

# The Remarkable $\text{Nb}_2(\text{CO})_{12}$ with Seven-Coordinate Niobium: Decarbonylation to $\text{Nb}_2(\text{CO})_{11}$ and $\text{Nb}_2(\text{CO})_{10}$

Lihong Tang,<sup>†</sup> Qiong Luo,<sup>\*,‡</sup> Qian-shu Li,<sup>‡,†</sup> Yaoming Xie,<sup>§</sup> R. Bruce King,<sup>\*,†,§</sup> and Henry F. Schaefer, III<sup>§</sup>

<sup>†</sup>The School of Sciences, Beijing Institute of Technology, Beijing 100081, P. R. China

<sup>‡</sup>School of Chemistry and Environment, South China Normal University, Guangzhou, Guangdong 510631, P. R. China

<sup>§</sup>Department of Chemistry and Center for Computational Chemistry, University of Georgia, Athens, Georgia 30602, United States

 Supporting Information

**ABSTRACT:** The dissociation of  $\text{Nb}_2(\text{CO})_{12}$  into two  $\text{Nb}(\text{CO})_6$  units is predicted to require  $\sim 13$  kcal/mol so that  $\text{Nb}_2(\text{CO})_{12}$  rather than  $\text{Nb}(\text{CO})_6$  is the anticipated initial oxidation product of the known  $\text{Nb}(\text{CO})_6^-$  anion. This differs from the corresponding vanadium carbonyl chemistry where  $\text{V}(\text{CO})_6$  rather than  $\text{V}_2(\text{CO})_{12}$  is found experimentally to be the oxidation product of  $\text{V}(\text{CO})_6^-$ . The lowest energy  $\text{Nb}_2(\text{CO})_{12}$  structure consists of two  $\text{Nb}(\text{CO})_6$  fragments joined by a  $\text{Nb}-\text{Nb}$  bond of  $\sim 3.4$  Å length so that each niobium atom is heptacoordinate, counting the metal–metal bond. These niobium coordination polyhedra can be approximated by capped octahedra. Among unsaturated binuclear niobium carbonyls the lowest energy  $\text{Nb}_2(\text{CO})_{11}$  structure has a formal four-electron donor bridging  $\eta^2\text{-}\mu\text{-CO}$  group and a formal  $\text{Nb}-\text{Nb}$  single bond rather than only two-electron donor carbonyl groups and a formal  $\text{Nb}=\text{Nb}$  double bond. The  $\text{Nb}_2(\text{CO})_{11}$  structures with formal  $\text{Nb}=\text{Nb}$  double bonds and exclusively two-electron donor carbonyl groups lie more than 13 kcal/mol above this low-energy  $\text{Nb}_2(\text{CO})_{10}(\eta^2\text{-}\mu\text{-CO})$  structure. However,  $\text{Nb}_2(\text{CO})_{11}$  is predicted to be thermodynamically disfavored, owing to disproportionation into  $\text{Nb}_2(\text{CO})_{12} + \text{Nb}_2(\text{CO})_{10}$ , a slightly exothermic process by  $\sim 4$  kcal/mol. The  $\text{Nb}_2(\text{CO})_{10}$  structures with formal  $\text{Nb}=\text{Nb}$  triple bonds and all two-electron donor carbonyl groups appear to be particularly favorable, as suggested by high CO dissociation energies and viability toward disproportionation. Such structures are isolobal with  $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ , which was the first stable metal carbonyl to be discovered with a short metal–metal distance, corresponding to a formal triple bond. Considerably higher energy  $\text{Nb}_2(\text{CO})_{10}$  structures (by more than 20 kcal/mol) have two four-electron donor bridging carbonyl groups and long niobium–niobium distances. Such structures can be considered to consist of a bidentate  $\text{Nb}(\text{CO})_6^-$  “ligand” coordinating to a  $\text{Nb}(\text{CO})_4$  unit through the two  $\eta^2\text{-}\mu\text{-CO}$  groups.

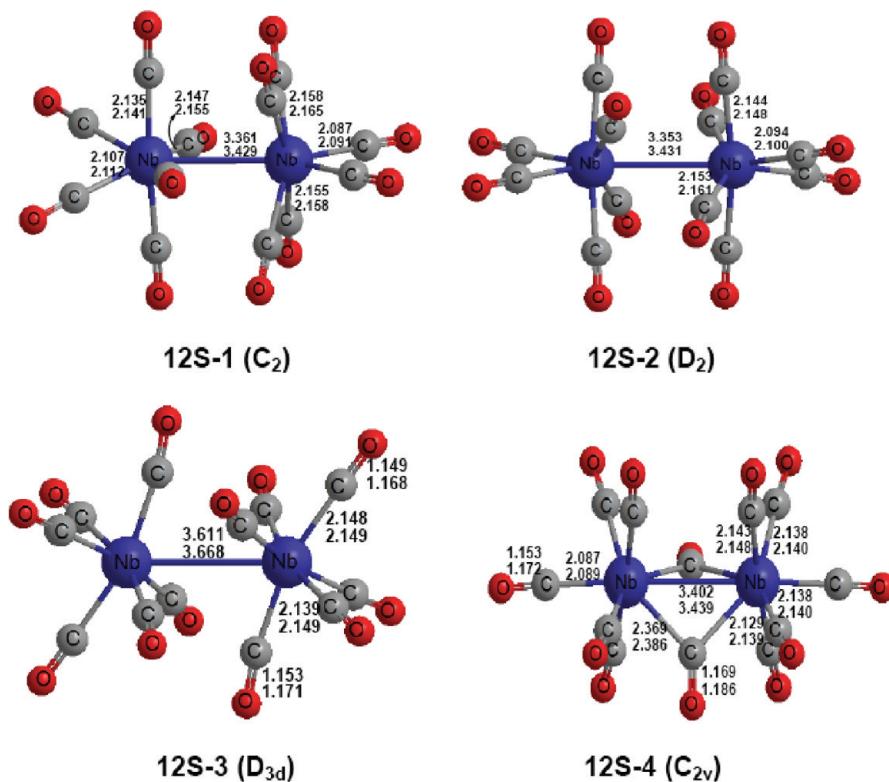
## 1. INTRODUCTION

The 18-electron rule has played an important role in the structure and bonding in simple metal carbonyls.<sup>1,2</sup> Thus, the well-known simple binary carbonyls of the first row transition metals from chromium to nickel, inclusive, namely,  $\text{Cr}(\text{CO})_6$ ,  $\text{Mn}_2(\text{CO})_{10}$ ,  $\text{Fe}(\text{CO})_5$ ,  $\text{Co}_2(\text{CO})_8$ , and  $\text{Ni}(\text{CO})_4$ , all obey the 18-electron rule. However, difficulties arise when applying the 18-electron rule to neutral binary carbonyls of the early transition metals of groups 4 and 5 because of the large numbers of carbonyl groups required to give the central metal the favored 18-electron configuration. Thus, the only binary carbonyl of vanadium which has been isolated<sup>3</sup> is the 17-electron complex  $\text{V}(\text{CO})_6$ . The hypothetical binuclear complex  $\text{V}_2(\text{CO})_{12}$  with a V–V bond has seven-coordinate vanadium atoms and is unstable with respect to dissociation to mononuclear  $\text{V}(\text{CO})_6$ , as suggested by both theory<sup>4</sup> and experiment.<sup>5</sup> No neutral binary carbonyls of titanium have been isolated, although the anion  $\text{Ti}(\text{CO})_6^{2-}$  with an 18-electron configuration for the central titanium has been isolated as a potassium-2,2,2-cryptate salt.<sup>6</sup> However, recent theoretical studies suggest that the titanium carbonyl species observed spectroscopically in low temperature matrices<sup>7,8</sup> is the hepta-coordinate  $\text{Ti}(\text{CO})_7$  in which the titanium atom has the favored 18-electron configuration. However,  $\text{Ti}(\text{CO})_7$  appears to be unstable under ambient conditions.

The existence of binary carbonyls of the early second and third row transition metals might be expected to be more favorable than that of the corresponding first row transition metals. Thus, the larger sizes of the second and third row metals might be expected to favor the larger coordination numbers required to accommodate enough carbonyl groups to give the central metal atoms the favored 18-electron configurations. However, no neutral binary carbonyl derivatives of zirconium, niobium, hafnium, or tantalum are known despite the fact that they are potentially accessible by mild oxidation of the known anions  $\text{M}(\text{CO})_6^{2-}$  ( $\text{M} = \text{Zr},^9 \text{Hf}^{10}$ ) and  $\text{M}(\text{CO})_6^-$  ( $\text{M} = \text{Nb},^{11} \text{Ta}^{12}$ ), all of which have the favored 18-electron configuration of the central metal atom. Such a synthetic method is analogous to the known method<sup>3</sup> for synthesizing the neutral  $\text{V}(\text{CO})_6$  from the anion  $\text{V}(\text{CO})_6^-$ . In this case, the hydride  $\text{HV}(\text{CO})_6$  initially formed by acidification of  $\text{V}(\text{CO})_6^-$  with a nonoxidizing acid such as phosphoric acid spontaneously evolves hydrogen to give directly the neutral  $\text{V}(\text{CO})_6$ . However, neither neutral  $\text{Nb}(\text{CO})_6$  nor its dimer  $\text{Nb}_2(\text{CO})_{12}$  has yet been reported as an oxidation product of the known  $\text{Nb}(\text{CO})_6^-$ . The experimental conditions tried so far<sup>13</sup> have had halide present so that the products are the niobium

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**Figure 1.** Optimized geometries of  $\text{Nb}_2(\text{CO})_{12}$ . The distances are given in Å. The upper numbers were determined by the MPW1PW91 method and the lower distances by the BP86 method.

**Table 1. Total Energies ( $E$  in hartrees), Relative Energies ( $\Delta E$  in kcal/mol), Numbers of Imaginary Vibrational Frequencies (Nimag), and Nb–Nb Distances (in Å) for the Lowest-Energy  $\text{Nb}_2(\text{CO})_{12}$  Structures**

	12S-1 ( $C_2$ )	12S-2 ( $D_2$ )	12S-3 ( $D_{3d}$ )	12S-4 ( $C_{2v}$ )
MPW1PW91	$E$	−1474.01069	−1474.01055	−1473.99678
	$\Delta E$	0.0	0.09	8.7
	Nimag	0	1 ( $17i$ )	2 ( $19i, 19i$ )
	Nb–Nb	3.361	3.353	3.611
BP86	$E$	−1474.58661	−1474.58652	−1474.57691
	$\Delta E$	0.0	0.06	6.1
	Nimag	0	1 ( $19i$ )	2 ( $10i, 10i$ )
	Nb–Nb	3.429	3.431	3.668

carbonyl halide anions  $[\text{Nb}_2(\mu\text{-X})_3(\text{CO})_8]^-$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ). However, binary niobium carbonyl derivatives have been generated in low-temperature neon matrices from laser ablated niobium atoms and carbon monoxide.<sup>14</sup>

This paper reports theoretical studies on the binuclear niobium carbonyl derivatives  $\text{Nb}_2(\text{CO})_n$  ( $n = 12, 11, 10$ ) with particular focus on the following points:

- (1) Does the larger size of niobium relative to vanadium favor the binuclear species  $\text{Nb}_2(\text{CO})_{12}$  with at least seven-coordinate niobium and an 18-electron configuration for the niobium over the mononuclear  $\text{Nb}(\text{CO})_6$  with a 17-electron configuration for the niobium? The tendency for niobium to favor larger coordination numbers than vanadium in metal carbonyls is shown by a recent gas phase study of the  $\text{M}(\text{CO})_n^+$  cations generated in a molecular beam by laser vaporization.<sup>15</sup> The vanadium system forms exclusively the hexacoordinate  $\text{V}(\text{CO})_6^+$  with a 16-electron configuration. However, the

niobium system forms both the hexacoordinate  $\text{Nb}(\text{CO})_6^+$  with a 16-electron configuration and the heptacoordinate  $\text{Nb}(\text{CO})_7^+$  with an 18-electron configuration.

