DOI: 10.1002/ejic.200601172

The Binuclear Cyclopentadienylvanadium Carbonyls $(\eta^5\text{-}C_5H_5)_2V_2(CO)_7$ and $(\eta^5\text{-}C_5H_5)_2V_2(CO)_6$: Comparison with Homoleptic Chromium Carbonyls

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Keywords: Binuclear cyclopentadienylvanadium carbonyls / Density functional theory

The cyclopentadienylvanadium carbonyls $CpV(CO)_n$ (n = 4, 3, 2, 1), $Cp_2V_2(CO)_7$, and $Cp_2V_2(CO)_6$ have been studied by density functional theory using the B3LYP and BP86 functionals. The optimized structure of $CpV(CO)_4$ is close to that found experimentally by X-ray and electron diffraction methods. For the coordinately unsaturated $CpV(CO)_n$ (n = 3, 2, 1) the computed ν(CO) frequencies by BP86 are related to those found in low-temperature matrix isolation experiments but show some significant differences for n = 3 and 2 in band spacings suggesting some matrix effects on the geometries. An optimized structure for $Cp_2V_2(CO)_7$ is found with one symmetrical bridging carbonyl group and a V–V distance of 3.306 Å (BP86) suggesting a single bond. Energetically competitive structures for $Cp_2V_2(CO)_6$ include a doubly symmetrically bridged singlet structure with only two-electron donor carbonyl groups, a triplet doubly semibridged structure, and a singlet structure with one four-electron donor bridging carbonyl group. Thermodynamic considerations rationalize why neither $Cp_2V_2(CO)_7$ nor $Cp_2V_2(CO)_6$ have yet been synthesized. Thus $Cp_2V_2(CO)_7$ is predicted to be unstable with respect to dissociation into $CpV(CO)_4$ + $CpV(CO)_3$. Furthermore, the dissociation energy of the lowest lying singlet isomer from $Cp_2V_2(CO)_6$ to $Cp_2V_2(CO)_5$ is only 10.8 kcal/mol (BP86) consistent with the formation of $Cp_2V_2(CO)_5$ rather than $Cp_2V_2(CO)_6$ upon decomposition of the presumed $CpV(CO)_3H_2$ dihydride generated by acidification of the dianion $CpV(CO)_3^{2-}$.

1. Introduction

Cyclopentadienylvanadium tetracarbonyl, $CpV(CO)_4$ ($Cp = \eta^5\text{-}C_5H_5$), which was originally synthesized in 1958 by E. O. Fischer,[1] can be regarded as an analogue of the long known $Fe(CO)_5$ or $Cr(CO)_6$ or the unknown $Ti(CO)_7$ depending on whether the $\eta^5\text{-}C_5H_5$ ring replaces one, two, or three carbonyl groups, respectively, in the corresponding homoleptic metal carbonyl. Photolysis of $Fe(CO)_5$ has been known[2] since 1927 to give $Fe_2(CO)_9$ (Figure 1), with the formal Fe–Fe single bond required to give each iron atom the favored 18-electron configuration.[3] However, no evidence has been found for any binuclear $Cr_2(CO)_n$ derivatives from the photolysis or thermolysis of $Cr(CO)_6$ including $Cr_2(CO)_{11}$ with a Cr–Cr single bond required to give each chromium atom the favored 18-electron configuration. This latter observation has been rationalized by our theoretical studies indicating even the lowest energy isomer of $Cr_2(CO)_{11}$ to be thermodynamically unstable with respect to mononuclear $Cr(CO)_6$ and $Cr(CO)_5$ fragments.[4] By comparison, laboratory photolysis of $CpV(CO)_4$ goes directly to $Cp_2V_2(CO)_5$ with the formal V≡V triple bond required to give both vanadium atoms the favored 18-electron configuration[5–8] (Figure 1) without any evidence for $Cp_2V_2(CO)_7$ and $Cp_2V_2(CO)_6$ intermediates expected to have formal V–V single and V = V double bonds, respectively, by the 18-electron rule.[3] We now present computational studies on these intermediate $Cp_2V_2(CO)_7$ and $Cp_2V_2(CO)_6$ molcules in order to predict structures and to understand why they have not been found in the photolysis of $CpV(CO)_4$ or other reactions of cyclopentadienylvanadium carbonyl derivatives.

