# Tetranuclear Iron Carbonyl Complexes with a Central Tin Atom: Relationship to Iron Carbonyl Carbides



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5/18

# Tetranuclear Iron Carbonyl Complexes with a Central Tin Atom: Relationship to Iron Carbonyl Carbides

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**Abstract**

The two tetranuclear iron carbonyl systems $EFe_4(CO)_n$ (E = Sn, C) containing central group 14 interstitial atoms differ in that spiropentane-like $SnFe_4(CO)_{16}$ has been synthesized in the tin system whereas the butterfly $CFe_4(CO)_{13}$, with three fewer carbonyl groups is the carbonyl-richest tetranuclear iron carbonyl carbide that has been synthesized. In order to clarify this point, the complete $SnFe_4(CO)_n$ ($n$ = 16, 15, 14, 13, 12) series has been studied by density functional theory for comparison with earlier similar studies on their $CFe_4(CO)_n$ analogues. The experimentally observed spiropentane-like $Sn[Fe_2(CO)_8]_2$ structure is found to be the lowest energy structure for the $SnFe_4(CO)_{16}$ system as it is for the experimentally unknown $CFe_4(CO)_{16}$ system. Loss of a CO group from $Sn[Fe_2(CO)_8]_2$ joins the two $Fe_2(CO)_8$ units by a third Fe–Fe bond to give an $SnFe_4(CO)_{15}$ structure with a bonded four-atom Fe–Fe–Fe–Fe chain. Further CO loss from $SnFe_4(CO)_{15}$ adds a fourth Fe–Fe bond in the lowest energy $SnFe_4(CO)_{14}$ structure. The lowest energy $SnFe_4(CO)_{13}$ structure is analogous to that of the experimentally known iron carbonyl carbide $CFe_4(CO)_{13}$ with a central $Fe_4$ butterfly having five Fe–Fe bonds. The energetics of CO dissociation from the $EFe_4(CO)_n$ (E = C, Sn; $n$ = 16, 15, 14, 13) species account for the experimentally observed differences between the systems with central tin and central carbon atoms. Thus for the tin systems the CO dissociation energy from $SnFe_4(CO)_{16}$ is relatively high at ~50 kcal/mol consistent with its experimental observation as a stable species. However, for the tetranuclear iron carbonyl carbides $CFe_4(CO)_n$ the CO dissociation energies of the species with more than 13 CO groups are all very small or even negative suggesting $CFe_4(CO)_{13}$ to be the carbonyl-richest viable iron tetracarbonyl carbide consistent with experiment.

# 1. Introduction

Very stable metal carbonyl complexes containing direct metal-tin bonds have long been known. The first such compounds were obtained from metal carbonyl anions and organotin halides.[1] Although most of the early chemistry was done with the tetracarbonylcobalt anion, Hieber and Breu in 1957 also reported the reaction of $K_2Fe(CO)_4$ with $nBu_2SnCl_2$ to give a species $nBu_2SnFe(CO)_4$, later shown to be a dimer with a central four-membered $Fe_2Sn_2$ ring (Figure 1).[2] Related $[R_2SnFe(CO)_4]_2$ dimers were obtained from thermal reactions of $Fe(CO)_5$ with various organotin compounds.[3,4] Under more forcing conditions reactions of organotin compounds with $Fe(CO)_5$ resulted in removal of all alkyl and/or aryl groups from the tin atom leading to a species of stoichiometry $Sn[Fe_2(CO)_8]_2$. This species was shown to have a spiropentane structure (Figure 1) with four iron-tin bonds to two $Fe_2(CO)_8$ units, each containing an iron-iron bond.[5] This structure can formally be regarded as a tetrahedral Sn(IV) derivative of the known $Fe_2(CO)_8^{2-}$ dianion in which the iron atom has the favored 18-electron configuration. Thus stripping all Sn–C bonds from the central tin atom in reactions of organotin compounds with iron carbonyls leads to the pairwise coupling of the external $Fe(CO)_4$ units by forming iron-iron bonds. Similar spiropentane-like $E[Fe_2(CO)_8]_2$ (E = Si, Pb) species have also been synthesized with silicon,[6] germanium, and lead[7] as the central atoms.

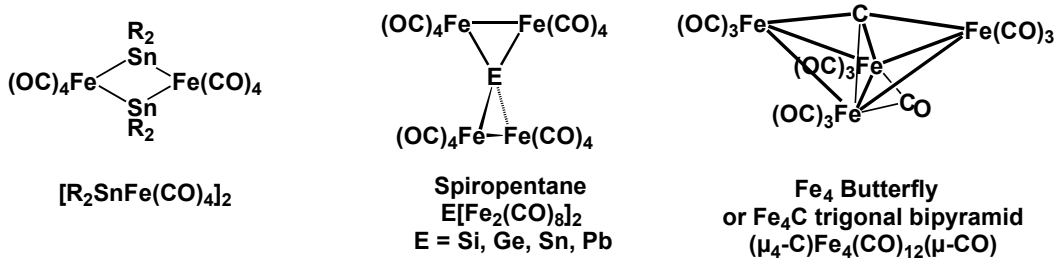


**Figure 1.** The first organotin complexes of iron carbonyl $(R_2SnFe(CO)_4]_2$; comparison of the experimentally spiropentane-like $E\{Fe_2(CO)_8]_2$ structures with the carbonyl-poorer stable tetranuclear iron carbonyl carbide structure $(\mu_4\text{-C})Fe_4(CO)_{12}(\mu\text{-CO})$.

