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Possibilities for Titanium−Titanium Multiple Bonding in Binuclear Cyclopentadienyltitanium Carbonyls: 16-Electron Metal Configurations and Four-Electron Donor Bridging Carbonyl Groups as Alternatives

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The structures for the binuclear $Cp_2Ti_2(CO)_n$ derivatives ($Cp = \eta^5\text{-}C_5H_5$; n = 8, 7, 6, 5, 4, 3, 2) have been optimized using density functional theory. Furthermore, the thermodynamics of CO dissociation, disproportionation into $Cp_2Ti_2(CO)_{n+1} + Cp_2Ti_2(CO)_{n-1}$, and dissociation into mononuclear fragments of these $Cp_2Ti_2(CO)_n$ derivatives have been studied. An unbridged $Cp_2Ti_2(CO)_8$ structure with a long ∼3.9 Å Ti−Ti bond is found. As expected from the long Ti−Ti bond, the predicted dissociation energy of this dimer into $CpTi(CO)_4$ fragments is relatively low at 7 ± 3 kcal/mol. The lowest energy $Cp_2Ti_2(CO)_6$ structure has two $CpTi(CO)_3$ units linked by a formal ∼2.8 Å Ti≡Ti triple bond and thus is the next member of the M≡M triply bonded series $Cp_2V_2(CO)_5$, $Cp_2Cr_2(CO)_4$, $Cp_2Mn_2(CO)_3$, all three of which are stable compounds. The lowest energy structures of $Cp_2Ti_2(CO)_7$, $Cp_2Ti_2(CO)_5$, and $Cp_2Ti_2(CO)_4$ all contain one or two four-electron donor bridging $\eta^2\text{-}\mu\text{-CO}$ groups. However, they are not likely to be stable molecules since their disproportionation energies into $Cp_2Ti_2(CO)_{n+1} + Cp_2Ti_2(CO)_{n-1}$ are either nearly thermoneutral (n = 5) or exothermic (n = 7 and 4). The lowest energy structure of $Cp_2Ti_2(CO)_3$, in which all three carbonyl groups are four-electron donor $\eta^2\text{-}\mu\text{-CO}$ groups bridging a ∼3.05 Å formal Ti−Ti single bond, is a promising synthetic target since it is thermodynamically stable with respect to both CO dissociation and disproportionation into $Cp_2Ti_2(CO)_4 + Cp_2Ti_2(CO)_2$. In the lowest energy $Cp_2Ti_2(CO)_2$ structure both carbonyl groups are four-electron donor $\eta^2\text{-}\mu\text{-CO}$ groups bridging a formal 2.74 Å Ti≡Ti triple bond. These low energy $Cp_2Ti_2(CO)_n$ (n = 3, 2) structures have only a 16-electron titanium configuration rather than the usually favorable 18-electron configuration for metal carbonyl complexes.

1. Introduction

One of the most important principles in transition metal organometallic chemistry, particularly metal carbonyl chemistry, is the so-called 18-electron rule, which states that the most favorable structures have an 18-electron configuration for the central transition metal.[1−5] This corresponds to a formal electron pair in each of the nine orbitals of the sp^3d^5 transition metal manifold. However, for the early transition metals there is a limit to the applicability of the 18-electron rule since for these relatively electron deficient metals the number of external ligands required to satisfy the 18-electron rule is so large as to create steric problems.

The carbonyls of titanium are of particular interest with respect to the applicability of the 18-electron rule. Such compounds are generally prepared by the reductive carbonylation of suitable titanium derivatives, particularly titanium halide derivatives, using rather potent reducing agents derived from alkali or alkaline earth metals. The first titanium carbonyl of any type to be prepared was the stable $Cp_2Ti(CO)_2$ ($Cp = \eta^5\text{-}C_5H_5$).[6] Subsequently the anions $CpTi(CO)_4^-$ and $Ti(CO)_6^{2-}$ were also prepared and isolated as stable salts.[7,8] The homoleptic $Ti(CO)_7$, which also satisfies the 18-electron rule, is not stable at room temperature but has been identified in low-temperature matrices.[9] The instability of $Ti(CO)_7$ does not arise solely from the difficulty of surrounding a metal atom with seven carbonyl groups, since

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the carbonyl dissociation of $Ti(CO)_7$ to $Ti(CO)_6$ is predicted to be substantial at 29 ± 5 kcal/mol by density functional theory (DFT).[9] Stable seven-coordinate derivatives of $Ti(CO)_7$ have been synthesized[10] in which two to four CO groups are replaced by highly basic chelating phosphines including $(Me_2PCH_2CH_2PMe_2)Ti(CO)_5$ and $[MeC(CH_2PMe_2)_3]Ti(CO)_4$. In addition the seven-coordinate titanium carbonyl anions $[R_3SnTi(CO)_6]^-$ (R = Ph)[11] and $[R_3PAu\rightarrow Ti(CO)_6]^-$ (R = Et)[12] have been synthesized and structurally characterized. All of these reported titanium carbonyl derivatives clearly satisfy the 18-electron rule.[1−5] No binuclear titanium carbonyl derivatives have been reported so that there are no experimental examples of titanium−titanium bonds of any order in titanium carbonyl derivatives.

Outside of titanium carbonyl chemistry, some very stable cyclopentadienyl titanium complexes are known with 16-electron rather than 18-electron titanium configurations. The first cyclopentadienyltitanium derivative to be synthesized was titanocene dichloride, Cp_2TiCl_2, in which the titanium has only a 16-electron configuration.[13,14] The chlorine atoms can be readily replaced by other ligands such as alkyl and aryl groups,[15] thereby leading to an extensive series of Cp_2TiR_2 derivatives in which the 16-electron titanium configuration is maintained. The chemistry of such 16-electron titanium complexes is significant in connection with the extensive technology of olefin polymerization under mild conditions, derived originally from Ziegler−Natta chemistry.[16] No unsupported Ti−Ti bonds are known in these cyclopentadienyltitanium derivatives, even in those with the titanium in formal oxidation states below four. The nature of titanium−titanium interactions in binuclear derivatives with bridging groups such as $Cp_4Ti_2(\mu\text{-}Cl)_2$,[17] $(Me_3P)_2Ti_2Cp_2(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)_2$,[17] and $(Me_3P)_4Ti_2I_4(\mu\text{-}I)_2$[18] is not completely clear and not particularly relevant to the molecules discussed in this paper.

This paper reports the use of DFT to investigate binuclear cyclopentadienyltitanium carbonyls of the type $Cp_2Ti_2(CO)_n$ (n = 8, 7, 6, 5, 4, 3, 2). Such molecules have not yet been synthesized. However, the known anion[7] $CpTi(CO)_4^-$ is a potential source of such molecules through mild oxidation. Thus a one-electron oxidation of $CpTi(CO)_4^-$ might be expected to give the 17-electron complex $CpTi(CO)_4$, analogous to the known[19] oxidation of $V(CO)_6^-$ to $V(CO)_6$. Such a $CpTi(CO)_4$ molecule might dimerize to form $Cp_2Ti_2(CO)_8$, which requires only a Ti−Ti single bond between the two $CpTi(CO)_4$ "halves" to give each titanium atom the favored 18-electron configuration. Structures of this type are of general interest in titanium chemistry since no examples of molecules containing unbridged titanium−titanium bonds of any order have yet been synthesized.

The unsaturated $Cp_2Ti_2(CO)_n$ ($n < 8$) derivatives are potential sources of structures containing one or more of the following features:

(1) Titanium−titanium multiple bonds, which so far are unknown experimentally.

(2) Four-electron donor bridging carbonyl groups, which bond to the metal through one of the π-bonds of the carbonyl group as well as the carbon atom. A carbonyl group of this type was first found in the stable compound[20,21] $(Ph_2PCH_2PPh_2)_2Mn_2(CO)_4(\eta^2\text{-}\mu\text{-}CO)$ and is recognized by a short metal−oxygen distance and an abnormally low ν(CO) frequency. The high oxophilicity of titanium makes such carbonyl groups likely features in unsaturated binuclear cyclopentadienyltitanium carbonyls.

(3) Metal configurations less than the normally favored 18-electron configuration. In view of the stability of the 16-electron Cp_2TiX_2 (X = halide, alkyl, aryl, etc.) derivatives[13−15] as well as other 16-electron titanium derivatives, such as $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)Ti$,[22] and $(\eta^6\text{-}CH_3C_6H_5)_2Ti$,[23] this is also a likely possibility.

2. Theoretical Methods

DFT methods have evolved as a practical and effective computational tool, especially for organometallic compounds.[24−38] Two DFT methods were used in this study. The first method (B3LYP) is the hybrid HF/DFT method using the combination of the three-parameter Becke functional (B3)[39] with the Lee−Yang−Parr (LYP) generalized gradient correlation functional.[40] The second method (BP86) is a pure DFT method combining Becke's 1988 exchange functional (B)[41] with Perdew's 1986 gradient corrected correlation functional (P86). The BP86[42] method has been

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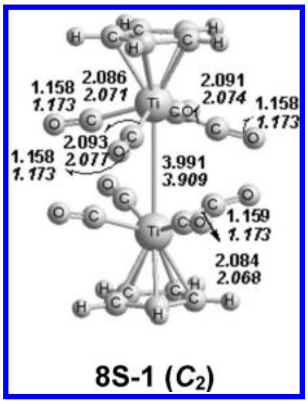

8S-1 (C_2)

Figure 1. Optimized geometry of $Cp_2Ti_2(CO)_8$. The distances in Figure 1−10 are given in angstrom. The upper structural parameters were determined by the B3LYP method and the lower values by the BP86 method.

shown to be somewhat more reliable than the B3LYP method for first row transition metal organometallic systems.[43]

All calculations were performed using double-ζ plus polarization (DZP) basis sets. The DZP basis sets used for carbon and oxygen add one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(C) = 0.75$ and $\alpha_d(O) = 0.85$ to the standard Huzinaga−Dunning contracted double-ζ contraction sets and are designated as (9s5p1d/4s2p1d).[44,45] For H, a set of p polarization functions, $\alpha_p(H) = 0.75$, was added to the Huzinaga−Dunning DZ set. For titanium the Wachters' primitive set[46] was used but is augmented by two sets of p functions and one set of d functions, contracted following Hood et al.,[47] and designated (14s11p6d/10s8p3d).

The geometries of all structures were fully optimized using the two selected DFT methods. The vibrational frequencies were determined by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates at the same levels. The corresponding infrared intensities were also evaluated analytically. The ν(CO) frequencies reported in the tables are those determined by the BP86 method, which has been shown to be more reliable than the B3LYP method for this purpose.[48,49]

All of the computations were carried out with the Gaussian 03 program.[50] The fine grid (75, 302) was the default for evaluating integrals numerically, and the tight (10^{-8} hartree) designation was the default for the energy convergence. The finer grid (120, 974) was used for investigating small imaginary vibrational frequencies.[51] All of the predicted triplet structures were found to have negligible spin contamination, that is, the values of $S(S+1)$ are very close to the ideal value of 2.0.

Table 1. Total Energies (E, in Hartree), Relative Energies (ΔE, in kcal/mol), Numbers of Imaginary Vibrational Frequencies (Nimg), and Ti−Ti bond distance (Å) for $Cp_2Ti_2(CO)_8$

singlet		**8S-1**(C_2)
B3LYP	E	−2993.01901
	ΔE	0.0
	Nimg	0
	Ti−Ti	3.991
BP86	E	−2993.30459
	ΔE	0.0
	Nimg	0
	Ti−Ti	3.909

3. Results

3.1. Geometries and Energies. The results predicted by both B3LYP and BP86 methods agree fairly well. For the sake of brevity, unless specifically noted, only the BP86 results are discussed in the text. However, both the B3LYP and BP86 results are shown in the figures and tables.

