

The Quest for Metal–Metal Quadruple and Quintuple Bonds in Metal Carbonyl Derivatives: $\text{Nb}_2(\text{CO})_9$ and $\text{Nb}_2(\text{CO})_8$

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Supporting Information

ABSTRACT: The synthesis by Power and co-workers of the first metal–metal quintuple bond (*Science* 2005, 310, 844) is a landmark in inorganic chemistry. The 18-electron rule suggests that $\text{Nb}_2(\text{CO})_9$ and $\text{Nb}_2(\text{CO})_8$ are candidates for binary metal carbonyls containing metal–metal quadruple and quintuple bonds, respectively. Density functional theory (MPW1PW91 and BP86) indeed predicts structures having very short Nb–Nb distances of $\sim 2.5 \text{ \AA}$ for $\text{Nb}_2(\text{CO})_9$ and $\sim 2.4 \text{ \AA}$ for $\text{Nb}_2(\text{CO})_8$ as well as relatively large Nb–Nb Wiberg bond indices supporting these high formal Nb–Nb bond orders. However, analysis of the frontier molecular orbitals of these unbridged structures suggests formal $\text{Nb} \equiv \text{Nb}$ triple bonds and 16-electron metal configurations. This contrasts with an analysis of the frontier orbitals in a model chromium(I) alkyl linear $\text{CH}_3\text{CrCrCH}_3$, which confirms the generally accepted presence of chromium–chromium quintuple bonds in such molecules. The presence of $\text{Nb} \equiv \text{Nb}$ triple bonds rather than quadruple or quintuple bonds in the $\text{Nb}_2(\text{CO})_n$ ($n = 9, 8$) structures frees up $d(xy)$ and $d(x^2-y^2)$ orbitals for $d\pi \rightarrow p\pi^*$ back-bonding to the carbonyl groups. The lowest energy $\text{Nb}_2(\text{CO})_n$ structures ($n = 9, 8$) are not these unbridged structures but structures having bridging carbonyl groups of various types and formal Nb–Nb orders no higher than three. Thus, the two lowest energy $\text{Nb}_2(\text{CO})_9$ structures have $\text{Nb} \equiv \text{Nb}$ triple bond distances of $\sim 2.8 \text{ \AA}$ and three semibridging carbonyl groups, leading to a 16-electron configuration rather than an 18-electron configuration for one of the niobium atoms. The lowest energy structure of the highly unsaturated $\text{Nb}_2(\text{CO})_8$ is unusual since it has a formal *single* Nb–Nb bond of length $\sim 3.1 \text{ \AA}$ and two four-electron donor $\eta^2\text{-}\mu\text{-CO}$ groups, thereby giving each niobium atom only a 16-electron configuration.

1. INTRODUCTION

In 2005, Power et al.¹ reported the laboratory preparation of the first arguably² quintuple bond in the dichromium compound ArylCrCrAryl (Aryl = 2,6-(2,6-iPr₂C₆H₃)₂C₆H₃) depicted in Figure 1. As noted recently by Noor et al.,³ Power

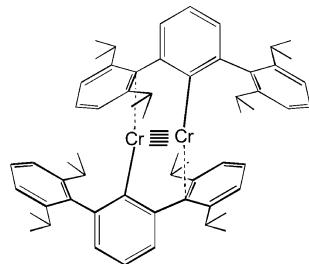


Figure 1. The first compound to be synthesized with a metal–metal quintuple bond.

et al.'s work has served to usher in exciting new chemistry.^{4–20} Thus far, the new quintuply bonded molecules involve either chromium or molybdenum, with tungsten as the next obvious candidate metal. Whether quintuple bonds for non-Cr/Mo/W transition metals can be made is a topic of lively discussion.⁹ The present paper seeks to move this discussion in the direction of niobium by density functional theory studies of the

highly unsaturated homoleptic niobium carbonyls $\text{Nb}_2(\text{CO})_n$ ($n = 9, 8$).

The chemistry of metal–metal multiple bonds dates back to the discovery by Cotton and Harris²¹ in 1965 of the rhenium–rhenium quadruple bond in the binuclear rhenium(III) halide complex $\text{Re}_2\text{Cl}_8^{2-}$. This was not only the first example of a metal–metal quadruple bond but also the first example of a quadruple bond of any type. The highest known formal metal–metal bond order in a stable molecule then remained four for 40 years until Power et al.'s discovery¹ of a binuclear chromium(I) aryl of the type RCrCrR , noted above. Subsequently, various research groups reported further experimental work on low oxidation state transition metal aryls of the type $\text{RMMR}^{22,23}$ as well as chromium(I) amidinate,^{24,25} 2-aminopyridine,²⁶ and diazadiene²⁷ complexes, apparently containing formal quintuple bonds.

The chemistry of binuclear metal carbonyl derivatives containing metal–metal multiple bonds^{28,29} dates back to the discovery of $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ derivatives (Cp = cyclopentadienyl or substituted cyclopentadienyl) in the late 1960s. Thus, in 1967, the simple thermal reaction of $\text{Mo}(\text{CO})_6$ with pentamethylcyclopentadiene³⁰ was reported to give the

Received: November 15, 2011

Published: January 30, 2012

tetracarbonyl ($\eta^5\text{-Me}_5\text{C}_5$)₂Mo₂(CO)₄ rather than the originally anticipated hexacarbonyl ($\eta^5\text{-Me}_5\text{C}_5$)₂Mo₂(CO)₆. Later, the analogous unsubstituted cyclopentadienyl derivative ($\eta^5\text{-C}_5\text{H}_5$)₂Mo₂(CO)₄ was also synthesized.³¹ Simple electron counting in these Cp₂Mo₂(CO)₄ derivatives and assuming 18-electron configurations^{32,33} for the molybdenum atoms suggest formal Mo≡Mo triple bonds. This proposal was later supported by structure determinations from X-ray crystallography, indicating very short Mo≡Mo distances, suggesting metal–metal multiple bonding. Thus, the metal–metal distance in ($\eta^5\text{-Me}_5\text{C}_5$)₂Mo₂(CO)₄, as determined by X-ray crystallography, was found to be 2.488 Å as compared with 3.235 Å for ($\eta^5\text{-C}_5\text{H}_5$)₂Mo₂(CO)₆, which clearly has a metal–metal single bond.³⁴

Subsequent work led to the discovery of other binuclear cyclopentadienyl metal carbonyls formulated with M≡M triple bonds on the basis of electron counting and short M≡M distances in their crystal structures, as exemplified by Cp₂V₂(CO)₅^{35,36} and Cp₂M'₂(CO)₃ (M' = Mn,³⁷ Re³⁸). However, no stable homoleptic binuclear metal carbonyls M₂(CO)_n have been synthesized in which electron counting and structural parameters suggest metal–metal multiple bonding of any order. In addition, no stable binuclear cyclopentadienylmetal carbonyls have been synthesized in which the combination of ultrashort metal–metal distances and electron counting suggest metal–metal multiple bonds of orders greater than three.

High order metal–metal multiple bonds are only one way of accommodating unsaturation in binuclear metal carbonyl derivatives. Another alternative is the conversion of one or two carbonyl groups in such structures from the usual two-electron donor carbonyl group to a four-electron donor bridging carbonyl group. The first example of a stable compound with a four-electron donor bridging carbonyl group was (Ph₂PCH₂PPh₂)₂Mn₂(CO)₄($\eta^2\text{-}\mu\text{-CO}$), which was synthesized by Colton and Commons³⁹ by heating Mn₂(CO)₁₀ with two molar equivalents of the Ph₂PCH₂PPh₂ ligand in boiling decane. Determination of the structure of this manganese complex by X-ray diffraction⁴⁰ indicated a very unusual bridging CO group with an abnormally short Mn–O distance of 2.29 Å, suggesting some direct manganese–oxygen bonding, as well as the usual manganese–carbon bonding to both manganese atoms expected for a bridging carbonyl group. The Mn–Mn distance of 2.934 Å in this complex suggested a single metal–metal bond so that the anomalous bridging CO group needed to be a formal four-electron donor for each manganese atom to have the favored 18-electron configuration. Such donation of four electrons can occur through one σ bond and one π bond. The π -bonding lowers the effective carbon–oxygen bond order, consistent with the very low bridging infrared $\nu(\text{CO})$ frequency of 1645 cm⁻¹ found experimentally for this metal complex.

The best candidates for binuclear metal carbonyls containing high order metal–metal bonds would seem to be the early transition metals, since they require the largest numbers of electrons from the surrounding ligands and metal–metal bonding to attain the favored 18-electron configuration. However, the early transition metals are also the most oxophilic of the transition metals so that their metal–metal bonds are most susceptible to being bridged by four-electron donor bridging carbonyl groups, which involve metal–oxygen as well as metal–carbon bonding to such carbonyl groups. In addition, the relatively large number of ligands required by early

transition metals to attain the favored 18-electron configuration suggests that such metals might form stable complexes in which the metal has fewer than the favored 18 valence electrons. For example, titanium forms an extensive series of stable compounds Cp₂TiX₂ (X = halogen^{41,42} or alkyl⁴³) in which the metal atom has only a 16-electron configuration.

The binuclear carbonyls M₂(CO)_n of the group 5 metals vanadium, niobium, and tantalum are possible candidates for species with metal–metal multiple bonds. Thus, the 18-electron rule^{32,33} predicts quadruple metal–metal bonds for M₂(CO)₉ derivatives and quintuple metal–metal bonds for M₂(CO)₈ derivatives (M = V, Nb, Ta). However, a previous theoretical study⁴⁴ did not find any evidence for structures with formal V⁴–V quadruple bonds for V₂(CO)₉. Instead, the low-energy V₂(CO)₉ structures were found to have a combination of vanadium–vanadium bonds of orders no greater than three, four-electron donor bridging carbonyl groups, and/or vanadium atoms with 16-electron configurations. For V₂(CO)₈, the lowest energy structures also have similar characteristics.⁴⁵ However, for V₂(CO)₈, higher energy structures lying 10–14 kcal/mol above the global minimum were found with extremely short V–V distances of ~1.95 Å. A possible interpretation of these very short V–V distances is the presence of the formal vanadium–vanadium quintuple bond required to give both vanadium atoms the favored 18-electron configuration in a V₂(CO)₈ structure.