- (2) Are there viable structures for  $\text{Nb}_2(\text{CO})_{10}$  where the possibility of a formal  $\text{Nb}\equiv\text{Nb}$  triple bond can lead to a structure with the favored 18-electron configuration with a possible metal coordination number of six? There is some evidence,<sup>4</sup> for the formation of an analogous vanadium derivative  $\text{V}_2(\text{CO})_{10}$  in the photolysis of gas-phase  $\text{V}(\text{CO})_6$ .<sup>16</sup>

## 2. THEORETICAL METHODS

Density functional theory (DFT) appears to be a powerful and effective computational tool to study organometallic compounds.<sup>17–32</sup> In this connection, two different density functional theory (DFT) methods were used in the present study. The first

**Table 2.** Infrared  $\nu(\text{CO})$  Vibrational Frequencies ( $\text{cm}^{-1}$ ) Predicted by the BP86 Method for the  $\text{Nb}_2(\text{CO})_{12}$  Structures<sup>a</sup>

	BP86
<b>12S-1 (<math>C_2</math>)</b>	1937 (307), 1944 (374), 1945 (300), 1959 (574), 1960 (714), 1963 (419)
<b>12S-2 (<math>D_2</math>)</b>	1973 (185), 1983 (1783), 1984 (38), 1990 (2433), 2019 (1730), 2067 (4)
<b>12S-3 (<math>D_{3d}</math>)</b>	1945 (13), 1949 (1), 1955 (842), 1960 (0), 1961 (891), 1969 (416)
<b>12S-4 (<math>C_{2v}</math>)</b>	1970 (0), 1972 (0), 1977 (2169) 1985 (2817), 2019 (1709), 2065 (0)
	1937 (0), 1937 (0), 1945 (703), 1961 (0), 1968 (1366), 1968 (1367)
	1973 (1867), 1973 (1867), 1977 (0), 1977 (0), 2019 (3122), 2069 (0)
	<b>1829 (402), 1836 (118), 1946 (246), 1959 (1208), 1962 (19), 1968 (0)</b>
	1973 (13), 1977 (2761), 1981 (2715), 1983 (171), 2019 (2226), 2064 (15)

<sup>a</sup> Infrared intensities are in parentheses (in km/mol). The bridging CO frequencies are in bold.

DFT method is the BP86 method, which uses Becke's 1988 exchange functional (B) with Perdew's 1986 gradient corrected correlation functional method (P86).<sup>33,34</sup> The second DFT method is a newer generation functional, MPW1PW91, which is a combination of the modified Perdew–Wang exchange functional with Perdew–Wang's 91 gradient-correlation functional.<sup>35</sup> This MPW1PW91 functional has been shown to be better than the first generation functionals for some heavy transition metal compounds.<sup>36</sup>

The Stuttgart/Dresden double- $\zeta$  (SDD) basis set with an effective core potential (ECP)<sup>37,38</sup> was used for the niobium atoms. In this basis set, the 28 core electrons for the niobium atoms are replaced by an effective core potential (ECP), and the valence basis set is contracted from (8s7p6d) primitive sets to (6s5p3d). The effective core approximation includes scalar relativistic contributions, which become significant for the heavy transition metal atoms. For the C and O atoms, the all-electron DZP basis sets are used. They are Huzinaga–Dunning contracted double- $\zeta$  sets<sup>39,40</sup> plus a set of spherical harmonic d polarization functions with the orbital exponents  $\alpha_d(\text{C}) = 0.75$  and  $\alpha_d(\text{O}) = 0.85$ . The DZP basis sets for C and O atoms may be designated as 9s5p1d/4s2p1d.

The geometries of all structures were fully optimized using the MPW1PW91 and 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 and Gaussian 09 programs,<sup>41</sup> exercising the fine grid option (75 radial shells, 302 angular points) for evaluating integrals numerically, while the tight designation is the default for the self-consistent field (SCF) convergence. For structures with small imaginary frequencies, the finer grid (120, 974) is used for the further confirmation.

In the search for minima, low magnitude imaginary vibrational frequencies are suspect, because of significant limitations in the numerical integration procedures used in standard DFT computations. Thus, imaginary vibrational frequencies with a magnitudes less than  $50i \text{ cm}^{-1}$  are considered questionable. In less critical cases, we do not follow the eigenvectors corresponding to imaginary frequencies less than  $50i \text{ cm}^{-1}$  in search of another minimum.<sup>42</sup>

In the present study, the MPW1PW91 and BP86 methods agree with each other fairly well in predicting the structural characteristics of the  $\text{Nb}_2(\text{CO})_n$  derivatives ( $n = 12, 11, 10$ ). However, the BP86 method was used in previous work<sup>20,43</sup> to predict  $\nu(\text{CO})$  frequencies closer to the experimental values.

### 3. RESULTS

#### 3.1. $\text{Nb}_2(\text{CO})_{12}$ .

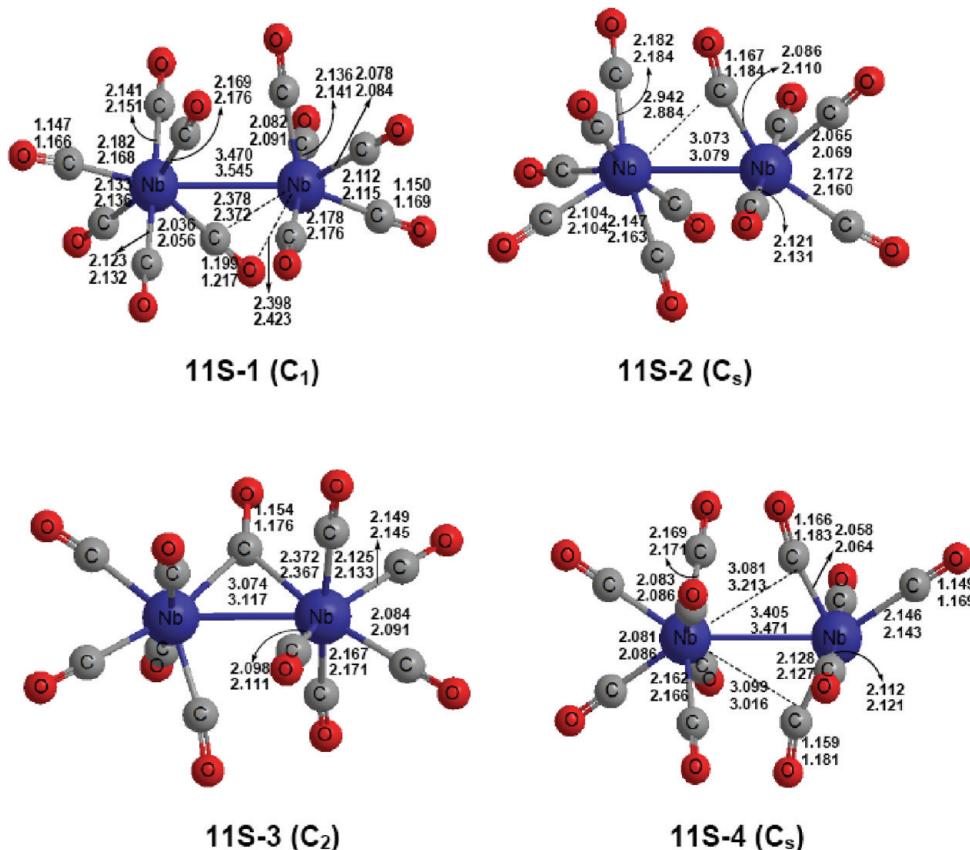
A total of 11 structures for  $\text{Nb}_2(\text{CO})_{12}$  were investigated. However, only four of these structures lie within

20 kcal/mol of the global minimum **12S-1** and are discussed in detail in this paper. All of these structures are singlet ( $S = 0$ ) electronic states. Attempts to optimize triplet  $\text{Nb}_2(\text{CO})_{12}$  structures led instead to mononuclear fragments  $\text{Nb}(\text{CO})_6$ .

The global minimum **12S-1** for  $\text{Nb}_2(\text{CO})_{12}$  (Figure 1 and Tables 1 and 2) is a  $C_2$  structure with 12 terminal CO groups. This structure is predicted to have all real vibrational frequencies by both the MPW1PW91 and BP86 methods. The Nb–C distances fall in the range of 2.087 to 2.158 Å (MPW1PW91) or 2.091 to 2.165 Å (BP86). The inward Nb–C distances of structure **12S-1** are all slightly longer than outward Nb–C distances, probably caused by steric hindrance between the inward Nb–C bonds. The six unique Nb–C–O angles are in the range of 170.8° to 179.4° (MPW1PW91) or 169.3° to 178.9° (BP86), which is close to linearity except for the two inward Nb–C–O bonds. All CO distances in **12S-1** are close to 1.150 Å, which is within the normal range. The Nb–Nb distance in **12S-1** is predicted to be 3.361 Å (MPW1PW91) or 3.429 Å (BP86), consistent with the Nb–Nb single bond required to give each niobium atom the favored 18-electron configuration.

The second stationary point of  $\text{Nb}_2(\text{CO})_{12}$  is **12S-2**, which is also an unbridged structure, but with higher symmetry than **12S-1**, i.e.,  $D_2$  for **12S-2** versus  $C_2$  for **12S-1** (Figure 1 and Table 1). Structure **12S-2** lies only 0.09 kcal/mol (MPW1PW91) or 0.06 kcal/mol (BP86) above **12S-1** (Figure 1 and Table 1). Furthermore, **12S-2** has a very small-magnitude imaginary vibrational frequency of  $17i \text{ cm}^{-1}$  (MPW1PW91) or  $19i \text{ cm}^{-1}$  (BP86). Following the corresponding normal mode leads to **12S-1** ( $C_2$  symmetry). The Nb–C distances in **12S-2** fall in the range of 2.100–2.161 Å. For the eight inward CO groups (two equivalent sets), the Nb–Nb–C angles are 75.2° and 85.8° (MPW1PW91) or 73.5° and 86.8° (BP86). The Nb–Nb distance of **12S-2** is predicted to be 3.353 Å (MPW1PW91) or 3.431 Å (BP86). This Nb–Nb distance is close to that of **12S-1** and can also be interpreted as the formal Nb–Nb single bond required to give each niobium atom the favored 18-electron configuration.

The third energetically low-lying  $\text{Nb}_2(\text{CO})_{12}$  structure **12S-3** lies 8.7 kcal/mol (MPW1PW91) or 6.1 kcal/mol (BP86) above **12S-1** (Figure 1 and Table 1). Structure **12S-3** is another unbridged  $(\text{CO})_6\text{Nb}–\text{Nb}(\text{CO})_6$  structure, but with  $D_{3d}$  symmetry. Structure **12S-3** is predicted to have negligible doubly degenerate imaginary vibrational frequencies at  $19i \text{ cm}^{-1}$  (MPW1PW91) or  $10i \text{ cm}^{-1}$  (BP86). Following one of the corresponding normal modes leads first to the  $D_2$  structure **12S-2** and then to the  $C_2$  structure **12S-1**. The Nb–Nb distance in **12S-3** is 3.611 Å (MPW1PW91) or 3.668 Å (BP86), which is ~0.3 Å longer than that of **12S-1** and thus suggests a relatively weak single bond. For the six inward CO groups in **12S-3**, the Nb–C distances are 2.139 Å



**Figure 2.** The four optimized singlet  $\text{Nb}_2(\text{CO})_{11}$  structures.

(MPW1PW91) or 2.149 Å (BP86), and the corresponding Nb–Nb–C angles are 69.7° (MPW1PW91) or 69.9° (BP86). For the six outward CO groups, the Nb–C distances are 2.148 Å (MPW1PW91) or 2.149 Å (BP86), and the relevant Nb–Nb–C angles are 125.9° (MPW1PW91) or 126.3° (BP86). The local coordination of each niobium atom in 12S-3 (including the Nb–Nb bond) approximates a  $C_{3v}$  capped octahedron. The Nb–C–O angles for the six outward CO groups are nearly linear, i.e., 178.6° (MPW1PW91) or 178.1° (BP86), while the Nb–C–O angles for the six inward CO groups are slightly bent, i.e., 172.4° (MPW1PW91) or 171.6° (BP86), probably owing to steric interactions.

The fourth  $\text{Nb}_2(\text{CO})_{12}$  structure, namely, the  $C_{2v}$  structure 12S-4 (Figure 1 and Table 1), lies 18.8 kcal/mol (MPW1PW91) or 12.7 kcal/mol (BP86) above the global minimum 12S-1. Structure 12S-4 is a doubly bridged structure,  $(\text{OC})_5\text{Nb}(\mu\text{-CO})_2\text{Nb}(\text{CO})_5$ . The Nb–C distances to the two bridging CO groups are 2.369 Å (MPW1PW91) or 2.386 Å (BP86), which is significantly longer than the Nb–C distances to the terminal CO groups ranging from 2.087 to 2.143 Å (MPW1PW91) or from 2.089 to 2.148 Å (BP86). The Nb–Nb distance in 12S-4 is 3.402 Å (MPW1PW91) or 3.439 Å (BP86), which is somewhat longer than that of 12S-1 but shorter than that of 12S-3. This is consistent with the formal Nb–Nb single bond required to give each niobium atom the favored 18-electron configuration. Structure 12S-4 has one large ( $>100i \text{ cm}^{-1}$ ) imaginary vibrational frequency. Following the corresponding normal mode leads to 12S-1.