3.1.1. $Cp_2Ti_2(CO)_8$. Only one optimized structure **8S-1** was found for $Cp_2Ti_2(CO)_8$ with a titanium−titanium distance short enough to imply any significant interaction between the two $CpTi(CO)_4$ fragments (Figure 1 and Table 1). Structure **8S-1** is a genuine minimum and has C_2 symmetry with eight terminal CO groups. The Ti−Ti distance of 3.909 Å, which is shorter than twice the atomic radius of 2.160 Å but longer than twice the covalent radius of 1.60 Å, is in accord with a weak single bond (between the two $CpTi(CO)_4$ halves) required to give both titanium atoms the favored 18-electron configuration.

3.1.2. $Cp_2Ti_2(CO)_7$. Three singlet structures and one triplet structure (Figure 2 and Table 2) were found for $Cp_2Ti_2(CO)_7$ within 15 kcal/mol of the global minimum **7S-1**. Structure **7S-1** has C_1 geometry with two semibridging and five terminal CO groups. The Ti−O distance to one semibridging carbonyl group is very short, namely, 2.309 Å, indicating that this semibridging carbonyl is a four-electron donor η^2-μ-CO group. This is consistent with its extremely low ν(CO) frequency of 1703 cm^{-1} and relatively long C−O distance of 1.214 Å, indicating a very low C−O bond order for the carbonyl group. The other semibridging carbonyl in **7S-1** is a very weakly semibridging carbonyl group, since its Ti−C distance is very long at 3.620 Å. The Ti−Ti distance in **7S-1** is 3.734 Å, corresponding to the formal single bond required to give each titanium atom in **7S-1** the favored 18-electron configuration with the single four-electron donor bridging carbonyl group.

The second singlet structure **7S-2** has C_s geometry with seven terminal carbonyls and lies 6.3 kcal/mol above **7S-1**. It is predicted to be a genuine minimum with all real harmonic vibrational frequencies by BP86. However, it has a very small imaginary vibrational frequency ($7i$ cm^{-1}) by B3LYP. This imaginary frequency becomes real with a finer (120, 974) integration grid, indicating it stems from the numerical integration error. The Ti=Ti distance in **7S-2** is 3.378 Å, which is ~0.3 Å shorter than that of **7S-1** and thus can be interpreted as the Ti=Ti double bond required to give each titanium atom the favored 18-electron configuration in a $Cp_2Ti_2(CO)_7$ structure in which all of the carbonyl groups are formal two-electron donors.

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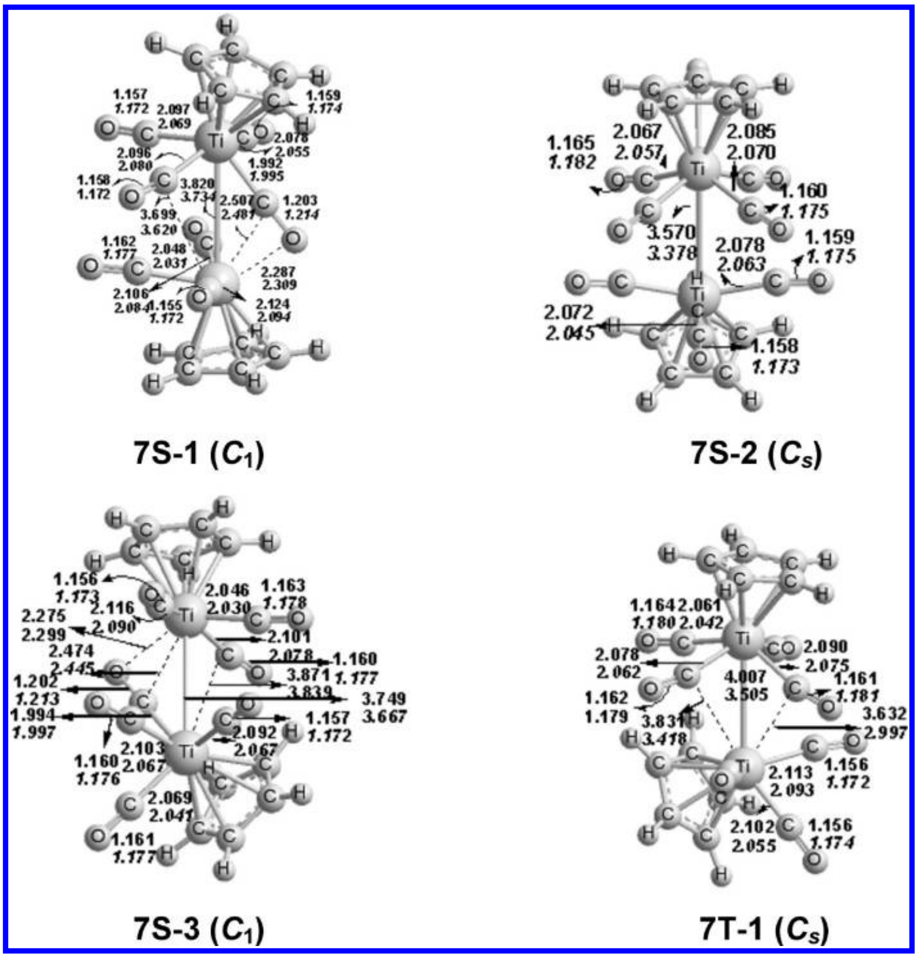

7S-1 (C_1) **7S-2 (C_s)** **7S-3 (C_1)** **7T-1 (C_s)**

Figure 2. Optimized geometries of $Cp_2Ti_2(CO)_7$.

Table 2. Total Energies (E, in Hartree), Relative Energies (ΔE, in kcal/mol), Numbers of Imaginary Vibrational Frequencies (Nimg), and Ti−Ti Bond Distances (Å) for the Four Lowest Energy $Cp_2Ti_2(CO)_7$ Structures

		7S-1 (C_1)	**7S-2** (C_s)	**7S-3** (C_1)	**7T-1** (C_s)
B3LYP	E	−2879.65783	−2879.64784	−2879.64279	−2879.64246
	ΔE	0.0	6.3	9.4	9.6
	Nimg	0	1 (7*i*)	0	1 (13*i*)
	Ti−Ti	3.820	3.570	3.749	4.007
BP86	E	−2879.94023	−2879.93020	−2879.92821	−2879.91941
	ΔE	0.0	6.3	7.5	13.1
	Nimg	0	0	0	1 (25*i*)
	Ti−Ti	3.734	3.378	3.667	3.505

The third singlet structure **7S-3** is a C_1 structure with two semibridging carbonyls and five terminal carbonyls lying 7.5 kcal/mol above **7S-1** (Figure 2 and Table 2). For one of the semibridging carbonyls, there is a very short Ti−O distance, namely, 2.299 Å, which indicates that this semibridging carbonyl is a four-electron donor η^2-μ-CO group, consistent with its very low ν(CO) frequency of 1709 cm^{-1}. The second semibridging carbonyl group is only weakly semibridging for its long Ti−C distance (3.839 Å). The Ti−Ti distance in **7S-3** is predicted to be 3.667 Å, which is 0.1 Å shorter than that of **7S-1**, but still consistent with the formal single bond required to give each titanium atom the favored 18-electron configuration. The singlet $Cp_2Ti_2(CO)_7$ structures **7S-1** and **7S-3** differ only in the orientations of the carbonyl and Cp ligands.

The lowest lying triplet structure **7T-1** (Figure 2 and Table 2) is a C_s structure lying 13.1 kcal/mol above the global minimum **7S-1**, with a small imaginary vibrational frequency at 25*i* cm^{-1}. Structure **7T-1** has three semibridging carbonyls and five terminal carbonyls. Two of the semibridging carbonyls in **7T-1** are only very weakly semibridging since the long Ti−C distances are 3.418 Å with corresponding ν(CO) frequencies of 1887 and 1895 cm^{-1}, essentially in the terminal carbonyl region. The Ti−Ti distance in **7T-1** is 3.505 Å corresponding to a formal single bond, thereby giving both titanium atoms the 17-electron configurations for a binuclear triplet.

3.1.3. $Cp_2Ti_2(CO)_6$.

Three singlet and two triplet structures (Figure 3 and Table 3) were found for $Cp_2Ti_2(CO)_6$. The global minimum **6S-1** is predicted to be a C_2 structure with two semibridging and four terminal CO groups. The predicted Ti≡Ti distance, namely, 2.795 Å, is consistent with the triple bond required to give each titanium atom the favored 18-electron configuration.

The second singlet structure **6S-2** is a C_i structure with two semibridging carbonyls and four terminal carbonyls, lying 6.3 kcal/mol above **6S-1**. The Ti≡Ti distance in **6S-2** is 2.820 Å, corresponding to the formal Ti≡Ti triple bond required to give both titanium atoms the favored 18-electron configuration. The main difference between the $Cp_2Ti_2(CO)_6$ structures **6S-1** and **6S-2** is the relative orientations of the Cp and CO ligands. The Ti≡Ti core is essentially the same for both structures.

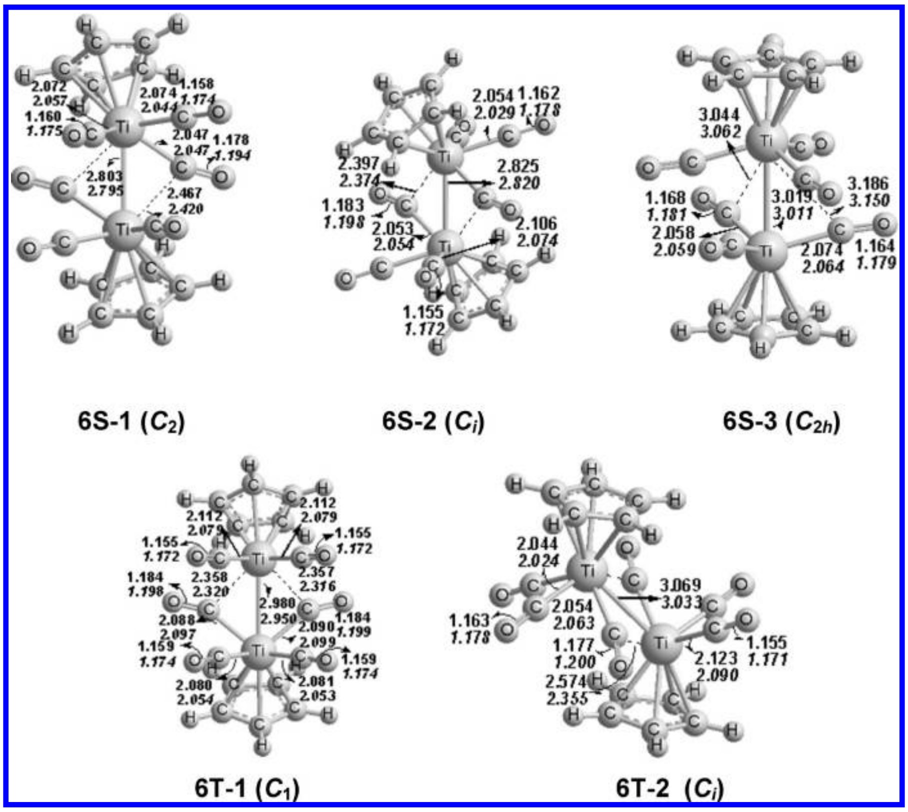

Figure 3. Optimized geometries of $Cp_2Ti_2(CO)_6$.