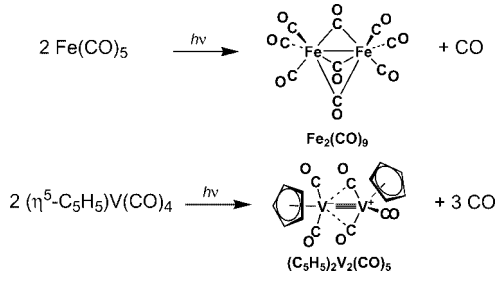

Figure 1. A comparison of the photolyses of $Fe(CO)_5$ and $CpV(CO)_4$.

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2. Theoretical Methods

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.[9–17] Two DFT methods were used in this study. The first functional is the hybrid 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.[18,19] The other DFT method used in this paper is BP86, which combines Becke's 1988 exchange functional (B) with Perdew's 1986 gradient corrected correlation functional method (P86).[20,21] 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.[22–24]

All calculations were performed using the double-ζ plus polarization (DZP) basis sets. The DZP basis sets used for carbon and oxygen add one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(C) = 0.75$ and $\alpha_d(O) = 0.85$ to the standard Huzinaga-Dunning contracted DZ sets[25,26] and are designated (9s5p1d/4s2p1d). For hydrogen, a set of p polarization functions $\alpha_p(H) = 0.75$ was added to the Huzinaga-Dunning DZ set. The loosely contracted DZP basis set for vanadium is the Wachters primitive set[27] augmented by two sets of p functions and a set of d functions, contracted following Hood, Pitzer and Schaefer,[28] designated (14s11p6d/10s8p3d).

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. All of the computations were carried out with the Gaussian 03 program,[29] exercising the fine grid option (75 radial shells, 302 angular points) for evaluating integrals numerically, while the tight (10^{-8} hartree) designation is the default for the self-consistent field (SCF) convergence.

The low-magnitude imaginary vibrational frequencies are suspect because of significant limitations in the numerical integration procedures used in the DFT computations. Ziegler et al.[30] have suggested that all imaginary vibrational frequencies with magnitudes less than 100 cm^{-1} may be suspect, owing to the possibility of numerical errors arising from the use of standard integration grids. Therefore, we do not always follow such low imaginary vibrational frequencies unless they appear to be chemically meaningful.

3. Results

3.1 Mononuclear Cyclopentadienylvanadium Carbonyl Derivatives

Figure 2 and Table 1 depict and describe the optimized structures for $CpV(CO)_n$ (n = 4, 3, 2, 1). Among these compounds $CpV(CO)_4$ is a stable 18-electron metal complex[1] whereas the coordinately unsaturated derivatives $CpV(CO)_n$ (n = 3, 2, 1) have been generated by the photolysis of $CpV(CO)_4$ in frozen gas matrices (argon, methane) at 12 K.[31]

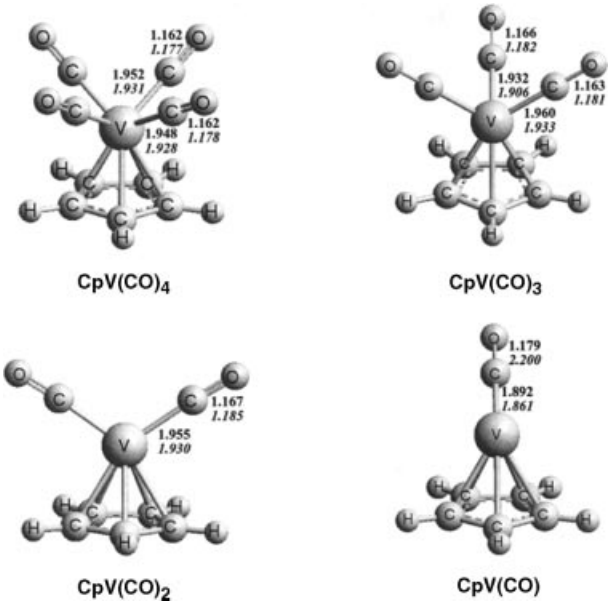

Figure 2. The optimized structures of $CpV(CO)_n$ (n = 4, 3, 2, 1).