Table 2 lists the infrared active  $\nu(\text{CO})$  frequencies predicted by the BP86 method for the four  $\text{Nb}_2(\text{CO})_{12}$  structures. Realistically, matrix isolation IR spectroscopy will probably be

the first experimental method to observe  $\text{Nb}_2(\text{CO})_{12}$ . Structures 12S-1, 12S-2, and 12S-3 exhibit only terminal  $\nu(\text{CO})$  frequencies, which fall in the typical range of 1937–2069  $\text{cm}^{-1}$  (BP86). For 12S-1, the three frequencies with high IR intensities (larger or close to 2000 km/mol) are 1983, 1990, and 2019  $\text{cm}^{-1}$ , while those for 12S-2 are very similar at 1977, 1985, and 2019  $\text{cm}^{-1}$ . For 12S-3, there are two frequencies, 1973  $\text{cm}^{-1}$  (doubly degenerate) and 2019  $\text{cm}^{-1}$ , with very large IR intensities (>3000 km/mol), while there is another, 1968  $\text{cm}^{-1}$  (doubly degenerate), with large IR intensities (>2000 km/mol). Structure 12S-4 has two bridging CO groups, which exhibit lower  $\nu(\text{CO})$  frequencies at 1829 and 1836  $\text{cm}^{-1}$  (BP86; Table 2 in bold face). However, these frequencies do not have high IR intensities. The three frequencies in 12S-4 with high IR intensities (>2000 km/mol) are 1977, 1981, and 2019  $\text{cm}^{-1}$ .

**3.2.  $\text{Nb}_2(\text{CO})_{11}$ .** A total of seven  $\text{Nb}_2(\text{CO})_{11}$  structures (four singlets and three triplets) are found within ~20 kcal/mol of the global minimum. The global minimum 11S-1 (Figure 2 and Table 3) is a  $C_1$  structure with one bridging CO group and 10 terminal CO groups. The bridging CO group is a four-electron donor  $\eta^2\text{-}\mu\text{-CO}$  group, as indicated by the short Nb–O distance of 2.398 Å (MPW1PW91) or 2.423 Å (BP86) as well as the extremely low  $\nu(\text{CO})$  frequency of 1701  $\text{cm}^{-1}$  (BP86). The relatively long C–O distance of 1.199 Å (MPW1PW91) or 1.217 Å (BP86) suggests a relatively low C–O bond order for this  $\eta^2\text{-}\mu\text{-CO}$  group. The short Nb–C distance to this bridging  $\eta^2\text{-}\mu\text{-CO}$  group is 2.036 Å (MPW1PW91) or 2.056 Å (BP86), and the long Nb–C distance is 2.378 Å (MPW1PW91) or 2.372 Å (BP86). The Nb–Nb distance in 11S-1 is predicted to be 3.470 Å (MPW1PW91) or 3.545 Å (BP86), which is close to

**Table 3.** Total Energies (*E* in hartrees), Relative Energies ( $\Delta E$  in kcal/mol), Numbers of Imaginary Vibrational Frequencies (Nimag), and Nb–Nb Distances (in Å) for the Singlet  $\text{Nb}_2(\text{CO})_{11}$  Structures

		11S-1 ( $C_1$ )	11S-2 ( $C_s$ )	11S-3 ( $C_2$ )	11S-4 ( $C_s$ )
MPW1PW91	<i>E</i>	−1360.68601	−1360.66366	−1360.65329	−1360.65167
	$\Delta E$	0.0	14.0	20.5	21.5
	Nimag	0	1 (22 <i>i</i> )	2 (384 <i>i</i> , 90 <i>i</i> )	0
	Nb–Nb	3.470	3.073	3.074	3.405
BP86	<i>E</i>	−1361.22921	−1361.20769	−1361.20125	−1361.19442
	$\Delta E$	0.0	13.5	17.5	21.8
	Nimag	0	2 (20 <i>i</i> , 6 <i>i</i> )	2 (355 <i>i</i> , 107 <i>i</i> )	0
	Nb–Nb	3.545	3.079	3.117	3.471

that in **12S-1**. This comparison suggests a formal Nb–Nb single bond in **11S-1**. Such an analysis gives each Nb atom the favored 18-electron configuration after considering the four-electron donor  $\eta^2\text{-}\mu\text{-CO}$  group. The  $\text{Nb}_2(\text{CO})_{11}$  global minimum structure **11S-1** appears to be a very favorable structure since it lies ~13 kcal/mol below any of the other  $\text{Nb}_2(\text{CO})_{11}$  structures found in this work.

The second singlet  $\text{Nb}_2(\text{CO})_{11}$  stationary point **11S-2** is a  $C_s$  structure with one semibridging carbonyl group and 10 terminal carbonyl groups (Figure 2 and Table 3). Structure **11S-2** lies 14.0 kcal/mol (MPW1PW91) or 13.5 kcal/mol (BP86) above **11S-1** (Figure 2 and Table 3). The short Nb–C distance to the semibridging CO group in **11S-2** is 2.086 Å (MPW1PW91) or 2.110 Å (BP86), whereas the long Nb–C distance is 2.942 Å (MPW1PW91) or 2.884 Å (BP86). The  $\nu(\text{CO})$  frequency at 1877 cm<sup>−1</sup> predicted for **11S-2** by the BP86 method can be assigned to this semibridging CO group. The six unique Nb–C distances to the 10 terminal carbonyls in **11S-2** range from 2.065 Å to 2.182 Å (MPW1PW91) or from 2.069 Å to 2.184 Å (BP86). The Nb=Nb distance of 3.073 Å (MPW1PW91) or 3.079 Å (BP86) in **11S-2** is significantly shorter than the Nb–Nb single bond distances in the  $\text{Nb}_2(\text{CO})_{12}$  structures (Figure 1) and in the  $\text{Nb}_2(\text{CO})_{10}(\eta^2\text{-}\mu\text{-CO})$  structure **11S-1**. Thus, the Nb=Nb bond in **11S-2** appears to be the formal double bond required to give each niobium atom the favored 18-electron configuration.

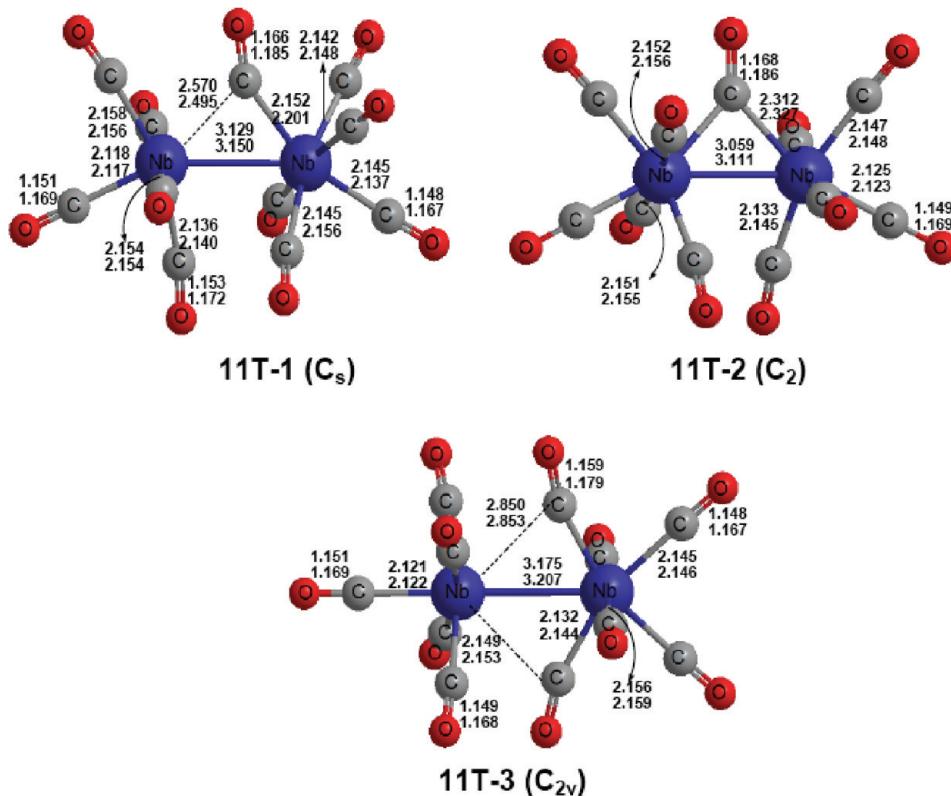
The next singlet  $\text{Nb}_2(\text{CO})_{11}$  structure **11S-3** is a singly bridged  $C_2$  structure, lying 20.5 kcal/mol (MPW1PW91) or 17.5 kcal/mol (BP86) in energy above the global minimum **11S-1** (Figure 2 and Table 3). The Nb–C distances to the symmetrically bridging CO group in **11S-3** are 2.372 Å (MPW1PW91) or 2.367 Å (BP86), while the five unique Nb–C distances to the 10 terminal carbonyls range from 2.084 Å to 2.167 Å (MPW1PW91) or from 2.091 Å to 2.172 Å (BP86). The Nb=Nb distance is predicted to be 3.074 Å (MPW1PW91) or 3.117 Å (BP86), consistent with the formal double bond needed to give both niobium atoms the favored 18-electron configuration. Structure **11S-3** has a significant imaginary vibrational frequency (>300*i* cm<sup>−1</sup>). Following the normal mode of this imaginary frequency leads to the global minimum **11S-1**.

The other singlet  $\text{Nb}_2(\text{CO})_{11}$  structure **11S-4** has  $C_s$  symmetry and lies 21.5 kcal/mol (MPW1PW91) or 21.8 kcal/mol (BP86) above **11S-1** (Figure 2 and Table 3). Structure **11S-4** has two very weakly semibridging carbonyls with short Nb–C distances of 2.058 Å and 2.128 Å (MPW1PW91) or 2.064 Å and 2.127 Å (BP86) and long Nb–C distances of 3.081 Å and 3.099 Å (MPW1PW91) or 3.213 Å and 3.016 Å (BP86). The Nb–O distances to these two unique semibridging carbonyls are very long (>3.5 Å), indicating that both of these carbonyls are

two-electron donor carbonyl groups. However, despite their weakly semibridging nature, these two carbonyl groups exhibit relatively low  $\nu(\text{CO})$  frequencies of 1877 cm<sup>−1</sup> and 1883 cm<sup>−1</sup> (BP86). The Nb–Nb bond distance of 3.405 Å (MPW1PW91) or 3.471 Å (BP86) in **11S-4** is close to that in **11S-1** and thus consistent with a formal single bond. This gives one niobium atom in **11S-4** the favored 18-electron configuration but the other niobium atom only a 16-electron configuration. The niobium atom in **11S-4** with only a 16-electron configuration is the niobium atom bonded to only five carbonyl groups rather than six carbonyl groups, namely, the “right” niobium atom depicted in Figure 2. The **11S-4** structure can be derived from one of the unbridged  $\text{Nb}_2(\text{CO})_{12}$  structures (**12S-1** through **12S-3**) by removal of a terminal carbonyl group.

The triplet  $\text{Nb}_2(\text{CO})_{11}$  structure **11T-1** has  $C_s$  symmetry with a semibridging CO group (Figure 3 and Table 4) and lies 12.7 kcal/mol (MPW1PW91) or 12.4 kcal/mol (BP86) above the global minimum **11S-1**. Structure **11T-1** is predicted by both methods to have a very small imaginary vibrational frequency ( $\leq 15i$  cm<sup>−1</sup>, Table 4). This imaginary frequency arises from numerical integration errors, since it becomes real when a finer integration grid (120, 974) is used for the optimization. Structure **11T-1** has one semibridging carbonyl and 10 terminal carbonyls. In **11T-1**, the short Nb–C distance to the semibridging carbonyl is 2.152 Å (MPW1PW91) or 2.201 Å (BP86), whereas the long Nb–C distance is 2.570 Å (MPW1PW91) or 2.495 Å (BP86). The seven unique Nb–C distances to the terminal carbonyls in **11T-1** fall in the range from 2.118 to 2.158 Å (MPW1PW91) or from 2.117 to 2.156 Å (BP86). The Nb=Nb distance of 3.129 Å (MPW1PW91) or 3.150 Å (BP86) is significantly shorter than the Nb–Nb single bonds of lengths 3.3–3.4 Å found in the  $\text{Nb}_2(\text{CO})_{12}$  structures (Figure 1 and Table 1). This gives each niobium atom in **11T-1** the favored 18-electron configuration. The triplet spin multiplicity in **11T-1** can arise from the Nb=Nb double bond being a  $\sigma + 2/2 \pi$  bond with the two unpaired electrons in two  $\pi$  “half bonds.” This is similar to dioxygen or the Fe=Fe double bond in the organometallic  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\mu\text{-CO})_3$ , which is stable enough to be isolated in the pure state and structurally characterized by X-ray diffraction.<sup>44–46</sup>

