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Vanadium Carbonyl Nitrosyl Compounds: The Carbonyl Nitrosyl Chemistry of an Oxophilic Early Transition Metal

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The vanadium carbonyl nitrosyl compounds $V(NO)(CO)_n$ (n = 5, 4, 3) and $V_2(NO)_2(CO)_n$ (n = 9, 8, 7) have been examined by density functional theory in order to assess the effect of the oxophilicity of vanadium on its metal carbonyl nitrosyl chemistry. The expected octahedral structure for the experimentally known, but surprisingly unstable, $V(NO)(CO)_5$, is confirmed by DFT. The optimized structures of the unsaturated derivatives $V(NO)(CO)_4$ and $V(NO)(CO)_3$ can be derived from the octahedral $V(NO)(CO)_5$ structure by loss of one or two carbonyl groups, respectively. This leads to a nearly square-planar predicted structure for $V(NO)(CO)_3$. The lowest energy structures for the binuclear derivatives $V_2(NO)_2(CO)_n$ (n = 9, 8, 7) have exclusively two-electron donor carbonyl groups and three-electron donor linear nitrosyl groups with metal–metal distances corresponding to the formal bond orders required for the favored 18-electron configurations. Bridging carbonyl groups appear to be preferred energetically over bridging nitrosyl groups in the $V_2(NO)_2(CO)_n$ structures in contrast to the similar carbonyl nitrosyl compounds of later transition metals. The saturated $V_2(NO)_2(CO)_9$, with a relatively long V–V distance of 3.583 Å (B3LYP) or 3.205 Å (BP86), is thermodynamically unstable with respect to dissociation into $V(NO)(CO)_5$ + $V(NO)(CO)_4$.

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1. Introduction

A number of metal carbonyl nitrosyl compounds are known that are isoelectronic with homoleptic metal carbonyl derivatives.[1] The most extensive such isoelectronic series consists of the tetrahedral molecules $Ni(CO)_4 \rightarrow Co(NO)(CO)_3 \rightarrow Fe(NO)_2(CO)_2 \rightarrow Mn(NO)_3CO \rightarrow Cr(NO)_4$. The extent of this tetrahedral isoelectronic series is particularly surprising because $Ni(CO)_4$ is by far the least thermally stable of the known homoleptic mononuclear carbonyl compounds of the first-row transition metals. Thus, $Ni(CO)_4$ readily decomposes to nickel metal and carbon monoxide only slightly above room temperature.

Similar series of stable mononuclear metal carbonyl nitrosyl compounds isoelectronic with the much more stable $Fe(CO)_5$ and $Cr(CO)_6$ are surprisingly much less extensive. Thus the only well-characterized five-coordinate mononuclear metal carbonyl nitrosyl isoelectronic with $Fe(CO)_5$ is the manganese derivative[2] $Mn(NO)(CO)_4$. What is even more striking is the observation that the only known metal carbonyl nitrosyl isoelectronic with the very stable octahedral $Cr(CO)_6$ is the vanadium derivative $V(NO)(CO)_5$. However, whereas $Cr(CO)_6$ is the most stable known homoleptic first-row transition metal carbonyl derivative, being stable enough for steam distillation in air, the isoelectronic $V(NO)(CO)_5$ is reported[3] to decompose at –10 °C. Furthermore, $V(NO)(CO)_5$ is much more reactive towards carbonyl substitution reactions[3] than $Cr(CO)_6$. Thus, $V(NO)(CO)_5$ reacts with ligands such as phosphanes, trimethylamine, and iodide at temperature in the range –30° to 0 °C to give carbonyl substitution products whereas $Cr(CO)_6$ generally requires temperatures in excess of 100 °C for analogous substitution reactions. These observations suggest that the oxophilic nature of the early transition metals, such as vanadium, limits the stability of their metal carbonyl nitrosyls.

In order to explore in more detail the chemistry of metal carbonyl nitrosyl compounds of relatively oxophilic early transition metals, we have used density functional theory (DFT) to examine both the mononuclear vanadium carbonyl nitrosyl compounds $V(NO)(CO)_n$ as well as the binuclear derivatives $V_2(NO)_2(CO)_n$ (n = 9, 8, 7) isoelectronic with homoleptic binuclear chromium carbonyls that have been investigated in previous work.[4–7] Previous papers from our group have used similar DFT methods to study the metal carbonyl nitrosyl compounds of the later first-row transition metal chromium,[8] manganese,[9] and iron.[10]

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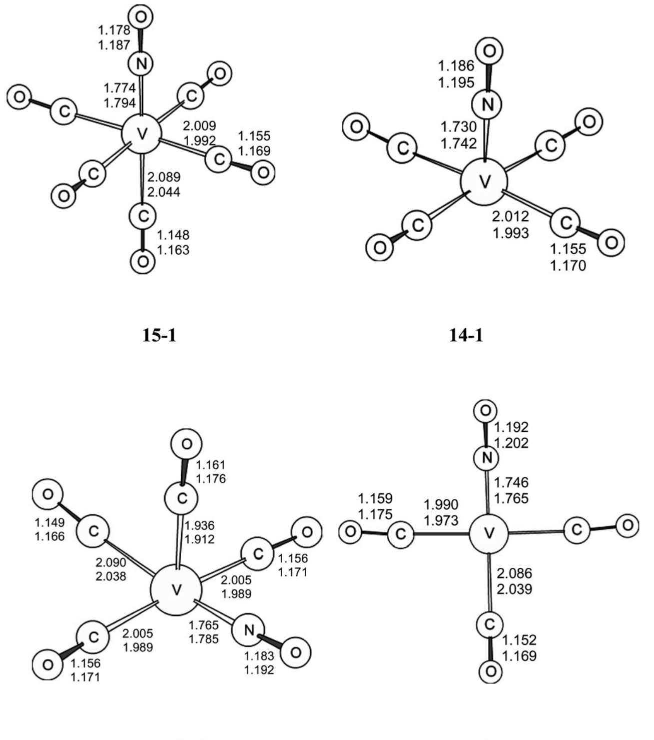
2. Theoretical Methods

Electron-correlation effects were included by employing density functional theory (DFT), which has been found to be a practical and effective computational tool, especially for organometallic compounds.[11–18] Two DFT methods were used in this study. The first functional is the hybrid B3LYP method, which incorporates Becke's three-parameter functional (B3)[19] with the Lee, Yang, and Parr (LYP) correlation functional.[20] The second approach is the BP86 method, which marries Becke's 1988 exchange functional (B)[21] with Perdew's 1986 correlation functional.[22]