The optimized structure for $CpV(CO)_4$ is close to those found experimentally by X-ray[32] and electron diffraction[33] for crystalline and gas-phase $CpV(CO)_4$, respectively, with the latter perhaps being more accurate since the X-ray diffraction study is a rather old one predating automatic diffractometers. Thus the theoretical V–CO and C–O distances from our DFT studies are 1.948/1.952 Å (B3LYP) or 1.928/1.931 Å (BP86) and 1.162 Å (B3LYP) or 1.178 Å (BP86), respectively. This compares with 1.88/1.94 Å and 1.18/1.12 Å found by X-ray diffraction and 1.963 Å and 1.135 Å found by electron diffraction.

Table 1. The total energies (E, Hartree) for $CpV(CO)_n$ (n = 4, 3, 2, 1). The number of imaginary vibrational frequencies (Nimg) for each structure is also listed.

Singlet		$CpV(CO)_4$ (C_s)	$CpV(CO)_3$ (C_s)	$CpV(CO)_2$ (C_s)	CpV(CO) (C_s)
B3LYP	E	–1591.065026	–1477.674671	–1364.278723	–1250.877952
	Nimg	1 (15i)[a]	0	0	0
BP86	E	–1591.244927	–1477.841138	–1364.430801	–1251.019000
	Nimg	1 (17i)[a]	0	0	0

[a] These imaginary frequencies were reduced to 0i (B3LYP) or 2i (BP86) by using the larger (120, 974) integration grid.

Table 2. Infrared-active ν(CO) vibrational frequencies (cm^{-1}) predicted for the mono-nuclear molecules: $CpV(CO)_n$ (n = 4, 3, 2, 1) (infrared intensities in parentheses are given in km/mol).

	B3LYP	BP86	Experimental[a]
$CpV(CO)_4$	2008 (1539), 2008 (1544), 2019 (7), 2085 (624)	1928 (1290), 1928 (1293), 1934 (4),[b] 2004 (497)	1931, 1952,[b] 2030
$CpV(CO)_3$	1983 (714), 1985 (1701), 2062 (718)	1892 (1406), 1896 (536), 1967 (581)	1857, 1887, 1953
$CpV(CO)_2$	1954 (1964), 2028 (741)	1854 (1634), 1924 (561)	1894, 1992
CpV(CO)	1929 (1370)	1823 (1039)	1830

[a] Data taken from the literature (R. B. Hitam, A. J. Rest, *Organometallics* **1989**, *8*, 1598) for the ν(CO) frequencies in methane matrices at 12 K averaging out reported matrix splitting. [b] The infrared "inactive" b_1 ν(CO) frequency for $CpV(CO)_4$.

The infrared ν(CO) frequencies computed for $CpV(CO)_n$ (n = 4, 3, 2, 1) are listed in Table 2 along with the experimental ν(CO) frequencies reported in methane matrices.[31]

The BP86 calculated frequencies for $CpV(CO)_4$ and CpV(CO) agree very well with the experimental frequencies. However, there are significant differences between the ν(CO) frequencies calculated by the usually more reliable BP86 method and those found in matrices for $CpV(CO)_3$ and $CpV(CO)_2$. In particular, although the positions of the calculated ν(CO) frequencies are reasonably close to those found experimentally, the calculated frequency separations are significantly different from those found experimentally. Thus for $CpV(CO)_2$ the two theoretical ν(CO) frequencies (Table 2) are separated by 74 cm^{-1} (B3LYP) or 70 cm^{-1} (BP86), whereas the experimental ν(CO) frequencies assigned to the matrix studies are separated by 98 cm^{-1}. The nature of the matrix experiments may be responsible for this discrepancy since the initial geometries generated by loss of a CO ligand may not fully relax to the optimized geometries at the low temperatures involved.