The second triplet  $\text{Nb}_2(\text{CO})_{11}$  structure **11T-2** is a singly symmetrically bridged  $C_2$  structure (Figure 3 and Table 4), which is geometrically similar to the singlet structure **11S-3**. Structure **11T-2** lies 13.2 kcal/mol (MPW1PW91) or 12.8 kcal/mol (BP86) above the global minimum **11S-1**. However, structure **11T-2** is a transition state with a large imaginary vibrational frequency at 165*i* cm<sup>−1</sup> (MPW1PW91) or 101*i* cm<sup>−1</sup> (BP86). Following the corresponding normal mode leads to **11T-1**. The Nb–C distances to the bridging CO group in **11T-2** are 2.312 Å

Figure 3. The triplet  $\text{Nb}_2(\text{CO})_{11}$  structures.**Table 4.** Total Energies ( $E$  in hartrees), Relative Energies ( $\Delta E$  in kcal/mol), Numbers of Imaginary Vibrational Frequencies (Nimg), and Nb–Nb Distances (in Å) for the Triplet  $\text{Nb}_2(\text{CO})_{11}$  Structures

	11T-1 ( $C_s$ )	11T-2 ( $C_2$ )	11T-3 ( $C_{2v}$ )
MPW1PW91	$E$ −1360.66572	−1360.66492	−1360.66489
	$\Delta E$ 12.7	13.2	13.3
	Nimg 1 (15 <i>i</i> )	1 (165 <i>i</i> )	2 (43 <i>i</i> , 10 <i>i</i> )
	Nb–Nb 3.129	3.059	3.175
BP86	$E$ −1361.20948	−1361.20889	−1361.20483
	$\Delta E$ 12.4	12.8	15.3
	Nimg 1 (11 <i>i</i> )	1 (101 <i>i</i> )	3 (58 <i>i</i> , 25 <i>i</i> , 17 <i>i</i> )
	Nb–Nb 3.151	3.111	3.207

(MPW1PW91) or 2.327 Å (BP86), whereas the five unique Nb–C distances for the 10 terminal CO groups fall in the range from 2.125 to 2.152 Å (MPW1PW91) or from 2.123 to 2.155 Å (BP86). The Nb=Nb distance in 11T-2 of 3.059 Å (MPW1PW91) or 3.111 Å (BP86) is close to that in 11T-1 and likewise can correspond to a formal double bond. This gives each niobium atom in 11T-2 the favored 18-electron configuration. The triplet spin multiplicity in 11T-2 arises from the Nb=Nb double bond being a  $\sigma + 2/2 \pi$  bond with two unpaired electrons similar to that in 11T-2 discussed above.

The other low-lying triplet  $\text{Nb}_2(\text{CO})_{11}$  structure 11T-3 is a  $C_{2v}$  structure with two semibridging carbonyls and nine (four unique) terminal carbonyls (Figure 3 and Table 4). Structure 11T-3 lies 13.3 kcal/mol (MPW1PW91) or 15.3 kcal/mol (BP86) above 11S-1. The MPW1PW91 method predicts 11T-3 to have two small imaginary vibrational frequencies (43*i* and 10*i* cm<sup>−1</sup>), while

the BP86 method predicts 11T-3 to have three small imaginary vibrational frequencies (58*i*, 25*i*, and 17*i* cm<sup>−1</sup>). Following the normal mode corresponding to the largest frequency leads to 11T-1. For the two equivalent semibridging carbonyls in 11T-3, the short Nb–C bond distances are 2.132 Å (MPW1PW91) or 2.144 Å (BP86), and the long Nb–C distances are 2.850 Å (MPW1PW91) or 2.853 Å (BP86). The  $\nu(\text{CO})$  frequencies at 1890 and 1900 cm<sup>−1</sup> (BP86) can be assigned to these two semibridging CO groups. The Nb=Nb distance of 11T-3 of 3.175 Å (MPW1PW91) or 3.207 Å (BP86) is similar to that in the triplets 11T-1 and 11T-2 and can likewise be interpreted as a  $\sigma + 2/2 \pi$  bond containing the two unpaired electrons of the triplet spin state.

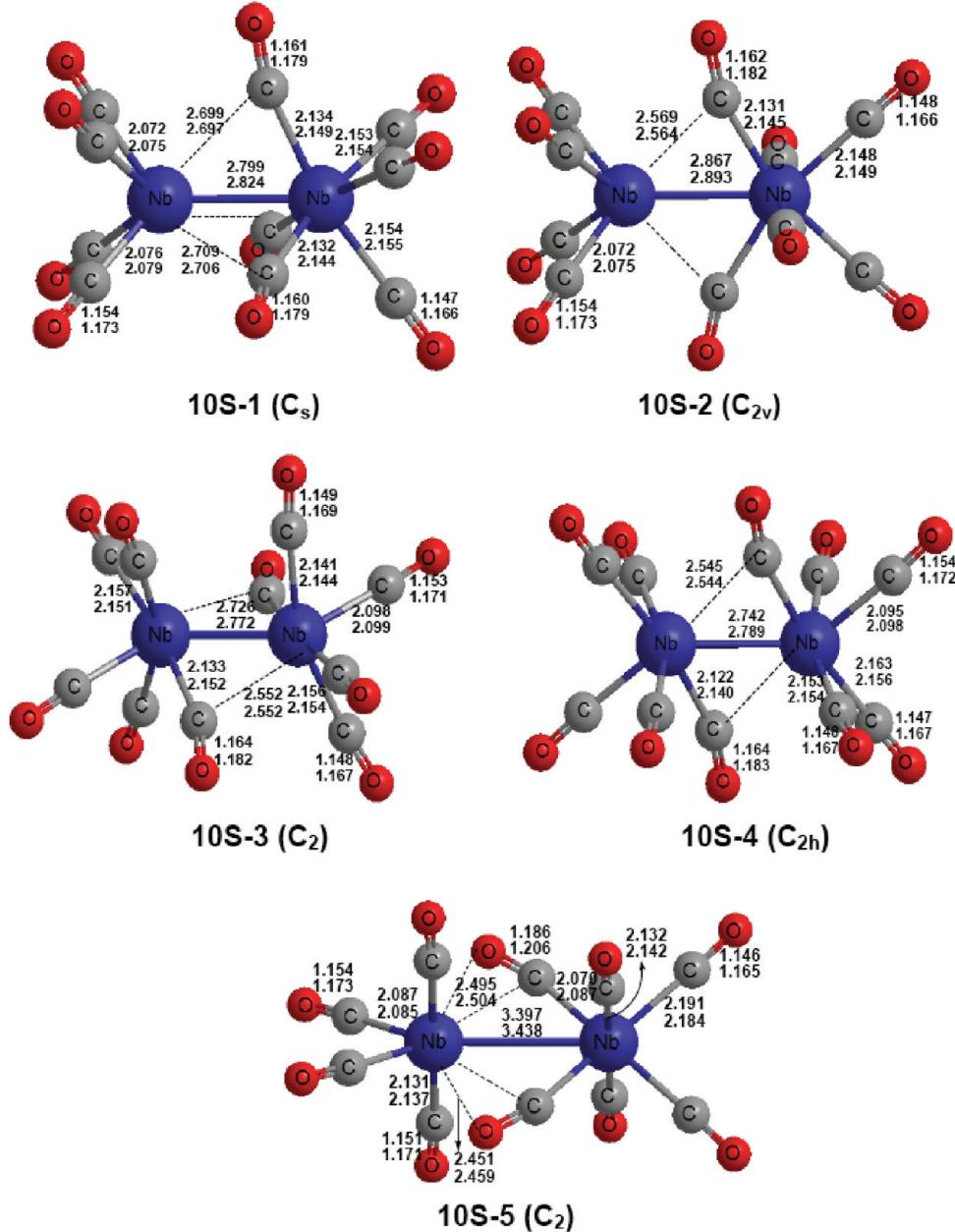
Table 5 lists the  $\nu(\text{CO})$  frequencies for the seven  $\text{Nb}_2(\text{CO})_{11}$  structures predicted by the BP86 method. The  $\nu(\text{CO})$  frequencies for the terminal CO groups fall in the range 1912–2065 cm<sup>−1</sup> (Table 5). The  $\nu(\text{CO})$  frequencies for the two-electron donor bridging CO groups are significantly lower in the range 1831–1900 cm<sup>−1</sup> (**bold face** in Table 5). The four-electron donor bridging  $\eta^2\text{-}\mu\text{-CO}$  group in 11S-1 exhibits an extremely low  $\nu(\text{CO})$  frequency at 1701 cm<sup>−1</sup> (BP86).

**3.3.  $\text{Nb}_2(\text{CO})_{10}$ .** A total of nine low-lying structures (five singlets and four triplets) were found for  $\text{Nb}_2(\text{CO})_{10}$  (Figures 4 and 5 and Tables 6 and 7). These nine structures can be classified into three general types: (a) structures with a Nb≡Nb distance of around 2.8 Å, suggesting a formal triple bond. This type includes the singlets 10S-1, 10S-2, 10S-3, and 10S-4; (b) structures with a Nb=Nb distance of around 3.0 Å, suggesting a formal double bond—this type includes the triplets 10T-1, 10T-2, and 10T-3; (c) structures with a long Nb–Nb distance (>3.4 Å), namely, 10S-5 and 10T-4. In such structures, a  $\text{Nb}(\text{CO})_6$  unit acts as a bidentate chelating ligand to a  $\text{Nb}(\text{CO})_4$

Table 5. Infrared  $\nu(\text{CO})$  Vibrational Frequencies ( $\text{cm}^{-1}$ ) Predicted by the BP86 Method for the  $\text{Nb}_2(\text{CO})_{11}$  Structures<sup>a</sup>

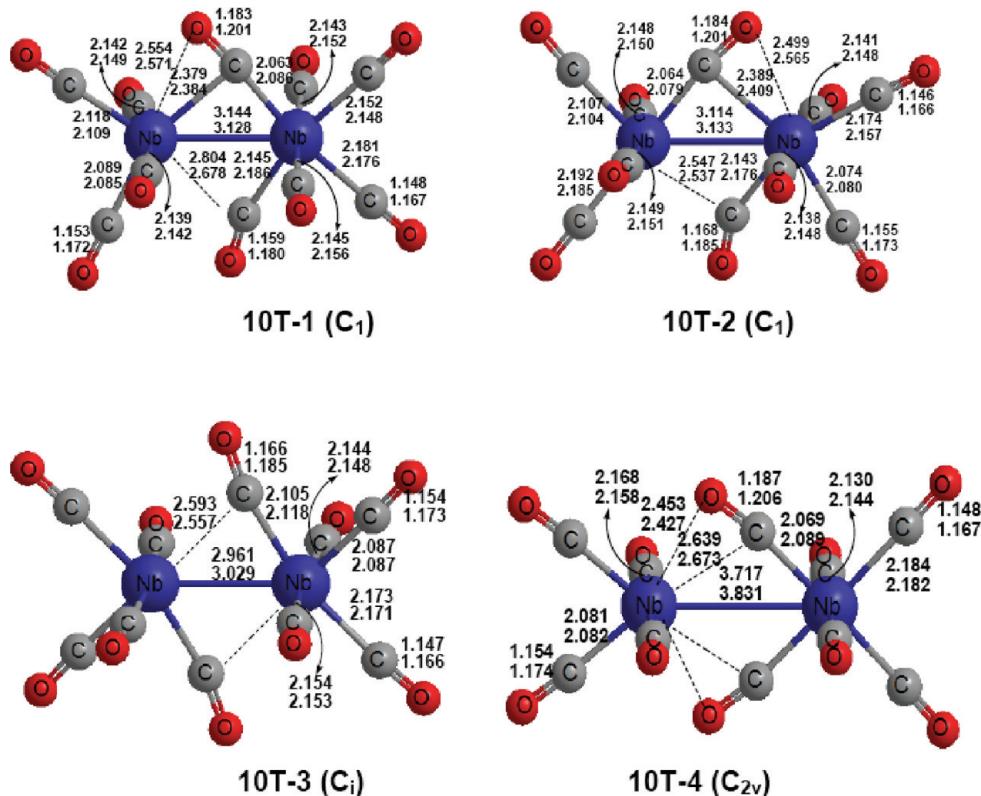
	BP86
11S-1 ( $C_1$ )	1701 (523), 1939 (188), 1952 (413), 1953 (454), 1968 (542), 1970 (1445), 1972 (754), 1983 (2544), 1986 (229), 2024 (1822), 2062 (27)
11S-2 ( $C_s$ )	1877 (269), 1912 (51), 1929 (499), 1942 (1431), 1948 (502), 1966 (988), 1967 (461), 1985 (1569), 2001 (565), 2008 (2587), 2060 (127)
11S-3 ( $C_2$ )	1896 (261), 1926 (102), 1936 (13), 1946 (261), 1953 (445), 1958 (1305), 1965 (1117), 1974 (660), 1976 (2154), 2000 (3327), 2058 (0)
11S-4 ( $C_s$ )	1877 (783), 1883 (103), 1913 (1024), 1946 (388), 1957 (633), 1973 (587), 1991 (956), 1992 (1191), 1998 (1912), 1999 (753), 2065 (83)
11T-1 ( $C_s$ )	1844 (263), 1936 (96), 1942 (2), 1961 (544), 1965 (1268), 1972 (733), 1972 (2843), 1974 (78), 1976 (556), 2004 (3637), 2062 (17)
11T-2 ( $C_2$ )	1831 (212), 1935 (56), 1943 (19), 1966 (980), 1966 (389), 1969 (653), 1971 (45), 1973 (2878), 1975 (971), 2003 (3672), 2062 (3)
11T-3 ( $C_{2v}$ )	1890 (396), 1900 (66), 1948 (8), 1963 (1333), 1964 (834), 1968 (0), 1973 (3012), 1976 (10), 1978 (1113), 2009 (3017), 2062 (7)

<sup>a</sup> Infrared intensities are in parentheses (in km/mol). The bridging CO frequencies are in bold.