For carbon, nitrogen, and oxygen, the double-ζ plus polarization (DZP) basis set used here, namely (9s5p/4s2p), adds one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(C) = 0.75$, $\alpha_d(N) = 0.80$ and $\alpha_d(O) = 0.85$ to the Huzinaga–Dunning standard contracted DZ sets.[23,24] For vanadium, our loosely contracted DZP basis set (14s11p6d/10s8p3d) uses the Wachters' primitive set augmented by two sets of p functions and one set of d functions contracted following Hood et al.[25,26] For $V(NO)(CO)_5$ and $V(NO)(CO)_4$ there are 229 and 199 contracted Gaussian basis functions. For the binuclear vanadium carbonyl nitrosyl compounds $V_2(NO)_2(CO)_9$, $V_2(NO)_2(CO)_8$, and $V_2(NO)_2(CO)_7$, there are 428, 398, and 368 contracted Gaussian basis functions, respectively.

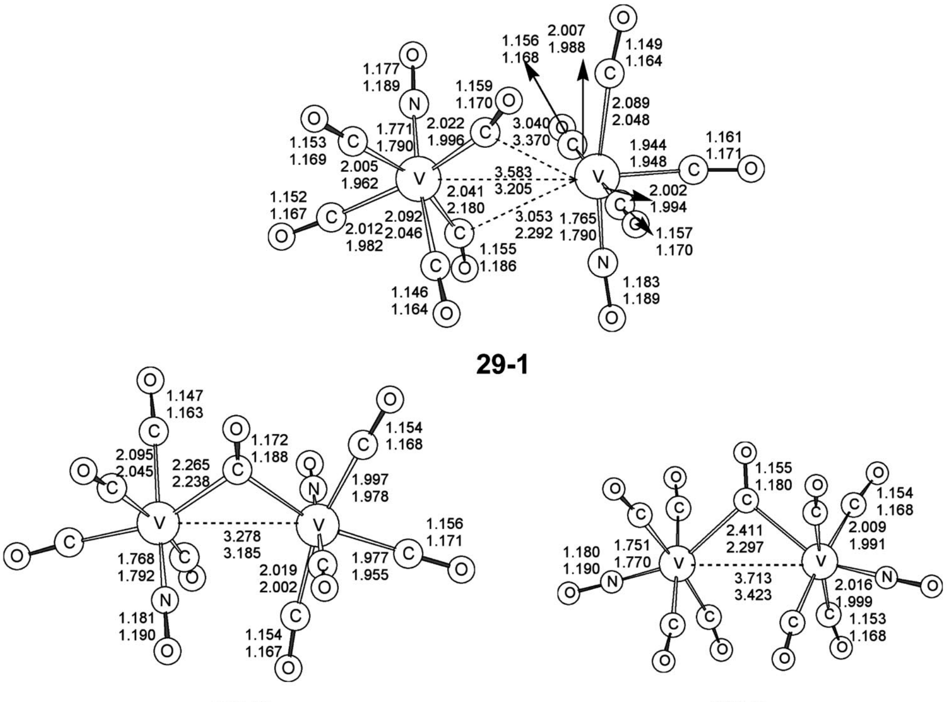
The geometries of all structures considered were fully optimized using both the DZP B3LYP and DZP BP86 methods. The vibrational frequencies were determined at the same levels by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. The corresponding infrared intensities were evaluated analytically as well. All of the predicted ν(CO) and ν(NO) frequencies discussed in this paper were obtained using the BP86 method, which has been shown to be more reliable



15-1 **14-1**

14-2 **13-1**

Figure 1. Optimized structures of the mononuclear $V(NO)(CO)_n$ (n = 5, 4, 3) derivatives.



29-1

29-2 **29-3**

Figure 2. The optimized structures of $V_2(NO)_2(CO)_9$.

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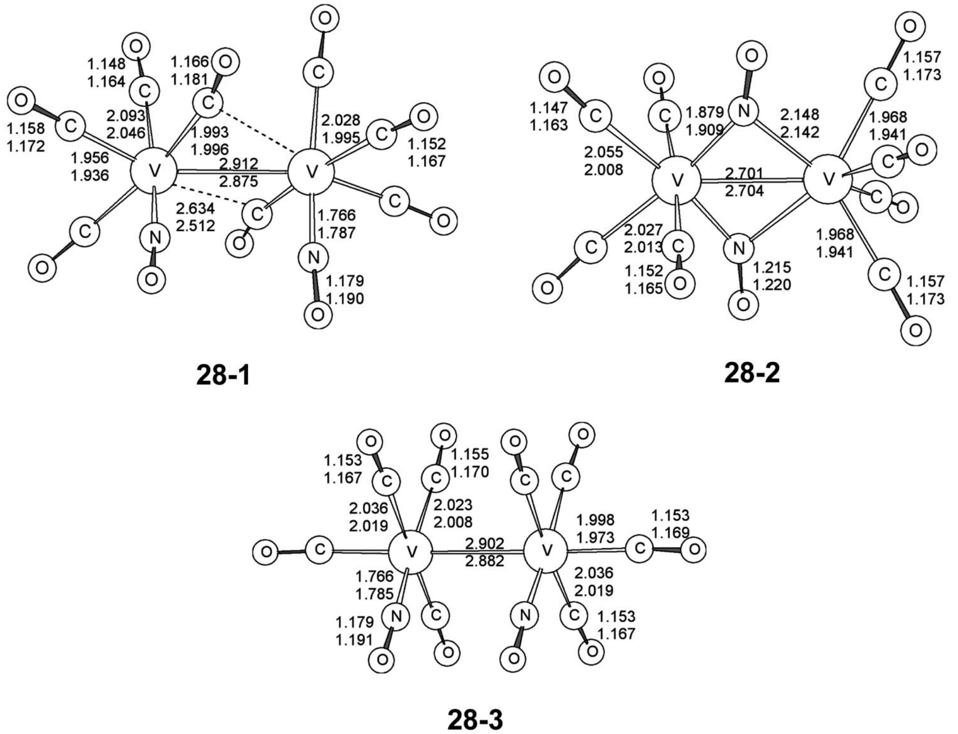
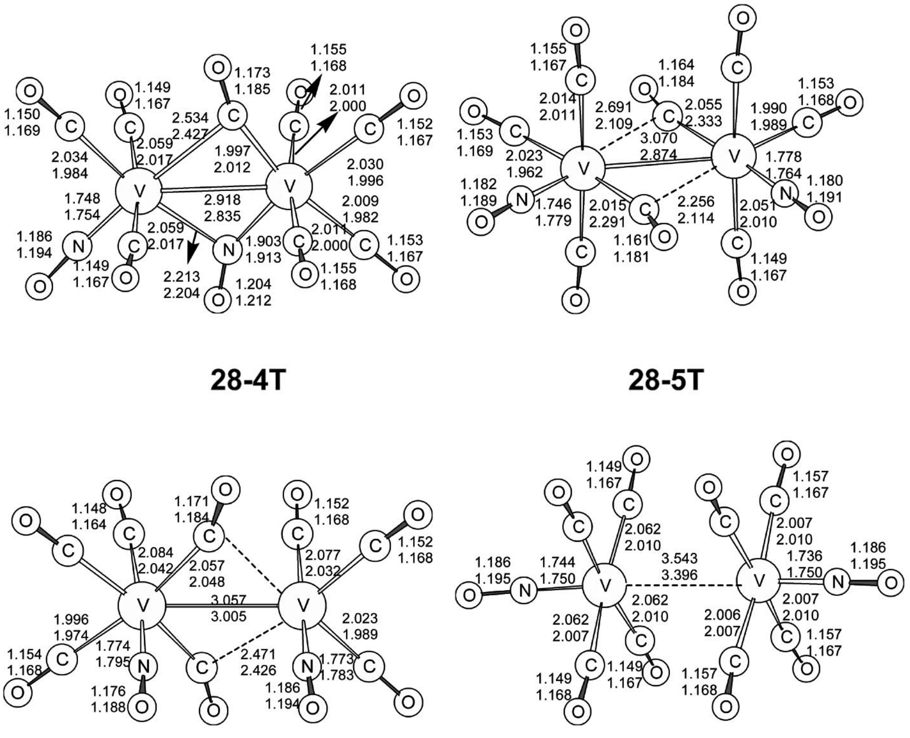
than the B3LYP method for such information. Complete vibrational frequency data by both the BP86 and B3LYP methods are given in the Supporting Information. All of the computations were carried out using the Gaussian 94 program[27] in which the fine grid (75, 302) is the default for evaluating integrals numerically,[28] and the tight (10^{-8}



