CO groups. Thus the V–V single bond is suggested by the 2.858 Å metal–metal distance and the four-electron bridging CO groups are suggested by the low $\nu(CO)$ frequencies at 1665 and 1670 cm^{-1} (Table 1). Structure 8S is to be contrasted with structure 8S′ of $V_2(CO)_8$ with a V≡V triple bond indicated by the much shorter metal–metal distance of 2.460 Å and the more normal bridging $\nu(CO)$ frequencies at 1812 and 1818 cm^{-1}. In both cases the metal atoms are seen to have only 16-electron configurations rather than the normally favored 18-electron configurations. Structure 8S′ with the V≡V triple bond and two-electron bridging CO groups lies 12.5 kcal/mol above structure 8S with a V–V single bond and two four-electron bridging CO groups. This appears to reflect the gain in energy in forming the two metal–oxygen bonds to the four-electron bridging

CO groups by the oxophilic early transition metal vanadium as compared with a metal–metal triple bond versus a metal–metal single bond.

A third structure 8S″ (Fig. 6) is also found for $V_2(CO)_8$ at 10.5 kcal/mol above the global minimum 8S [17]. Structure 8S″ has no bridging CO groups but simply consists of two V(CO)$_4$ units linked by a very short vanadium–vanadium bond. The 1.967 Å vanadium–vanadium bond distance in 8S″ is ∼0.5 Å shorter than the ∼2.5 Å V≡V bond distances found in the triply bonded derivatives 10S, 9T, and 9S suggesting a V≡V quintuple bond. The five orbitals required for the σ, 2π, and 2δ components of this V≡V quintuple bond plus the four additional orbitals required for the σ bonds to each of the four CO groups of a V(CO)$_4$ unit use all nine orbitals of the sp^{3}d^5 vanadium manifolds leaving no metal orbitals available for π^* backbonding to the CO groups. However, the normal $\nu(CO)$ frequencies for the CO groups in 8S″ are similar to the terminal $\nu(CO)$ frequencies of other homoleptic metal carbonyl derivatives [17] suggesting that such π^* backbonding must occur in 8S″. The electrons for this backbonding to the CO groups must come from the V≡V quintuple bond, probably the electrons in the weakly bonding δ components, thereby lowering the effective vanadium–vanadium bond order. This is consistent with the fact that the V≡V distance of 1.967 Å in isomer 8S″ of $V_2(CO)_8$ is 0.14 Å
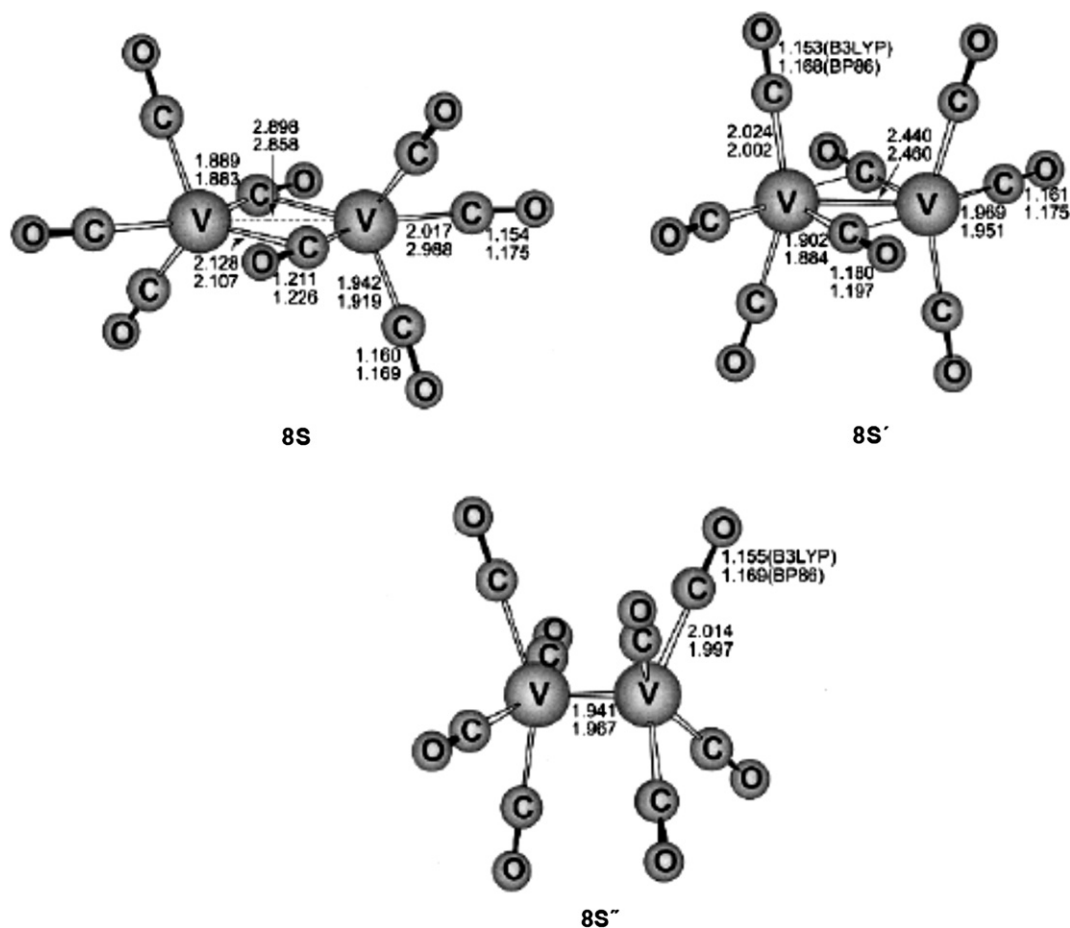
Fig. 6. Structures of $V_2(CO)_8$.