3.2 The Binuclear Derivatives $Cp_2V_2(CO)_n$ (n = 7, 6)

3.2.1 $Cp_2V_2(CO)_7$

Only one optimized structure was found for $Cp_2V_2(CO)_7$ with a V–V distance short enough to imply any significant interaction between the $CpV(CO)_4$ and $CpV(CO)_3$ fragments. This structure (**7S-1** in Figure 3 and Table 3) has C_2 symmetry with one symmetrical bridging CO group and six terminal CO groups. The bridging CO group has V–C distances of 2.214 Å (B3LYP) or 2.185 Å (BP86) and leads to a predicted ν(CO) frequency (Table 4) of 1759 cm^{-1} (BP86). The V–C distances to the terminal CO groups are in the range 1.933–1.988 Å (B3LYP) or 1.918–1.972 Å (BP86). The V–V distance of 3.382 Å (B3LYP) or 3.306 Å (BP86) is in agreement with the single bond required to give both vanadium atoms the favored 18-electron configuration.

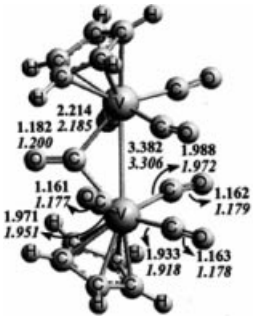

Figure 3. Optimized structure of $Cp_2V_2(CO)_7$ (**7S-1**).

Table 3. The total energy (E, Hartree), number of imaginary vibrational frequencies, (Nimg), and V–V distances for $Cp_2V_2(CO)_7$ (**7S-1**) by B3LYP and BP86.

Singlet		$Cp_2V_2(CO)_7$ (C_2) (**7S-1**)
B3LYP	E	–3068.725630
	V–V	3.382 Å
	Nimg	1 (19i)
BP86	E	–3069.086435
	V–V	3.306 Å
	Nimg	1 (18i)

This structure for $Cp_2V_2(CO)_7$ exhibits a very small imaginary vibrational frequency at 19i cm^{-1} (B3LYP) or 18i cm^{-1} (BP86). Following the corresponding normal mode causes $Cp_2V_2(CO)_7$ to dissociate into $CpV(CO)_4$ + $CpV(CO)_3$ fragments with an energy minimum at a clearly non-bonding vanadium-vanadium distance of 5.307 Å (B3LYP) or 5.283 Å (BP86). In addition, energy calculations indicate that the dissociation [Equation (1)]

$$Cp_2V_2(CO)_7 \rightarrow CpV(CO)_4 + CpV(CO)_3 \quad (1)$$

is either exothermic by 8.8 kcal/mol (B3LYP) or only very slightly endothermic by 0.2 kcal/mol (BP86). All of these observations indicate that $Cp_2V_2(CO)_7$ is unstable with respect to dissociation into $CpV(CO)_4$ + $CpV(CO)_3$ [Equation (1)] and thus unlikely to be prepared as an isolable molecule.

3.2.2 $Cp_2V_2(CO)_6$

Five low-lying stationary points are found for $Cp_2V_2(CO)_6$ (Figure 4 and Table 4 and Table 5). The B3LYP and BP86 methods disagree with respect to the relative energies of these isomers as well as key features of the optimized lowest energy triplet structure **6T-1**.

The global minimum for $Cp_2V_2(CO)_6$ using the BP86 method is a C_{2v} singlet **6S-1** (Figure 4) with two symmetrical bridging carbonyl groups having equal V–C distances of

Table 4. Infrared active ν(CO) vibrational frequencies (cm^{-1}) predicted for $Cp_2V_2(CO)_7$ (**7S-1**) and the $Cp_2V_2(CO)_6$ isomers [infrared intensities in parentheses are in km/mol; bridging ν(CO) frequencies are printed in **bold**].