28-1 **28-2**

28-3

Figure 3. The three optimized singlet structures of $V_2(NO)_2(CO)_8$.



28-4T **28-5T**

28-6T **28-7T**

Figure 4. The four triplet structures of $V_2(NO)_2(CO)_8$.

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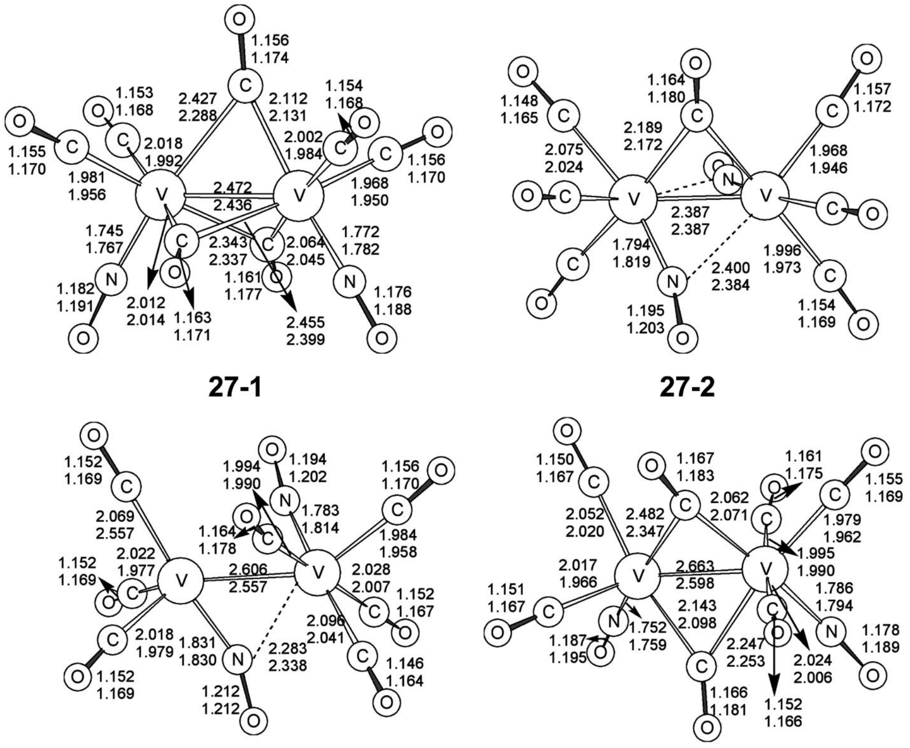

27-1 **27-2**

27-3T **27-4T**

Figure 5. The four optimized structures of $V_2(NO)_2(CO)_7$.

hartree) designation is the default for the energy convergence.

In the search for minima, low magnitude imaginary vibrational frequencies are suspect, because the numerical integration procedures used in existing DFT methods have significant limitations.[28] Thus, an imaginary vibrational frequency of magnitude less than 100*i* cm^{-1} should imply that there is a minimum with energy very similar to that of the stationary point in question. In most cases we do not follow the eigenvectors corresponding to imaginary frequencies less than 100*i* cm^{-1} in search of other minima.[29]

The optimized geometries from these computations are depicted in Figures 1, 2, 3, 4, and 5, with all bond lengths given in angstroms for both B3LYP (upper numbers) and BP86 (lower numbers). The structures are designated by the labels **ab-c** where **a** is the number of vanadium atoms (equal to the number of nitrosyl groups), **b** is the number of carbonyl groups, and **c** orders the isomeric structures by the relative energies. Triplet structures are designated with a **T** at the end. Thus the global minimum of $V(NO)(CO)_5$, a singlet, is designated as **15-1**.

3. Results

3.1 Molecular Structures

3.1.1 $V(NO)(CO)_n$ (n = 5, 4, 3): The single structure found for $V(NO)(CO)_5$, namely **15-1** (Figure 1 and Tables 1 and 2), is the expected octahedral structure with an essentially linear V–N–O unit consistent with a three-electron donor nitrosyl group as required by the 18-electron rule. The calculated ν(CO) frequencies for $V(NO)(CO)_5$ fall within 40 cm^{-1} of the experimental values[3] on the high side. However, the calculated ν(NO) frequency for $V(NO)(CO)_5$ at 1787 cm^{-1} lies 92 cm^{-1} above the experimental ν(NO) frequency[3] of 1695 cm^{-1}.