Figure 4. Optimized singlet  $\text{Nb}_2(\text{CO})_{10}$  geometries.

unit through its doubly bridging CO groups acting as four-electron donors.

The global minimum for  $\text{Nb}_2(\text{CO})_{10}$  is the asymmetric singlet  $C_s$  structure **10S-1** with one Nb atom bonded to six CO groups



**Figure 5.** Optimized triplet  $\text{Nb}_2(\text{CO})_{10}$  geometries.

Table 6. Total Energies ( $E$ , in Hartree), Relative Energies ( $\Delta E$ , in kcal/mol), Numbers of Imaginary Vibrational Frequencies ( $N_{\text{imag}}$ ), and Nb–Nb Bond Distances (Å) for the Singlet  $\text{Nb}_2(\text{CO})_{10}$  Structures

		<b>10S-1 (<math>C_s</math>)</b>	<b>10S-2 (<math>C_{2v}</math>)</b>	<b>10S-3 (<math>C_2</math>)</b>	<b>10S-4 (<math>C_{2h}</math>)</b>	<b>10S-5 (<math>C_2</math>)</b>
MPW1PW91	$E$	-1247.36824	-1247.35463	-1247.35234	-1247.35149	-1247.33452
	$\Delta E$	0.0	8.5	10.3	10.5	21.2
	Nimg	0	1 ( $S4i$ )	1 ( $12i$ )	1 ( $18i$ )	0
	Nb–Nb	2.799	2.867	2.726	2.742	3.397
BP86	$E$	-1247.87732	-1247.86496	-1247.86293	-1247.86192	-1247.84404
	$\Delta E$	0.0	7.8	9.0	9.7	20.9
	Nimg	0	1 ( $S3i$ )	1 ( $20i$ )	1 ( $22i$ )	0
	Nb–Nb	2.824	2.893	2.772	2.789	3.438

Table 7. Total Energies ( $E$ , in Hartree), Relative Energies ( $\Delta E$ , in kcal/mol), Numbers of Imaginary Vibrational Frequencies ( $N_{\text{imag}}$ ), and Nb–Nb Bond Distances (Å) for the Triplet  $\text{Nb}_2(\text{CO})_{10}$  Structures

		<b>10T-1 (<math>C_1</math>)</b>	<b>10T-2 (<math>C_1</math>)</b>	<b>10T-3 (<math>C_i</math>)</b>	<b>10T-4 (<math>C_{2v}</math>)</b>
MPW1PW91	$E$	-1247.33730	-1247.33678	-1247.33308	-1247.32399
	$\Delta E$	19.4	19.7	22.1	27.8
	Nimg	0	0	1 ( $5i$ )	0
	Nb–Nb	3.144	3.114	2.960	3.717
BP86	$E$	-1247.84553	-1247.84649	-1247.84456	-1247.83232
	$\Delta E$	19.9	19.3	20.6	28.2
	Nimg	0	0	1 ( $10i$ )	0
	Nb–Nb	3.128	3.133	3.029	3.831

(the “right” Nb atom in Figure 4) and the other Nb atom bonded to only four CO groups (the “left” Nb atom in Figure 4). The

inward three CO groups of the  $\text{Nb}(\text{CO})_6$  group are actually semibridging carbonyls to the  $\text{Nb}(\text{CO})_4$  group. In these three

semibridging carbonyls, the short Nb–C distances fall in the range from 2.132 to 2.134 Å (MPW1PW91) or from 2.144 to 2.149 Å (BP86), while the long Nb–C distances fall in the range from 2.699 to 2.709 Å (MPW1PW91) or from 2.697 to 2.706 Å (BP86). The C–O distances of ~1.16 Å (MPW1PW91) or ~1.18 Å (BP86) in the semibridging CO groups of **10S-1** are slightly longer than the C–O distances in the terminal CO groups. The Nb–C–O angles for the three semibridging CO groups deviate significantly from linearity (165° and 164°), while those for the terminal CO groups are almost linear. The predicted Nb≡Nb distances of 2.799 Å (MPW1PW91) or 2.824 Å (BP86) in **10S-1** correspond to a formal triple bond, thereby giving each niobium atom the favored 18-electron configuration.

The next  $\text{Nb}_2(\text{CO})_{10}$  structure **10S-2** is a  $C_{2v}$  doubly semibridged structure lying ~8 kcal/mol above the global minimum **10S-1** (Figure 4 and Table 6). In **10S-2**, one Nb atom (the “right” Nb atom in Figure 4) is bonded to six CO groups, whereas the other Nb atom (the “left” Nb atom in Figure 4) is bonded to only four CO groups, similar to **10S-1**. The two inward CO groups of the  $\text{Nb}(\text{CO})_6$  unit in **10S-2** are bonded to the  $\text{Nb}(\text{CO})_4$  unit as semibridging carbonyls with short Nb–C distances of 2.131 Å (MPW1PW91) or 2.145 Å (BP86) and long Nb–C distances of 2.569 Å (MPW1PW91) or 2.564 Å (BP86). The Nb–C–O angles for these semibridging CO groups deviate significantly from linearity, i.e., 162° (MPW1PW91) or 161° (BP86), while those for the terminal CO groups are almost linear. The Nb≡Nb distance in structure **10S-2** is 2.867 Å (MPW1PW91) or 2.893 Å (BP86), which is slightly longer than that of **10S-1** but still consistent with the formal triple bond required to give each Nb atom the favored 18-electron configuration. Structure **10S-2** has an imaginary vibrational frequency of  $54i\text{ cm}^{-1}$  (MPW1PW91) or  $53i\text{ cm}^{-1}$ . By following the corresponding normal mode, structure **10S-2** collapses to **10S-1**.

The next two singlet  $\text{Nb}_2(\text{CO})_{10}$  structures in terms of energy are **10S-3** ( $C_2$ ) and **10S-4** ( $C_{2h}$ ). These structures are both doubly semibridged  $(\text{CO})_4\text{Nb}(\mu\text{-CO})_2\text{Nb}(\text{CO})_4$  structures, differing only in the orientations of the CO groups (Figure 4 and Table 6). Structure **10S-3** lies 10.3 kcal/mol (MPW1PW91) or 9.0 kcal/mol (BP86) above the global minimum **10S-1**, whereas structure **10S-4** lies 10.5 kcal/mol (MPW1PW91) or 9.7 kcal/mol (BP86) above **10S-1**. In structures **10S-3** and **10S-4**, the Nb–C distances to the terminal carbonyl groups (four unique ones for **10S-3**, and three for **10S-4**) fall in the range from ~2.09 to ~2.16 Å. The short Nb–C distances to the semibridging carbonyl groups are ~2.14 Å, and the long Nb–C distances to the semibridging carbonyl groups are ~2.55 Å. The bridging Nb–C–O angles for both structures **10S-3** and **10S-4** deviate significantly from linearity (~162°). The Nb≡Nb distances for structure **10S-3** of 2.726 Å (MPW1PW91) or 2.772 Å (BP86) and for structure **10S-4** of 2.742 Å (MPW1PW91) or 2.789 Å (BP86) correspond to the formal triple bonds required to give each niobium atom the favored 18-electron configuration. Both structures **10S-3** and **10S-4** are predicted to have small imaginary vibrational frequencies at  $\sim 20i\text{ cm}^{-1}$  (Table 6), which cannot be removed by using a finer integration grid (120, 974). By following the corresponding normal modes, both **10S-3** and **10S-4** collapse to **10S-1**.

Three triplet  $\text{Nb}_2(\text{CO})_{10}$  structures, **10T-1**, **10T-2**, and **10T-3**, without bidentate  $\text{Nb}(\text{CO})_6$  ligands were found having Nb–Nb distances of ~3.1 Å (Figure 5 and Table 7). Structure **10T-1** is a doubly bridged  $C_1$  structure. For one of the bridging CO groups, the Nb–O distance is very short, namely, 2.55 Å (MPW1PW91)

or 2.57 Å (BP86), indicating a four-electron donor bridging  $\eta^2\text{-}\mu\text{-CO}$  group. The two Nb–C distances to this carbonyl are 2.379 Å (MPW1PW91) or 2.384 Å (BP86) and 2.804 Å (MPW1PW91) or 2.678 Å (BP86), respectively, and its Nb–C–O angle is ~174°, deviating only ~6° from linearity. The corresponding C–O distance is relatively long at 1.183 Å (MPW1PW91) or 1.201 Å (BP86), and the  $\nu(\text{CO})$  frequency is very low at  $1773\text{ cm}^{-1}$  (BP86). The Nb···O distance to the other bridging CO group in **10T-1** is very long, namely, 3.52 Å (MPW1PW91) or 3.49 Å (BP86). This indicates no direct Nb–O interaction and thus a normal two-electron donor bridging CO group. The Nb–C–O angle to this bridging carbonyl group of ~163° deviates significantly from linearity. The C–O distance in this bridging CO group is shorter, i.e., 1.159 Å (MPW1PW91) or 1.180 Å (BP86), than that to the  $\eta^2\text{-}\mu\text{-CO}$  group. This is consistent with its predicted  $\nu(\text{CO})$  frequency of  $1878\text{ cm}^{-1}$  (BP86). The Nb≡Nb distance in **10T-1** of 3.144 Å (MPW1PW91) or 3.128 Å (BP86) can be interpreted as a formal double bond, thereby giving each niobium atom the favored 18-electron configuration for a  $\text{Nb}_2(\text{CO})_{10}$  structure with a single four-electron donor  $\eta^2\text{-}\mu\text{-CO}$  group. This Nb≡Nb double bond can be a  $\sigma + 2/2\pi$  double bond similar to that in **11T-1**, **11T-2**, and **11T-3** discussed above and thus contains the two unpaired electrons for the triplet spin state.

The triplet  $\text{Nb}_2(\text{CO})_{10}$  structure **10T-2** is a doubly bridged  $C_1$  structure with a geometry and energy very close to **10T-1** (Figure 5 and Table 7). The main difference between these two  $\text{Nb}_2(\text{CO})_{10}$  structures is the orientation of the bridging CO groups, suggesting that the two structures can interconvert by motion of the bridging carbonyls. For one of the bridging CO groups in **10T-2**, the Nb–O distance is very short, i.e., 2.50 Å (MPW1PW91) or 2.56 Å (BP86); the C–O distance is relatively long at 1.184 Å (MPW1PW91) or 1.201 Å (BP86); and the predicted  $\nu(\text{CO})$  frequency of  $1769\text{ cm}^{-1}$  is very low. All of these characteristics indicate a four-electron donor bridging  $\eta^2\text{-}\mu\text{-CO}$  group. In contrast, for the other bridging CO group in **10T-2**, the Nb–O distance is very long, namely, 3.28 Å (MPW1PW91) or 3.31 Å (BP86), indicating a typical two-electron donor bridging CO group. The related C–O distance is 0.02 Å shorter, i.e., 1.168 Å, and its corresponding  $\nu(\text{CO})$  frequency is  $1847\text{ cm}^{-1}$  (BP86). The structure **10T-2** ( $C_1$ ) is a genuine minimum with all real vibrational frequencies (Table 7). The Nb≡Nb distance in **10T-2** is 3.114 Å (MPW1PW91) or 3.133 Å (BP86), which is consistent with the formal double bond required to give each niobium atom the favored 18-electron configuration. However, as for many of the other triplet  $\text{Nb}_2(\text{CO})_{11}$  and  $\text{Nb}_2(\text{CO})_{10}$  structures, this Nb≡Nb double bond can be of the  $\sigma + 2/2\pi$  type, thereby containing the two unpaired electrons for the triplet spin state.