	B3LYP	BP86
7S-1	**1847** (**495**), 1982 (68), 1992 (439),	**1759** (**405**), 1896 (97), 1907 (431),
(C_2)	2006 (48), 2006 (987), 2027 (2172), 2074 (664)	1922 (121), 1923 (733), 1945 (1726), 1988 (577)
6S-1	**1780** (**755**), **1833** (**283**), 2008 (0),	**1733** (**587**), **1767** (**221**), 1922 (0),
(C_{2v})	2013 (758), 2025 (1531), 2076 (1206)	1934 (555), 1939 (1249), 1987 (995)
6T-1	1929 (802), 1944 (671), 1988 (627),	**1799** (**609**), **1810** (**311**), 1915 (1),
(C_2)	2001 (8), 2025 (1556), 2072 (1087)	1915 (885), 1934 (1127), 1982 (1091)
6T-2	**1791** (**756**), **1836** (**284**), 2000 (1604),	**1778** (**629**), **1798** (**226**), 1907 (0),
(C_{2v})	2019 (0), 2021 (1486), 2071 (1346)	1920 (654), 1935 (1095), 1978 (1142)
6S-2	**1731** (**446**), 1970 (166), 1989 (1297),	**1678** (**353**), 1880 (97), 1902 (1081),
(C_1)	2015 (827), 2031 (879), 2086 (489)	1925 (307), 1931 (1205), 1985 (434)
6S-3	1958 (123), 1976 (200), 2002 (580),	1871 (7),1893 (28), 1909 (404),
(C_s)	2011 (888), 2015 (2108), 2070 (853)	1918 (1814), 1923 (926), 1978 (806)

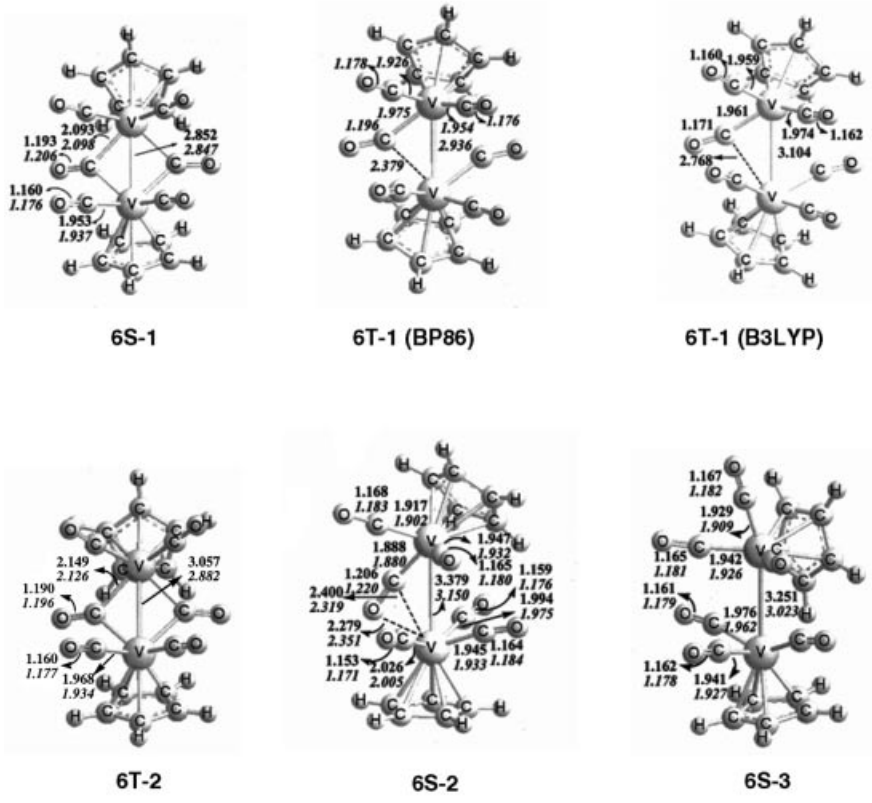

Figure 4. The stationary points of $Cp_2V_2(CO)_6$ showing the different structures for **6T-1** by BP86 and B3LYP.

Table 5. The total energies (*E*, hartree), relative energies (Δ*E*, kcal/mol), number of imaginary vibrational frequencies (Nimg), and V–V distances for the $Cp_2V_2(CO)_6$ stationary states.