Two structures are predicted for $V(NO)(CO)_4$. Both of these structures have linear V–C–O and V–N–O bonds. The lower energy $V(NO)(CO)_4$ structure **14-1** is derived from $V(NO)(CO)_5$ (**15-1**) by removal of the carbonyl group *trans* to the nitrosyl group. The higher energy $V(NO)(CO)_4$ structure, namely **14-2** at 8.1 kcal/mol (B3LYP) or 6.9 kcal/mol (BP86) above **14-1**, is also derived from **15-1**, but by removal of a carbonyl group *cis* to the nitrosyl group. The lower energy of **14-1** than **14-2** may relate to the fact that a nitrosyl group has a stronger *trans* effect than a carbonyl group.

A nearly planar C_s structure **13-1** (Figure 1) is predicted for $V(NO)(CO)_3$. In contrast to the structures for $V(NO)(CO)_5$ and $V(NO)(CO)_4$, the V–N–O angle in **13-1** is slightly bent at 152.7° (B3LYP) or 156.8° (BP86). Structure **13-1** can be derived from the $V(NO)(CO)_5$ structure **15-1** by loss of a *trans* pair of carbonyl groups with some distortion of the remaining atoms, possibly arising from a Jahn–Teller effect in this unsaturated 14-electron system.

Structures for $V(NO)(CO)_n$ (n = 5, 4, 3) with the nitrosyl group bonded to the vanadium through the oxygen atom rather than the nitrogen atom were also explored owing to

Table 1. The bond lengths [Å], total energies E [Hartree], and relative energies ΔE [kcal/mol] for $V(NO)(CO)_n$ (n = 5, 4, 3).

	$V(NO)(CO)_5$ (**15-1**) (C_{4v})		$V(NO)(CO)_4$ (**14-1**) (C_{4v})		$V(NO)(CO)_4$ (**14-2**) (C_s)		$V(NO)(CO)_3$ (**13-1**) (C_s)	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
M–N/C(ax.)	1.774/2.089	1.794/2.044	1.730	1.742	1.936	1.912	1.746/2.086	1.765/2.039
N/C–O(ax.)	1.178/1.148	1.187/1.163	1.186	1.195	1.161	1.176	1.192/1.152	1.202/1.169
M–C/N(eq.)	2.009	1.992	2.012	1.993	2.005/1.765	1.989/1.785	1.990	1.973
C/N–O(eq.)	1.155	1.169	1.155	1.170	1.156/1.183	1.171/1.192	1.159	1.175
M–N–O(ax.)	180.0	180.0	180.0	180.0	–	–	168.8	168.8
M–N–O(eq.)	–	–	–	–	176.2	174.4	–	–
N–M–C	91.2	91.7	92.6	92.2	87.6	86.4	152.7	156.8
–Energy	1640.82503	1641.02769	1527.45321	1527.64867	1527.44027	1527.63772	1414.04228	1414.22872
ΔE	–	–	0.0	0.0	8.1	6.9	–	–
Imaginary frequencies	none	none	none	none	none	none	none	none

Table 2. Infrared ν(CO) and ν(NO) frequencies predicted for the $V(NO)(CO)_n$ structures using the BP86 method (calculated infrared intensities are given in parentheses in km/mol).

Structure	ν(NO) Frequencies	ν(CO) Frequencies
$V(NO)(CO)_5$ (**15-1**)	1787 (a_1, 1156)	1972 (e, 1713), 1982 (b_2, 0), 2012 (a_1, 457), 2066 (a_1, 155)
$V(NO)(CO)_5$ (expt.[3])	1695 (m)	1990 (s), 2050 (w), 2100 (w)
$V(NO)(CO)_4$ (**14-1**)	1754 (a_1, 820)	1972 (a_1, 0), 1960 (b_1, 1828), 1960 (b_2, 1828), 2048 (a_1, 27)
$V(NO)(CO)_4$ (**14-2**)	1764 (a′, 1124)	1943 (a′, 768), 1951 (a′′, 1968), 1987 (a′, 462), 2043 (a′, 225)
$V(NO)(CO)_4$ (**13-1**)	1723 (a′, 1048)	1922 (a′′, 2140), 1954 (a′, 605), 2017 (a′, 291)

the oxophilicity of vanadium. However, such structures were found to be 35 kcal/mol or more above the global minima. Therefore, oxygen-bonded structures of the vanadium carbonyl nitrosyls were not investigated in further detail. It thus appears that the oxophilic character of vanadium is not sufficient to make oxygen-bonded nitrosyl structures energetically competitive with the usual nitrogen-bonded nitrosyl structures, at least in vanadium carbonyl nitrosyls.

3.1.2 $V_2(NO)_2(CO)_9$: Three energetically low-lying structures were found for singlet $V_2(NO)_2(CO)_9$ (Figure 2 and Tables 3 and 4). The structure **29-1** has only real harmonic vibrational frequencies, indicating that it is a true minimum rather than a transition state. The global minimum structure **29-1** of $V_2(NO)_2(CO)_9$ has only a weakly semibridging CO group by the B3LYP method but a single bridging CO group by the BP86 method. The other $V_2(NO)_2(CO)_9$ structures with a single bridging CO group lie close to **29-1** in energy and have one or more imaginary vibrational frequencies, suggesting that they are transition states to lower energy structures. Thus the entire potential energy surface for these molecules appears to be very flat as was found several years ago[4] for the isoelectronic

Table 3. Bond lengths [Å], total energies E [Hartree], and relative energies ΔE [kcal/mol] for the three $V_2(NO)_2(CO)_9$ structures.

	29 1 (C_1)		**29-2** (C_2)		**29-3** (C_{2v})	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
V–V	3.583	3.205	3.278	3.185	3.713	3.423
V–C(bridge)	–	–	2.265	2.238	2.411	2.297
V–N(terminal)	1.771/1.765	1.790	1.768	1.792	1.751	1.770
V–N–O angle	179.1	177.7	178.7	177.6	177.9/174.9	179.5/177.7
–Energy	3168.26374	3168.67252	3168.26041	3168.67130	3168.25901	3168.66520
ΔE	0.0	0.0	2.1	0.8	3.0	4.6
Imaginary frequencies	none	none	33i	16i	141i, 23i	24i

Table 4. Infrared ν(CO) and ν(NO) frequencies predicted for the $V_2(NO)_2(CO)_9$ structures using the BP86 method (calculated infrared intensities are given in parentheses in km/mol).