This tetranuclear iron carbonyl tin chemistry stands in direct contrast with tetranuclear iron carbonyl carbide chemistry. Thus the stable tetranuclear iron carbonyl carbide has the stoichiometry $CFe_4(CO)_{13}$ and structurally consists of a tin atom imbedded into an $Fe_4$ butterfly with five Fe–Fe bonds.[8] An analogous tin compound of

stoichiometry $SnFe_4(CO)_{13}$ or $SnFe_4(CO)_n$ ($n$ = 15, 14) with intermediate numbers of carbonyl groups remains unknown. Furthermore, a density functional theory study[9] shows spiropentane-like $C[Fe_2(CO)_8]_2$ structures analogous to the experimental $Sn[Fe_2(CO)_8]_2$ structure to be the lowest energy structures for the stoichiometry $CFe_4(CO)_{16}$. However, the calculated CO dissociation energies for the $CFe_4(CO)_n$ ($n$ = 16, 15, 14) carbonyl richer structures than the known $CFe_4(CO)_{13}$ suggest such structures to be disfavored relative to CO dissociation.

In order to understand the experimentally observed differences between the $CFe_4(CO)_n$ and $SnFe_4(CO)_n$ systems, we have now p;erformed a theoretical study of the $SnFe_4(CO)_n$ ($n$ = 16, 15, 14, 13, 12) systems. This paper reports our results thereby enabling a comparison between the tetranuclear iron carbonyl derivatives with central carbon and those with central tin atoms. In particular the different patterns of the CO dissociation energies for the two sequences $EFe_4(CO)_n$ (E = C, Sn) are able to account for $CFe_4(CO)_{13}$ and $Sn[Fe_2(CO)_8]_2$ being the stable species, respectively.

## 2. Theoretical Methods

Two density functional theory (DFT) methods were used in this paper. The BP86 method combines Becke's 1988 exchange functional (B) with Perdew's 1986 gradient-corrected correlation functional (P86) [10, 11] and usually provides better vibrational frequencies.[12,13] Thus, we discuss the vibrational frequencies predicted by the BP86/ DZP method in the work. The second functional is M06-L, a meta-GGA DFT method, developed by Truhlar and Zhao.[14] They suggest M06-L for transition-metal compounds, since it predicts relative energies closer to experimental values. Thus, we adopt the energy orderings predicted by the M06-L method, but list the results from the BP86 method in the Supporting Information. Standard double-ζ plus polarization (DZP) and triple-ζ plus polarization (TZP) basis sets were adopted in the present study. The TZP and DZP basis sets are designated as (10s6p2d1f/5s3p2d1f) and (9s5p1d/4s2p1d) for carbon and oxygen, (16s13p6d2f1g/9s6p3d2f1g) and (15s12p5d1f/8s6p2d1f) for iron, and (20s16p9d2f1g/9s7p4d2f1g) and (19s15p8d1f/8s6p3d1f) for tin, respectively.

The geometries of all structures were fully optimized using the two DFT methods, i.e., M06-L/TZP and BP86/DZP. Harmonic vibrational frequencies and the corresponding infrared intensities were determined by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. All computations were performed with the Gaussian 09 program package.[15] The ultra fine grid (99, 590) was the default for evaluating two-electron integrals numerically.[16] The tight ($10^{-8}$ hartree) designation was the default for the self-consistent-field (SCF) convergence except for **16S-1** and **16S-2**.

Natural bond orbital (NBO) analyses[17,18,19] were carried out using the two DFT methods to provide information on the chemical bonding in these system. All of the predicted triplet structures in the present study are found to have negligible spin contamination, with S(S+1) values close to the ideal 2.0.

A given $SnFe_4(CO)_n$ structure is designated as **nA-c** where **n** is the number of CO groups, **c** orders the structures according to their relative energies, and **A** indicates whether the structure is a singlet (**S**) or triplet (**T**). Thus the lowest energy singlet structure of $SnFe_4(CO)_{16}$ is designated **16S-1**.