The  $\text{Nb}_2(\text{CO})_{10}$  structure **10T-3** is a  $C_i$  structure with two equivalent semibridging carbonyls and eight (four unique) terminal carbonyls (Figure 5 and Table 7). Structure **10T-3** lies 22.1 kcal/mol (MPW1PW91) or 20.6 kcal/mol (BP86) above **10S-1**. Structure **10T-3** has a negligible imaginary vibrational frequency ( $5i\text{ cm}^{-1}$  by MPW1PW91 or  $10i\text{ cm}^{-1}$  by BP86). The former ( $5i\text{ cm}^{-1}$ ) becomes real when a finer integration grid (120, 974) is used. The predicted  $\nu(\text{CO})$  frequencies of 1850 and  $1862\text{ cm}^{-1}$  (BP86) in **10T-3** correspond to the semibridging carbonyl groups. The short Nb–C bond distances to the identical semibridging carbonyl groups in **10T-3** are 2.105 Å (MPW1PW91) or 2.118 Å (BP86), whereas the long Nb–C distances are 2.593 Å (MPW1PW91) or 2.557 Å (BP86). The four unique Nb–C distances to the terminal carbonyls in **10T-3**

**Table 8.** Infrared  $\nu(\text{CO})$  Vibrational Frequencies ( $\text{cm}^{-1}$ ) Predicted by the BP86 Method for the  $\text{Nb}_2(\text{CO})_{10}$  Structures (Infrared Intensities in Parentheses Are in  $\text{km/mol}$ )

	BP86
10S-1 ( $C_s$ )	1900 (514), 1900 (464), 1916 (373), 1950 (733), 1951 (1612), 1952 (881), 1992 (714), 1992 (736), 2015 (1901), 2053 (285)
10S-2 ( $C_{2v}$ )	1877 (756), 1885 (404), 1946 (1481), 1947 (287), 1949 (0), 1967 (2471), 1982 (113), 1991 (724), 2017 (1686), 2051 (286)
10S-3 ( $C_2$ )	1874 (57), 1890 (804), 1958 (63), 1960 (2), 1964 (2257), 1978 (163), 1979 (1537), 1983 (1190), 2012 (2669), 2058 (4)
10S-4 ( $C_{2h}$ )	1867 (0), 1888 (840), 1957 (0), 1960 (2116), 1966 (0), 1979 (323), 1985 (2856), 1987 (0), 2013 (2616), 2060 (0)
10S-5 ( $C_2$ )	1729 (650), 1754 (430), 1934 (234), 1942 (563), 1943 (543), 1967 (2851), 1979 (217), 1995 (779), 2015 (1976), 2052 (188)
10T-1 ( $C_1$ )	1773 (368), 1878 (235), 1935 (205), 1943 (687), 1947 (481), 1969 (2672), 1976 (36), 1987 (863), 1998 (3499), 2054 (138)
10T-2 ( $C_1$ )	1769 (333), 1847 (353), 1939 (21), 1949 (724), 1956 (552), 1968 (2919), 1969 (849), 1980 (71), 2003 (3467), 2053 (8)
10T-3 ( $C_t$ )	1850 (0), 1862 (876), 1939 (0), 1948 (1615), 1950 (0), 1968 (981), 1970 (2598), 1975 (0), 2001 (3396), 2053 (0)
10T-4 ( $C_{2v}$ )	1720 (695), 1735 (70), 1922 (667), 1943 (66), 1951 (886), 1969 (3016), 1970 (240), 1982 (877), 1998 (3644), 2049 (56)

**Table 9.** Formal Nb–Nb Single Bonds in Binuclear Niobium Carbonyls and Related Compounds

compound	bridges	Nb–Nb distance, Å
$\text{Nb}_2(\text{CO})_{12}$		
12S-1		3.40
12S-2		3.39
12S-3		3.64
12S-4	2 CO	3.42
$\text{Nb}_2(\text{CO})_{11}$		
11S-1	$\eta^2\text{-}\mu\text{-CO}$	3.51
11S-4		3.44
$\text{Nb}_2(\text{CO})_{10}$		
10S-5	2 $\eta^2\text{-}\mu\text{-CO}$	3.42
$\text{Cp}_2\text{Nb}_2(\text{CO})_7$ (ref 49)		3.40
$\text{Cp}_2\text{Nb}_2(\text{CO})_5(\eta^2\text{-}\mu\text{-CO})$ (ref 49)	$\eta^2\text{-}\mu\text{-CO}$	3.21
$\text{Cp}_3\text{Nb}_3(\text{CO})_6(\eta^2\text{-}\mu_3\text{-CO})$ (theory) <sup>48</sup>	variable	3.08, 3.24, 3.37
$\text{Cp}_3\text{Nb}_3(\text{CO})_6(\eta^2\text{-}\mu_3\text{-CO})$ (exptl.) <sup>47</sup>	variable	3.04, 3.18, 3.32

range from 2.087 to 2.173 Å (MPW1PW91) or 2.087 to 2.171 Å (BP86). The Nb=Nb distance in **10T-3** is 2.961 Å (MPW1PW91) or 3.029 Å (BP86). This is consistent with the formal double bond required to give each niobium atom the 17-electron configuration for a binuclear  $\text{Nb}_2(\text{CO})_{10}$  triplet structure with only two-electron donor carbonyl groups.

The  $\text{Nb}_2(\text{CO})_{10}$  structures with a chelating bidentate  $\text{Nb}(\text{CO})_6$  “ligand” bonded to the  $\text{Nb}(\text{CO})_4$  unit are **10S-5** ( $C_2$ ) and **10T-4** ( $C_{2v}$ ). These structures are characterized by very long Nb–Nb distances (>3.4 Å), suggesting very weak, if any, direct interactions between the two Nb atoms. Thus, the  $\text{Nb}(\text{CO})_6$  and  $\text{Nb}(\text{CO})_4$  units in these structures are linked mainly by the two bridging CO groups, which are four-electron donor CO groups. These two four-electron donor CO groups are characterized by very short Nb–O distances (<2.460 Å) and  $\nu(\text{CO})$  frequencies below 1800 cm<sup>-1</sup> (BP86). For **10S-5**, the Nb–Nb distance of 3.397 Å (MPW1PW91) or 3.438 Å (BP86) suggests the weak single bond required to give both niobium atoms the favored 18-electron configuration. The bridging CO groups in **10S-5** have short Nb–C distances of 2.070 Å (MPW1PW91) or 2.087 Å (BP86) to one niobium atom and long Nb–C distances of 2.495 Å (MPW1PW91) or 2.504 Å (BP86) to the other niobium atom. For the triplet structure **10T-4**, the Nb···Nb distance is even longer, namely, 3.717 Å (MPW1PW91) or 3.831 Å (BP86). This suggests a lack of niobium–niobium bonding, thereby giving each

**Table 10.** Formal Nb=Nb Double Bonds in Binuclear Niobium Carbonyls and Related Compounds

compound	bridges	Nb–Nb distance, Å
$\text{Nb}_2(\text{CO})_{11}$		
11S-2		3.08
11S-3	CO	3.09
11T-1		3.14
11T-2	CO	3.08
11T-3		3.19
10T-1	$\eta^2\text{-}\mu\text{-CO}$	3.13
10T-2	$\eta^2\text{-}\mu\text{-CO}$	3.12
$\text{Nb}_2(\text{CO})_{10}$ ( <b>10T-3</b> )		2.99
$\text{Cp}_2\text{Nb}_2(\text{CO})_6$ (ref 49)		2.99
$\text{Cp}_2\text{Nb}_2(\text{CO})_2(\eta^2\text{-}\mu\text{-CO})_2$ (ref 49)	2 $\eta^2\text{-}\mu\text{-CO}$	2.97

**Table 11.** Formal Nb≡Nb Triple Bonds in Binuclear Niobium Carbonyls and Related Compounds

compound	bridges	Nb–Nb distance, Å
$\text{Nb}_2(\text{CO})_{10}$		
10S-1		2.81
10S-2		2.88
10S-3		2.75
$\text{Cp}_2\text{Nb}_2(\text{CO})_5$ (ref 49)		2.74
$\text{Cp}_2\text{Nb}_2(\text{CO})(\eta^2\text{-}\mu\text{-CO})_2$ (ref 49)	2 $\eta^2\text{-}\mu\text{-CO}$	2.84

niobium atom a 17-electron configuration, consistent with a binuclear triplet. Both **10S-5** and **10T-4** are genuine minima, having all real vibrational frequencies. However, these two structures lie at relatively high energies, namely, ~21 kcal/mol above **10S-1** for **10S-5** and ~28 kcal/mol above **10S-1** for **10T-4**.

Table 8 lists the infrared  $\nu(\text{CO})$  frequencies for the nine  $\text{Nb}_2(\text{CO})_{10}$  structures, predicted by the BP86 method. The  $\nu(\text{CO})$  frequencies for the terminal CO groups fall between 1922 and 2060 cm<sup>-1</sup>, whereas those for the two-electron donor bridging CO groups are appreciably lower between 1850 and 1916 cm<sup>-1</sup> (**bold face** in Table 8). The four-electron donor bridging  $\eta^2\text{-}\mu\text{-CO}$  groups in **10S-5**, **10T-1**, **10T-2**, and **10T-4** are predicted to exhibit even lower  $\nu(\text{CO})$  frequencies between 1720 and 1773 cm<sup>-1</sup> (BP86; **bold face** in Table 8).

**3.4. Niobium–Niobium Bonding.** Tables 9, 10, and 11 compare formal Nb–Nb single bonds, Nb=Nb double bonds,

**Table 12.** Atomic Charges and Wiberg Bond Indices for the  $\text{Nb}_2(\text{CO})_n$  Structures Using the BP86 Method

structure	number of CO bridges	Nb–Nb distance, Å	formal bond order	natural charge on Nb(left)/ Nb(right)
$\text{Nb}_2(\text{CO})_{12}$				
12S-1	0	3.40	0.27	1    -1.92/-1.80
12S-2	0	3.39	0.27	1    -1.86/-1.86
12S-3	0	3.64	0.38	1    -1.85/-1.85
12S-4	2	3.42	0.14	1    -1.90/-1.90
$\text{Nb}_2(\text{CO})_{11}$				
11S-1	$\eta^2\text{-}\mu\text{-CO}$	3.51	0.29	1    -1.90/-1.37
11S-2	1 (semi)	3.07	0.42	2    -1.71/-1.56
11S-3	1	3.10	0.47	2    -1.70/-1.70
11S-4	0	3.44	0.27	1    -1.79/-1.19
11T-1	1	3.14	0.45	2    -1.57/-1.80
11T-2	1	3.08	0.47	2    -1.70/-1.70
11T-3	2 (semi)	3.19	0.37	2    -1.44/-1.89
$\text{Nb}_2(\text{CO})_{10}$				
10S-1	3 (semi)	2.81	0.64	3    -0.99/-2.01
10S-2	2 (semi)	2.88	0.58	3    -0.88/-2.09
10S-3	3 (semi)	2.75	0.86	3    -1.54/-1.54
10S-4	2 (semi)	2.76	0.88	3    -1.55/-1.55
10S-5	$2\eta^2\text{-}\mu\text{-CO}$	3.42	0.39	1    -1.05/-1.84
10T-1	$\eta^2\text{-}\mu\text{-CO}$	3.13	0.45	2    -1.09/-1.84
10T-2	$\eta^2\text{-}\mu\text{-CO}$	3.12	0.46	2    -1.45/-1.44
10T-3	2 (semi)	2.99	0.52	2    -1.44/-1.44
10T-4	$2\eta^2\text{-}\mu\text{-CO}$	3.77	0.19	0    -0.89/-1.86

and  $\text{Nb}\equiv\text{Nb}$  triple bonds, respectively, in various  $\text{Nb}_2(\text{CO})_n$  derivatives ( $n = 12, 11, 10$ ) with similar bonds in other niobium carbonyl species. However, the only niobium carbonyl derivative for which experimental data are available on Nb–Nb distances<sup>47</sup> is the unusual trinuclear species  $\text{Cp}_3\text{Nb}_3(\text{CO})_6(\eta^2\text{-}\mu_3\text{-CO})$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) with an unusual six-electron donor  $\eta^2\text{-}\mu_3\text{-CO}$  group bridging all three niobium atoms in the central  $\text{Nb}_3$  triangle. Because of this limited amount of experimental data, niobium–niobium distances in the binuclear cyclopentadienyl-niobium carbonyl derivatives  $\text{Cp}_2\text{Nb}_2(\text{CO})_n$  ( $n = 7, 6, 5, 4, 3$ ) predicted in previous theoretical studies<sup>48,49</sup> are also included in the tables. However, only the Nb–Nb distances for the lowest energy predicted  $\text{Cp}_2\text{Nb}_2(\text{CO})_n$  structures of a given type are included. The theoretical values of the Nb–Nb distances in the tables are the means of the values predicted by the MPW1PW91 and BP86 methods.