Structure	ν(NO) Frequencies	ν(CO) Frequencies
29-1	1768 (154) 1777 (1345)	1850 (344), 1951 (377), 1969 (452), 1973 (1207), 1981 (747) 1997 (662), 2003 (1105), 2018 (1699), 2058 (75)
29-2	1791 (a, 160) 1807 (b, 1687)	1912 (a, 289), 2057 (a, 84), 2065 (a, 2240), 2103 (a, 245), 2154 (a, 55), 2041 (b, 677), 2055 (b, 1145), 2087 (b, 1643), 2130 (b, 1385),
29-3	1779 (a_1,71) 1774 (b_2, 2179)	1877 (a_1, 139), 1987 (a_1, 2362), 2060 (a_1, 6), 1958 (a_2, 0), 1977 (a_2, 0), 1982 (a_2, 2292), 1992 (b_1, 465), 1958 (b_2, 33), 2027 (b_2, 488),

$Cr_2(CO)_{11}$ system. Thus a C_2 structure **29-2** of $V_2(NO)_2(CO)_9$ lies above **29-1** by only 2.1 kcal/mol (B3LYP) or 0.8 kcal/mol (BP86). Similarly a C_{2v} structure **29-3** of $V_2(NO)_2(CO)_9$ lies only 3.0 kcal/mol (B3LYP) or 4.6 kcal/mol (BP86) above **29-1**. Both **29-2** and **29-3** have a single bridging carbonyl group, which exhibits ν(CO) frequencies at 1912 cm^{-1} for **29-2** and 1877 cm^{-1} for 29-3 (Table 4).

The relatively long V···V bond length of 3.583 Å by the B3LYP method in the global minimum **29-1** of $V_2(NO)_2(CO)_9$ (Figure 2 and Table 3), suggests only a weak direct vanadium–vanadium interaction. However, by using the BP86 method the V–V bond length in **29-1** is found to be appreciably shorter at 3.205 Å. This can correspond to the single bond required by the 18-electron rule assuming the single bridging CO group to be a two-electron donor and assuming the linear terminal NO groups to be three-electron donors. An attempt to optimize a triplet $V_2(NO)_2(CO)_9$ structure led instead to rupture into $V(NO)(CO)_4$ and $V(NO)(CO)_5$ fragments.

3.1.3 $V_2(NO)_2(CO)_8$: A total of three singlet and four triplet structures are predicted for $V_2(NO)_2(CO)_8$ (Figures 3 and 4, Tables 5, 6, and 7). The global minimum **28-1** of $V_2(NO)_2(CO)_8$ is a singlet C_2 structure with two semibridging carbonyl groups. This structure was obtained by optimizing a starting structure with two carbonyl bridges. A second singlet $V_2(NO)_2(CO)_8$ structure **28-2** of $V_2(NO)_2(CO)_8$ with two bridging NO groups lies above **28-1** by 4.1 kcal/mol (B3LYP) or 7.5 kcal/mol (BP86). Both structures exhibit only real harmonic vibrational frequencies. The V=V bond lengths of 2.912 Å (B3LYP) or 2.875 Å (BP86) in **28-1** and 2.701 Å (B3LYP) or 2.704 Å (BP86) in **28-2** are significantly shorter than the V–V distances in any of the $V_2(NO)_2(CO)_9$ structures. Therefore, they can correspond to the double bonds required by the 18-electron rule, assuming that both nitrosyl groups are formal three-electron donors. The ν(NO) frequencies for the bridging NO groups in **28-2** are 1563 cm^{-1} and 1578 cm^{-1} (Table 7), which are lower than the ν(NO) frequencies predicted for the terminal NO groups in **28-1**, namely 1748 and 1787 cm^{-1}.

The third singlet structure of $V_2(NO)_2(CO)_8$, namely **28-3** (Figure 3) is a relatively high-energy structure staggered C_{2v} unbridged structure at 22.0 kcal/mol (B3LYP) or 21.1 kcal/mol (BP86) above **28-1**. Furthermore, structure **28-3** has a large imaginary vibrational frequency at 356*i* cm^{-1} (B3LYP) or 196*i* cm^{-1}. Following the corresponding normal modes lead to **28-1**.

Four energetically low-lying triplet structures were found for $V_2(NO)_2(CO)_8$ (Figure 4 and Table 6). These structures all have only real vibrational frequencies, confirming that they are genuine minima on the energy hypersurface. The energies of the triplet structures are higher than those of the singlet structures. The structure **28-4T** of $V_2(NO)_2(CO)_8$ with one bridging NO group and one bridging CO

Table 5. Bond lengths [Å], total energies *E* [Hartree] and relative energies Δ*E* [kcal/mol] for the singlet $V_2(NO)_2(CO)_8$ structures.

	28-1 (C_2)		**28-2** (C_2)		**28-3** (C_{2v})	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
V–V	2.912	2.875	2.701	2.704	2.902	2.882
V–C(bridge)	1.993/2.634	1.996/2.512	–	–	–	
V–N(bridge)	–	–	1.879/2.148	1.909/2.142	–	–
V–N(terminal)	1.766	1.787	–	–	1.766	1.785
V–N–O angle	176.5	175.2	147.4/128.6	146.7/129.8	176.7	176.1
–Energy	3054.90375	3055.31025	3054.89713	3055.29830	3054.86863	3055.27656
Δ*E*	0.0	0.0	4.1	7.5	22.0	21.1
Imaginary frequencies	none	none	none	none	356*i*	196*i*

Table 6. Bond lengths [Å], total energies *E* [Hartree] and relative energies Δ*E* [kcal/mol] relative to the singlet global minimum **28-1** for the triplet $V_2(NO)_2(CO)_8$ structures.

	28-4T (C_s)		**28-5T** (C_s)		**28-6T** (C_s)		**28-7T** (C_{2v})	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
V–V	2.918	2.835	3.070	2.874	3.057	3.005	3.543	3.396
V–C(bridge)	2.534 1.997	2.427 2.012	2.691 2.055 2.015 2.256	2.109 2.333 2.291 2.114	2.084 2.471	2.042 2.426	–	–
V–N(bridge)	2.059 1.903	2.017 1.913	–	–	–	–	–	–
V–N(terminal)	1.748	1.754	1.746 1.778	1.779 1.764	1.774 1.773	1.795 1.783	1.744 1.736	1.750 1.750
V–N–O angle	176.1 149.5	175.8 149.2	179.3 177.9	176.6 178.4	179.3 177.9	175.3 177.0	180.0	180.0
–Energy	3054.89028	3055.29405	3054.88963	3055.29356	3054.88710	3055.28650	3054.88647	3055.14153
Δ*E*	8.4	10.2	8.9	10.5	10.4	14.9	10.8	10.6
Imaginary frequencies	none	none	8*i*	none	none	none	none	none

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Table 7. Infrared ν(CO) and ν(NO) frequencies predicted for the $V_2(NO)_2(CO)_8$ structures using the BP86 method (calculated infrared intensities are given in parentheses in km/mol).