Table 3. Total Energies (E, in Hartree), Relative Energies (ΔE, in kcal/mol), Numbers of Imaginary Vibrational Frequencies (Nimg), and Ti−Ti Bond Distances (Å) for the Five Lowest Energy $Cp_2Ti_2(CO)_6$ Structures

		6S-1 (C_2)	**6S-2** (C_i)	**6S-3** (C_{2h})	**6T-1** (C_1)	**6T-2** (C_i)
B3LYP	E	−2766.30769	−2766.29614	−2766.25351	−2766.29432	−2766.28060
	ΔE	0.0	7.3	34.0	8.4	17.0
	Nimg	0	0	0	0	0
	Ti−Ti	2.803	2.825	3.019	2.980	3.069
BP86	E	−2766.59494	−2766.58496	−2766.54674	−2766.57486	−2766.56281
	ΔE	0.0	6.3	30.2	12.6	20.2
	Nimg	0	0	0	0	0
	Ti−Ti	2.795	2.820	3.011	2.950	3.033

The third singlet structure **6S-3** has C_{2h} symmetry with a relatively high energy, lying 30.2 kcal/mol above **6S-1**. Structure **6S-3** has two semibridging carbonyls and four terminal carbonyls. The Ti−Ti distance in **6S-3** of 3.011 Å corresponds to a formal single bond. This gives both titanium atoms 16-electron configurations, since all of the carbonyl groups in **6S-3**, like those in **6S-1** and **6S-2**, are formal two-electron donors.

The triplet structure **6T-1** (Figure 3 and Table 3) exhibits a C_1 *cis* structure with two semibridging and four terminal carbonyl groups. It is a genuine minimum lying 12.6 kcal/mol above **6S-1**. The two semibridging carbonyl groups in **6T-1** exhibit ν(CO) frequencies at 1761 and 1788 cm^{-1}. The Ti=Ti distance in **6T-1** is 2.950 Å, which is about 0.2 Å longer than the Ti≡Ti triple bond in **6S-1**, in accord with the double bond required to give each titanium atom a 17-electron configuration consistent with the binuclear triplet structure.

Another triplet structure **6T-2** is a C_i structure with two semibridging carbonyls and four terminal carbonyls lying 20.2 kcal/mol above **6S-1**. The two semibridging carbonyl groups in **6T-1** exhibit ν(CO) frequencies at 1760 and 1743 cm^{-1}. The Ti=Ti distance in **6T-2** is 3.033 Å, which is very close to that for **6T-1** and can also be interpreted as the formal double bond required to give each titanium atom a 17-electron configuration, in accord with the binuclear triplet structure.

3.1.4. $Cp_2Ti_2(CO)_5$. Four singlet structures (Figure 4 and Table 4) and three triplet structures (Figure 5 and Table 5) were found for $Cp_2Ti_2(CO)_5$. The global minimum **5S-1** is predicted to be a singlet C_1 *trans* structure with two semibridging and three terminal CO groups. For one semibridging carbonyl, the Ti−O distance is very short, namely, 2.293 Å, indicating that this semibridging carbonyl is a four-electron donor η^2-μ-CO group, which is consistent with its extremely low ν(CO) frequency of 1623 cm^{-1} and relatively long C−O distance of 1.232 Å, indicating a relatively low C−O bond order for the carbonyl group. For the other semibridging carbonyl, the predicted ν(CO) frequency is 1818 cm^{-1}. The predicted Ti≡Ti distance, namely, 2.809 Å, is consistent with the formal triple bond required to give each titanium

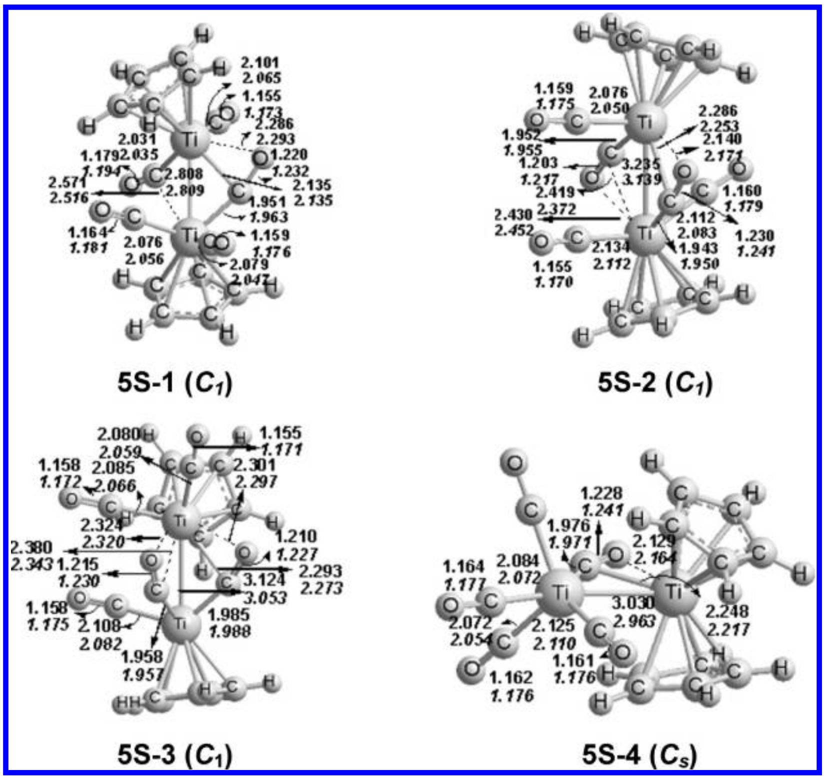

Figure 4. Optimized geometries for the four singlet structures of $Cp_2Ti_2(CO)_5$.

Table 4. Total Energies (E, in Hartree), Relative Energies (ΔE, in kcal/mol), Numbers of Imaginary Vibrational Frequencies (Nimg), and Ti−Ti Bond Distances (Å) for the Five Singlet $Cp_2Ti_2(CO)_5$ Structures

singlet		**5S-1** (C_1)	**5S-2** (C_1)	**5S-3** (C_1)	**5S-4** (C_s)
B3LYP	E	−2652.95046	−2652.95026	−2652.94138	−2652.92165
	ΔE	0.0	0.1	5.7	18.1
	Nimg	0	0	0	0
	Ti−Ti	2.808	3.235	3.124	3.030
BP86	E	−2653.23237	−2653.22272	−2653.21612	−2653.19692
	ΔE	0.0	6.1	10.2	22.2
	Nimg	0	0	0	1 (31i)
	Ti−Ti	2.809	3.139	3.053	2.963

atom the favored 18-electron configuration with the single four-electron donor bridging carbonyl group.

The second energetically low-lying singlet structure **5S-2** is a C_1 structure and lies above **5S-1** by 6.1 kcal/mol, with all real harmonic vibrational frequencies. Structure **5S-2** has two semibridging carbonyls and three terminal carbonyls. The Ti−O distances of both semibridging carbonyls are very short, namely, 2.171 Å and 2.452 Å, indicating that both semibridging carbonyls are four-electron donor η^2-μ-CO groups, consistent with their extremely low ν(CO) frequencies of 1571 and 1695 cm^{-1}. The Ti═Ti bond distance in **5S-2** of 3.139 Å (BP86) is ~0.3 Å longer than that in **5S-1** and consistent with the formal (albeit weak) double bond required to give each titanium atom a 18-electron configuration with two four-electron donor bridging carbonyl groups.

The third energetically low-lying singlet structure **5S-3** lies 10.2 kcal/mol above **5S-1**. Structure **5S-3** is a C_1 structure with two semibridging carbonyls and three terminal carbonyls. The Ti−O distances to the two semibridging carbonyl groups are both very short, namely, ~2.3 Å, indicating four-electron donor η^2-μ-CO groups consistent with their extremely low ν(CO) frequencies of 1603 and 1659 cm^{-1}. The Ti═Ti bond distance of 3.053 Å corresponds to a formal double bond, thereby giving each titanium an 18-electron configuration after considering the two four-electron donor bridging carbonyl groups.

The next singlet structure **5S-4** lies 22.2 kcal/mol above **5S-1** with all real harmonic vibrational frequencies by B3LYP but a small imaginary vibrational frequency at 31i cm^{-1} by BP86. Structure **5S-4** is of a very different type than the singlet structures reported above. Thus **5S-4** has the two Cp rings bonded to one titanium atom and only carbonyl groups bonded to the other titanium atom. One of the carbonyl groups in **5S-4** is a semibridging carbonyl, and the related Ti−O distance is very short, namely, 2.164 Å, indicating that this semibridging carbonyl is a four-electron donor η^2-μ-CO group. This is consistent with its extremely low ν(CO) frequency of 1574 cm^{-1} and relatively long C−O distance of 1.241 Å, indicating a very low C−O bond order for the carbonyl group. The Ti═Ti distance in **5S-4** is 2.963 Å, corresponding to a formal double bond, which, with the single four-electron donor bridging carbonyl group, gives the titanium atom bearing the two Cp rings the favored 18-electron configuration. However, this gives the titanium atom bearing only carbonyl groups only a 16-electron configuration.

The lowest lying triplet structure **5T-1** (Figure 5 and Table 5) is a C_1 *trans* structure with three semibridging carbonyls and two terminal carbonyls. Structure **5T-1** lies 12.2 kcal/mol above the global minimum **5S-1**, with all real harmonic vibrational frequencies. The predicted ν(CO) frequencies of 1805, 1849, and 1881 cm^{-1} correspond to the three semibridging carbonyl groups, which

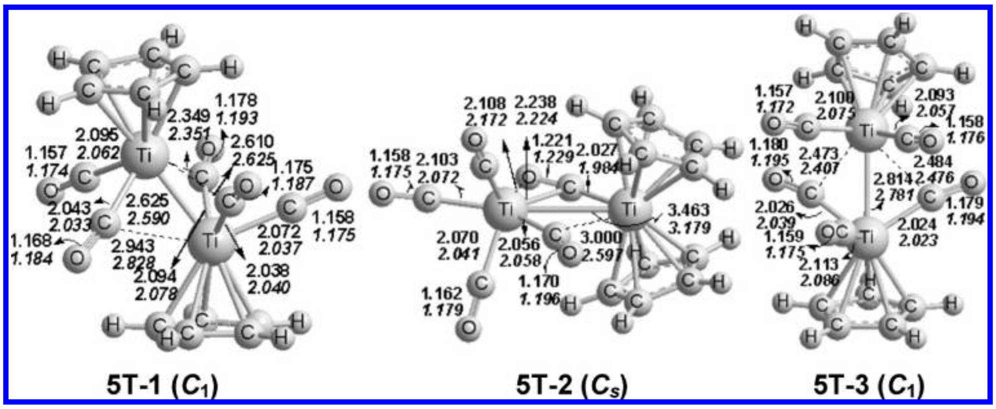

Figure 5. Optimized geometries for the three triplet structures of $Cp_2Ti_2(CO)_5$.

Table 5. Total Energies (E, in Hartree), Relative Energies (ΔE, relative to **5S-1** in kcal/mol), Number of Imaginary Vibrational Frequencies (Nimg), and Ti−Ti Bond Distances (Å) for the Three Triplet $Cp_2Ti_2(CO)_5$ Structures

triplet		**5T-1** (C_1)	**5T-2** (C_s)	**5T-3** (C_1)
B3LYP	E	−2652.93720	−2652.93459	−2652.93057
	ΔE	8.3	10.0	12.5
	Nimg	0	0	0
	Ti−Ti	2.625	3.463	2.814
BP86	E	−2653.21292	−2653.20197	−2653.20418
	ΔE	12.2	19.1	17.7
	Nimg	0	0	0
	Ti−Ti	2.590	3.179	2.781

all have relatively long Ti−O distances and thus are the usual two-electron donors. The Ti≡Ti distance in **5T-1** is 2.590 Å, which is 0.2 Å shorter than that of **5S-1**. This can be interpreted as a formal $\sigma + 2\pi + {}^2/_2\delta$ quadruple bond giving both titanium atoms in **5T-1** the favorable 18-electron configuration. The triplet spin multiplicity of **5T-1** then arises from the unpaired electrons in the two orthogonal δ "half-bond" components in the Ti≡Ti quadruple bond of the $3^2/_2$ type.