The early observations of formal metal–metal triple bonds in the stable Cp₂Mo₂(CO)₄ derivatives containing the second row transition metal molybdenum^{30,31} as well as a formal metal–metal quadruple bond in the stable Re₂Cl₈²⁻ containing the third row transition metal rhenium²⁸ suggest that binuclear homoleptic metal carbonyl derivatives M₂(CO)_n of second and third row transition metals might be more promising candidates than those of the first row transition metals for stable structures with metal–metal quadruple and quintuple bonds of a given type. In order to explore such possibilities, we have investigated Nb₂(CO)₉ and Nb₂(CO)₈ using density functional theory. The results are reported in this paper.

2. THEORETICAL METHODS

Density functional theory (DFT) appears to be a powerful and effective computational tool to study organometallic compounds.^{46–52} Two different density functional theory (DFT) methods were used in the present study. The first DFT method is the BP86 method, which uses Becke's 1988 exchange functional (B) with Perdew's 1986 gradient corrected correlation functional method (P86).^{53,54} The second DFT method is MPW1PW91, which is a combination of the modified Perdew–Wang exchange functional with the Perdew–Wang's 91 gradient functional.⁵⁵ This MPW1PW91 functional has been shown to be better than the first generation functionals for some heavy transition metal compounds.⁵⁶

The Stuttgart/Dresden double- ζ (SDD) basis set with an effective core potential (ECP)^{57,58} 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- ζ sets^{59,60} plus a set of spherical harmonic d

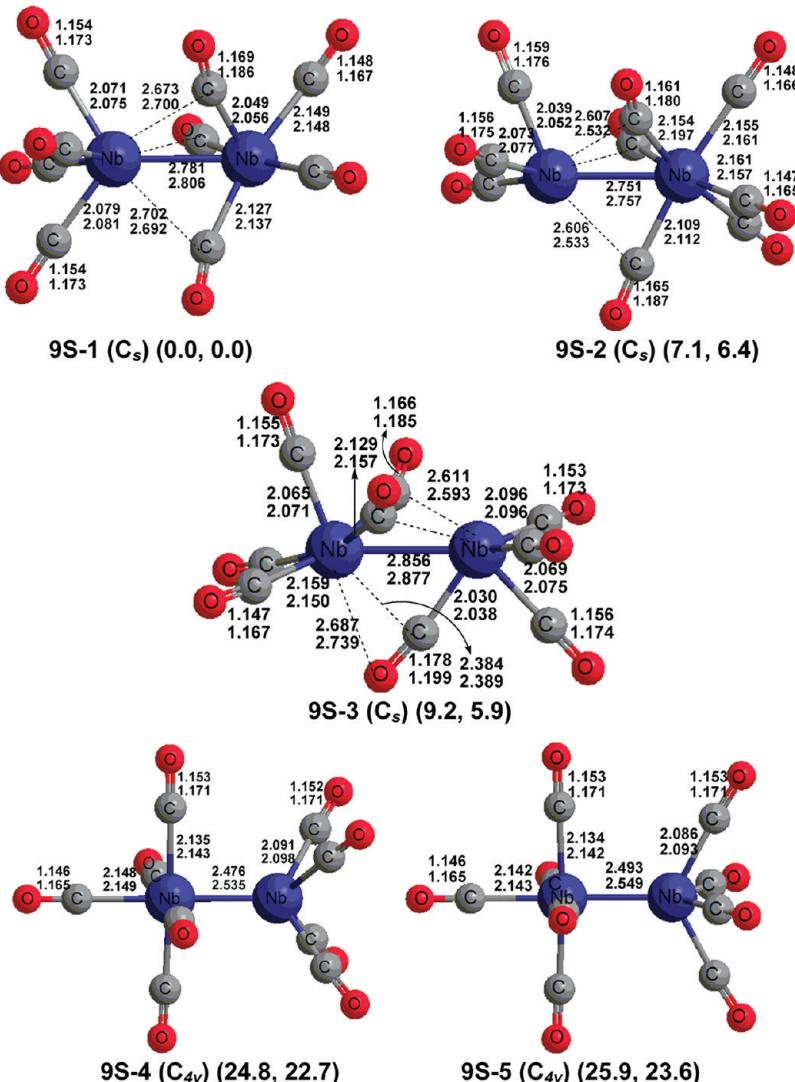


Figure 2. Optimized geometries of the singlet Nb₂(CO)₉ complexes. The distances are given in Å. The upper distances were determined by the MPW1PW91 method and the lower distance by the BP86 method. The relative energies (kcal/mol) predicted by the MPW1PW91 and BP86 methods, respectively, are shown in parentheses.

polarization functions with the orbital exponents $\alpha_d(C) = 0.75$ and $\alpha_d(O) = 0.85$. 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. 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,⁶¹ 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.

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.⁶² Thus, imaginary vibrational frequencies with a magnitudes less than $50i\text{ cm}^{-1}$ are considered questionable. For structures with small imaginary frequencies, the finer grid (120, 974) is used for further confirmation. In less critical cases, we do not follow the

eigenvectors corresponding to imaginary frequencies less than $50i\text{ cm}^{-1}$ in search of other minima.⁶³

In the present study, the MPW1PW91 and BP86 methods agree with each other fairly well in predicting the structural characteristics of the Nb₂(CO)_n derivatives ($n = 9, 8$). However, the BP86 method was found in previous work^{64,65} to predict $\nu(\text{CO})$ frequencies closer to the experimental values.

3. RESULTS

3.1. Nb₂(CO)₉. A total of 13 structures were found for Nb₂(CO)₉. However, only the 10 structures (five singlets and five triplets) with energies within 25 kcal/mol of the global minimum are discussed in detail in this paper (Figures 2 and 3). The Nb₂(CO)₉ global minimum 9S-1 (C_s symmetry) is an unusual singlet structure with three semibridging carbonyl groups and an unsymmetrical distribution of the remaining six CO groups, i.e., four CO groups on one niobium and only two CO groups on the other niobium. The very small imaginary vibrational frequency at $10i\text{ cm}^{-1}$ (MPW1PW91) or $13i\text{ cm}^{-1}$ (BP86) using the default (75, 302) integration grid is removed by using the (120, 974) finer integration grid. The shorter Nb–

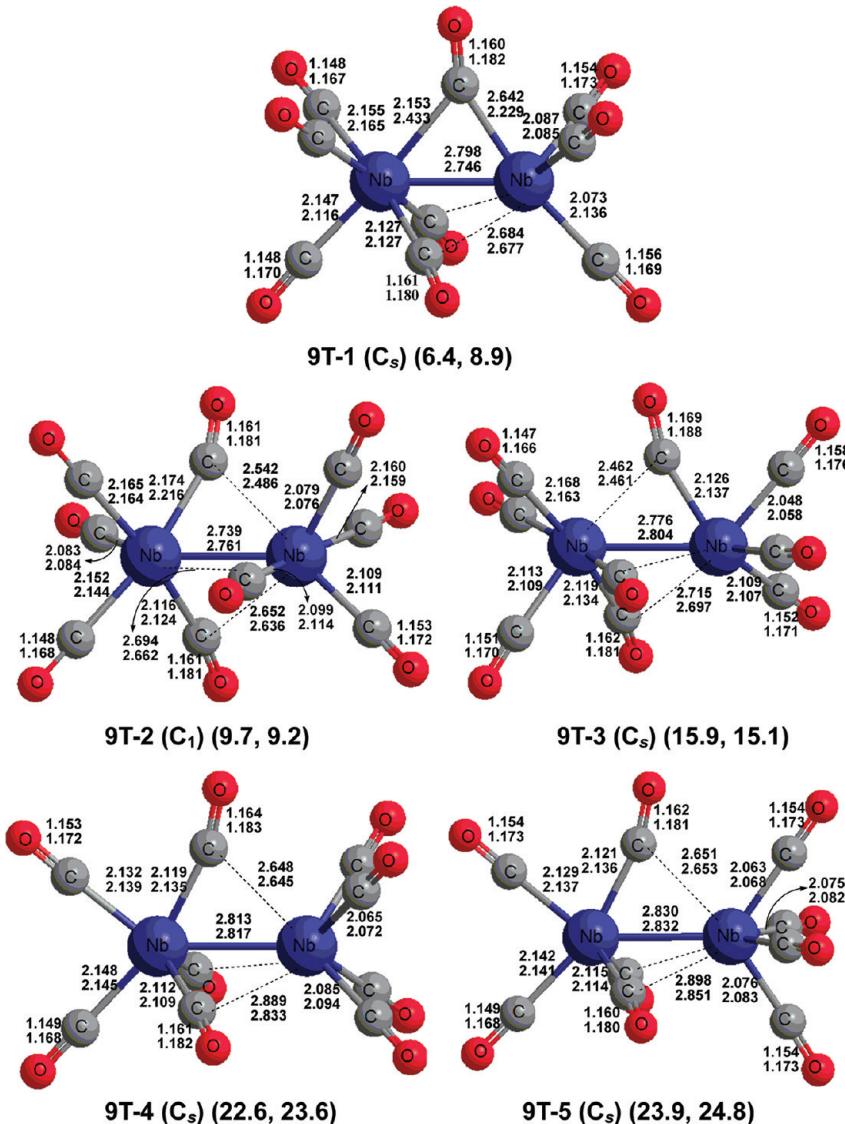


Figure 3. Optimized geometries of the triplet $\text{Nb}_2(\text{CO})_9$ structures. The distances are in Å. The upper distances were determined by the MPW1PW91 method, and the lower distances by BP86. The relative energies (kcal/mol) predicted by the MPW1PW91 and BP86 methods, respectively, are shown in parentheses.