Structure	ν(NO) Frequencies	ν(CO) Frequencies
28-1	1748 (16) 1787 (1582)	1887 (12), 1905 (894), 1966 (7), 1969 (1737), 1990 (606), 1998 (609) 2009 (1858), 2052 (396)
28-2	1563 (b, 635) 1578 (a, 62)	1945 (b, 819), 1947 (b, 1015), 1954 (a, 0), 1995 (b, 1625) 2002 (a, 1041), 2009 (a, 812), 2012 (b, 722), 2056 (a, 447)
28-3	1733 (b_2, 26) 1791 (a_1, 1432)	1946 (a_2, 0), 1954 (b_2, 114), 1978 (b_2, 57), 1980 (a_1, 356), 1987 (b_2, 3296), 1990 (a_1, 445), 1998 (b_1, 2106), 2055 (a_1, 159)
28-4T	1604 (a′, 276), 1761 (a′, 923)	1856 (a′, 360), 1958 (a″, 28), 1976 (a′, 390), 1982 (a′, 154) 1987 (a″, 2493), 1987 (a′, 765), 1999 (a′, 2342), 2053 (a′, 179)
28-5T	1770 (a′, 770) 1772 (a′, 781)	1855 (a′, 382), 1891 (a′, 670), 1962 (a″, 10), 1975 (a′, 179) 1981 (a′, 769), 1987 (a′, 2038), 1990 (a″, 2457), 2050 (a′, 138)
28-6T	1737 (a′, 147) 1787 (a′, 1388)	1863 (a″, 649), 1867 (a′, 112), 1971 (a′, 301), 1976 (a″, 480) 1984 (a″, 1055), 1998 (a′, 1590), 2006 (a′, 1264), 2048 (a′, 440)
28-7T	1750 (a′, 2038), 1756 (a′, 2)	1953 (a′, 13), 1955 (a″, 0), 1956 (a′, 2477), 1973 (a′, 1) 1987 (a′, 2358), 1988 (a″, 2406), 1992 (a′, 52), 2054 (a′, 0)

group, which was obtained from the optimization of a starting structure with two bridging NO groups, lies 8.4 kcal/mol (B3LYP) or 10.2 kcal/mol (BP86) above the global minimum **28-1**. The two NO groups in **28-4T** exhibit ν(NO) frequencies at 1604 and 1761 cm^{-1} (Table 7), corresponding to bridging and terminal NO groups, respectively. The triplet structures **28-5T** and **28-6T** (Figure 4 and Table 6) with two semibridging CO groups and terminal NO groups in different relative positions are higher in energy by 8.9 kcal/mol (B3LYP) or 10.5 kcal/mol (BP86) for **28-5T** and 10.4 kcal/mol (B3LYP) or 14.9 kcal/mol (BP86) for **28-6T** relative to the analogous singlet structure **28-1**. The semibridging CO groups in **28-5T** and **28-6T** exhibit ν(CO) frequencies in the range 1855 to 1891 cm^{-1} (Table 7), which are appreciably below the terminal ν(CO) frequencies. The vanadium–vanadium distances in the triplet structures are 3.070 Å (B3LYP) for **28-5T** and 3.057 Å (B3LYP) for **28-6T**, which are longer than these in the corresponding singlet structures. These suggest the V–V single bonds required to give each metal atom a 17-electron configuration leading to a triplet binuclear structure.

The final triplet $V_2(NO)_2(CO)_8$ structure, namely **28-7T** (Figure 4 and Table 6), is an unbridged structure lying 10.8 kcal/mol (B3LYP) or 10.6 kcal/mol (BP86) above **28-1**. The V–V distance of 3.543 Å (B3LYP) or 3.396 Å (BP86) can be interpreted as a rather long single bond holding the two $V(NO)(CO)_4$ halves together giving each vanadium atom the 17-electron configuration required for a binuclear triplet structure.

3.1.4 $V_2(NO)_2(CO)_7$: Both singlet and the triplet structures were optimized for $V_2(NO)_2(CO)_7$ (Figure 5 and Tables 8 and 9). The global minimum structure **27-1** of $V_2(NO)_2(CO)_7$ has three bridging CO groups similar to the known structure[30] for the stable isoelectronic $(\eta^6\text{-}C_6H_6)_2\text{-}Cr_2(\mu\text{-}CO)_3$ and related to the known structure[31,32] for $Fe_2(CO)_9$, which however has four more electrons than $V_2(NO)_2(CO)_7$. A higher energy C_2 structure **27-2** of $V_2(NO)_2(CO)_7$ with two bridging NO groups and one bridging CO group lies 3.3 kcal/mol (B3LYP) or 7.4 kcal/mol (BP86) above **27-1**. Both structures have only real harmonic vibrational frequencies. The predicted ν(NO) frequencies (Table 9) for the terminal NO groups in **27-1** are 1766 and 1778 cm^{-1}. Similarly, the predicted ν(NO) frequencies (Table 9) for the bridging NO groups for **27-2** are 1688 and 1693 cm^{-1}. The lower ν(NO) frequencies for bridging NO groups relative to terminal NO groups by ca. 80 cm^{-1} in this case are normal. The V–V bond lengths of 2.472 Å (B3LYP) or 2.436 Å (BP86) in **27-1** and 2.387 Å (B3LYP/BP86) in **27-2** are reasonable for the V≡V triple bonds required by the 18–electron rule assuming the bridging NO groups and linear terminal NO groups to be three-electron donors.

An attempt to optimize a triply bridged structure for triplet $V_2(NO)_2(CO)_7$ analogous to the singlet structure led

Table 8. Bond lengths [Å], total energies *E* [Hartree] and relative energies Δ*E* [kcal/mol] for the $V_2(NO)_2(CO)_7$ structures.