The second triplet structure **5T-2** has the two Cp rings bonded to one titanium atom and only carbonyl groups bonded to the second titanium atom, as found for the singlet structure **5S-4**. Structure **5T-2** is a C_s structure, lying 19.1 kcal/mol above the global minimum **5S-1**. Structure **5T-2** has two semibridging carbonyls and three terminal carbonyls. For one semibridging carbonyl, the Ti−O distance is very short, namely, 2.172 Å, indicating a four-electron donor η^2-μ-CO group. This is consistent with its extremely low ν(CO) frequency of 1649 cm^{-1} and relatively long C−O distance of 1.229 Å, implying a very low C−O bond order. For the other semibridging carbonyl in **5T-2**, the predicted ν(CO) frequency is at 1788 cm^{-1}. The Ti−Ti distance in **5T-2** is 3.179 Å.

The third energetically low-lying triplet structure **5T-3** lies 17.7 kcal/mol above **5S-1**. Structure **5T-3** is a C_1 *cis* structure with three terminal carbonyls and two semibridging carbonyls and the ν(CO) frequencies of 1780 and 1820 cm^{-1} correspond to these two semibridging CO groups. The Ti≡Ti distance in **5T-3** is 2.781 Å corresponding to the formal triple bond required to give both titanium atoms 17-electron configurations in a binuclear triplet $Cp_2Ti_2(CO)_5$ structure, in which all of the carbonyl groups are two-electron donor carbonyl groups.

3.1.5. $Cp_2Ti_2(CO)_4$.

Three singlet (Figure 6 and Table 6) and four triplet structures (Figure 7 and Table 7) were found for $Cp_2Ti_2(CO)_4$. The global minimum **4S-1** is a C_s structure with three semibridging CO groups and one terminal CO group (Figure 6). The Ti−O distances to the two equivalent semibridging CO groups are very short, namely, 2.110 Å, indicating that these two semibridging carbonyls are four-electron donor η^2-μ-CO groups. This is consistent with their extremely low ν(CO) frequencies of 1472 and 1543 cm^{-1} and relatively long C−O distances of 1.253 Å, indicating a very low C−O bond order for the carbonyl groups. The ν(CO) frequency in **4S-1** of 1864 cm^{-1} is assigned to the third semibridging CO group, which is a two-electron donor with a long Ti···O distance rather than a four-electron donor with a short Ti−O distance. The Ti−Ti distance in **4S-1** is 3.012 Å. This can correspond to a formal single bond thereby giving each titanium atom in **4S-1** a 16-electron configuration in this $Cp_2Ti_2(CO)_4$ structure with two four-electron donor bridging carbonyl groups. However, this formal Ti−Ti single bond is shortened drastically over the unbridged formal Ti−Ti single bonds in $Cp_2Ti_2(CO)_8$ (Figure 1) because of the geometrical requirements of the two four-electron donor η^2-μ-CO bridges.

The B3LYP and BP86 methods disagree with respect to the relative energies and the key features of the singlet C_2 structure **4S-2** (Figure 6 and Table 6). The B3LYP method predicts **4S-2** with two semibridging CO groups exhibiting ν(CO) frequencies of 1850 and 1868 cm^{-1}, lying above **4S-1** by 23.0 kcal/mol. The B3LYP Ti≡Ti bond distance is 2.739 Å, corresponding to a formal triple bond and thereby giving the titanium atoms 16-electron configurations with all four carbonyl groups functioning as two-electron donors. The BP86 method also predicts **4S-2** to have two semibridging CO groups, but the Ti−O distances for the two semibridging CO groups are very short, namely, 2.127 Å (BP86), indicating that these two CO groups are four-electron donor η^2-μ-CO groups. This is consistent with their extremely low ν(CO) frequencies of 1529 and 1556 cm^{-1} (BP86) and relatively long C−O distances of 1.248 Å (BP86), indicating a very low C−O bond order. With the BP86 method, **4S-2** lies 2.8 kcal/mol lower than **4S-1** and the Ti−Ti bond distance is 3.219 Å. This corresponds to a formal Ti−Ti single bond, again giving both titanium atoms 16-electron configurations in a $Cp_2Ti_2(CO)_4$ structure with two four-electron donor bridging η^2-μ-CO groups.

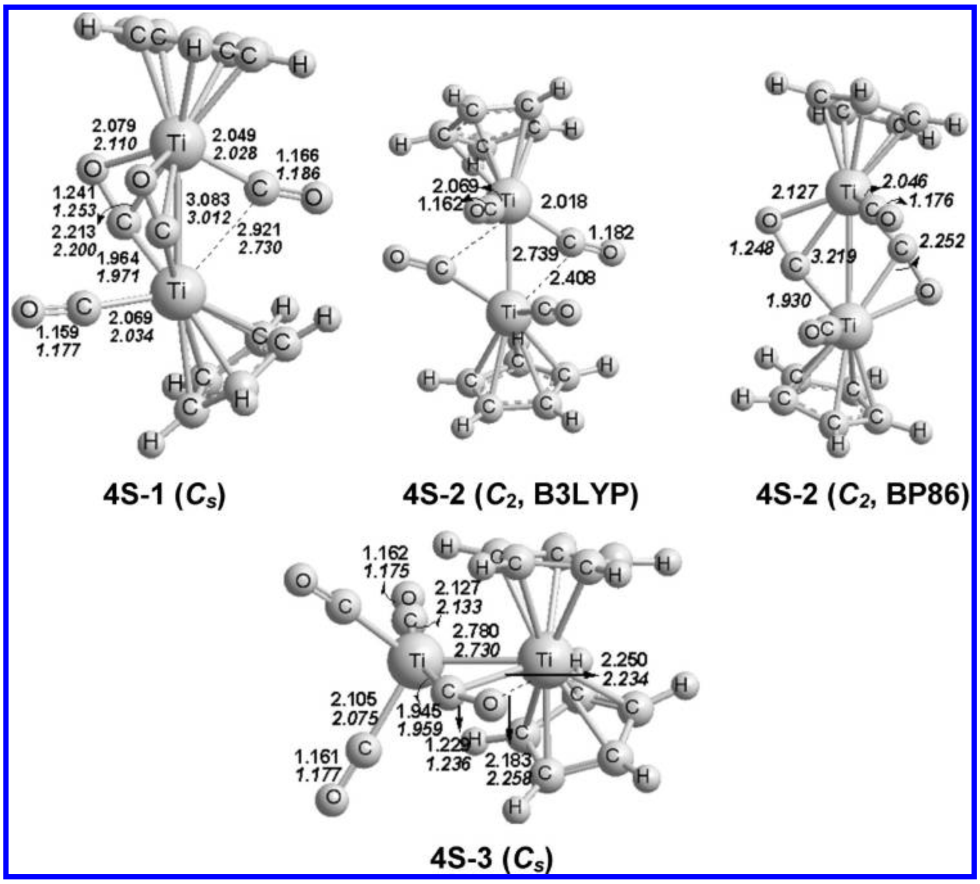

Figure 6. Optimized geometries of the singlet structures of $Cp_2Ti_2(CO)_4$.

Table 6. Total Energies (E, in Hartree), Relative Energies (ΔE, in kcal/mol), Numbers of Imaginary Vibrational Frequencies (Nimg), and Ti−Ti Bond Distances (Å) for the Three Singlet $Cp_2Ti_2(CO)_4$ Structures

		4S-1 (C_s)	**4S-2** (C_2)	**4S-3** (C_s)
B3LYP	E	−2539.59342	−2539.55669	−2539.54982
	ΔE	0.0	23.0	27.4
	Nimg	0	0	0
	Ti−Ti	3.083	2.739	2.780
BP86	E	−2539.86728	−2539.87170	−2539.82325
	ΔE	0.0	−2.8	27.6
	Nimg	0	0	0
	Ti−Ti	3.012	3.219	2.730

The third singlet structure **4S-3** has the two Cp rings bonded to one titanium atom and only carbonyl groups bonded to the other titanium atom. Structure **4S-3** is a C_s structure, lying 27.6 kcal/mol above the global minimum **4S-1**. The $Cp_2Ti_2(CO)_4$ structure **4S-3** has one semibridging carbonyl and three terminal carbonyls. For the semibridging carbonyl, the Ti−O distance is very short, namely, 2.258 Å, indicating that this semibridging carbonyl is a four-electron donor η^2-μ-CO group. This is consistent with its extremely low ν(CO) frequency of 1587 cm^{-1} and relatively long C−O distance of 1.236 Å, implying a very low C−O bond order. The predicted Ti≡Ti distance of 2.730 Å can be interpreted as a formal triple bond. This gives the titanium atom bearing the two Cp rings the favored 18-electron configuration with a formal positive charge and the other titanium atom a 16-electron configuration with a formal negative charge.

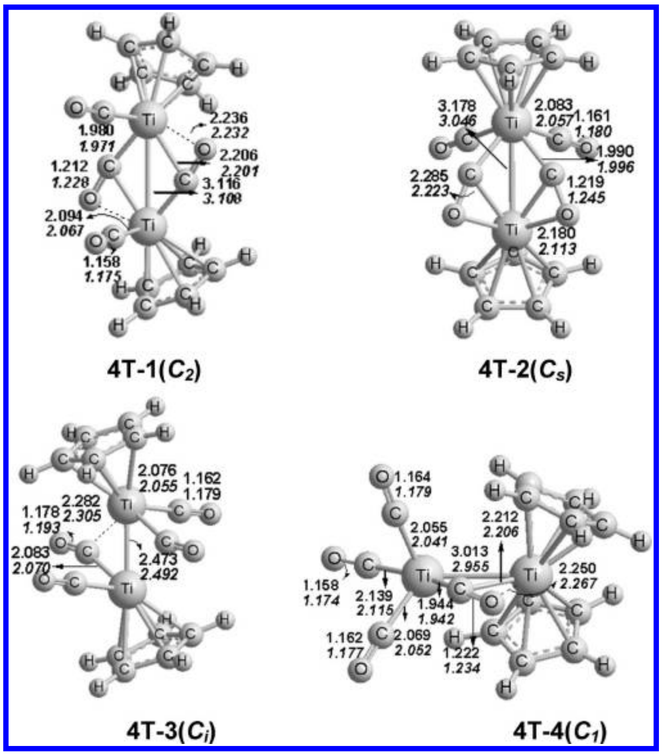

Figure 7. Optimized geometries of the triplet structures of $Cp_2Ti_2(CO)_4$.