C distances for the three semibridging carbonyls in **9S-1** range from 2.049 to 2.127 Å (MPW1PW91) or 2.056 to 2.137 Å (BP86), whereas the longer Nb–C distances range from 2.673 to 2.702 Å (MPW1PW91) or 2.692 to 2.700 Å (BP86). The lowest $\nu(\text{CO})$ frequencies at 1867, 1884, and 1901 cm^{-1} (BP86) in **9S-1** can be assigned to these three semibridging CO groups (Table S2S, in the Supporting Information). The six terminal carbonyl Nb–C distances range from 2.071 to 2.149 Å (MPW1PW91) or 2.075 to 2.148 Å (BP86), and the corresponding $\nu(\text{CO})$ frequencies range from 1947 to 2037 cm^{-1} (BP86). The Nb≡Nb distance of **9S-1** is 2.781 Å (MPW1PW91) or 2.806 Å (BP86), which is similar to the predicted Nb≡Nb triple bond distances in other binuclear niobium carbonyls⁶⁶ such as $\text{Cp}_2\text{Nb}_2(\text{CO})_6$ and $\text{Nb}_2(\text{CO})_{10}$, using similar theoretical methods. This gives one niobium atom in **9S-1** the favored 18-electron configuration but the other niobium atom only a 16-electron configuration. The niobium atom with the 16-electron configuration appears to be the “right” niobium atom in Figure 1, since there is an obvious gap

in its coordination sphere *trans* to one of the semibridging carbonyl groups.

The second low-lying singlet $\text{Nb}_2(\text{CO})_9$ structure **9S-2**, also with C_s symmetry, lies 7.1 kcal/mol (MPW1PW91) or 6.4 kcal/mol (BP86) in energy above **9S-1** with all real vibrational frequencies (Figure 2). Structure **9S-2** also has three semibridging CO groups and six terminal carbonyls, but in different positions for the terminal CO groups from **9S-1**. Thus, in structure **9S-2**, the six terminal CO groups are distributed equally between the two niobium atoms in contrast to **9S-1**. The shorter Nb–C bond distances for the semibridging carbonyls in **9S-2** range from 2.109 to 2.154 Å (MPW1PW91) or from 2.112 to 2.197 Å (BP86), whereas the longer Nb–C distances range from 2.606 to 2.607 Å (MPW1PW91) or 2.532 to 2.533 Å (BP86). The low $\nu(\text{CO})$ frequencies at 1858, 1891, and 1894 cm^{-1} (BP86) in **9S-2** can be assigned to the three semibridging CO groups. The Nb–C distances to the terminal carbonyls range from 2.039 to 2.161 Å (MPW1PW91) or from 2.052 to 2.161 Å (BP86), and the corresponding $\nu(\text{CO})$ frequencies range from 1921 to

2047 cm⁻¹ (BP86). The Nb≡Nb distance in **9S-2** is 2.751 Å (MPW1PW91) or 2.757 Å (BP86), similar to that in **9S-1** and likewise interpreted as a formal triple bond. Again, one of the niobium atoms in **9S-2** has the favored 18-electron configuration, but the other niobium atom has only a 16-electron configuration. In this case, the “left” niobium atom in Figure 2 appears to be the one with the 16-electron configuration, as indicated by the gap in the coordination sphere *trans* to one of the semibridging carbonyl groups.

A third low-lying singlet Nb₂(CO)₉ structure **9S-3** (C_s symmetry) lies 9.2 kcal/mol (MPW1PW91) or 5.9 kcal/mol (BP86) in energy above **9S-1** (Figure 2). Like **9S-1** and **9S-2**, the Nb₂(CO)₉ structure **9S-3** has three semibridging CO groups. However, in **9S-3**, unlike in **9S-1** and **9S-2**, the Nb—O distance to one of the semibridging CO groups is very short, i.e., 2.687 Å (MPW1PW91) or 2.739 Å (BP86), indicating a four-electron donor bridging $\eta^2\text{-}\mu\text{-CO}$ group. This is consistent with the very low $\nu(\text{CO})$ frequency of 1792 cm⁻¹ (BP86) for this carbonyl group (Table S25, in the Supporting Information). The shorter Nb—C bond distance to this $\eta^2\text{-}\mu\text{-CO}$ group is 2.030 Å (MPW1PW91) or 2.038 Å (BP86), whereas the longer Nb—C distance to this $\eta^2\text{-}\mu\text{-CO}$ group is 2.384 Å (MPW1PW91) or 2.389 Å (BP86). For the other two semibridging CO groups, which are symmetry equivalent, the shorter Nb—C bond distances are 2.129 Å (MPW1PW91) or 2.157 Å (BP86) and the longer Nb—C distances are 2.611 Å (MPW1PW91) or 2.593 Å (BP86). The $\nu(\text{CO})$ frequencies for these two-electron donor bridging CO groups are 1865 and 1870 cm⁻¹ (BP86), which lie between the $\nu(\text{CO})$ frequencies for the four-electron donor bridging CO group and the terminal CO groups. The Nb—C distances for the terminal carbonyls range from 2.065 to 2.159 Å (MPW1PW91) or from 2.071 to 2.150 Å (BP86). The Nb≡Nb distance in **9S-3** of 2.856 Å (MPW1PW91) or 2.877 Å (BP86) corresponds to a formal triple bond. This gives each niobium atom in **9S-3** the favored 18-electron configuration after considering the four-electron donor bridging $\eta^2\text{-}\mu\text{-CO}$ group.

The remaining two lower energy singlet Nb₂(CO)₉ structures, namely **9S-4** and **9S-5**, are unbridged structures with significantly shorter Nb—Nb distances than those in the first three singlet Nb₂(CO)₉ structures **9S-1**, **9S-2**, and **9S-3** (Figure 2). These very short Nb—Nb distances suggest the formal quadruple bonds required to give both niobium atoms in **9S-4** and **9S-5** the favored 18-electron configuration. Structures **9S-4** and **9S-5** differ by having staggered and eclipsed arrangements, respectively, of the carbonyl groups in the Nb(CO)₄ unit relative to those in the Nb(CO)₅ unit. Structures **9S-4** and **9S-5** are high energy structures relative to the triply bridged Nb₂(CO)₉ structures **9S-1**, **9S-2**, and **9S-3**. Thus, structures **9S-4** and **9S-5** lie 24.8 and 25.9 kcal/mol (MPW1PW91) or 22.7 and 23.6 kcal/mol, respectively, in energy above **9S-1**. The Nb—C distances for the nine terminal carbonyls in **9S-4** and **9S-5** fall in a narrow range, i.e., from 2.086 Å to 2.148 Å (MPW1PW91) or from 2.093 Å to 2.149 Å (BP86). The Nb—Nb distances of 2.476 Å and 2.493 Å (MPW1PW91) or 2.535 Å and 2.549 Å (BP86) for **9S-4** and **9S-5**, respectively, are \sim 0.3 Å shorter than those in **9S-1**, **9S-2**, and **9S-3**, consistent with the suggestion of formal Nb—Nb quadruple bonds in **9S-4** and **9S-5**.

The lowest lying triplet structure of Nb₂(CO)₉, namely **9T-1**, is a genuine C_s minimum with three semibridging carbonyls lying 6.4 kcal/mol (MPW1PW91) or 8.9 kcal/mol (BP86) in

energy above **9S-1** (Figure 3). For the two symmetry equivalent semibridging carbonyls in **9T-1**, the shorter Nb—C bond distances are 2.127 Å (MPW1PW91 or BP86) and the longer Nb—C distances are 2.684 Å (MPW1PW91) or 2.677 Å (BP86). The other semibridging carbonyl is predicted to be in different positions by the two different DFT methods. The MPW1PW91 method predicts this third semibridging carbonyl group to be tilted in the same way as the other two semibridging carbonyls with a shorter Nb—C distance of 2.153 Å and a longer Nb—C distance of 2.642 Å. However, the BP86 method predicts it to be tilted in the opposite direction with a longer Nb—C distance of 2.229 Å and a longer Nb—C distance of 2.433 Å. The three lowest $\nu(\text{CO})$ frequencies at 1874, 1888, and 1897 cm⁻¹ (BP86) in **9T-1** can be assigned to the three semibridging CO groups. The Nb—C distances to the terminal carbonyls in **9T-1** range from 2.073 Å to 2.155 Å (MPW1PW91) or 2.085 Å to 2.165 Å (BP86). The Nb≡Nb distance in the triplet structure **9T-1** of 2.798 Å (MPW1PW91) or 2.746 Å (BP86) is similar to the Nb≡Nb distances in the singlet structures **9S-1**, **9S-2**, and **9S-3** and likewise suggests a formal triple bond. This gives each niobium atom in **9T-1** the 17-electron configuration for a binuclear triplet.

The other two low-lying triplet Nb₂(CO)₉ structures, namely **9T-2** (C_1 symmetry) and **9T-3** (C_s symmetry), also have three semibridging CO groups and three terminal CO groups on each Nb atom (Figure 3). Structure **9T-2** lies 9.7 kcal/mol (MPW1PW91) or 9.2 kcal/mol (BP86) in energy above **9S-1**, whereas structure **9T-3** lies 15.9 kcal/mol (MPW1PW91) or 15.1 kcal/mol (BP86) in energy above **9S-1**. Structures **9T-2** and **9T-3** differ in the arrangement of the three semibridging CO groups relative to the terminal CO groups. Structure **9T-2** is a genuine minimum with no imaginary vibrational frequencies. However, structure **9T-3** has a small imaginary vibrational frequency of 17*i* cm⁻¹ (MPW1PW91) or 21*i* cm⁻¹ (BP86), which is not eliminated using the (120, 974) finer integration grid. By following the corresponding normal mode, structure **9T-3** collapses to **9T-1**. For the semibridging carbonyls in **9T-2** and **9T-3**, the shorter Nb—C bond distances range from 2.099 Å to 2.174 Å (MPW1PW91) or from 2.114 Å to 2.216 Å (BP86), and the longer Nb—C distances for the semibridging carbonyls fall in a wide range from 2.462 Å to 2.715 Å (MPW1PW91) or from 2.461 Å to 2.697 Å (BP86). The lowest $\nu(\text{CO})$ frequencies of 1879, 1886, and 1892 cm⁻¹ (BP86) for **9T-2** and 1830, 1883, and 1890 cm⁻¹ (BP86) for **9T-3** can be assigned to these three semibridging CO groups (Table S25, in the Supporting Information). The Nb—C distances for the terminal carbonyls in **9T-2** and **9T-3** range from 2.048 Å to 2.168 Å (MPW1PW91) or 2.052 Å to 2.164 Å (BP86), corresponding to significantly higher $\nu(\text{CO})$ vibrational frequencies ranging from 1936 to 2039 cm⁻¹ (BP86). The Nb≡Nb distances of 2.739 Å (MPW1PW91) or 2.761 Å (BP86) for **9T-2** and 2.776 Å (MPW1PW91) or 2.804 Å (BP86) for **9T-3** are similar to the Nb≡Nb triple bond distances in the singlet Nb₂(CO)₉ structures **9S-1**, **9S-2**, and **9S-3**, thereby suggesting formal Nb≡Nb triple bonds in **9T-2** and **9T-3**. This gives each niobium atom in **9T-2** and **9T-3** the 17-electron configurations for a binuclear triplet.