longer than the Cr≡Cr distance of 1.835 Å in the chromium(I) alkyl [11] RCr≡CrR.

It is instructive to compare the high order vanadium–vanadium bond in isomer **8S″** of $V_2(CO)_8$ with the high order iron–iron bond linking the two $Fe(CO)_3$ units in $Fe_2(CO)_6$ without any bridging CO groups, a species found in a DFT search for new unsaturated homoleptic binuclear iron carbonyls [6]. In $Fe_2(CO)_6$ an iron–iron quadruple bond is required to give both iron atoms the favored 18-electron configuration. Formation of an iron–iron quadruple bond and Fe–C σ bonds to the three CO groups on each iron uses only seven of the nine orbitals in the iron sp^3d^5 manifolds leaving two electron pairs on each iron atom available for π^* backbonding to the CO groups. However, a detailed analysis [43] of the molecular orbitals in $Fe_2(CO)_6$ shows that these electron pairs are not nonbonding. Thus the σ^* and δ^* orbitals of this iron–iron multiple bond are occupied by these electron pairs leaving only an effective Fe=Fe double bond with two orthogonal π components. This 2π Fe=Fe double bond is suggested to be shorter than a normal $\sigma + \pi$ double bond because of the absence of the σ component.

The mechanisms for reduction of the effective metal–metal bond order is seen to be quite different in $Fe_2(CO)_6$ and $V_2(CO)_8$ (**8S″** in Fig. 6). In $Fe_2(CO)_6$ otherwise non-

bonding electron pairs move into two of the metal–metal antibonding orbitals thereby neutralizing the σ and δ components of the iron–iron quadruple bond and thus leaving only two π components for the iron–iron bonding corresponding to an Fe=Fe double bond. This secondary bonding in $Fe_2(CO)_6$ reduces the effective metal–metal bond order by addition of electrons to metal–metal antibonding orbitals. However, in $V_2(CO)_8$ (**8S″**) electron density moves out of metal–metal bonding orbitals for π^* backbonding to the CO groups thereby also lowering the order of the vanadium–vanadium bond. This secondary bonding in $V_2(CO)_8$ (**8S″**) reduces the effective metal–metal bond order by removal of electrons from metal–metal bonding orbitals.