	27-1 (C_1)		**27-2** (C_2)		**27-3T** (C_1)		**27-4T** (C_1)	
	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86	B3LYP	BP86
V–V	2.472	2.436	2.387	2.387	2.606	2.557	2.663	2.598
V–C(bridge)	2.236 (ave.)	2.045 (ave.)	2.189	2.172	–	–	2.234 (ave.)	2.192 (ave.)
V–N(bridge)	–	–	1.794/2.400	1.819/2.384	1.831/2.283	1.830/2.338	–	–
V–N(terminal)	1.745/1.772	1.767/1.782	–	–	1.783	1.814	1.752/1.786	1.759/1.794
V–N–O angle	178.2/175.1	178.0/176.2	165.8/126.5	164.8/127.4	171.0/117.8 157.7/124.5	169.1/120.5 160.9/124.6	177.6/175.9	177.5/176.6
–Energy	2941.55177	2941.95639	2941.54656	2941.94454	2941.53131	2941.92045	2941.52961	2941.92691
Δ*E*	0.0	0.0	3.3	7.4	12.8	22.6	13.9	18.5
Imaginary frequencies	none	none	none	none	none	none	none	none

Table 9. Infrared ν(CO) and ν(NO) frequencies predicted for the $V_2(NO)_2(CO)_7$ structures using the BP86 method (calculated infrared intensities are given in parentheses in km/mol).

Structure	ν(NO) Frequencies	ν(CO) Frequencies
27-1	1766 (715) 1778 (1061)	1923 (593), 1924 (745), 1929 (429), 1973 (3), 1977 (1745), 1996 (1707), 2039 (283)
27-2	1688 (a, 231) 1693 (b, 821)	1898 (a, 433),1965 (a, 1118), 1987 (a, 588), 2044 (a, 27), 1961 (b, 649), 1983 (b, 913), 2006 (b, 2396)
27-3T	1628 (372) 1692 (530)	1912 (432), 1962 (768), 1964 (472), 1974 (1499), 1990 (2101), 1996 (1291), 2043 (151)
27-4T	1751 (797) 1770 (876)	1867 (626), 1898 (479), 1932 (633), 1973 (510), 1981 (1664), 1994 (1548), 2038 (325)

instead to structures **27-3T** and **27-4T** (Figure 5 and Table 8). The triplet (S = 1) structures of $V_2(NO)_2(CO)_7$ were found to be significantly higher in energy than the singlet structures. Thus the triplet structure **27-3T** with one bridging CO group and two bridging NO groups lies 12.8 kcal/mol (B3LYP) or 22.6 kcal/mol (BP86) above **27-1**. The ν(NO) frequencies for the bridging NO groups in **27-3T** are predicted to be 1628 and 1692 cm^{-1} (Table 9), which are very close to the ν(NO) frequencies predicted for the bridging NO groups in **27-2**. The $V{=}V$ distances of 2.606 Å (B3LYP) or 2.557 Å (BP86) in **27-3T** and of 2.663 Å (B3LYP) or 2.598 Å in **27-4T** (Figure 5 and Table 8) are ca. 0.2 Å longer than the $V{\equiv}V$ distances in **27-1** and **27-2**, interpreted as formal triple bonds. They can thus be interpreted as the formal double bonds required to give both vanadium atoms in both **27-3T** and **27-4T** the 17-electron configurations required for a binuclear triplet structure.

3.2 Dissociation Energies

Table 10 lists the energies for removal of one CO group from the $V(NO)(CO)_n$ (n = 5, 4, 3) and $V_2(NO)_2(CO)_n$ (n = 9, 8, 7) derivatives based on the lowest energy structures. For comparison the reported[19] CO dissociation energies are 37 ± 2, and 41 ± 2 kcal/mol for $Cr(CO)_6$, and $Fe(CO)_5$, respectively. Thus, the CO dissociation energy of $V(NO)(CO)_5$, although still rather endothermic, is distinctly lower than that of the isoelectronic $Cr(CO)_6$. This may relate to the effect of the NO group in $V(NO)(CO)_5$ labilizing the CO groups because of the stronger π-accepting ability of NO relative to CO.

Table 11 lists the dissociation energies of the binuclear $V_2(NO)_2(CO)_n$ into mononuclear fragments. The binuclear $V_2(NO)_2(CO)_9$ is seen to be thermodynamically unstable with respect to dissociation into the mononuclear fragments $V(NO)(CO)_5$ and $V(NO)(CO)_4$.

4. Discussion

4.1 Mononuclear Derivatives

Table 12 compares the M–C/N and C/N–O distances to the CO and NO ligands in the lowest energy structures of $V(NO)(CO)_n$ (n = 5, 4) derivatives with the corresponding isoelectronic $Cr(CO)_{n+1}$ derivatives. Thus the V–C(equatorial) bond length is longer by 0.118 Å (BP86) in $V(NO)(CO)_4$ and 0.076 Å (BP86) in $V(NO)(CO)_5$ as compared with the Cr–C(equatorial) bond lengths in $Cr(CO)_5$ and $Cr(CO)_6$.[17,18] However, the V–N(axial) bond lengths in $V(NO)(CO)_4$ and $V(NO)(CO)_5$ are shorter by 0.110 Å (BP86) and 0.122 Å (BP86), respectively, than the corresponding Cr–C(axial) bond length in $Cr(CO)_5$ and $Cr(CO)_6$. The significantly shorter V–N bond lengths in

Table 12. Bond lengths [Å] for the lowest energy vanadium carbonyl nitrosyl and their isoelectronic chromium carbonyl structures (BP86 results).

Compound	Symmetry	M–C/N(b) distances	C/N–O(b) distances
$V(NO)(CO)_5$ (**15-1**)	C_{4v}	1.992 (eq. V–C)	1.169 (eq.)
		1.794 (ax. V–N)	1.187 (ax.)
$Cr(CO)_6$	O_h	1.916[18]	1.140[18]
$V(NO)(CO)_4$ (**14-1**)	C_{4v}	1.993 (eq. V–C)	1.170 (eq.)
		1.742 (ax. V–N)	1.195 (ax.)
$Cr(CO)_5$	C_{4v}	1.865 (eq.)[17]	1.145 (eq.)[17]
		1.852 (ax.)[17]	1.152 (ax.)[17]

Table 10. Energies [kcal/mol] for carbonyl dissociation of $V(NO)(CO)_n$ (n = 5, 4, 3) and $V_2(NO)_2(CO)_n$ (n = 9, 8, 7) structures.