The C_s structures **9T-4** and **9T-5** have geometries similar to each other, with three semibridging carbonyls and six terminal carbonyls (Figure 3). However, structures **9T-4** and **9T-5** have a less symmetrical placement of the six carbonyl groups on the two niobium atoms than **9T-2** and **9T-3**, since in both **9T-4** and **9T-5** four terminal carbonyl groups are located on one

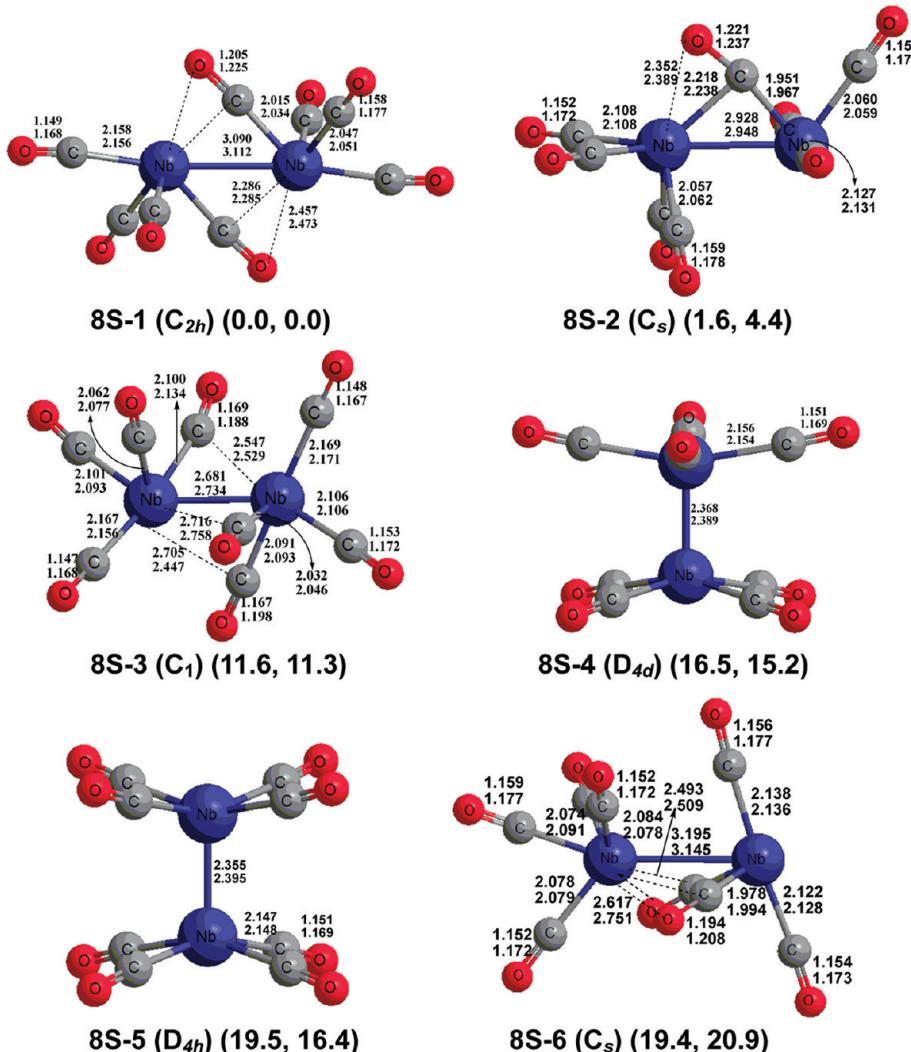


Figure 4. Optimized geometries of the singlet $\text{Nb}_2(\text{CO})_8$ structures. The distances are given in Å. The upper distances were determined by the MPW1PW91 method and the lower distances by the BP86 method. The relative energies (kcal/mol) predicted by the MPW1PW91 and BP86 methods, respectively, are shown in parentheses.

niobium atom, whereas only two carbonyl groups are located on the other niobium atom. The “unsymmetrical” triplet structures **9T-4** and **9T-5** are significantly higher energy structures than the “symmetrical” triplet structures **9T-2** and **9T-3**. Thus, both **9T-4** and **9T-5** lie more than 22 kcal/mol above the global minimum **8S-1**. The Nb–C distances in structures **9T-4** and **9T-5** are similar to those in the other triplet structures. The lowest $\nu(\text{CO})$ frequencies at 1874, 1875, and 1887 cm⁻¹ (BP86) for **9T-4** and 1878, 1881, and 1895 cm⁻¹ (BP86) for **9T-5** can be assigned to the three semibridging CO groups. The Nb≡Nb distances in **9T-4** and **9T-5** of ~2.8 Å suggest formal triple bonds, thereby giving both niobium atoms 17-electron configurations consistent with binuclear triplets.

3.2. $\text{Nb}_2(\text{CO})_8$. Eleven structures were found for the $\text{Nb}_2(\text{CO})_8$ complexes. However, only the nine $\text{Nb}_2(\text{CO})_8$ structures lying within 25 kcal/mol of the global minimum are discussed in this paper (Figures 4 and 5). The global minimum $\text{Nb}_2(\text{CO})_8$ structure **8S-1** is a beautiful C_{2h} structure having two symmetry equivalent bridging CO groups and six terminal CO groups. For the two semibridging CO groups, the shorter Nb–C distances are 2.015 Å (MPW1PW91) or 2.034 Å

(BP86) and the longer Nb–C distances are 2.286 Å (MPW1PW91) or 2.285 Å (BP86). The short Nb–O distances of 2.457 Å (MPW1PW91) or 2.473 Å (BP86) to these two bridging carbonyl groups suggest that they both are four-electron donor $\eta^2\text{-}\mu\text{-CO}$ groups. This is consistent with the relatively long C–O distances of 1.205 Å (MPW1PW91) or 1.225 Å (BP86) and the extremely low $\nu(\text{CO})$ frequencies of 1640 and 1670 cm⁻¹ (BP86), indicating relatively low C–O bond orders for these two carbonyl groups. The Nb–C distances for the terminal CO groups range from 2.047 to 2.158 Å (MPW1PW91) or 2.051 to 2.156 Å (BP86). The predicted Nb–Nb distance of 3.090 Å (MPW1PW91) or 3.112 Å (BP86) suggests a formal single bond, thereby giving each niobium atom a 16-electron configuration.

The second singlet $\text{Nb}_2(\text{CO})_8$ structure, **8S-2**, is a C_s symmetry structure with one semibridging carbonyl and seven terminal carbonyls, lying 1.6 kcal/mol (MPW1PW91) or 4.4 kcal/mol (BP86) in energy above **8S-1** (Figure 4). For the semibridging carbonyl, the shorter Nb–C distance is 1.951 Å (MPW1PW91) or 1.967 Å (BP86) and the longer Nb–C distance is 2.218 Å (MPW1PW91) or 2.238 Å (BP86). The short Nb–O distance of 2.352 Å (MPW1PW91) or

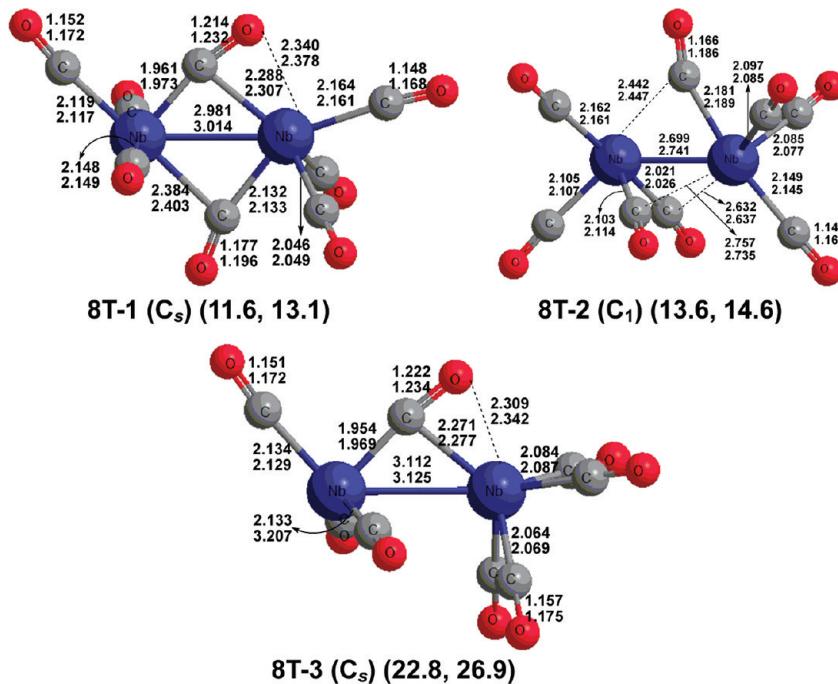


Figure 5. Optimized geometries of the triplet $\text{Nb}_2(\text{CO})_8$ structures. The distances are given in Å. The upper distances were determined by the MPW1PW91 method and the lower distances by the BP86 method. The relative energies (kcal/mol) predicted by the MPW1PW91 and BP86 methods, respectively, are shown in parentheses.