8. Summary

Octahedral or nearly octahedral $V(CO)_6$ units, similar to the known monomeric $V(CO)_6$, appear to be fundamental building blocks in the lowest energy structures of the homoleptic binuclear vanadium carbonyls $V_2(CO)_n$ ($n = 12, 11, 10$, and 9). A $V(CO)_6$ unit often links to a second $V(CO)_n$ unit to form the binuclear vanadium carbonyl through one or two four-electron donor CO groups as a consequence of the oxophilicity of vanadium. Single and triple vanadium–vanadium bonds are favored but double

and quadruple vanadium–vanadium bonds are avoided. Thus the global minimum of $V_2(CO)_{11}$ (**11S** in Fig. 2) has a $V(CO)_6$ unit linked to a $V(CO)_5$ unit through a single four-electron bridging CO group so that only a V–V single bond is required to give both vanadium atoms the favored 18-electron configuration. For $V_2(CO)_{10}$ favorable structures (Fig. 3) have such a $V(CO)_6$ unit is linked to a $V(CO)_4$ unit either through a V≡V triple bond (**10S**) or through two four-electron donor bridging CO groups and a V–V single bond for the singlet **10S′** or no V···V bond for the triplet **10T**. Among the many structures found for $V_2(CO)_9$ the lowest energy structures (Fig. 5) include both triplet and singlet structures with a $V(CO)_6$ unit linked to a $V(CO)_3$ unit through a V≡V triple bond. Structures for $V_2(CO)_9$ with a four-electron donor bridging CO group are also found (**9S′** and **9T′** in Fig. 5). However, structures of $V_2(CO)_9$ with a V≡V quadruple bond are not found.

Removal of a carbonyl group from $V_2(CO)_9$ gives $V_2(CO)_8$, which is so highly unsaturated that the vanadium atoms typically have 16- rather than 18-electron configurations. Structures of $V_2(CO)_8$ with a V–V single bond and two four-electron bridging CO groups (**8S** in Fig. 6) and with a V≡V triple bond and two two-electron bridging CO groups (**8S′** in Fig. 6) are found with the latter being of lower energy. An interesting structure for $V_2(CO)_8$ (**8S″** in Fig. 6) is found consisting of two $V(CO)_4$ linked only by a vanadium–vanadium bond, which is short enough to be the quintuple bond required by the 18-electron rule.

References

[1] C.M. Lukehart, Fundamental Transition Metal Organometallic Chemistry, Brooks-Cole/Wadsworth, Belmont, CA, 1985 (Chapters 1 and 2).

[2] R.H. Crabtree, The Organometallic Chemistry of the Transition Metals, second ed., Wiley, New York, 1994.

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

[4] Cr: R.B. King, Y. Xie, H.F. Schaefer, N. Richardson, S. Li, Inorg. Chim. Acta 358 (2005) 1442.

[5] Mn: Y. Xie, J.H. Jang, R.B. King, H.F. Schaefer, Inorg. Chem. 42 (2003) 5219.

[6] Fe: Y. Xie, H.F. Schaefer, R.B. King, J. Am. Chem. Soc. 122 (2000) 8746.

[7] Co: J.P. Kenny, R.B. King, H.F. Schaefer III, Inorg. Chem. 40 (2001) 900.

[8] Ni: I.S. Ignatyev, H.F. Schaefer, R.B. King III, J. Am. Chem. Soc. 122 (2000) 1989.

[9] Fe, Co, Ni overview: H.F. Schaefer III, R.B. King, Pure Appl. Chem. 73 (2001) 1059.

[10] T.A. Ford, H. Huber, W. Klotzbücher, M. Moskovits, G.A. Ozin, Inorg. Chem 15 (1976) 1666.

[11] T. Nguyen, A.D. Sutton, M. Brynda, J.C. Fettinger, G.J. Long, P.P. Power, Science 310 (2005) 844.