Singlet		**6S-1** (C_{2v})	**6T-1** (C_2)	**6T-2** (C_{2v})	**6S-2** (C_1)	**6S-3** (C_s)
B3LYP	*E*	–2955.369144	–2955.380720	–2955.361110	–2955.374370	–2955.359829
	Δ*E*	7.3	0.0	12.3	4.0	13.1
	Nimg	0	0	3 (304*i*, 8*i*, 6*i*)	0	0
	V–V	2.852	3.104	3.057	3.379	3.251
BP86	*E*	–2955.732464	–2955.728933	–2955.724138	–2955.722935	–2955.709504
	Δ*E*	0.0	2.2	5.2	6.0	14.4
	Nimg	0	0	1 (371*i*)	0	0
	V–V	2.847	2.936	2.882	3.150	3.023

2.093 Å (B3LYP) or 2.098 Å (BP86) and exhibiting ν(CO) frequencies in the normal range for such bridging carbonyl groups, namely 1767 and 1733 cm^{-1} (BP86, Table 4). For the four terminal carbonyls in **6S-1**, the V–C distances are 1.953 Å (B3LYP) or 1.937 Å (BP86). The V–V distance in **6S-1** is 2.852 Å (B3LYP) or 2.847 Å (BP86), which is the shortest vanadium-vanadium distance found in any of the $Cp_2V_2(CO)_6$ isomers and consistent with the V=V double bond required to give each vanadium atom in $Cp_2V_2(CO)_6$ the favored 18-electron configuration[3] when all of the CO groups are the usual two-electron donors. The dissociation energy of $Cp_2V_2(CO)_6$ (**6S-1**) to 2 $CpV(CO)_3$ is 31.5 kcal/mol (BP86) indicating that $Cp_2V_2(CO)_6$, unlike $Cp_2V_2(CO)_7$, is stable with respect to dissociation.

The two methods disagree on the structure of the lowest lying triplet **6T-1** of $Cp_2V_2(CO)_6$ (Figure 4). The BP86 method predicts **6T-1** to be a structure with two semibridging CO groups having V–C distances of 1.975 Å and 2.379 Å and exhibiting ν(CO) frequencies in the usual bridging range at 1799 and 1810 cm.$^{-1}$ (Table 4). The V–V bond length of 2.936 Å in **6T-1** can be interpreted as a single bond somewhat shortened by the presence of the two semibridging CO groups thereby giving both metal atoms the 17-electron configurations expected for a binuclear triplet. Using the B3LYP method gives a significantly different structure for **6T-1** with two much more unsymmetrical semibridging CO groups having V–C distances of 1.961 Å and 2.768 Å. The latter V–C distance indicates very weak interactions so that these highly unsymmetrical bridging CO groups are essentially undistinguishable from terminal CO groups consistent with their V–C–O angles close to 180°. Thus these two semibridging CO groups give ν(CO) frequencies in the terminal CO range. The V–V distance of 3.104 Å in **6T-1** found by B3LYP is nearly 0.2 Å longer than that found by BP86. This can be rationalized by the fact that the semibridging CO groups in **6T-1** found by B3LYP are so highly unsymmetrical that they function effectively as terminal CO groups and thus do not shorten the V–V distance. By either method isomer **6T-1** for $Cp_2V_2(CO)_6$ is found to have relatively little spin contamination ($<S^2>$ = 2.05 and 2.01 for B3LYP and BP86, respectively).

A triplet stationary point for $Cp_2V_2(CO)_6$ similar to **6S-1** is **6T-2**, which lies 12.3 kcal/mol above **6T-1** (B3LYP) or 5.2 kcal/mol above **6S-1** (BP86). The apparent spin contamination in **6T-2** is quite small ($<S^2>$ = 2.07 and 2.02 for B3LYP and BP86, respectively). Structure **6T-2** has one substantial imaginary vibrational frequency, namely, 304*i* cm^{-1} (B3LYP) or 371*i* cm^{-1} (BP86). Following the corresponding normal mode leads to structure **6T-1**. For the bridging carbonyls, the V–C distances in **6T-2** are 2.149 Å (B3LYP) or 2.126 Å (BP86) and their ν(CO) frequencies are the normal values of 1798 and 1778 cm^{-1}. The V–C distances to the terminal carbonyls are 1.968 Å (B3LYP) or 1.934 Å (BP86). The V–V distance in **6T-2** is 3.057 Å (B3LYP) or 2.882 Å (BP86) consistent with the single bond required to give each vanadium the 17-electron configuration for a binuclear triplet with only two-electron donor CO groups.