Four triplet states of $Cp_2Ti_2(CO)_4$ are very low-lying energetically (Figure 7 and Table 7). The lowest energy of these triplet structures, namely, **4T-1**, is a C_2 structure

Table 7. Total Energies (E, in Hartree), Relative Energies (ΔE, related to **4S-1** in kcal/mol), Number of Imaginary Vibrational Frequencies (Nimg), and Ti−Ti Bond Distances (Å) for the Four Triplet $Cp_2Ti_2(CO)_4$ Structures

		4T-1 (C_2)	**4T-2** (C_s)	**4T-3** (C_i)	**4T-4** (C_1)
B3LYP	E	−2539.59765	−2539.59781	−2539.56533	−2539.55929
	ΔE	−2.7	−2.8	17.6	21.4
	Nimg	1 (57*i*)	0	0	0
	Ti−Ti	3.116	3.178	2.473	3.013
BP86	E	−2539.86367	−2539.85996	−2539.83644	−2539.82042
	ΔE	2.3	4.6	19.4	29.4
	Nimg	0	1(10*i*)	0	0
	Ti−Ti	3.108	3.046	2.492	2.955

Table 8. Total Energies (E, in Hartree), Relative Energies (ΔE, in kcal/mol), Number of Imaginary Vibrational Frequencies (Nimg), and Ti−Ti Bond Distances (Å) for the Four Lowest Energy Structures of $Cp_2Ti_2(CO)_3$

		3S-1 (C_s)	**3S-2** (C_1)	**3T-1** (C_1)	**3T-2** (C_1)
B3LYP	E	−2426.25261	−2426.23422	−2426.23017	−2426.22845
	ΔE	0.0	11.5	14.1	15.2
	Nimg	0	0	0	0
	Ti−Ti	3.065	2.912	3.200	2.820
BP86	E	−2426.51765	−2426.49987	−2426.48502	−2426.49156
	ΔE	0.0	11.2	20.5	16.4
	Nimg	0	0	0	0
	Ti−Ti	3.031	2.836	3.079	2.811

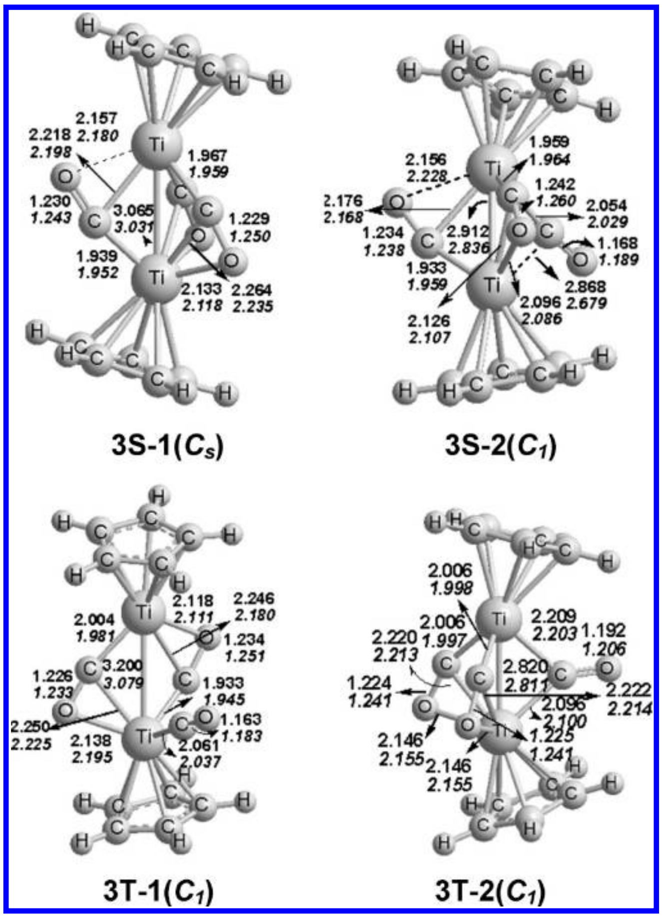

Figure 8. Optimized geometries of $Cp_2Ti_2(CO)_3$.

with two semibridging carbonyls and two terminal carbonyls. Structure **4T-1** lies only 2.3 kcal/mol higher than that of **4S-1** by BP86 and 2.7 kcal/mol lower than that of **4S-1** by B3LYP. Structure **4T-1** has all real harmonic vibrational frequencies by BP86 but a small imaginary vibrational frequency at 57*i* cm^{-1} by B3LYP. For the two semibridging carbonyls in **4T-1**, the Ti−O distances are very short, namely, 2.232 Å, indicating that these two semibridging carbonyls are both four-electron donor η^2-μ-CO groups. This is consistent with their extremely low ν(CO) frequencies of 1619 and 1658 cm^{-1}. The predicted Ti=Ti distance in **4T-1** of 3.108 Å is consistent with the formal double bond required to give each titanium atom the favored 17-electron configuration in a triplet structure with two four-electron donor carbonyl groups.

The second energetically low-lying triplet $Cp_2Ti_2(CO)_4$ structure **4T-2** is a C_s structure lying 2.8 kcal/mol below **4S-1** by B3LYP but 4.6 kcal/mol above **4S-1** by BP86. Structure **4T-2** has all real harmonic vibrational frequencies by B3LYP but a very small imaginary vibrational frequency at 10*i* cm^{-1} by BP86. Structure **4T-2** has two four-electron donor η^2-μ-CO bridging carbonyl groups and two terminal carbonyl groups. The Ti−O distances to the two η^2-μ-CO bridging carbonyl groups of 2.113 Å and their very low ν(CO) frequencies of 1531 and 1574 cm^{-1} are consistent with these two semibridging carbonyl groups being formal four-electron donors. The predicted Ti=Ti distance in **4T-2** of 3.046 Å is consistent with the formal double bond required to give each titanium atom the favored 17-electron configuration for a binuclear triplet structure with two four-electron donor carbonyl groups.

The third triplet $Cp_2Ti_2(CO)_4$ structure **4T-3** lies 19.4 kcal/mol above **4S-1**. Structure **4T-3** is a C_i structure with two equivalent semibridging carbonyls and two equivalent terminal carbonyls. The ν(CO) frequencies to the semibridging carbonyls in **4T-3** are 1809 and 1814 cm^{-1}. The Ti≡Ti distance in **4T-3** is very short at 2.492 Å and can be interpreted as the formal quadruple bond required to give each titanium atom the favored 17-electron configuration for a binuclear triplet structure.

Another triplet $Cp_2Ti_2(CO)_4$ structure **4T-4** has the two Cp rings bonded to one titanium atom and only carbonyl groups bonded to the second titanium atom. Structure **4T-4** lies 29.4 kcal/mol above the global minimum **4S-1**. One of the carbonyl groups in **4T-4** is a four-electron donor η^2-μ-CO group, as indicated by a short Ti−O distance of 2.267 Å, a relatively long C−O distance of 1.234 Å, and a very low ν(CO) frequency of 1613 cm^{-1}. The Ti≡Ti distance in **4T-4** is 2.955 Å. Simple electron counting suggests a formal Ti≡Ti triple bond required to give each titanium atom in $Cp_2Ti_2(CO)_4$ the favored 17-electron configuration with the one four-electron donor bridging carbonyl group in a triplet structure.

3.1.6. $Cp_2Ti_2(CO)_3$. Two singlet structures and two triplet structures (Figure 8 and Table 8) are predicted for $Cp_2Ti_2(CO)_3$ within 20 kcal/mol of the global minimum. The global minimum **3S-1** is predicted to be a singlet C_s structure with three four-electron donor η^2-μ-CO carbonyl groups. Two of the three four-electron donor carbonyl groups in **3S-1** are equivalent and are characterized by short Ti−O distances of 2.118 Å, very long C−O distances of 1.250 Å, and extremely low ν(CO) frequencies of 1501 and 1540 cm^{-1}. The third carbonyl group in **3S-1** can also be interpreted as a four-electron donor carbonyl group on the basis of its short Ti−O distance of 2.180 Å, and extremely low ν(CO) frequency

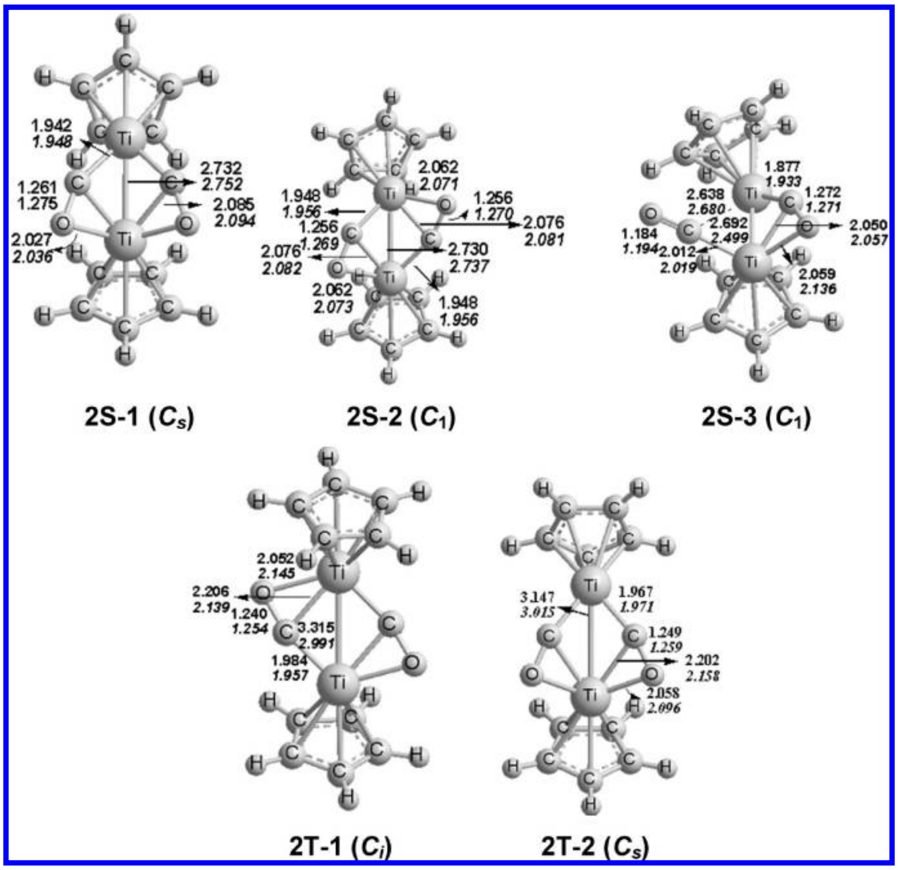

Figure 9. Optimized geometries of $Cp_2Ti_2(CO)_2$.

Table 9. Total Energies (E, in Hartree), Relative Energies (ΔE, in kcal/mol), Numbers of Imaginary Vibrational Frequencies (Nimg), and Ti−Ti Bond Distances (Å) for Each of the Singlet $Cp_2Ti_2(CO)_2$ Structures

singlet		**2S-1** (C_s)	**2S-2** (C_1)	**2S-3** (C_1)
B3LYP	E	−2312.86767	−2312.86268	−2312.82287
	ΔE	0.0	3.1	28.1
	Nimg	0	0	0
	Ti−Ti	2.732	2.730	2.692
BP86	E	−2313.12657	−2313.12140	−2313.08472
	ΔE	0.0	3.2	26.3
	Nimg	0	0	0
	Ti−Ti	2.752	2.737	2.499

of 1603 cm^{-1}. The predicted Ti−Ti distance of 3.031 Å in **3S-1** can be interpreted as a formal single bond thereby giving each titanium atom a 16-electron configuration.

The second singlet structure **3S-2** is a C_1 structure lying 11.2 kcal/mol in energy above **3S-1**. Two of the three carbonyl groups in **3S-2** are four-electron donor η^2-μ-CO carbonyls, as indicated by short Ti−O distances of 2.086 Å and 2.228 Å, as well as their very low ν(CO) frequencies of 1491 and 1592 cm^{-1}. The predicted Ti=Ti distance of 2.836 Å in **3S-2** can be interpreted as a formal double bond thereby giving each titanium atom a 16-electron configuration with two four-electron donor bridging carbonyl groups. The formal Ti=Ti double bond in **3S-2** is ~0.2 Å shorter than the formal Ti−Ti single bond in **3S-1**.

The lowest lying $Cp_2Ti_2(CO)_3$ triplet structure **3T-1** is a C_1 structure with all real vibrational frequencies. Structure **3T-1** lies 20.5 kcal/mol in energy above **3S-1** and has two semibridging carbonyl groups and one terminal carbonyl group. Both semibridging carbonyl groups are four-electron donor η^2-μ-CO carbonyls, as indicated by the short Ti−O distances of 2.111 Å and 2.195 Å, long C−O bond distances of 1.251 Å and 1.233 Å, and low predicted ν(CO) frequencies of 1526 and 1613 cm^{-1}. The Ti−Ti bond distance in **3T-1** is predicted to be 3.079 Å, consistent with a formal single bond and giving each titanium atom a 15-electron configuration.