[12] J.D. Zeinstra, J.L. De Boer, J. Organomet. Chem 54 (1973) 207.

[13] U. Thewalt, T. Woehrle, J. Organomet. Chem. 464 (1994) C17.

[14] G.G. Tairova, O.N. Krasochka, V.I. Ponomarev, E.F. Kvashina, Yu.A. Shvetsov, E.M. Lisetskii, D.P. Kiryukhin, L.O. Atovmyan, Yu.G. Borod'ko, Transition Met. Chem. 7 (1982) 189.

[15] $V_2(CO)_{12}$, $V_2(CO)_{11}$, $V_2(CO)_{10}$: Z. Liu, Q.S. Li, Y. Xie, R.B. King, H.F. Schaefer, Inorg. Chem. 46 (2007) 1803.

[16] $V_2(CO)_9$: Q.S. Li, Z. Liu, Y. Xie, R.B. King, H.F. Schaefer, J. Phys. Chem. A 109 (2005) 11064.

[17] $V_2(CO)_8$: Q.S. Li, Z. Liu, Y. Xie, H.F. Schaefer, R.B. King, Mol. Phys. 104 (2006) 763.

[18] T.H. Dunning, J. Chem. Phys. 53 (1970) 2823.

[19] S. Huzinaga, J. Chem. Phys. 42 (1965) 1293.

[20] A.J.H. Wachters, J. Chem. Phys. 52 (1970) 1033.

[21] D.M. Hood, R.M. Pitzer, H.F. Schaefer, J. Chem. Phys. 71 (1979) 705.

[22] A.W. Ehlers, G. Frenking, J. Am. Chem. Soc. 116 (1994) 1514.

[23] B. Delley, M. Wrinn, H.P. Lüthi, J. Chem. Phys. 100 (1994) 5785.

[24] J. Li, G. Schreckenbach, T. Ziegler, J. Am. Chem. Soc. 117 (1995) 486.

[25] V. Jonas, W. Thiel, J. Chem. Phys. 102 (1995) 8474.

[26] T.A. Barckholtz, B.E. Bursten, J. Am. Chem. Soc. 120 (1998) 1926.

[27] S. Niu, M.B. Hall, Chem. Rev. 100 (2000) 353.

[28] P. Macchi, A. Sironi, Coord. Chem. Rev. 238 (2003) 383.

[29] J.-L. Carreon, J.N. Harvey, Phys. Chem. Chem. Phys 8 (2006) 93.

[30] M. Bühl, H. Kabrede, J. Chem. Theory Comput. 2 (2006) 1282.

[31] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.

[32] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.

[33] A.D. Becke, Phys. Rev. A 38 (1988) 3098.

[34] J.P. Perdew, Phys. Rev. B 33 (1986) 8822.

[35] See especially F. Furche, J.P. Perdew, J. Chem. Phys. 124 (2006) 044103.

[36] H.Y. Wang, Y. Xie, R.B. King, H.F. Schaefer, J. Am. Chem. Soc. 127 (2005) 11646.

[37] H.Y. Wang, Y. Xie, R.B. King, H.F. Schaefer, J. Am. Chem. Soc. 128 (2006) 11376.

[38] GAUSSIAN 94, Revision B.3, Gaussian Inc., Pittsburgh, PA, 1995 (see Supporting Information for details).

[39] B.N. Papas, H.F. Schaefer, J. Mol. Struct. THEOCHEM 768 (2006) 175.

[40] H.J. Keller, P. Laubereau, D. Nöthe, Z. Naturforsch. 24B (1969) 257.

[41] J.C. Bernier, O. Kahn, Chem. Phys. Lett. 19 (1973) 414.

[42] M.D. Curtis, W.M. Butler, J. Organomet.Chem. 155 (1978) 131.

[43] E.D. Jemmis, B. Pathak, R.B. King, H.F. Schaefer, Chem. Commun. (2006) 2164.