	B3LYP	BP86
$V(NO)(CO)_5$ (**Id**) → $V(NO)(CO)_4$ (**Ib**) + CO	27.1	32.5
$V(NO)(CO)_4$ (**Ib**) → $V(NO)(CO)_3$ (**Ia**) + CO	51.6	58.2
$V_2(NO)_2(CO)_9$ (**IIa-s**) → $V_2(NO)_2(CO)_8$ (**IIIa-s**) + CO	19.7	22.0
$V_2(NO)_2(CO)_8$ (**IIIa-s**) → $V_2(NO)_2(CO)_7$ (**IVa-s**) + CO	14.6	16.7

Table 11. Dissociation energies [kcal/mol] for dissociation of the binuclear $V_2(NO)_2(CO)_n$ (n = 9, 8, 7) into mononuclear fragments.

	B3LYP	BP86
$V_2(NO)_2(CO)_9$ (**IIa-s**) → $V(NO)(CO)_5$ (**Id**) + $V(NO)(CO)_4$(**Ib**)	–9.1	–2.4
$V_2(NO)_2(CO)_8$ (**IIIa-s**) → $V(NO)(CO)_5$ (**Id**) + $V(NO)(CO)_3$ (**Ia**)	22.9	33.8
$V_2(NO)_2(CO)_7$ (**IVa-s**) → $V(NO)(CO)_4$ (**Ib**) + $V(NO)(CO)_3$ (**Ia**)	35.3	49.6

Table 13. Bond lengths (in Å) and formal metal–metal bond orders for the lowest energy structures of analogous $V_2(NO)_2(CO)_n$ (n = 9, 8, 7) and $Cr_2(CO)_{n+2}$ derivatives (BP86 results).

	Symmetry	Number of bridges	M–M distance	M–C/N distances (bridging)	C/N–O distances (bridging)	Formal bond order
$V_2(NO)_2(CO)_9$ **(29-1)**	C_1	1(CO)	3.205	2.180/2.292	1.186	1
$Cr_2(CO)_{11}$	C_s	1(CO)	3.148	2.074/2.279	1.185	1
$V_2(NO)_2(CO)_8$ **(28-1)**	C_2	2(CO)	2.875	1.996/2.512	1.181	2
$Cr_2(CO)_{10}$	C_{2h}	2(CO)	2.832	1.920/2.463	1.178	2
$V_2(NO)_2(CO)_7$ **(27-1)**	C_1	3(CO)	2.436	2.063/2.334	1.174(ave.)	3
$Cr_2(CO)_9$	C_s	3(CO)	2.285	1.981/2.125	1.162 (ave.)	3

$V(NO)(CO)_4$ and $V(NO)(CO)_5$ relative to the corresponding Cr–C bond lengths in $Cr(CO)_5$ and $Cr(CO)_6$ can be related to the fact that NO is a stronger π-acceptor than CO.

4.2 Binuclear Derivatives

Table 13 compares the lowest energy structures of analogous $V_2(NO)_2(CO)_n$ (n = 9, 8, 7) and $Cr_2(CO)_{n+2}$ derivatives using previous BP86 results[4–7] for the $Cr_2(CO)_{n+2}$ data. In general, the structures are seen to be quite analogous in terms of the formal metal–metal bond orders and number of bridging groups. The vanadium–vanadium distances for a given formal bond order in the $V_2(NO)_2(CO)_n$ derivatives are 0.04 to 0.15 Å longer than the chromium–chromium distances in the corresponding $Cr_2(CO)_{n+2}$ derivatives. In all cases $V_2(NO)_2(CO)_n$ structures with bridging carbonyl groups are preferred over structures with bridging nitrosyl groups in contrast to the binuclear metal carbonyl nitrosyls of manganese[9] and iron,[10] where bridging nitrosyls are energetically preferred over bridging carbonyls.

The following more specific observations can be made concerning the lowest energy structures of the isoelectronic pairs in Table 13. The semibridging carbonyl groups for the molecules in Table 13 can be characterized by Δ(M–C), which is the difference between the long and short M–C distances to a semibridging carbonyl group.

(1) $Cr_2(CO)_{11}$ vs. $V_2(NO)_2(CO)_9$: Both structures have a single slightly unsymmetrical bridging carbonyl group with Δ(M–C) of ca. 0.2 Å for $Cr_2(CO)_{11}$ but only ca. 0.1 Å for $V_2(NO)_2(CO)_9$. The dissociation of $Cr_2(CO)_{11}$ to $Cr(CO)_6$ + $Cr(CO)_5$ and the dissociation of $V_2(NO)_2(CO)_9$ to $V(NO)(CO)_5$ + $V(NO)(CO)_4$ are both slightly exothermic with dissociation energies of ca. 2 kcal/mol by the BP86 method. This is consistent with their relatively long metal–metal distances exceeding 3.1 Å.

(2) $Cr_2(CO)_{10}$ vs. $V_2(NO)_2(CO)_8$: Both structures have two highly unsymmetrical semibridging carbonyl groups with Δ(M–C) values of ca. 0.5 Å. For both compounds the M=M distances are around ca. 2.8 Å, which can be interpreted as the formal double bonds required to give the metal atoms the favored 18-electron configuration.

(3) $Cr_2(CO)_9$ vs. $V_2(NO)_2(CO)_7$: Both structures have three unsymmetrical semibridging carbonyl groups. The Δ(M–C) value for $Cr_2(CO)_9$ is 0.14 Å whereas that for the isoelectronic $V_2(NO)_2(CO)_7$ is much larger at 0.27 Å. The relatively short M≡M distances in the lowest energy structures of both $Cr_2(CO)_9$ and $V_2(NO)_2(CO)_9$ can be interpreted as the formal triple bonds required to give the metal atoms the favored 18-electron configuration.

A noteworthy point in view of the oxophilicity of the early transition metal vanadium is that no structures with either formal four-electron donor η^2-μ-CO groups or formal five-electron donor η^2-μ-NO groups were found in any of the energetically accessible unsaturated $V_2(NO)_2(CO)_n$ structures (n = 8 and 7). Thus, vanadium appears to form formal double and triple bonds in binuclear derivatives in preference to four-electron donor carbonyl groups or five-electron donor nitrosyl groups.

Supporting Information (see also the footnote on the first page of this article): Tables S1 to S18: Harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (in parentheses, in km/mol) for $V(NO)(CO)_n$ (n = 5, 4, 3) and $V_2(NO)_2(CO)_n$ (n = 9, 8, 7); complete Gaussian reference[27].

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