2.389 Å (BP86) to this carbonyl group indicates a four-electron donor $\eta^2\text{-}\mu\text{-CO}$ group. This is consistent with the extremely low $\nu(\text{CO})$ frequency of 1623 cm⁻¹ (BP86) and relatively long C–O distance of 1.221 Å (MPW1PW91) or 1.237 Å (BP86), indicating a low C–O bond order for this carbonyl group. The Nb–C distances for the terminal CO groups range from 2.057 to 2.127 Å (MPW1PW91) or from 2.059 to 2.131 Å (BP86). The predicted Nb=Nb distance of 2.928 Å (MPW1PW91) or 2.948 Å (BP86) can be interpreted as a formal double bond. This gives both niobium atoms in **8S-2** 16-electron configurations consistent with the clear gaps in the coordination spheres of each niobium atom (Figure 4).

The third singlet structure, **8S-3** (Figure 4), lying 11.6 kcal/mol (MPW1PW91) or 11.3 kcal/mol (BP86) in energy above **8S-1**, is predicted to have C_1 symmetry with three semibridging CO groups. For the three semibridging CO groups, the shorter Nb–C bond distances range from 2.032 to 2.100 Å (MPW1PW91) or 2.046 to 2.134 Å (BP86), whereas the longer Nb–C distances range from 2.547 to 2.716 Å (MPW1PW91) or 2.529 to 2.758 Å (BP86). The Nb–C distances for the terminal carbonyls in **8S-3** range from 2.062 to 2.169 Å (MPW1PW91) or 2.077 to 2.171 Å (BP86). The three lowest $\nu(\text{CO})$ frequencies at 1796, 1850, and 1877 cm⁻¹ (BP86) in **8S-3** can be assigned to the three semibridging CO groups. The Nb≡Nb distance in **8S-3** of 2.681 Å (MPW1PW91) or 2.734 Å (BP86) can correspond to a formal triple bond, thereby giving each niobium atom a 16-electron configuration.

The $\text{Nb}_2(\text{CO})_8$ structures **8S-4** and **8S-5** are similar in energy and in geometry. Both are highly symmetric unbridged structures consisting of two $\text{Nb}(\text{CO})_4$ halves linked together by very short Nb–Nb bonds, obviously of high formal bond orders (Figure 4). The D_{4d} structure **8S-4** has a staggered configuration of the two $\text{Nb}(\text{CO})_4$ units, whereas the D_{4h} structure **8S-5** has an eclipsed configuration of the two

$\text{Nb}(\text{CO})_4$ units. Structure **8S-4** lies 16.5 kcal/mol (MPW1PW91) or 15.2 kcal/mol (BP86) above **8S-1**, whereas structure **8S-5** lies 19.5 kcal/mol (MPW1PW91) or 16.4 kcal/mol (BP86) above **8S-1**. Structure **8S-4** is a genuine minimum, whereas structure **8S-5** has a small imaginary vibrational frequency. By following the corresponding normal mode, structure **8S-5** goes to **8S-4**. Both **8S-4** and **8S-5** have all terminal CO groups with Nb–C distances of 2.156 Å (MPW1PW91) or 2.154 Å (BP86) for **8S-4** and 2.147 Å (MPW1PW91) or 2.148 Å (BP86) for **8S-5**. The Nb–Nb–C angles are predicted to be $\sim 98.7^\circ$ for **8S-4** and $\sim 101.2^\circ$ for **8S-5**. The very short Nb–Nb distances of 2.368 Å (B3LYP) or 2.389 Å (BP86) in **8S-4** or 2.355 Å (B3LYP) or 2.395 Å (BP86) in **8S-5** suggest the formal quintuple bonds required to give both niobium atoms the favored 18-electron configuration.

The last singlet $\text{Nb}_2(\text{CO})_8$ structure, **8S-6**, lying 19.4 kcal/mol (MPW1PW91) or 20.9 kcal/mol (BP86) in energy above **8S-1**, is a C_s structure with two semibridging carbonyl groups and a very unsymmetrical distribution of the terminal carbonyl groups (Figure 4). For the two semibridging carbonyls, the shorter Nb–C distances are 1.978 Å (MPW1PW91) or 1.994 Å (BP86) and the longer Nb–C distances are 2.493 Å (MPW1PW91) or 2.509 Å (BP86). The short Nb–O distances for the semibridging carbonyls of 2.617 Å (MPW1PW91) or 2.751 Å (BP86), indicating four-electron donor $\eta^2\text{-}\mu\text{-CO}$ ligands. This is with the very low $\nu(\text{CO})$ vibrational frequencies of 1723 and 1775 cm⁻¹ (BP86) as well as the relatively long C–O distance of 1.194 Å (MPW1PW91) or 1.208 Å (BP86), indicating a low C–O bond order for the two carbonyl groups. The Nb–C distances for the terminal carbonyls in **8S-6** range from 2.074 Å to 2.138 Å (MPW1PW91) and from 2.078 Å to 2.136 Å (BP86). The Nb–Nb distance of 3.195 Å (MPW1PW91) or 3.145 Å (BP86) suggests a formal single bond to give one niobium atom (the “left” Nb atom in Figure 4) the favored 18-electron configuration, and the other niobium

atom (the “right” Nb atom in Figure 4) only a 14-electron configuration. The niobium atom with only a 14-electron configuration in **8S-6** has a major gap in its coordination sphere *trans* to the bridging carbonyl groups and the Nb–Nb bond.

The lowest lying triplet structure of $\text{Nb}_2(\text{CO})_8$, namely, **8T-1** (Figure 5), is a C_s genuine minimum with two semibridging carbonyls lying 11.6 kcal/mol (MPW1PW91) or 13.1 kcal/mol (BP86) in energy above **8S-1** (Figure 4). The short Nb–O distance to one of the semibridging CO groups of 2.340 Å (MPW1PW91) or 2.378 Å (BP86) indicates a four-electron donor bridging CO group, which is consistent with the very low $\nu(\text{CO})$ frequency of 1627 cm⁻¹ (BP86). For the four-electron donor $\eta^2\text{-}\mu\text{-CO}$ group in **8T-1**, the shorter Nb–C bond distances are 1.961 Å (MPW1PW91) or 1.973 Å (BP86) and the longer Nb–C distances are 2.288 Å (MPW1PW91) or 2.307 Å (BP86). For the two-electron donor bridging carbonyl group in **8T-1**, the shorter Nb–C distance is 2.132 Å (MPW1PW91) or 2.133 Å (BP86) and the longer Nb–C distance is 2.384 Å (MPW1PW91) or 2.403 Å (BP86). This bridging carbonyl group exhibits a $\nu(\text{CO})$ frequency of 1794 cm⁻¹ (BP86), which lies between the very low $\nu(\text{CO})$ frequency of the four-electron donor $\eta^2\text{-}\mu\text{-CO}$ group and the normal $\nu(\text{CO})$ frequencies of the terminal carbonyl groups. The Nb–C distances for the terminal carbonyls in **8T-1** range from 2.046 to 2.164 Å (MPW1PW91) or from 2.049 to 2.161 Å (BP86). The Nb–Nb distance in **8T-1** of 2.981 Å (MPW1PW91) or 3.014 Å (BP86) suggests a formal single bond. This leads to a 15-electron configuration for each niobium atom, consistent with a binuclear triplet.

The triplet $\text{Nb}_2(\text{CO})_8$ structure **8T-2** (Figure 5), lying 13.6 kcal/mol (MPW1PW91) or 14.6 kcal/mol (BP86) in energy above **8S-1**, is predicted to have C_1 symmetry with three semibridging CO groups. For these three semibridging carbonyls, the shorter Nb–C bond distances range from 2.021 to 2.181 Å (MPW1PW91) or from 2.026 to 2.189 Å (BP86), whereas the longer Nb–C distances range from 2.442 to 2.757 Å (MPW1PW91) or 2.447 to 2.735 Å (BP86). The Nb–C distances to the terminal carbonyls in **8T-2** range from 2.085 to 2.162 Å (MPW1PW91) or from 2.077 to 2.161 Å (BP86). The low $\nu(\text{CO})$ frequencies at 1838, 1854, and 1885 cm⁻¹ (BP86) in **8T-2** can be assigned to the three semibridging CO groups. The Nb≡Nb distance in **8T-2** of 2.699 Å (MPW1PW91) or 2.741 Å (BP86) suggests a formal triple bond, thereby giving one niobium atom a 17-electron configuration but the other niobium atom only a 15-electron configuration. This is consistent with a binuclear triplet.

The third triplet $\text{Nb}_2(\text{CO})_8$ structure, **8T-3**, lying 22.8 kcal/mol (MPW1PW91) or 26.9 kcal/mol (BP86) in energy above **8S-1**, is a C_s structure with one semibridging carbonyl and seven terminal carbonyls (Figure 5). Structure **8T-3** has a negligible imaginary vibrational frequency ($2i$ cm⁻¹ by MPW1PW91 or $7i$ cm⁻¹ by BP86). Following the corresponding normal mode leads to **8T-1**, with one of the terminal carbonyls in **8T-3** becoming a bridging carbonyl in **8T-1**. For the semibridging carbonyl, the shorter Nb–C distance is 1.954 Å (MPW1PW91) or 1.969 Å (BP86) and the longer Nb–C distance is 2.271 Å (MPW1PW91) or 2.277 Å (BP86). The short Nb–O distance of 2.309 Å (MPW1PW91) or 2.342 Å (BP86) indicates a four-electron donor $\eta^2\text{-}\mu\text{-CO}$ group. In **8T-3**, the four-electron donor CO group exhibits the typical very low $\nu(\text{CO})$ frequency of 1610 cm⁻¹ (BP86) and a relatively long C–O distance of 1.222 Å (MPW1PW91) or 1.234 Å (BP86), indicating a low C–O bond order. The Nb–C

distances for the terminal CO groups range from 2.064 to 2.134 Å (MPW1PW91) or 2.069 to 2.129 Å (BP86). The predicted Nb–Nb distance of 3.112 Å (MPW1PW91) or 3.125 Å (BP86) in **8T-3** is close to that in **8T-1** and suggests a formal single bond. This gives each niobium in **8T-3** a 15-electron configuration consistent with a binuclear triplet.