The Nb–Nb single bond distances in singlet  $\text{Nb}_2(\text{CO})_n$  structures are seen to be very close to 3.4 Å (Table 9). A similar Nb–Nb single bond distance is predicted<sup>49</sup> for the unknown  $\text{Cp}_2\text{Nb}_2(\text{CO})_7$ , which also has a singlet spin state.

The Nb=Nb double bond distances in both singlet and triplet  $\text{Nb}_2(\text{CO})_n$  structures are consistently shorter than the formal Nb–Nb single bonds. Thus, the Nb=Nb double bond distances fall in the narrow range of 2.99–3.19 Å (Table 10). This range is similar to that previously predicted<sup>49</sup> for the Nb=Nb distances in the lowest energy singlet  $\text{Cp}_2\text{Nb}_2(\text{CO})_6$  and  $\text{Cp}_2\text{Nb}_2(\text{CO})_2(\eta^2\text{-}\mu\text{-CO})_2$  structures.

The only binuclear niobium carbonyls found in this work with formal  $\text{Nb}\equiv\text{Nb}$  triple bonds have singlet spin states. The predicted Nb≡Nb triple bond lengths in such  $\text{Nb}_2(\text{CO})_n$  structures are consistently shorter than formal Nb=Nb double bond lengths and fall in the narrow range of 2.75–2.81 Å (Table 11). This range is bracketed by the predicted<sup>49</sup> Nb≡Nb triple bond lengths of 2.74 Å in  $\text{Cp}_2\text{Nb}_2(\text{CO})_5$  and 2.84 Å in  $\text{Cp}_2\text{Nb}_2(\text{CO})(\eta^2\text{-}\mu\text{-CO})_2$ .

Table 12 lists the Wiberg bond indices (WBIs)<sup>50</sup> and bond distances for the Nb–Nb bonds in the  $\text{Nb}_2(\text{CO})_n$  derivatives. The results with the BP86 method are used, since less spin contamination was found in the triplet structures, relative to the MPW1PW91 method. The WBIs are seen to correlate reasonably with the formal bond orders estimated from the niobium–niobium distances and electron counting. In this connection, previous studies on the WBIs in metal–metal bonded derivatives suggest typical values of 0.2–0.3 for unbridged formal metal–metal single bonds.<sup>51</sup> The WBIs for the single Nb–Nb bonds in the unbridged  $\text{Nb}_2(\text{CO})_{12}$  structures fall in a similar range from 0.27 to 0.39. The likewise long Nb–Nb formal single bonds of ~3.5 Å in the  $\text{Nb}_2(\text{CO})_{11}$  structures 11S-1 and 11S-4, which are clearly derived from the lowest energy  $\text{Nb}_2(\text{CO})_{12}$  structure 12S-1 by loss of a terminal carbonyl group, have similar WBIs of 0.27–0.29. The Nb=Nb double bonds in the  $\text{Nb}_2(\text{CO})_{11}$  and  $\text{Nb}_2(\text{CO})_{10}$  structures 11S-2, 11T-1, 10S-5, 10T-1, and 10T-2 have significantly higher WBIs from 0.42 to 0.52. The Nb≡Nb triple bonds in the singlet  $\text{Nb}_2(\text{CO})_{10}$  structures 10S-1, 10S-2, 10S-3, and 10S-4 have still higher WBIs falling in the range from 0.58 to 0.88. The WBI for the nonbonding Nb atoms in 10T-4 is very small, i.e., 0.19.

The major factor affecting the natural charges on the niobium atoms in the  $\text{Nb}_2(\text{CO})_n$  derivatives is the number of carbonyl groups to which they are bonded (Table 12). This suggests that the  $\pi$  back-bonding of the niobium atom to the antibonding orbitals of the carbonyl groups is not sufficient to remove all of the negative charge arising from the  $\sigma$  forward bonding. Thus, the natural charges on the niobium atoms bearing six carbonyl groups such as the unbridged  $\text{Nb}_2(\text{CO})_{12}$  structures fall in the narrow range –1.80 to –1.92. Niobium atoms bonded to five terminal carbonyl groups are less negative with natural charges in the range –1.19 to –1.57. Similarly for the two  $\text{Nb}_2(\text{CO})_{10}$  structures, in which one of the niobium atoms is bonded to only four terminal carbonyl groups, namely, 10S-1 and 10S-5 (Figure 4), the natural charges on the niobium atoms are even less negative, from –0.88 to –0.99.

**3.5. Thermochemistry.** Table 13 lists the dissociation energies for the reactions  $\text{Nb}_2(\text{CO})_n \rightarrow \text{Nb}_2(\text{CO})_{n-1} + \text{CO}$  ( $n = 12, 11, 10$ ) considering the lowest energy structures of  $\text{Nb}_2(\text{CO})_n$ , e.g., 12S-1, 11S-1, and 10S-1. The dissociation energies for the loss of one carbonyl group from  $\text{Nb}_2(\text{CO})_{12}$  and  $\text{Nb}_2(\text{CO})_{11}$  are relatively low, namely, ~18 kcal/mol and ~15 kcal/mol, respectively. However, the predicted energy for the loss of one CO group from  $\text{Nb}_2(\text{CO})_{10}$  is much higher at ~37 kcal/mol. For comparison, the experimental BDEs<sup>52</sup> for  $\text{Ni}(\text{CO})_4$ ,  $\text{Fe}(\text{CO})_5$ , and  $\text{Cr}(\text{CO})_6$  are 27 kcal/mol, 41 kcal/mol, and 37 kcal/mol, respectively.

Table 13 also lists the energies of the disproportionation reactions  $2\text{Nb}_2(\text{CO})_n \rightarrow \text{Nb}_2(\text{CO})_{n+1} + \text{Nb}_2(\text{CO})_{n-1}$ . The disproportionation of  $\text{Nb}_2(\text{CO})_{11}$  into  $\text{Nb}_2(\text{CO})_{12} + \text{Nb}_2(\text{CO})_{10}$  is slightly exothermic by ~4 kcal/mol, suggesting that  $\text{Nb}_2(\text{CO})_{11}$  might not be a viable species. However, the disproportionation of  $\text{Nb}_2(\text{CO})_{10}$  into  $\text{Nb}_2(\text{CO})_9 + \text{Nb}_2(\text{CO})_{11}$  is endothermic by ~22 kcal/mol.

**Table 13.** Dissociation Energies (kcal/mol) for the Successive Removal of Carbonyl Groups, Dissociation Energies into Mononuclear Fragments (kcal/mol), and Disproportionation Energies (kcal/mol) for  $\text{Nb}_2(\text{CO})_n$  ( $n = 12, 11, 10$ )<sup>a</sup>

	MPW1PW91	BP86
$\text{Nb}_2(\text{CO})_{12} \rightarrow \text{Nb}_2(\text{CO})_{11} + \text{CO}$	18.7	18.9
$\text{Nb}_2(\text{CO})_{11} \rightarrow \text{Nb}_2(\text{CO})_{10} + \text{CO}$	14.4	15.5
$\text{Nb}_2(\text{CO})_{10} \rightarrow \text{Nb}_2(\text{CO})_9 + \text{CO}$	36.5	37.4
$2\text{Nb}_2(\text{CO})_{11} \rightarrow \text{Nb}_2(\text{CO})_{12} + \text{Nb}_2(\text{CO})_{10}$	-4.3	-3.5
$2\text{Nb}_2(\text{CO})_{10} \rightarrow \text{Nb}_2(\text{CO})_{11} + \text{Nb}_2(\text{CO})_9$	22.1	21.9
$\text{Nb}_2(\text{CO})_{12} \rightarrow 2\text{Nb}(\text{CO})_6$	12.2	13.9
$\text{Nb}_2(\text{CO})_{11} \rightarrow \text{Nb}(\text{CO})_5 + \text{Nb}(\text{CO})_6$	29.5	32.2
$\text{Nb}_2(\text{CO})_{10} \rightarrow 2\text{Nb}(\text{CO})_5$	51.3	53.8
$\text{Nb}_2(\text{CO})_{10} \rightarrow \text{Nb}(\text{CO})_4 + \text{Nb}(\text{CO})_6$	51.1	54.3

<sup>a</sup> All results reported refer to the lowest energy structures of  $\text{Nb}_2(\text{CO})_n$ .

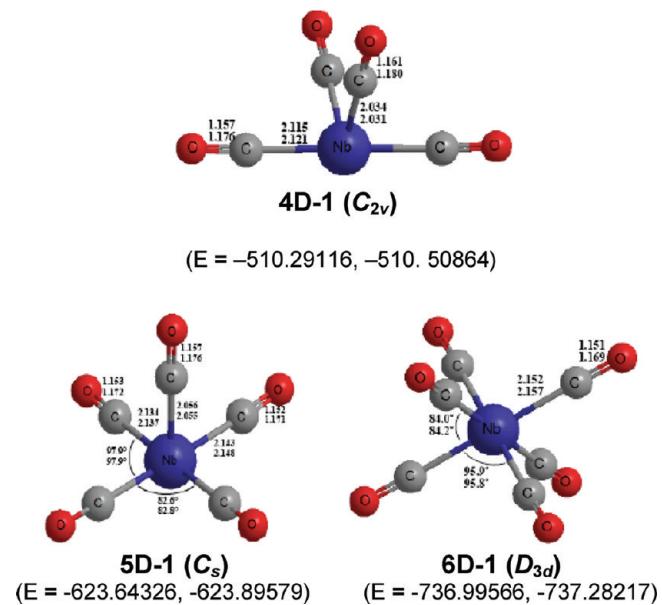
The dissociation of  $\text{Nb}_2(\text{CO})_n$  into mononuclear fragments is also shown in Table 13. In order to obtain these data, the global minima for the mononuclear  $\text{Nb}(\text{CO})_m$  ( $m = 6, 5, 4$ ) were optimized by the same DFT methods (Figure 6). The dissociation reactions of all  $\text{Nb}_2(\text{CO})_n$  structures ( $n = 12, 11, 10$ ) are all endothermic. The dissociation energy of the saturated  $\text{Nb}_2(\text{CO})_{12}$  into the  $\text{Nb}(\text{CO})_6$  fragments is found to be  $\sim 13$  kcal/mol, that for  $\text{Nb}_2(\text{CO})_{11}$  into  $\text{Nb}(\text{CO})_5$  and  $\text{Nb}(\text{CO})_6$  is  $\sim 30$  kcal/mol, and that for unsaturated  $\text{Nb}_2(\text{CO})_{10}$  is predicted to reach  $\sim 50$  kcal/mol. Thus, the binuclear  $\text{Nb}_2(\text{CO})_n$  complexes, even including  $\text{Nb}_2(\text{CO})_{12}$ , are viable with respect to dissociation into mononuclear fragments. The dissociation energies of  $\text{Nb}_2(\text{CO})_n$  monotonically increase with decreasing  $n$ , in accord with the increasing formal Nb–Nb bond orders.

A single  $\nu(\text{CO})$  frequency at  $1984.1 \text{ cm}^{-1}$  assigned to  $\text{Nb}(\text{CO})_6$  was observed by Zhou and Andrews<sup>14</sup> in the mixture of niobium carbonyls obtained by co-deposition of laser-ablated niobium atoms and carbon monoxide molecules in excess neon. Our theoretical structure for the doublet  $\text{Nb}(\text{CO})_6$  (Figure 6) has  $D_{3d}$  symmetry rather than ideal  $O_h$  symmetry, owing to the Jahn–Teller effect. For the six CO groups, the infrared active  $\nu(\text{CO})$  frequencies are only the  $e_u$  and  $a_{2u}$  modes. Both of these  $\nu(\text{CO})$  frequencies are predicted to occur at  $1961 \text{ cm}^{-1}$  using the BP86 method (Table 14). This is in good agreement with the experimental result of Zhou and Andrews and supports their assignment of this  $\nu(\text{CO})$  frequency to  $\text{Nb}(\text{CO})_6$ .

#### 4. DISCUSSION

The stable binary vanadium carbonyl is the 17-electron mono-nuclear  $\text{V}(\text{CO})_6$  rather than its dimer  $\text{V}_2(\text{CO})_{12}$ , consisting of two  $\text{V}(\text{CO})_6$  units linked by a V–V single bond. In  $\text{V}(\text{CO})_6$ , the vanadium atom is clearly six-coordinate, whereas in  $\text{V}_2(\text{CO})_{12}$  the vanadium atom is necessarily seven-coordinate. For the larger niobium atom, the binuclear  $\text{Nb}_2(\text{CO})_{12}$ , with a seven-coordinate niobium atom, is predicted to be the stable species, requiring an energy of  $\sim 13$  kcal/mol for dissociation into two  $\text{Nb}(\text{CO})_6$  units.