The next singlet structure **6S-2** for $Cp_2V_2(CO)_6$ lies 6.0 kcal/mol above **6S-1** (BP86) or 4.0 kcal/mol above **6T-1** (B3LYP). This structure has one semibridging CO group with V–C distances of 1.888 Å (B3LYP) or 1.880 Å (BP86) and 2.400 Å (B3LYP) or 2.319 Å (BP86). The V–C–O bond angle is almost linear. One of these semibridging CO group has a relatively short V–O distance of 2.279 Å (B3LYP) or 2.351 Å (BP86) indicating that it is a η^2-μ-CO group donating four electrons using both a σ-bond and a π-bond. This four-electron donor CO group is responsible for the very low bridging ν(CO) frequency of 1678 cm^{-1} (Table 4). The V–V distance in **6S-2** is 3.379 Å (B3LYP) or 3.150 Å (BP86). This is longer than that in **6T-1** by ca. 0.3 Å (B3LYP) or ca. 0.2 Å (BP86) but consistent with the single bond needed to give both vanadium atoms in **6S-2** the favored 18-electron configuration in a structure with one four-electron donor bridging CO group.

The last isomer **6S-3** of $Cp_2V_2(CO)_6$ is a C_s unbridged structure lying above **6T-1** by 13.1 kcal/mol (B3LYP) or above **6S-1** by 14.4 kcal/mol (BP86). Structure **6S-3** has all real vibrational frequencies. For the six carbonyls, the V–C distances are in the range of 1.929–1.976 Å (B3LYP) or 1.909–1.962 Å (BP86). The V–C–O bond angles are almost linear. The V–V distance in **6S-3** is 3.251 Å (B3LYP) or 3.023 Å (BP86), which is longer than that of **6T-1** by ca. 0.1 Å.

3.3 Dissociation Energies

Table 6 summarizes the calculated dissociation energies for the successive removal of carbonyl groups from the lowest lying singlet isomers of $Cp_2V_2(CO)_7$ and $Cp_2V_2(CO)_6$, namely isomers **7S-1** (Figure 2) and **6S-1** (Figure 3) for $Cp_2V_2(CO)_7$ and $Cp_2V_2(CO)_6$, respectively, as well as the calculated lowest energy singlet isomers of $Cp_2V_2(CO)_5$ and $Cp_2V_2(CO)_4$. Note that the dissociation energy for decarbonylation of $Cp_2V_2(CO)_5$ to $Cp_2V_2(CO)_4$ is considerably larger than that for decarbonylation of $Cp_2V_2(CO)_7$ to $Cp_2V_2(CO)_6$ or for $Cp_2V_2(CO)_6$ to $Cp_2V_2(CO)_5$. This thermodynamic factor may be one reason why the photochemical decarbonylation[6] of $CpV(CO)_4$ goes all the way to $Cp_2V_2(CO)_5$ without stopping at $Cp_2V_2(CO)_7$ or $Cp_2V_2(CO)_6$. In addition, $Cp_2V_2(CO)_5$ was first synthesized[5] by acidification of the anion $CpV(CO)_3^{2-}$, with the expected carbonyl dihydride $CpV(CO)_3H_2$ decomposing according to the following Equation (2).

$$2\ CpV(CO)_3H_2 \rightarrow Cp_2V_2(CO)_5 + 2\ H_2 + CO \quad (2)$$

Table 6. Dissociation energies (kcal/mol) for the successive removal of carbonyl groups from the lowest lying singlet isomers of $Cp_2V_2(CO)_n$ (n = 7, 6, 5, 4).