3.3. Thermochemistry. Table 1 lists the carbonyl dissociation energy for $\text{Nb}_2(\text{CO})_9$ and the dissociation energies

Table 1. Energies (kcal/mol) for the Loss of Carbonyl Groups, Dissociation into Mononuclear Fragments (kcal/mol), and Disproportionation into $\text{Nb}_2(\text{CO})_{n+1} + \text{Nb}_2(\text{CO})_{n-1}$ for the Lowest Energy $\text{Nb}_2(\text{CO})_n$ Structures ($n = 9, 8$)

	MPW1PW91	BP86
$\text{Nb}_2(\text{CO})_9 \rightarrow \text{Nb}_2(\text{CO})_8 + \text{CO}$	29.6	29.5
$\text{Nb}_2(\text{CO})_9 \rightarrow \text{Nb}(\text{CO})_5 + \text{Nb}(\text{CO})_4$	50.7	54.0
$\text{Nb}_2(\text{CO})_8 \rightarrow 2\text{Nb}(\text{CO})_4$	57.0	62.0
$\text{Nb}_2(\text{CO})_8 \rightarrow \text{Nb}(\text{CO})_5 + \text{Nb}(\text{CO})_3$	70.5	80.0
$2\text{Nb}_2(\text{CO})_9 \rightarrow \text{Nb}_2(\text{CO})_{10} + \text{Nb}_2(\text{CO})_8$	-6.8	-7.7

for $\text{Nb}_2(\text{CO})_9$ and $\text{Nb}_2(\text{CO})_8$ into mononuclear fragments. The dissociation energy for the loss of one carbonyl group from $\text{Nb}_2(\text{CO})_9$ is ~30 kcal/mol, which is comparable with the experimental carbonyl dissociation energies for $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, and $\text{Cr}(\text{CO})_6$ of 27 kcal/mol, 41 kcal/mol, and 37 kcal/mol, respectively.⁶⁷ The energy for dissociation of $\text{Nb}_2(\text{CO})_9$ into the mononuclear fragments $\text{Nb}(\text{CO})_5 + \text{Nb}(\text{CO})_4$ is found to be substantial, i.e., $\sim 52 \pm 2$ kcal/mol. The energies for the dissociation of $\text{Nb}_2(\text{CO})_8$ into $2\text{Nb}(\text{CO})_4$ or $\text{Nb}(\text{CO})_5 + \text{Nb}(\text{CO})_3$ are also both substantial. Thus, the binuclear $\text{Nb}_2(\text{CO})_9$ and $\text{Nb}_2(\text{CO})_8$ are viable with respect to dissociation into mononuclear fragments. The energy for the disproportionation of $\text{Nb}_2(\text{CO})_9$ into $\text{Nb}_2(\text{CO})_{10} + \text{Nb}_2(\text{CO})_8$ is slightly exothermic by ~7 kcal/mol, suggesting that $\text{Nb}_2(\text{CO})_9$ might not be a viable species.

3.4. Natural Bond Orbital (NBO) Analysis. Table 2 lists the Nb–Nb bond distances, Wiberg bond indices (WBI), and

Table 2. Natural Atomic Charges and Wiberg Bond Indices (WBI) for the Singlet $\text{Nb}_2(\text{CO})_n$ Structures ($n = 8, 9$)

structure	Nb–Nb distance, Å	WBI	formal bond order	natural charge on Nb(left)/Nb(right)
$\text{Nb}_2(\text{CO})_9$				
9S-1	2.806	0.46	3	-0.38/-0.58
9S-2	2.757	0.64	3	-0.18/-0.97
9S-3	2.877	0.36	2	-0.77/-0.22
9S-4	2.535	0.90	4	-0.98/-0.33
9S-5	2.549	0.87	4	-0.99/-0.31
$\text{Nb}_2(\text{CO})_8$				
8S-1	3.112	0.25	1	-0.12/-0.12
8S-2	2.948	0.43	2	-0.09/-0.20
8S-3	2.734	0.77	3	-0.40/-0.22
8S-4	2.389	2.16	5	-0.49/-0.49
8S-5	2.395	2.15	5	-0.47/-0.47
8S-6	3.145	0.27	1	-0.29/-0.14

natural atomic charges from a NBO analysis⁶⁸ of $\text{Nb}_2(\text{CO})_9$ and $\text{Nb}_2(\text{CO})_8$ using the BP86 method. Previous studies⁶⁹ on the WBIs of metal carbonyls such as $\text{Fe}_2(\text{CO})_9$ and $\text{Fe}_3(\text{CO})_{12}$ show that the WBIs are relatively low compared with the formal

bond orders, particularly when the metal–metal bonds are bridged by carbonyl groups. Thus, the WBIs for the Fe–Fe formal single bonds in the lowest energy unbridged $\text{Fe}_3(\text{CO})_{12}$ structure are only 0.18. The WBI for the triply bridged formal Fe–Fe single bond in $\text{Fe}_2(\text{CO})_9$ is even lower at 0.11. With these considerations in mind, the WBIs of the singlet $\text{Nb}_2(\text{CO})_9$ and $\text{Nb}_2(\text{CO})_8$ structures correlate well with the formal Nb–Nb bond orders suggested by the Nb–Nb distances. Thus, the WBIs for the formal Nb–Nb single bonds in the $\text{Nb}_2(\text{CO})_8$ structures 8S-1 and 8S-6 are 0.26 ± 0.01 . The WBIs for the formal Nb=Nb double bonds in the $\text{Nb}_2(\text{CO})_9$ structure 9S-3 and the $\text{Nb}_2(\text{CO})_8$ structure 8S-2 are consistently higher at 0.36 and 0.43, respectively. The WBIs for the formal Nb≡Nb triple bonds in the $\text{Nb}_2(\text{CO})_9$ structures 9S-1, 9S-2, and 8S-3 are still higher at 0.46, 0.64, and 0.77, respectively. The trend continues with the higher order Nb–Nb multiple bonds with WBIs of 0.87–0.90 for the presumed Nb^4Nb quadruple bonds in the $\text{Nb}_2(\text{CO})_9$ structures 9S-4 and 9S-5. The presumed Nb^5Nb quintuple bonds in the $\text{Nb}_2(\text{CO})_8$ structures 8S-4 and 8S-5 have extraordinarily high WBIs of 2.15 for metal–metal bonds.

Analysis of the formal charges on the metal atoms is more complicated since at least two factors appear to be significant. For metal atoms with the favored 18-electron configurations, the formal negative charges increase with increasing numbers of carbonyl groups. This suggests that the $d\pi \rightarrow p\pi^*$ back-bonding from the filled metal d orbitals to the antibonding orbitals of the CO ligands is not sufficient to remove all of the negative charge accumulated from the $\text{OC} \rightarrow \text{M} \sigma$ forward bonding. Simple examples are the $\text{Nb}_2(\text{CO})_9$ structures 9S-4 and 9S-5 where both of the niobium atoms have the favored 18-electron configuration, assuming a formal Nb^4Nb quadruple bond. Thus, the niobium atoms bearing five CO groups in these structures have negative charges of -0.99 , whereas those bearing only four carbonyl groups have negative charges of -0.32 .

In addition to the numbers of carbonyl groups, the natural charges on the metal atoms are also affected by the metal electronic configurations and the presence of four-electron donor bridging $\eta^2\text{-}\mu\text{-CO}$ groups. Metal atoms with 16-electron configurations and a given number of carbonyl groups are less negative than those with 18-electron configurations and the same number of carbonyl groups. This is reasonable since a “missing” lone electron pair in a metal atom with a 16-electron configuration corresponds to “missing” negative charge, thereby leading to a more positive metal atom. Thus, for $\text{Nb}_2(\text{CO})_8$, the formal negative charges on the metal atoms bearing four CO groups in structures 8S-4 and 8S-5 where the metal has a formal 18-electron configuration are -0.48 \AA . However, for the $\text{Nb}_2(\text{CO})_8$ structure 8S-1, in which there are two four-electron donor bridging $\eta^2\text{-}\mu\text{-CO}$ groups and the niobium atoms have 16- rather than 18-electron configurations, the niobium atoms, which also bear four CO groups each, are appreciably less negative with natural charges of -0.12 .

3.5. Frontier Molecular Orbitals in the Unbridged $\text{Nb}_2(\text{CO})_n$ Structures ($n = 9, 8$): The Nature of Their Niobium–Niobium Multiple Bonds. The niobium–niobium distances, WBIs, and the 18-electron rule all suggest formal quintuple Nb–Nb bonds in the two unbridged $\text{Nb}_2(\text{CO})_8$ structures 8S-4 and 8S-5. However, a formal quintuple bond between the two niobium atoms combined with the four Nb–C σ bonds to the four carbonyl groups on each niobium atom is expected to use all nine orbitals of the

sp^3d^5 valence orbital manifolds on each niobium atom. This leaves no nonbonding d orbitals with electron pairs for back-donation into the π^* orbitals of the carbonyl groups as typically occurs in metal carbonyl chemistry. However, the $\nu(\text{CO})$ frequencies of these two unbridged $\text{Nb}_2(\text{CO})_8$ structures 8S-4 and 8S-5 are in the usual region for terminal $\nu(\text{CO})$ frequencies, suggesting a similar amount of $d\pi \rightarrow p\pi^*$ back bonding as found in other metal carbonyl derivatives. A key question thus is how there can be $d\pi \rightarrow p\pi^*$ back bonding in a metal carbonyl structure when all nine orbitals of the sp^3d^5 manifold are already required for the M–C σ bonds to the terminal carbonyl groups and the presumed order of the metal–metal multiple bond.