The second triplet structure **3T-2** lies 16.4 kcal/mol in energy above the global minimum **3S-1**. Structure **3T-2** is a C_1 structure with two four-electron donor η^2-μ-CO bridging carbonyls and one normal two-electron donor semibridging carbonyl. Both four-electron donor carbonyl groups are characterized by short Ti−O distances of 2.155 Å and very low ν(CO) frequencies of 1543 and 1601 cm^{-1}. The Ti≡Ti distance in **3T-2** is predicted to be 2.811 Å, consistent with the formal triple bond required to give each titanium atom the 17-electron configuration for a binuclear triplet.

3.1.7. $Cp_2Ti_2(CO)_2$. A total of five energetically low-lying $Cp_2Ti_2(CO)_2$ structures were found (Figure 9 and Tables 9 and 10), including two triplet and three singlet structures. The global minimum **2S-1** is predicted to be a singlet C_s structure. The two carbonyl groups in **2S-1** are both predicted to be four-electron donor η^2-μ-CO bridging carbonyl groups as indicated by their short Ti−O distances of 2.036 Å and extremely low ν(CO) frequencies of 1421 and 1468 cm^{-1}. The Ti≡Ti bond distance in **2S-1** is predicted to be 2.752 Å consistent with a formal triple bond to give each titanium atom a 16-electron configuration.

Table 10. Total Energies (E, in Hartree), Relative Energies (ΔE, related to **2S-1** in kcal/mol), Numbers of Imaginary Vibrational Frequencies (Nimg), and Ti−Ti Bond Distances (Å) for Each of the Triplet $Cp_2Ti_2(CO)_2$ Structures

triplet		**2T-1**(C_i)	**2T-2** (C_s)
B3LYP	E	−2312.85213	−2312.85016
	ΔE	9.8	11.0
	Nimg	0	1 (12i)
	Ti−Ti	3.315	3.147
BP86	E	−2313.09668	−2313.09567
	ΔE	18.8	19.4
	Nimg	0	0
	Ti−Ti	2.991	3.015

The second singlet $Cp_2Ti_2(CO)_2$ structure **2S-2** also has two semibridging carbonyl groups and lies 3.2 kcal/mol above **2S-1**. The Ti−C distances to the semibridging carbonyls in **2S-2** are ~1.96 Å and ~2.08 Å. The low ν(CO) frequencies of **2S-2** at 1436 and 1491 cm^{-1} and short Ti−O distances of ~2.07 Å indicate that these two semibridging CO groups are both four-electron donor η^2-μ-CO bridging carbonyl groups. The Ti≡Ti distance in **2S-2** of 2.737 Å again corresponds to a formal triple bond, giving both titanium atoms 16-electron configurations. The $Cp_2Ti_2(CO)_2$ structures **2S-1** and **2S-2** are similar except for the locations of the two short Ti−O distances from the carbonyl groups. In structure **2S-1** the short Ti−O distances are to the same titanium atom, whereas in structure **2S-2** the short Ti−O distances are to different titanium atoms.

The third singlet $Cp_2Ti_2(CO)_2$ structure **2S-3** is a C_1 structure with one four-electron donor η^2-μ-CO bridging carbonyl group and one terminal carbonyl group. Structure **2S-3** lies 26.3 kcal/mol above the global minimum **2S-1**. The four-electron donor bridging carbonyl group in **2S-3** is characterized by a very short Ti−O distance of 2.136 Å and a very low ν(CO) frequency of 1438 cm^{-1}. The Ti$\equiv$Ti bond distance in **2S-3** of 2.499 Å is shorter than the Ti≡Ti distances of ~2.74 Å in **2S-1** and **2S-2** attributed to formal triple bonds. Therefore the Ti$\equiv$Ti bond in **2S-3** is interpreted as the formal quadruple bond, giving each titanium atom a 16-electron configuration in a $Cp_2Ti_2(CO)_2$ structure with one four-electron bridging η^2-μ-CO group and one normal two-electron terminal carbonyl group. This quadruple bond is polarized so that the titanium atom bonded to both carbonyl groups (the "bottom" titanium atom in Figure 9) bears a formal positive charge and the titanium atom bonded only to the bridging carbonyl group (the "top" titanium atom in Figure 9) bears a formal negative charge.

The lowest lying triplet $Cp_2Ti_2(CO)_2$ structure **2T-1** (Figure 9 and Table 10) has two semibridging carbonyls and lies 18.8 kcal/mol above the global minimum **2S-1**, with all real harmonic vibrational frequencies. The Ti−O distances for the two semibridging carbonyls in **2T-1** are very short, namely, 2.145 Å, indicating that these two semibridging carbonyls are four-electron donor η^2-μ-CO groups. This is consistent with their extremely low ν(CO) frequencies of 1493 and 1535 cm^{-1} and relatively long C−O distances of 1.254 Å, indicating a very low C−O bond order for the carbonyl groups. The Ti=Ti bond distance in **2T-1** of 3.315 Å (B3LYP) can correspond to a formal double bond, thereby giving each titanium atom a 15-electron configuration for the binuclear triplet. However, the BP86 method predicts a much shorter Ti=Ti bond distance of 2.991 Å (BP86).

Table 11. Dissociation Energies (kcal/mol) for the Successive Removal of Carbonyl Groups from the $Cp_2Ti_2(CO)_n$(n = 8, 7, 6, 5, 4, 3, 2) Derivatives

	B3LYP/DZP	BP86/DZP
$Cp_2Ti_2(CO)_8$ (**8S-1**) → $Cp_2Ti_2(CO)_7$ (**7S-1**) + CO	20.4	23.3
$Cp_2Ti_2(CO)_7$ (**7S-1**) → $Cp_2Ti_2(CO)_6$ (**6S-1**) + CO	13.5	11.3
$Cp_2Ti_2(CO)_6$ (**6S-1**) → $Cp_2Ti_2(CO)_5$ (**5S-1**) + CO	17.9	22.2
$Cp_2Ti_2(CO)_5$ (**5S-1**) → $Cp_2Ti_2(CO)_4$ (**4S-1**) + CO	17.8	23.8
$Cp_2Ti_2(CO)_4$ (**4S-1**) → $Cp_2Ti_2(CO)_3$ (**3S-1**) + CO	7.6	14.1
$Cp_2Ti_2(CO)_3$ (**3S-1**) → $Cp_2Ti_2(CO)_2$ (**2S-1**) + CO	35.3	40.1
$Cp_2Ti_2(CO)_2$ (**2S-1**) → $Cp_2Ti_2(CO)$ (**1S-1**) + CO	67.4	69.7

Table 12. Disproportionation Energies (kcal/mol) of the $Cp_2Ti_2(CO)_n$ (n = 7, 6, 5, 4, 3, 2) Species Based on the Lowest Energy Structures

	B3LYP/DZP	BP86/DZP
$2Cp_2Ti_2(CO)_7$ (**7S-1**) → $Cp_2Ti_2(CO)_8$ (**8S-1**) + $Cp_2Ti_2(CO)_6$(**6S-1**)	−6.9	−12.0
$2Cp_2Ti_2(CO)_6$(**6S-1**) → $Cp_2Ti_2(CO)_7$ (**7S-1**) + $Cp_2Ti_2(CO)_5$(**5S-1**)	4.4	10.8
$2Cp_2Ti_2(CO)_5$(**5S-1**) → $Cp_2Ti_2(CO)_6$ (**6S-1**) + $Cp_2Ti_2(CO)_4$(**4S-1**)	−0.1	1.6
$2Cp_2Ti_2(CO)_4$(**4S-1**) → $Cp_2Ti_2(CO)_5$ (**5S-1**) + $Cp_2Ti_2(CO)_3$(**3S-1**)	−10.2	−9.7
$2Cp_2Ti_2(CO)_3$(**3S-1**) → $Cp_2Ti_2(CO)_2$ (**2S-1**) + $Cp_2Ti_2(CO)_4$(**4S-1**)	27.7	26.0
$2Cp_2Ti_2(CO)_2$(**2S-1**) → $Cp_2Ti_2(CO)$ (**1S-1**) + $Cp_2Ti_2(CO)_3$(**3S-1**)	32.1	29.6

The other triplet $Cp_2Ti_2(CO)_2$ structure **2T-2** lies 19.4 kcal/mol above **2S-1** with all real harmonic vibrational frequencies by BP86, but a very small imaginary vibrational frequency (12i cm^{-1}) with B3LYP. This small imaginary vibrational frequency is from the numerical integration error since it becomes real by using a finer (120, 974) integration grid. Structure **2T-2** is a C_s structure with two semibridging carbonyls. These two semibridging carbonyls are both four-electron donor bridging carbonyl groups, which are characterized by short Ti−O distances of 2.096 Å and very low ν(CO) frequencies of 1459 and 1523 cm^{-1}. The Ti=Ti distance in **2T-2** is 3.015 Å, which can correspond to a formal double bond, thereby giving each titanium atom a 15-electron configuration for the binuclear triplet.

3.2. Dissociation and Disproportionation Reactions.

Table 11 lists the carbonyl dissociation energies for the reactions $Cp_2Ti_2(CO)_n \rightarrow Cp_2Ti_2(CO)_{n-1} + CO$ (n = 8, 7, 6, 5, 4, 3, 2), based on the lowest energy structures. For the thermodynamics of reactions giving the monocarbonyl $Cp_2Ti_2(CO)$ as a product, the optimized structure was taken from a previous study[52] using the same DFT methods.

The bond dissociation energy (BDE) values for the losses of one carbonyl group from $Cp_2Ti_2(CO)_n$ (n = 8, 7, 6, 5, 4) are seen from Table 11 to be relatively low at

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Table 13. Total Energies (E, in Hartree) and Numbers of Imaginary Vibrational Frequencies (Nimg) of the Global Minima of CpTi(CO)$_m$ (m = 4, 3, 2, 1)

		CpTi(CO)$_4$ (C_s)	CpTi(CO)$_3$ (C_s)	CpTi(CO)$_2$ (C_s)	CpTi(CO) (C_s)
B3LYP	E	−1496.50593	−1383.12693	−1269.74641	−1156.35122
	Nimg	1 (9i)[a]	0	0	1 (6i)[a]
BP86	E	−1496.64488	−1383.25874	−1269.87066	−1156.46725
	Nimg	1 (16i)[a]	0	0	1 (15i)[a]

[a] When a finer (120, 974) integration grid was used, this imaginary frequency disappeared.

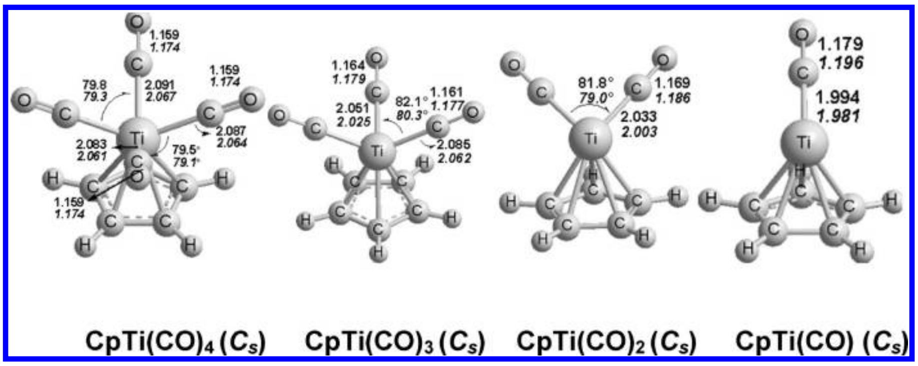

Figure 10. Optimized structures of the mononuclear fragments CpTi(CO)$_n$ (n = 4, 3, 2, 1) with distances in Å.

<24 kcal/mol. However, the energies for the loss of one carbonyl group from $Cp_2Ti_2(CO)_n$ (n = 3, 2) are significantly higher at >40 kcal/mol suggesting the favorabilities of these structures. For comparison, the experimental BDEs[53] are 27 kcal/mol, 41 kcal/mol, and 37 kcal/mol for $Ni(CO)_4$, $Fe(CO)_5$, and $Cr(CO)_6$, respectively.