The  $\text{Nb}_2(\text{CO})_{12}$  structures found in this work (Figure 1 and Table 1) provide an interesting illustration of how symmetry breaking can reduce the energy of the optimized structures. Structure **12S-3** has relatively high  $D_{3d}$  symmetry with the CO groups occupying the octahedral positions and the Nb–Nb bond occupying the capping positions of the capped octahedral niobium coordination polyhedron. Structure **12S-3** has a pair of



**Figure 6.** Optimized geometries for the mononuclear  $\text{Nb}(\text{CO})_n$  ( $n = 6, 5, 4$ ). Total energies predicted by the MPW1PW91 and BP86 methods, respectively, are listed under each structure.

small imaginary vibrational frequencies ( $19i \text{ cm}^{-1}$  by MPW1PW91 or  $10i \text{ cm}^{-1}$  by BP86), which might be considered to be negligible. However, following the corresponding normal mode reduces the symmetry from  $D_{3d}$  to  $D_2$  and the energy by 8.7 kcal/mol (MPW1PW91) or 6.1 kcal/mol (BP86) to give structure **12S-2**. The collapse of **12S-3** to **12S-2** is accompanied by a shortening of the unusually long Nb–Nb bond of  $\sim 3.62 \text{ \AA}$  in **12S-3** to a more normal length of  $\sim 3.39 \text{ \AA}$  in **12S-2**. The  $\text{Nb}_2(\text{CO})_{12}$  structure **12S-2** still has a residual imaginary vibrational frequency of  $17i \text{ cm}^{-1}$  (MPW1PW91) or  $19i \text{ cm}^{-1}$  (BP86). Following the corresponding normal mode reduces the symmetry from  $D_2$  to  $C_2$  to give **12S-1**. However, the energy changes in going from **12S-2** are minimal (<0.1 kcal/mol) and the structural changes very subtle. These structures, closely spaced in energy, suggest  $\text{Nb}_2(\text{CO})_{12}$  to be a highly fluxional system.

The 18-electron rule requires  $\text{Nb}_2(\text{CO})_{11}$  to have a formal Nb=Nb double bond if all of the carbonyl groups are the usual two-electron donors. However, the lowest energy  $\text{Nb}_2(\text{CO})_{11}$  structure by  $\sim 12$  kcal/mol, namely, **11S-1** (Figure 2), has a relatively long Nb–Nb distance of  $\sim 3.5 \text{ \AA}$  and a four-electron donor bridging  $\eta^2\text{-}\mu\text{-CO}$  group. A closely related  $\text{V}_2(\text{CO})_{10}$  ( $\eta^2\text{-}\mu\text{-CO}$ ) structure is predicted<sup>4</sup> to be the lowest energy structure for  $\text{V}_2(\text{CO})_{11}$ , indicating the similarly of the vanadium and niobium carbonyl systems in this respect. However,  $\text{Nb}_2(\text{CO})_{11}$  is found to be disfavored with respect to disproportionation to give  $\text{Nb}_2(\text{CO})_{12} + \text{Nb}_2(\text{CO})_{10}$  (Table 12).

The lowest energy  $\text{Nb}_2(\text{CO})_{10}$  structure, namely, **10S-1** (Figure 4), has an unsymmetrical distribution of carbonyl groups and a short Nb≡Nb distance indicative of a formal triple bond. A closely related structure is predicted<sup>4</sup> to be the lowest energy structure of  $\text{V}_2(\text{CO})_{10}$ . Also, if the isolobal nature of  $\text{Nb}(\text{CO})_3$  and CpMo moieties is recognized, where Cp is a pentahapto cyclopentadienyl ring, then  $\text{Nb}_2(\text{CO})_{10}$  is isolobal with the stable  $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ , obtained by thermal reactions of  $\text{Mo}(\text{CO})_6$  with cyclopentadiene derivatives.<sup>53,54</sup> Thermochemistry suggests  $\text{Nb}_2(\text{CO})_{10}$  to be a viable species. Thus, the CO dissociation

**Table 14.** Infrared  $\nu(\text{CO})$  Vibrational Frequencies ( $\text{cm}^{-1}$ ) Predicted for  $\text{Nb}(\text{CO})_6$  (Infrared Intensities Are in Parentheses, in  $\text{km/mol}$ )<sup>a</sup>

Nb(CO) <sub>6</sub>	MPW1PW91	BP86
16S-1 ( $D_{3d}$ )	2082 (0), 2084 (5035), 2085 (1784), 2196 (0)	1959 (0), 1961 (4086), 1961 (1496), 2065 (0)

<sup>a</sup>The IR intensities are doubled for the doubly degenerate modes.

energy of  $\text{Nb}_2(\text{CO})_{10}$  is reasonably high at  $\sim 37 \text{ kcal/mol}$ , which is essentially the same as that of the very stable  $\text{Cr}(\text{CO})_6$ .<sup>52</sup> Furthermore, the energy required for disproportionation of  $\text{Nb}_2(\text{CO})_{10}$  into  $\text{Nb}_2(\text{CO})_{11} + \text{Nb}_2(\text{CO})_9$  is also reasonably high at  $\sim 22 \text{ kcal/mol}$ .

A second type of  $\text{Nb}_2(\text{CO})_{10}$  structure is found in which a  $\text{Nb}(\text{CO})_6$  unit acts as a chelating ligand toward a  $\text{Nb}(\text{CO})_4$  unit by using the oxygen atoms of two of its carbonyl groups. The lowest energy such  $\text{Nb}_2(\text{CO})_{10}$  structure, namely, 10S-5, lies  $\sim 21 \text{ kcal/mol}$  above the lowest energy  $\text{Nb}\equiv\text{Nb}$  triply bonded  $\text{Nb}_2(\text{CO})_{10}$  structure 10S-1 with only two-electron donor carbonyl groups (Figure 4). In the  $\text{Nb}_2(\text{CO})_{10}$  structures with a chelating  $\text{Nb}(\text{CO})_6$  “ligand”, both niobium atoms are hexa-coordinate, not counting any niobium–niobium interactions. The involvement of the oxygen atoms of the chelating carbonyl groups of the  $\text{Nb}(\text{CO})_6$  “ligand” in these  $\text{Nb}_2(\text{CO})_{10}$  structures makes the chelating carbonyl groups four-electron donors so that relatively low Nb–Nb bond orders are required to give each niobium atom a suitable electronic configuration.

The neutral homoleptic 17-electron vanadium carbonyl  $\text{V}(\text{CO})_6$  is synthesized by very mild oxidation of the 18-electron  $\text{V}(\text{CO})_6^-$  anion.<sup>3</sup> Such an oxidation is very delicate since  $\text{V}(\text{CO})_6^-$  is very sensitive toward further oxidation and indeed is spontaneously flammable in air under ambient conditions. In fact, the standard synthesis of  $\text{V}(\text{CO})_6$  involves acidification of  $\text{V}(\text{CO})_6^-$ , effectively using the proton as an oxidizing agent via an unstable  $\text{HV}(\text{CO})_6$  intermediate. A homoleptic niobium carbonyl has not yet been obtained by an analogous oxidation of the known  $\text{Nb}(\text{CO})_6^-$  anion, possibly because a suitably mild and selective oxidant has not yet been found. Studies by Ellis and co-workers<sup>11</sup> suggests that the use of coordinating solvents for  $\text{Nb}(\text{CO})_6^-$  oxidations prevents the oxidation from stopping at the zerovalent niobium oxidation state. This is consistent with the synthesis of  $[\text{Nb}_2(\mu-\text{X})_3(\text{CO})_8]^-$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) performed by Calderazzo and Pampaloni by the oxidation of  $\text{Nb}(\text{CO})_6^-$  in the presence of halide sources.<sup>13</sup> Thus, possible mild oxidation reactions of  $\text{Nb}(\text{CO})_6^-$  to neutral zerovalent homoleptic niobium carbonyl derivatives must be limited to noncoordinating solvents.

The theoretical study reported here suggests that the neutral homoleptic niobium carbonyls potentially obtainable by oxidation of  $\text{Nb}(\text{CO})_6^-$  are likely to be singlet binuclear derivatives with the favored 18-electron configuration for the niobium atoms rather than mononuclear  $\text{Nb}(\text{CO})_6$  analogous to the known  $\text{V}(\text{CO})_6$ .<sup>3</sup> The most obvious such oxidation product would be  $\text{Nb}_2(\text{CO})_{12}$  with a formal Nb–Nb single bond and total niobium coordination numbers of seven, e.g., structure 12S-1 (Figure 1). However, the relatively low CO dissociation energies of  $\text{Nb}_2(\text{CO})_{12}$  and  $\text{Nb}_2(\text{CO})_{11}$  as well as the instability of  $\text{Nb}_2(\text{CO})_{11}$  toward disproportionation into  $\text{Nb}_2(\text{CO})_{12} + \text{Nb}_2(\text{CO})_{10}$  suggests  $\text{Nb}_2(\text{CO})_{10}$  as another neutral homoleptic niobium carbonyl as a possible oxidation product of  $\text{Nb}(\text{CO})_6^-$ . The lowest energy  $\text{Nb}_2(\text{CO})_{10}$  structure 10S-1 (Figure 4) has a formal  $\text{Nb}\equiv\text{Nb}$  triple bond and is related to the known<sup>53,54</sup>

$\text{Cp}_2\text{Mo}_2(\text{CO})_4$  by replacement of the  $\text{CpMo}$  units in the latter structure with isoelectronic and isolobal  $\text{Nb}(\text{CO})_3$  units. Also, there is some experimental evidence for the production of the analogous  $\text{V}_2(\text{CO})_{10}$  from the excimer laser photolysis of  $\text{V}(\text{CO})_6$  vapor at 308 nm.<sup>16</sup>

## 5. CONCLUSIONS

Our theoretical studies predict the binuclear unbridged  $\text{Nb}_2(\text{CO})_{12}$  rather than the mononuclear  $\text{Nb}(\text{CO})_6$  to be a possible oxidation product of the known  $\text{Nb}(\text{CO})_6^-$  anion under conditions avoiding overoxidation or the formation of side products. Thus, the dissociation of  $\text{Nb}_2(\text{CO})_{12}$  to  $2\text{Nb}(\text{CO})_6$  is predicted to require an energy of  $\sim 13 \text{ kcal/mol}$ . This binuclear  $\text{Nb}_2(\text{CO})_{12}$  structure is particularly interesting since the niobium atoms are seven-coordinate, counting the Nb–Nb bond. The niobium coordination polyhedra in these structures can be approximated by capped octahedra.

The lowest energy  $\text{Nb}_2(\text{CO})_{11}$  structure is predicted to have a formal four-electron donor bridging  $\eta^2\text{-}\mu\text{-CO}$  group and a formal Nb–Nb single bond rather than only two-electron donor carbonyl groups and a formal  $\text{Nb}=\text{Nb}$  double bond. The  $\text{Nb}_2(\text{CO})_{11}$  structures with formal  $\text{Nb}=\text{Nb}$  double bonds and exclusively two-electron donor carbonyl groups lie more than 13 kcal/mol above this  $\text{Nb}_2(\text{CO})_{10}(\eta^2\text{-}\mu\text{-CO})$  structure. However,  $\text{Nb}_2(\text{CO})_{11}$  is predicted to be thermodynamically disfavored, owing to disproportionation into  $\text{Nb}_2(\text{CO})_{12} + \text{Nb}_2(\text{CO})_{10}$ , a slightly exothermic process by  $\sim 4 \text{ kcal/mol}$ .

The  $\text{Nb}_2(\text{CO})_{10}$  structures with formal  $\text{Nb}\equiv\text{Nb}$  triple bonds and all two-electron donor groups appear to be particularly favorable, as suggested by high CO dissociation energies and viability toward disproportionation. Such structures are isolobal with  $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ , which was the first stable metal carbonyl to be discovered with a short metal–metal distance corresponding to a formal triple bond. Considerably higher energy  $\text{Nb}_2(\text{CO})_{10}$  structures by more than 20 kcal/mol have two four-electron donor bridging carbonyl groups and long niobium–niobium distances. Such structures can be considered to consist of a chelating bidentate  $\text{Nb}(\text{CO})_6$  “ligand” coordinating to a  $\text{Nb}(\text{CO})_4$  unit through the two  $\eta^2\text{-}\mu\text{-CO}$  groups.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Tables S1–S26. Harmonic vibrational frequencies and infrared intensities for  $\text{Nb}_2(\text{CO})_{12}$  (4 structures),  $\text{Nb}_2(\text{CO})_{11}$  (7 structures), and  $\text{Nb}_2(\text{CO})_{10}$  (9 structures); Cartesian coordinates of the optimized structures; complete Gaussian reference (reference<sup>41</sup>). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Authors

\*E-mail: rbking@chem.uga.edu (R.B.K.); kelly.luo@126.com (Q.L.).

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