In order to gain some insight into this dilemma, the frontier molecular orbitals of the unbridged $\text{Nb}_2(\text{CO})_n$ ($n = 9, 8$) structures were examined. The unbridged D_{4d} and D_{4h} structures of $\text{Nb}_2(\text{CO})_8$, namely 8S-4 and 8S-5, are simpler than the unbridged $\text{Nb}_2(\text{CO})_9$ structure since both $\text{Nb}(\text{CO})_4$ halves of these unbridged $\text{Nb}_2(\text{CO})_8$ structures are equivalent. Analysis of the frontier orbitals of such structures provides some insight into the nature of the niobium–niobium bonding using structure 8S-4 as an example (Figure 6). A similar

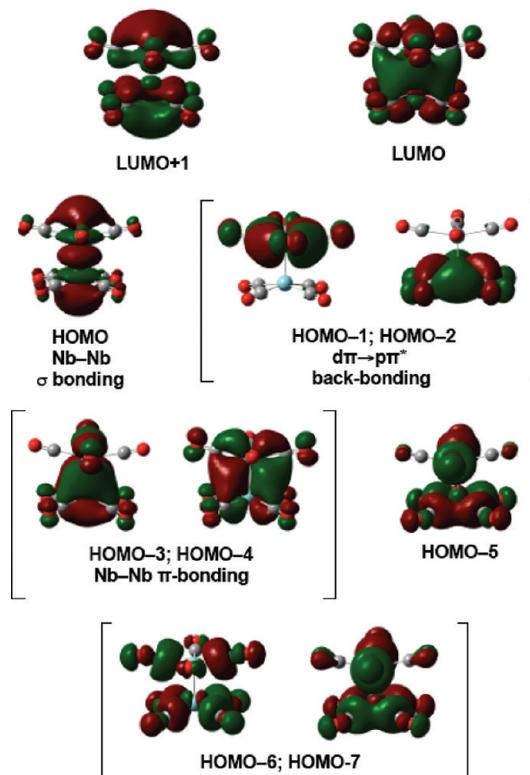


Figure 6. The frontier molecular orbitals for the D_{4d} unbridged $\text{Nb}_2(\text{CO})_8$ structure 8S-4. Pairs of degenerate orbitals are enclosed in brackets [].

approach was used in previous work⁷⁰ to study the metal–metal multiple bonding in the bent metallocene derivatives $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}_2$ of the third row transition metals from tantalum to osmium inclusive. This approach was used to identify the $\sigma + 2\pi + 2\delta$ components in a formal quintuple bond in a singlet $(\eta^5\text{-C}_5\text{H}_5)_2\text{Os}_2$ structure.

The pattern of the frontier molecular orbitals for the $\text{Nb}_2(\text{CO})_8$ structure 8S-4 suggests a formal Nb≡Nb triple

bond in this structure rather than the expected formal $\text{Nb}^5\text{—Nb}$ quintuple bond. Thus, the HOMO in 8S-4 corresponds to the σ component of this $\text{Nb}\equiv\text{Nb}$ triple bond in which the $d(z^2)$ orbitals are used. Similarly, the degenerate HOMO-3/HOMO-4 pair corresponds to the two orthogonal π components of this $\text{Nb}\equiv\text{Nb}$ triple bond. The two d orbitals, namely the $d(xy)$ and $d(x^2-y^2)$ orbitals, that would be used to form the δ components of a formal $\text{Nb}^5\text{—Nb}$ quintuple bond instead are used for $d\pi\rightarrow p\pi^*$ back-bonding to the carbonyl groups as indicated by the degenerate HOMO-1/HOMO-2 molecular orbital pair.

This observation on the molecular orbitals of the unbridged $\text{Nb}_2(\text{CO})_8$ structure 8S-4 suggests a $\text{Nb}\equiv\text{Nb}$ formal triple bond with a 16-electron configuration for each niobium atom (Figure 7). In this triple bonded $\text{Nb}_2(\text{CO})_8$ model, each

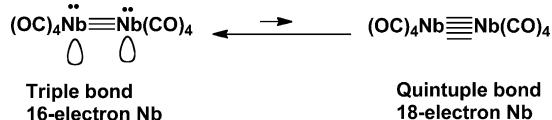


Figure 7. Schematic representations of unbridged $\text{Nb}_2(\text{CO})_8$ structures with formal triple and quintuple Nb–Nb bonds.

niobium atom uses four orbitals for the Nb–C σ bonds to the carbonyl groups and three more orbitals for the $\text{Nb}\equiv\text{Nb}$ triple bond. This leaves two orbitals from the sp^3d^5 manifold on each niobium atom. One of these orbitals is empty, relating to the 16-electron rather than 18-electron configuration of the niobium atom. The other orbital on each niobium atom has an electron pair, which can be used for $d\pi\rightarrow p\pi^*$ back-bonding to the carbonyl groups.

The analysis of the niobium–niobium bonding in the less symmetrical unbridged $\text{Nb}_2(\text{CO})_9$ structures 9S-4 and 9S-5 follows a similar pattern. In this case, a $\text{Nb}^4\text{—Nb}$ quadruple bond incorporating an $\text{Nb}(\text{CO})_5$ unit uses all nine orbitals of the sp^3d^5 niobium manifold leaving no orbitals from this niobium atom to participate in $d\pi\rightarrow p\pi^*$ back-bonding to the carbonyl groups. Again, the pattern of the frontier molecular orbitals in the $\text{Nb}_2(\text{CO})_9$ structure 9S-4 shows only a $\text{Nb}\equiv\text{Nb}$ triple bond (Figure 8). The σ component of this triple bond appears in HOMO-1, whereas the two orthogonal π components of this triple bond correspond to the degenerate HOMO-3/HOMO-4 pair. The d orbitals are again used for the $d\pi\rightarrow p\pi^*$ back-bonding to the carbonyl groups as shown by HOMO and HOMO-2. In this $\text{Nb}_2(\text{CO})_9$ structure, the frontier orbitals involved in this back-bonding have different energies, in contrast to the more symmetrical $\text{Nb}_2(\text{CO})_8$ structure 8S-4, where they form a degenerate pair.

For an unbridged $\text{Nb}_2(\text{CO})_9$ molecule, the two types of structures are shown in Figure 9. In the structure with a $\text{Nb}^4\text{—Nb}$ quadruple bond, suggested by the niobium–niobium distance and the WBI, each niobium atom has the favored 18-electron configuration. However, for each niobium atom to have the favored 18-electron configuration, the $\text{Nb}(\text{CO})_5$ niobium must have a formal positive charge and the $\text{Nb}(\text{CO})_4$ niobium must bear a formal negative charge. However, for the unbridged $\text{Nb}_2(\text{CO})_9$ structure with the formal $\text{Nb}\equiv\text{Nb}$ triple bond suggested by the frontier molecular orbitals, the niobium atom of the $\text{Nb}(\text{CO})_5$ group has the favored 18-electron configuration, but the niobium atom of the $\text{Nb}(\text{CO})_4$ group has

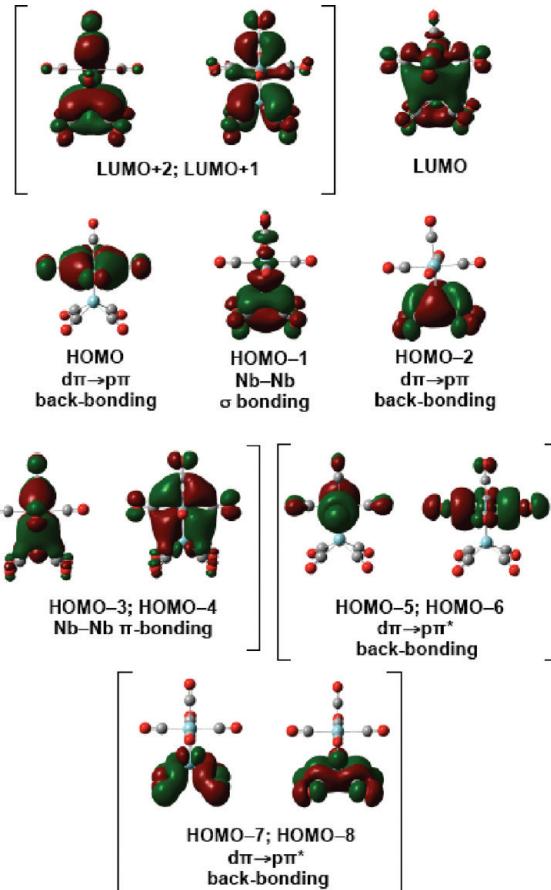


Figure 8. The frontier molecular orbitals for the C_{4v} unbridged $\text{Nb}_2(\text{CO})_9$ structure 9S-4. Pairs of degenerate orbitals are enclosed in brackets [].

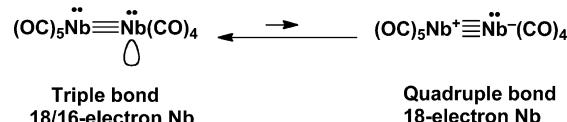


Figure 9. Schematic representations of unbridged $\text{Nb}_2(\text{CO})_9$ structures with formal triple and quadruple Nb–Nb bonds.

only a 16-electron configuration. Both niobium atoms have lone pairs, which can participate in the $d\pi\rightarrow p\pi^*$ back-bonding.

This analysis of the niobium–niobium multiple bonding in these unbridged $\text{Nb}_2(\text{CO})_n$ ($n = 9, 8$) structures shows that the metal–metal distances, WBIs, and electron counting are not unequivocal indications of the metal–metal bond order. A similar conclusion was reached several years ago with an unbridged $\text{Fe}_2(\text{CO})_6$ structure.⁷¹ In this case, the very short Fe–Fe distance of $\sim 2.0 \text{ \AA}$ and electron counting suggested an $\text{Fe}^4\text{—Fe}$ quadruple bond, thereby giving both iron atoms the favored 18-electron configuration. However, an analysis of the molecular orbitals suggested only a formal Fe=Fe double bond, thereby giving each iron atom only a 16-electron rather than an 18-electron configuration.