Table 12 lists the predicted energy changes of the disproportionation reactions $2Cp_2Ti_2(CO)_n \rightarrow Cp_2Ti_2(CO)_{n+1} + Cp_2Ti_2(CO)_{n-1}$ based on the lowest energy structures. These results indicate that the structures $Cp_2Ti_2(CO)_n$ (n = 2 and 3) are viable with respect to such disproportionations by >26 kcal/mol. In addition $Cp_2Ti_2(CO)_6$ is also modestly favored toward such disproportionations by 10.8 kcal/mol. However, for the lowest energy structures of $Cp_2Ti_2(CO)_7$, $Cp_2Ti_2(CO)_5$, and $Cp_2Ti_2(CO)_4$ such disproportionation reactions are exothermic (Table 12). Therefore $Cp_2Ti_2(CO)_7$, $Cp_2Ti_2(CO)_5$, and $Cp_2Ti_2(CO)_4$ are not likely to be stable molecules.

The binuclear derivatives $Cp_2Ti_2(CO)_n$ (n = 8, 7, 6, 5, 4, 3, 2) can dissociate into $CpTi(CO)_p + CpTi(CO)_q$, where $p + q = n$ and each fragment has a cyclopentadienyl ring bonded to the titanium atom. The structures of the mononuclear $CpTi(CO)_m$ (m = 4, 3, 2, 1) were optimized at the same levels of theory as the binuclear derivatives to obtain the energetic standards for the dissociation of the $Cp_2Ti_2(CO)_n$ derivatives into mononuclear $CpTi(CO)_m$ fragments. The structures and total energies of the global minima for the $CpTi(CO)_m$ fragments (m = 4, 3, 2, 1) are shown in Table 13 and Figure 10. The dissociation reactions for the lowest energy $Cp_2Ti_2(CO)_n$ structures are all predicted to be endothermic (Table 14). However, the predicted dissociation energy of the saturated dimer $Cp_2Ti_2(CO)_8$ into two mononuclear $CpTi(CO)_4$ fragments is predicted to be only slightly endothermic at 9.3 kcal/mol. This indicates that $Cp_2Ti_2(CO)_8$ is marginal with respect to dissociation into two $CpTi(CO)_4$ fragments and thus unlikely to be prepared as an isolable molecule. The situation is somewhat similar to the dissociation of $V_2(CO)_{12}$ into $V(CO)_6$ fragments.[54] In that case $V(CO)_6$ rather than $V_2(CO)_{12}$ is the stable isolable molecule.[55] This suggest that the 17-electron complex $CpTi(CO)_4$ might be an isolable molecule, possibly obtained by the mild one-electron oxidation of the experimentally known[7] anion $CpTi(CO)_4^-$.

Table 14. Dissociation Energies of the Cp$_2$Ti$_2$(CO)$_n$ (n = 8, 7, 6, 5, 4, 3, 2) into Mononuclear Fragments CpTi(CO)$_m$ (m = 4, 3, 2, 1) in kcal/mol

	B3LYP/DZP	BP86/DZP
$Cp_2Ti_2(CO)_8 \rightarrow 2\ CpTi(CO)_4$	4.5	9.3
$Cp_2Ti_2(CO)_7 \rightarrow CpTi(CO)_3 + CpTi(CO)_4$	15.7	23.0
$Cp_2Ti_2(CO)_6 \rightarrow 2\ CpTi(CO)_3$	33.8	48.6
$Cp_2Ti_2(CO)_6 \rightarrow CpTi(CO)_2 + CpTi(CO)_4$	34.7	49.8
$Cp_2Ti_2(CO)_5 \rightarrow CpTi(CO)_3 + CpTi(CO)_2$	48.4	64.6
$Cp_2Ti_2(CO)_5 \rightarrow CpTi(CO)_4 + CpTi(CO)$	58.6	75.5
$Cp_2Ti_2(CO)_4 \rightarrow 2\ CpTi(CO)_2$	63.1	79.0
$Cp_2Ti_2(CO)_4 \rightarrow CpTi(CO)_3 + CpTi(CO)$	72.3	88.7
$Cp_2Ti_2(CO)_3 \rightarrow CpTi(CO)_2 + CpTi(CO)$	97.3	112.8
$Cp_2Ti_2(CO)_2 \rightarrow 2\ CpTi(CO)$	103.7	120.5

The dissociation energies of the unsaturated $Cp_2Ti_2(CO)_n$ (n = 7, 6, 5, 4, 3, 2) derivatives into the mononuclear fragments increase monotonically with decreasing number of carbonyl groups as expected by the increased Ti−Ti bond order and increased number of four-electron donor η^2-μ-CO groups. In addition, the more unsymmetrical the dissociation of $Cp_2Ti_2(CO)_n$ into the mononuclear fragments, the higher is the dissociation energy. Clearly it is not energetically feasible for the mononuclear fragments $CpTi(CO)_m$ to play a role in the mechanisms of the reactions of the unsaturated $Cp_2Ti_2(CO)_n$ (n = 7, 6, 5, 4, 3, 2) derivatives.

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4. Discussion

4.1. $Cp_2Ti_2(CO)_n$ Structures. Only one structure was found for $Cp_2Ti_2(CO)_8$, namely, **8S-1** (Figure 1) in which two $CpTi(CO)_4$ "halves" are held together by only a relatively long (~3.9 Å) Ti−Ti single bond. Attempts to optimize other $Cp_2Ti_2(CO)_8$ structures led to separation of the two $CpTi(CO)_4$ fragments. Furthermore, the predicted dissociation energy of the $Cp_2Ti_2(CO)_8$ structure **8S-1** into mononuclear $CpTi(CO)_4$ fragments is relatively low at 9.3 kcal/mol, suggesting that the mononuclear complex $CpTi(CO)_4$ with a 17-electron configuration is viable. This is similar to the experimentally observed[19] stability of the 17-electron mononuclear $V(CO)_6$ relative to the binuclear $V_2(CO)_{12}$.

The 18-electron rule suggests a structure for $Cp_2Ti_2(CO)_7$ with a formal Ti═Ti double bond. Structure **7S-2** (Figure 2) is of this type with a predicted Ti═Ti distance of ~3.4 Å. Although this Ti═Ti double bond distance may seem long, it is nevertheless ~0.5 Å shorter than the Ti−Ti single bond distance in the lowest energy $Cp_2Ti_2(CO)_8$ structure **8S-1**. The other two $Cp_2Ti_2(CO)_7$ structures (**7S-1** and **7S-3** in Figure 2) have a four-electron donor bridging carbonyl group with Ti−Ti distances of ~3.7 Å, suggesting a formal single bond giving both titanium atoms the favored 18-electron configuration. A triplet $Cp_2Ti_2(CO)_7$ structure **7T-1** (Figure 2) is also found with only two-electron donor CO groups and a Ti−Ti distance of 3.5 to 4.0 Å. This suggests a formal single bond, providing both titanium atoms with the 17-electron configurations for a binuclear triplet. The reluctance of $Cp_2Ti_2(CO)_7$ to form structures with a formal Ti═Ti double bond is reminiscent of the experimentally observed[56] instability of $Cp_2Cr_2(CO)_5$, which analogously requires a formal Cr═Cr double bond to give both chromium atoms the favored 18-electron configuration. Thus $Cp_2Cr_2(CO)_5$, when generated in the laboratory from $Cp_2Cr_2(CO)_6$ and trimethylsilyldiazomethane, is seen to disproportionate into $Cp_2Cr_2(CO)_6$ with a Cr−Cr single bond and $Cp_2Cr_2(CO)_4$ with a Cr≡Cr triple bond.[56]

The two lowest energy structures for $Cp_2Ti_2(CO)_6$, namely, **6S-1** and **6S-2** (Figure 3), have only two-electron donor terminal and weakly semibridging CO groups and a short Ti≡Ti distance of ~2.8 Å suggesting the Ti≡Ti bond required to give both titanium atoms the favored 18-electron configuration. Thus, $Cp_2Ti_2(CO)_6$ is the next member of the series of M≡M formally triply bonded derivatives $(\eta^5\text{-}R_5C_5)_2V_2(CO)_5$,[57,58] $(\eta^5\text{-}R_5C_5)_2Cr_2(CO)_4$ (R = H,[59] Me[60,61]), and $(\eta^5\text{-}R_5C_5)_2M'_2(CO)_3$ (M′ = Mn,[62] Re[63]), all of which are sufficiently stable to be isolated and characterized structurally by X-ray diffraction.

The low energy structures of the more highly unsaturated $Cp_2Ti_2(CO)_n$ derivatives (n = 5, 4, 3, 2) all have at least one four-electron donor bridging η^2-μ-CO carbonyl group and formal titanium−titanium bond orders no higher than three as deduced by the Ti−Ti distances. This is consistent with the high oxophilicity of titanium relative to the later first-row transition metals. Such η^2-μ-CO groups are characterized by relatively short Ti−O bonding distances in the range 2.0 to 2.3 Å, very low ν(CO) frequencies in the range 1420 to 1710 cm^{-1}, and relatively long C−O distances indicating a relatively low formal bond order for a metal carbonyl group. In general both the Ti−O distances and the ν(CO) frequencies decrease as the total number of CO groups in the $Cp_2Ti_2(CO)_n$ derivatives decrease. Thus the lowest energy structure of $Cp_2Ti_2(CO)_5$, namely, **5S-1** (Figure 4), has one four-electron donor bridging carbonyl group and a Ti≡Ti distance of ~2.8 Å consistent with a formal triple bond. A second low energy $Cp_2Ti_2(CO)_5$ structure, namely, **5S-2** (Figure 4), has two four-electron donor bridging carbonyl groups and a longer Ti═Ti distance of ~3.2 Å consistent with a formal double bond. In both of these $Cp_2Ti_2(CO)_5$ structures both titanium atoms have the favored 18-electron configurations.

The still more highly unsaturated $Cp_2Ti_2(CO)_n$ derivatives (n = 4, 3, 2) have structures in which the titanium atoms have only 16-electron configurations rather than the normally favorable 18-electron configurations of most stable transition metal carbonyl derivatives. They thus resemble many known carbonyl-free organotitanium derivatives such as Cp_2TiX_2 (X = halide, alkyl, aryl, etc) derivatives[13−15] as well as other 16-electron titanium derivatives, such as $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)Ti$,[22] and $(\eta^6\text{-}CH_3C_6H_5)_2Ti$.[23] Thus the lowest energy structure for $Cp_2Ti_2(CO)_4$ (**4S-1** in Figure 6) has a Ti−Ti distance of ~3.0 Å, interpreted as a formal single bond shortened by the constraint of the two four-electron donor bridging η^2-μ-CO groups.

In the lowest energy structures for $Cp_2Ti_2(CO)_n$ (n = 3, 2) all of the carbonyl groups are four-electron donor η^2-μ-CO groups, consistent with the high oxophilicity of titanium. In the lowest energy $Cp_2Ti_2(CO)_3$ structure **3S-1** (Figure 8) the combination of the three η^2-μ-CO groups and a ~3.0 Å Ti−Ti single bond gives both titanium atoms 16-electron configurations. Similarly in the two lowest energy $Cp_2Ti_2(CO)_2$ structures **2S-1** and **2S-2** (Figure 9), the combinations of the two η^2-μ-CO groups and a ~2.7 Å formal Ti≡Ti triple bond again give both titanium atoms 16-electron configurations.