	B3LYP	BP86
$Cp_2V_2(CO)_7 \rightarrow Cp_2V_2(CO)_6 + CO$	17.5	16.8
$Cp_2V_2(CO)_6 \rightarrow Cp_2V_2(CO)_5 + CO$	1.2	10.8
$Cp_2V_2(CO)_5 \rightarrow Cp_2V_2(CO)_4 + CO$	29.5	34.7

The fact that $Cp_2V_2(CO)_5$, rather than the expected dimer $Cp_2V_2(CO)_6$, is produced in this reaction relates to our calculation of a low dissociation energy of one CO group from $Cp_2V_2(CO)_6$ to give $Cp_2V_2(CO)_5$ (Table 6).

4. Discussion

A cyclopentadienyl ring is electronically equivalent to three carbonyl groups[34] but, because of its compact nature, sterically equivalent to only two carbonyl groups. Using the latter relationship the binuclear cyclopentadienylvanadium carbonyls studied in this work can be compared with the corresponding homoleptic chromium carbonyls studied previously[4,35] by replacing two carbonyl groups in the chromium derivatives with a single cyclopentadienyl ring in the vanadium derivatives. In this way $Cp_2V_2(CO)_7$ is an analogue of $Cr_2(CO)_{11}$ and thus was found to be unstable with respect to dissociation into $CpV(CO)_4$ + $CpV(CO)_3$ just as $Cr_2(CO)_{11}$ was found earlier[4] to be unstable with respect to dissociation into $Cr(CO)_6$ + $Cr(CO)_5$. The monobridged structure for $Cp_2V_2(CO)_7$, namely $Cp_2V_2(CO)_6(\mu\text{-CO})$, found in this work (Figure 2) is analogous to a monobridged structure $Cr_2(CO)_{10}(\mu\text{-CO})$ found for $Cr_2(CO)_{11}$ in the previous work.[4]

The other binuclear cyclopentadienylvanadium carbonyl derivative discussed in this paper, namely $Cp_2V_2(CO)_6$, is an analogue of $Cr_2(CO)_{10}$.[35] Both $Cp_2V_2(CO)_6$ and $Cr_2(CO)_{10}$ are predicted to be thermodynamically stable with respect to dissociation into the corresponding mononuclear fragments, namely $CpV(CO)_3$ and $Cr(CO)_5$, respectively. For $Cp_2V_2(CO)_6$ the global minimum using the BP86 functional, namely **6S-1**, is a doubly bridged structure with a V=V distance of 2.85 Å suggesting the double bond required to give both vanadium atoms the favored 18-electron configuration. Similar Cr=Cr distances are found in the lowest lying $Cr_2(CO)_{10}$ isomers, which are also doubly bridged singlets.[35] Using the B3LYP functional for $Cp_2V_2(CO)_6$ leads to a different global minimum, namely an essentially unbridged triplet **6T-1** with a predicted V–V single-bond length of 3.10 Å. This triplet structure, with 17-electron configurations for the vanadium atoms, is closely related to the structure of the experimentally known singlet $Cp_2Cr_2(CO)_6$ determined by X-ray crystallography[36] to have no bridging CO groups and a Cr–Cr single bond length of 3.28 Å consistent with 18-electron configurations for the chromium atoms. The triplet structure for $Cr_2(CO)_{10}$ corresponding to this triplet structure for $Cp_2V_2(CO)_6$ lies 12.7 kcal/mol (B3LYP) or 13.2 kcal/mol (BP86) above its singlet global minimum.[35] The singlet structure **6S-2** for $Cp_2V_2(CO)_6$, with one four-electron donor bridging carbonyl group and a V–V distance of 3.150 Å (BP86) suggesting a single bond, has no counterpart in the singlet structures[35] predicted for $Cr_2(CO)_{10}$ in previous research.

Supporting Information (see also the footnote on the first page of this article): Tables S1–S6: The theoretical harmonic vibrational frequencies for the $Cp_2V_2(CO)_7$ and $Cp_2V_2(CO)_6$ structures using the BP86 method; Tables S7–S12: The theoretical Cartesian coordinates for the $Cp_2V_2(CO)_7$ and $Cp_2V_2(CO)_6$ structures using the BP86 method.

Acknowledgments

We are indebted to the National Science Foundations of the U. S. (grant CHE-0209857) and the 111 Project (B07012) in China for support of this work.

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Received: November 20, 2006
Published Online: March 6, 2007