The suggestion from this analysis of the molecular orbitals depicted in Figures 6 and 8 that the niobium–niobium bonds in $\text{Nb}_2(\text{CO})_9$ and $\text{Nb}_2(\text{CO})_8$ are formal $\text{Nb}\equiv\text{Nb}$ triple bonds rather than the quadruple and quintuple bonds suggested by the metal–metal distances, WBIs, and electron counting is quite surprising. For this reason, we did an analogous analysis

of the frontier molecular orbitals of the binuclear chromium(I) alkyls and aryls RCrCrR ($\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$) as models for the more complicated ArylCrCrAryl (Aryl = 2,6-(2,6-*i*Pr₂C₆H₃)₂C₆H₃) synthesized by Power and co-workers¹ and generally accepted to contain a formal Cr—Cr quintuple bond (Figure 1). Both the simple linear structures and bent structures closer to the experimental structure for ArylCrCrAryl (Aryl = 2,6-(2,6-*i*Pr₂C₆H₃)₂C₆H₃) were considered. Analysis of the molecular orbital patterns of the bent structures was complicated by their low symmetries, which lifted the degeneracy of the pairs of π and δ components of the Cr—Cr quintuple bond. In addition, mixing of metal–alkyl bonding and metal–metal bonding in the same molecular orbitals in the bent systems makes their assignments more difficult. However, in the frontier orbitals of the linear RCrCrR derivatives ($\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$) all five components ($\sigma + 2\pi + 2\delta$) of the Cr—Cr quintuple bond are found. The pattern is particularly clear for the frontier molecular orbitals of the linear methyl derivative $\text{CH}_3\text{CrCrCH}_3$ where all five components of the Cr—Cr quintuple bond in the range from HOMO down to HOMO-5 are clearly seen (Figure 10). Thus, HOMO and

very short Nb—Nb distances and high Wiberg bond indices for the Nb—Nb bonds, suggesting formal quadruple and quintuple bonds, respectively. However, analysis of the frontier molecular orbitals of these unbridged $\text{Nb}_2(\text{CO})_n$ ($n = 9, 8$) structures (Figures 6 and 8) indicates that the Nb≡Nb interactions in these structures are only triple bonds with one σ component and two orthogonal π components. The $d(xy)$ and $d(x^2-y^2)$ orbitals in these structures, instead of forming δ components of formal quadruple and quintuple bonds, participate in $d\pi \rightarrow p\pi^*$ back-bonding to the carbonyl groups. However, similar frontier molecular orbital analysis of the chromium–chromium bonding in the binuclear chromium alkyls and aryls analogous to ArylCrCrAryl (Aryl = 2,6-(2,6-*i*Pr₂C₆H₃)₂C₆H₃) synthesized by Power and co-workers¹ confirms the generally accepted formulation of their chromium–chromium bonding as formal quintuple bonds. The molecular orbital pattern for a formal Cr—Cr quintuple bond is particularly clear in the D_{3d} linear methyl derivative $\text{CH}_3\text{CrCrCH}_3$ (Figure 10).

These unbridged $\text{Nb}_2(\text{CO})_n$ ($n = 9, 8$) structures are not the lowest energy structures for these binary niobium carbonyls. Lower energy singlet structures are found with various arrangements of two-electron donor bridging and semibridging carbonyl groups as well as some examples of four-electron donor bridging $\eta^2\text{-}\mu\text{-CO}$ groups. The latter are recognized by unusually low $\nu(\text{CO})$ frequencies and short Nb—O distances, indicating direct Nb—O interactions. For $\text{Nb}_2(\text{CO})_9$, the lowest energy structures **9S-1** and **9S-2** (Figure 2) have Nb≡Nb distances and WBIs suggesting formal triple bonds as well as only two-electron donor carbonyl groups. This gives one niobium atom the favored 18-electron configuration but the other niobium atom only a 16-electron configuration. The niobium atom with a 16-electron configuration is recognized by a gap in its coordination sphere, corresponding to the empty orbital of its nine-orbital sp^3d^5 valence orbital manifold relating to the 16-electron configuration. In addition to the $\text{Nb}_2(\text{CO})_9$ structures **9S-1** and **9S-2**, a third slightly higher energy singlet $\text{Nb}_2(\text{CO})_9$ structure **9S-3** was found with a four-electron donor bridging $\eta^2\text{-}\mu\text{-CO}$ group and a similar Nb≡Nb distance, likewise suggesting a formal triple bond (Figure 2). In this structure, both niobium atoms have the favored 18-electron configuration. All of these singlet bridged $\text{Nb}_2(\text{CO})_9$ structures have counterparts in low-energy $\text{V}_2(\text{CO})_9$ structures found in a previous theoretical study.⁴⁴

The lowest energy $\text{Nb}_2(\text{CO})_8$ structures are singlet structures with various arrangements of bridging carbonyl groups (Figure 4). Interestingly enough, in the lowest energy $\text{Nb}_2(\text{CO})_8$ structure **8S-1**, the Nb—Nb distance is relatively long at ~3.1 Å, corresponding to a single bond in this highly unsaturated system. However, structure **8S-1** has two four-electron donor bridging $\eta^2\text{-}\mu\text{-CO}$ groups so that each niobium atom has a 16-electron configuration. This contrasts with the next highest lying $\text{Nb}_2(\text{CO})_8$ structure **8S-2**, having only two-electron donor carbonyl groups and a shorter Nb≡Nb distance, suggesting a formal double bond. In **8S-2** as in **8S-1**, both niobium atoms have 16-electron configurations.

Triplet structures for $\text{Nb}_2(\text{CO})_9$ and $\text{Nb}_2(\text{CO})_8$ are also found. For $\text{Nb}_2(\text{CO})_9$, the lowest energy triplet structure **9T-1** lies 6.4 kcal/mol (MPW1PW91) or 8.9 kcal/mol (BP86) above the lowest energy singlet structure **9S-1** (Figure 3). This contrasts with the analogous $\text{V}_2(\text{CO})_9$, where the lowest energy structure is a triplet structure with an arrangement of carbonyl groups similar to that in **9T-1**. All of the triplet $\text{Nb}_2(\text{CO})_9$ structures have only two-electron donor carbonyl groups and

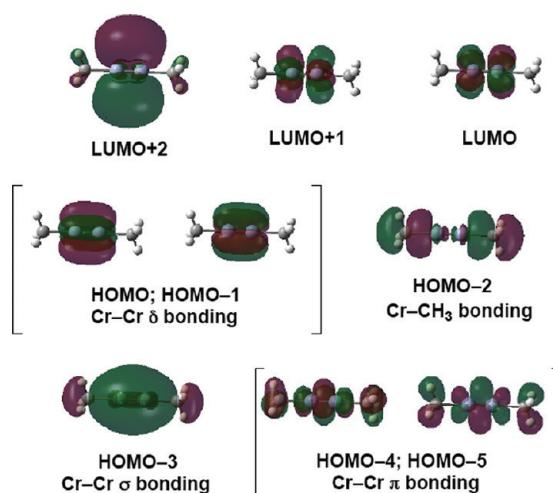


Figure 10. Frontier molecular orbitals for the D_{3h} linear $\text{CH}_3\text{CrCrCH}_3$. Pairs of degenerate orbitals are enclosed in brackets [].

HOMO-1 correspond to the two degenerate δ components, HOMO-3 corresponds to the σ component, and HOMO-4 and HOMO-5 correspond to the two degenerate π components. Only HOMO-2 corresponds to chromium–methyl bonding rather than chromium–chromium bonding.

The fact that the five components of the Cr—Cr quintuple bond are clearly found in the frontier bonding orbitals of representative RCrCrR derivatives indicates the validity of this type of frontier molecular orbital analysis for assessing the formal orders of metal–metal multiple bonds.

4. DISCUSSION

The 18-electron rule suggests structures with formal niobium–niobium quadruple and quintuple bonds for $\text{Nb}_2(\text{CO})_9$ and $\text{Nb}_2(\text{CO})_8$, respectively. Indeed, our search for low-energy structures for these binuclear niobium carbonyls has led to the unbridged $\text{Nb}_2(\text{CO})_9$ structures **9S-4** and **9S-5** (Figure 2) and unbridged $\text{Nb}_2(\text{CO})_8$ structures **8S-5** and **8S-6** (Figure 4) with

Nb≡Nb distances in the range 2.73–2.83 Å, suggesting formal triple bonds (Figure 3). This gives each niobium atom in these Nb₂(CO)₉ structures a 17-electron configuration consistent with binuclear triplets. The triplet Nb₂(CO)₈ structures (Figure 4) lie at least 11 kcal/mol above the lowest energy singlet structure and exhibit various combinations of formal Nb–Nb bond orders from 1 to 4, two-electron donor and four-electron donor bridging carbonyl groups, and 15- and 17-electron metal configurations.

■ ASSOCIATED CONTENT

Supporting Information

Tables S1–S5: Harmonic vibrational frequencies and infrared intensities for five singlet structures of Nb₂(CO)₉. Tables S6–S10: Harmonic vibrational frequencies and infrared intensities for five triplet structures of Nb₂(CO)₉. Tables S11–S16: Harmonic vibrational frequencies and infrared intensities for six singlet structures of Nb₂(CO)₈. Tables S17–S19: Harmonic vibrational frequencies and infrared intensities for three triplet structures of Nb₂(CO)₈. Tables S20 and S21: Cartesian coordinates of Nb₂(CO)₉. Tables S22 and S23: Cartesian coordinates of Nb₂(CO)₈. Figures S1–S3: Linear CH₃CrCrCH₃ and its frontier molecular orbitals. Figures S4–S6: Linear C₆H₅CrCrC₆H₅ and its frontier molecular orbitals. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are indebted to the National Natural Science Foundation (20873045 and 20802093) of China, the Scientific Research Fund of the State Key Laboratory of Explosion Science and Technology (QNKT10-11), the Excellent Talent Training Fund of Beijing (2010D009011000003), the Natural Science Foundation of Beijing (2112036), and the U.S. National Science Foundation (Grants CHE-1054286 and CHE-1057466) for support of this research.

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