4.2. Titanium−Titanium Bond Distances. The standard 1.60 Å covalent radius of titanium is significantly larger than the covalent radii of the later first row transition metals (vanadium through copper). Therefore a titanium−titanium bond of a given order would be expected to be longer than metal−metal bonds of the later first row transition metals of similar order. In this context the lengths of the presumed Ti−Ti single bonds, Ti═Ti double bonds, and Ti≡Ti triple bonds are listed in Tables 15, 16, and 17, respectively, using the means of the lengths predicted by the B3LYP and BP86 methods for a given structure. Only structures with one Cp ring bonded

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Table 15. Formal Ti−Ti Single Bonds in $Cp_2Ti_2(CO)_n$ Derivatives [a]

compound	bridging groups	Ti−Ti distance, Å	Ti electronic configuration
$Cp_2Ti_2(CO)_8$ (**8S-1**)	none	3.94	18
$Cp_2Ti_2(CO)_7$ (**7S-1**)	η^2-μ-CO	3.66	18
$Cp_2Ti_2(CO)_7$ (**7S-3**)	η^2-μ-CO	3.71	18
$Cp_2Ti_2(CO)_7$ (**7T-1**)	2 weakly semibridging CO	3.75	17
$Cp_2Ti_2(CO)_4$ (**4S-1**)	2 η^2-μ-CO	3.05	16
$Cp_2Ti_2(CO)_4$ (**4S-2**)[b]	2 η^2-μ-CO	3.22	16
$Cp_2Ti_2(CO)_3$ (**3S-1**)	3 η^2-μ-CO	3.05	16
$Cp_2Ti_2(CO)_3$ (**3T-1**)	2 η^2-μ-CO	3.14	15

[a] Mean of values from B3LYP and BP86 optimizations. [b] The data are for the BP86 structure **4S-2**.

Table 16. Formal Ti═Ti Double Bonds in $Cp_2Ti_2(CO)_n$ Derivatives[a]

compound	bridging groups	Ti═Ti distance, Å	Ti electronic configuration
$Cp_2Ti_2(CO)_7$ (**7S-2**)	none	3.47	18
$Cp_2Ti_2(CO)_6$ (**6T-1**)	2 semibridging CO	2.97	17
$Cp_2Ti_2(CO)_6$ (**6T-2**)	2 semibridging CO	3.05	17
$Cp_2Ti_2(CO)_5$ (**5S-2**)	2 η^2-μ-CO	3.18	18
$Cp_2Ti_2(CO)_5$ (**5S-3**)	2 η^2-μ-CO	3.09	18
$Cp_2Ti_2(CO)_4$ (**4T-1**)	2 η^2-μ-CO	3.11	17
$Cp_2Ti_2(CO)_4$ (**4T-2**)	2 η^2-μ-CO	3.11	17
$Cp_2Ti_2(CO)_3$ (**3S-2**)	2 η^2-μ-CO	2.87	16
$Cp_2Ti_2(CO)_2$ (**2T-1**)	2 η^2-μ-CO	3.15	15
$Cp_2Ti_2(CO)_2$ (**2T-2**)	2 η^2-μ-CO	3.08	15

[a] Mean of values from B3LYP and BP86 optimizations.

to each titanium atom are considered in these tables. Thus, the typically higher energy structures with two Cp rings on one titanium atom and only carbonyl groups on the other titanium atom are excluded from consideration.

The longest Ti−Ti formal single bond (Table 15) is seen to be the ~3.94 Å unbridged bond in $Cp_2Ti_2(CO)_8$ (**8S-1**). Here the steric hindrance between the four carbonyl groups on each titanium atom is expected to lengthen the Ti−Ti bond. Also the energy for dissociation of $Cp_2Ti_2(CO)_8$ into mononuclear $CpTi(CO)_4$ fragments is rather small at ~7 kcal/mol. This is consistent with the weakness of such a long Ti−Ti bond (Table 15). The other example of an unbridged Ti−Ti bond is in the lowest energy triplet structure of $Cp_2Ti_2(CO)_7$, namely, **7T-1**. This is the next longest Ti−Ti bond in Table 15 at 3.75 Å.

Almost all of the other Ti−Ti formal single bonds found in this work (Table 15) are bridged by one to three four-electron donor bridging η^2-μ-CO groups. Such Ti−Ti single bonds are shorter than the unbridged Ti−Ti bonds in **8S-1** and **7T-1**. However, they have a wide range of lengths from ~3.0 Å to ~3.7 Å and generally become shorter in the lower end of this range (~3.0 to ~3.2 Å) when there are two or three η^2-μ-CO groups and the titanium atoms have 16-electron configurations. Apparently the geometrical constraints of two or three four-electron donor bridging η^2-μ-CO groups shorten drastically the lengths of formal Ti−Ti single bonds.

Table 17. Formal Ti≡Ti Triple Bonds in $Cp_2Ti_2(CO)_n$ Derivatives [a]

compound	bridging groups	Ti−Ti distance, Å	Ti electronic configuration
$Cp_2Ti_2(CO)_6$ (**6S-1**)	2 semibridging CO	2.80	18
$Cp_2Ti_2(CO)_6$ (**6S-2**)	2 semibridging CO	2.82	18
$Cp_2Ti_2(CO)_5$ (**5S-1**)	η^2-μ-CO	2.81	18
$Cp_2Ti_2(CO)_5$ (**5T-3**)	2 semibridging CO	2.80	17
$Cp_2Ti_2(CO)_3$ (**3T-2**)	2 η^2-μ-CO	2.82	17
$Cp_2Ti_2(CO)_2$ (**2S-1**)	2 η^2-μ-CO	2.74	16
$Cp_2Ti_2(CO)_2$ (**2S-2**)	2 η^2-μ-CO	2.74	16

[a] Mean of values from B3LYP and BP86 optimizations.

Table 16 lists the formal Ti═Ti double bonds found in the $Cp_2Ti_2(CO)_n$ derivatives studied in this work. The assignment of the formal bond order is based on electron counting to give the singlet or triplet spin multiplicity of the structure in question as well as a reasonable electron configuration for the titanium atoms. Most of the formal double bonds listed in Table 16 are bridged by two four-electron donor bridging η^2-μ-CO groups and have lengths in the range ~3.0 to ~3.2 Å. These bond lengths are also at the lower end of the range for formal Ti−Ti single bonds (Table 15). It thus appears that when there are two bridging η^2-μ-CO groups there is no longer a reasonable correlation between bond length and formal bond order, at least for formal single and double bonds.

A number of $Cp_2Ti_2(CO)_n$ derivatives are found which appear to contain formal Ti≡Ti triple bonds (Table 17). The lengths of such formal triple bonds generally fall in the range ~2.8 to ~2.7 Å, which are distinctly shorter than the bond lengths for formal single and double titanium−titanium bonds (Tables 15 and 16). Here there appears to be a correlation between bond length and formal bond order.

Formal quadruple Ti≣Ti bonds were encountered in only a few relatively high energy highly unsaturated $Cp_2Ti_2(CO)_n$ structures, namely, the triplet $Cp_2Ti_2(CO)_4$ structure **4T-3** with a mean Ti≣Ti distance of 2.48 Å (Figure 7) and the singlet $Cp_2Ti_2(CO)_2$ structure **2S-3** with a mean Ti≣Ti distance of 2.59 Å (Figure 9). In addition, the short Ti≣Ti distance of 2.61 Å in the triplet $Cp_2Ti_2(CO)_5$ structure **5T-1** can be interpreted as a $\sigma + 2\pi + {}^2/_2$ δ quadruple bond with the two unpaired electrons of the triplet spin state in the two δ "half bond" components of the formal titanium−titanium bond of order $3^2/_2$ (= 4). The lengths of all of these formal quadruple Ti≣Ti bonds are thus significantly (~0.2 Å) shorter than the Ti≡Ti triple bond lengths in Table 17.

4.3. Synthetic Prospects. No $Cp_2Ti_2(CO)_n$ derivatives are known experimentally. The obvious synthetic entry into such structures is the oxidation[7] of the known anion $CpTi(CO)_4^-$ to the neutral $CpTi(CO)_4$. Our studies suggest that this monomer would be in equilibrium with the dimer $Cp_2Ti_2(CO)_8$ (**8S-1** in Figure 1). The oxidation of the anion $CpTi(CO)_4^-$ with the titanium in the formal zero oxidation state to the neutral $CpTi(CO)_4$ with the titanium in the formal +1 oxidation state would need to be done under very mild conditions with a selective one-electron oxidizing agent to avoid overoxidation of the titanium to higher oxidation states.

Another interesting synthetic target is $Cp_2Ti_2(CO)_6$ (**6S-1** in Figure 3), which is the next member of the series of M≡M formally triply bonded derivatives (η^5-$R_5C_5)_2$-$V_2(CO)_5$,[57,58] (η^5-$R_5C_5)_2Cr_2(CO)_4$ (R = H,[59] Me[60,61]), and $(\eta^5\text{-}R_5C_5)_2M'_2(CO)_3$ (M′ = Mn,[62] Re,[63]). Decarbonylation of a $CpTi(CO)_4/Cp_2Ti_2(CO)_8$ equilibrium mixture might lead to $Cp_2Ti_2(CO)_6$ (**6S-1**), analogous to the reported[58] photochemical decarbonylation of $CpV(CO)_4$ to $Cp_2V_2(CO)_5$.

Our analysis of the thermodynamics of $Cp_2Ti_2(CO)_n$ systems (Tables 11, 12, and 14) suggests that the most promising $Cp_2Ti_2(CO)_n$ synthetic target is probably not $Cp_2Ti_2(CO)_8$ or $Cp_2Ti_2(CO)_6$ but instead $Cp_2Ti_2(CO)_3$ (**3S-1** in Figure 8). The predicted lowest energy structure **3S-1** (Figure 8) of $Cp_2Ti_2(CO)_3$, in which all three carbonyl groups are four-electron donor bridging $\eta^2\text{-}\mu\text{-CO}$ groups with a Ti−Ti single bond, has no analogues in the binuclear cyclopentadienylmetal carbonyl chemistry of the later first row transition metals. The favorable thermodynamics of the $Cp_2Ti_2(CO)_3$ structure **3S-1** include the following:

(1) The much higher CO dissociation energy of ~37 kcal/mol compared with the $Cp_2Ti_2(CO)_n$ (n = 8, 7, 6, 5, 4) structures with larger numbers of carbonyl groups (Table 11);

(2) The predicted stability of $Cp_2Ti_2(CO)_3$ with respect to disproportionation into $Cp_2Ti_2(CO)_4 + Cp_2Ti_2(CO)_2$ by ~27 kcal/mol (Table 12).

It thus appears that $Cp_2Ti_2(CO)_3$ might be a thermodynamic “sink” in the $Cp_2Ti_2(CO)_n$ system, possibly because of the high oxophilicity of the early transition metal titanium, making the three four-electron donor $\eta^2\text{-}\mu\text{-CO}$ groups in the $Cp_2Ti_2(CO)_3$ structure **3S-1** with Ti−O bonding energetically favorable.

The final observation from the thermodynamics in Table 12 is that $Cp_2Ti_2(CO)_7$, $Cp_2Ti_2(CO)_5$, and $Cp_2Ti_2(CO)_4$ are not promising synthetic targets because the predicted energies for the disproportionations of these three $Cp_2Ti_2(CO)_n$ derivatives into $Cp_2Ti_2(CO)_{n+1} + Cp_2Ti_2(CO)_{n-1}$ range from essentially thermoneutral for $n = 5$ to clearly exothermic for $n = 7$ and 4.

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Supporting Information Available: Tables S1−S10: The theoretical harmonic vibrational frequencies for the 33 structures of $Cp_2Ti_2(CO)_n$ (n = 8 to 2) using the BP86 method; Tables S11−S43: Theoretical Cartesian coordinates for the 33 structures of $Cp_2Ti_2(CO)_n$ (n = 8 to 2) using the B3LYP method; complete Gaussian 03 reference (Reference 50). This material is available free of charge via the Internet at http://pubs.acs.org.