## 3. Results and Discussion

**3.1. $SnFe_4(CO)_n$ ($n$ = 16 to 12) structures.** The $SnFe_4$ skeletons in the $SnFe_4(CO)_n$ ($n$ = 16 to 12) compounds studied in the present paper are of five different types, namely spiropentane, distorted spiropentane, twisted spiropentane, distorted triangular pyramidal, and butterfly (Figure 2). Each skeletal type has four Fe-Sn bonds except the twisted spiropentane type, which has only three Fe-Sn bonds. In the spiropentane and twisted spiropentane skeleton the four iron atoms are partitioned into two bonded $Fe_2$ pairs. The twisted spiropentane skeleton can be dissected into a Sn(II) ligand with an $SnFe_2$ three-membered ring using a lone pair on the tin atom to form a dative bond with an $Fe_2$ unit involving the other two iron atoms. The distorted spiropentane skeleton has these two bonded $Fe_2$ pairs linked by an additional Fe–Fe bond to form a bonded $Fe_4$ chain. The distorted triangular pyramidal skeleton and butterfly skeleton have four and five Fe-Fe bonds, respectively. All of the $SnFe_4(CO)_n$ ($n$ = 12 to 16) structures are predicted to be genuine minima with all real vibrational frequencies except for **16S-2**, which is predicted to have two small imaginary frequencies of 41$i$ and 15$i$ $cm^{-1}$.

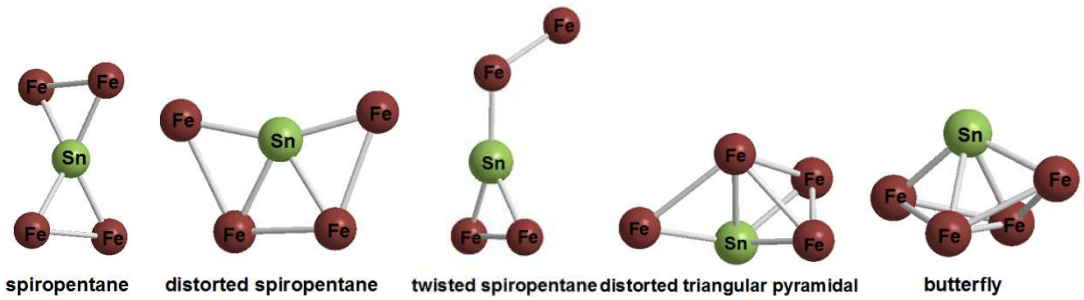


**Figure 2.** The fundamental $SnFe_4$ skeletons in the $SnFe_4(CO)_n$ ($n$ = 16 to 12) compounds.

*3.1.1 $SnFe_4(CO)_{16}$ structures.* Two low-energy singlet $SnFe_4(CO)_{16}$ structures, namely the unbridged $D_{2d}$ structure **16S-1** and the doubly CO-bridged $C_{2v}$ structure **16S-2**, were found. (Figure 3). Structure **16S-1** corresponds to the experimental structure as determined by X-ray crystallography.[5] The symmetry equivalent two Fe–Fe and four Sn-Fe distances in **16S-1** of 2.872 and 2.520 Å, respectively, are very close to the experimental Fe-Fe and Sn-Fe bond distances of 2.87 and 2.54 Å in $SnFe_4(CO)_{16}$. These Fe-Fe and Sn-Fe bond distances in **16S-1** coupled with their WBIs of 0.19 and 0.37 suggest formal single bonds, thereby giving each iron atom the favored 18-electron configuration.

The doubly CO-bridged $C_{2v}$ spiropentane $SnFe_4(CO)_{16}$ structure **16S-2**, lying 7.3 kcal/mol in energy above **16S-1**, has two Fe–Fe bonds and four Sn-Fe bonds, In **16S-2** the unbridged Fe1–Fe2 distance of 2.876 Å is essentially identical to that in **16S-1**. The doubly bridged Fe3–Fe4 distance at 2.601 Å is significantly shorter than the unbridged Fe1-Fe2 distance by 0.275 Å, which is the typical effect of two bridging CO groups across a metal-metal bond. In **16S-2** the WBI of 0.18 for the Fe1-Fe2 bond and that of 0.14 for the Fe3-Fe4 both suggest formal single bonds, thereby giving each iron atom the favored 18-electron configuration. The bridging ν(CO) frequencies in **16S-2** of 1859 and 1876 $cm^{-1}$ are significantly lower than the lowest terminal ν(CO) frequency by ~200 $cm^{-1}$ in accord with expectation.

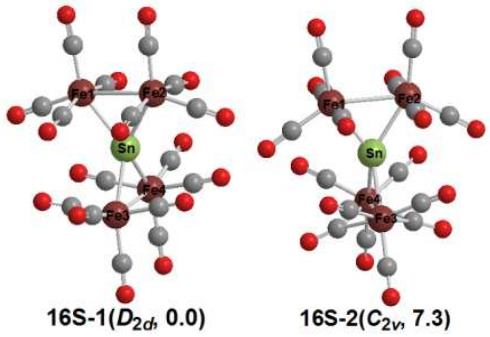


**Figure 3.** Optimized $SnFe_4(CO)_{16}$ structures. Relative energies (in kcal/mol) by M06-L are shown under each structure.

*3.1.2. $SnFe_4(CO)_{15}$ structures.* Two singlet structures **15S-1** and **15S-2** and one triplet structure **15T-1** for $SnFe_4(CO)_{15}$ were found within 18 kcal/mol of the global minimum (Figure 4). The lowest energy structure **15S-1** is predicted to have a distorted spiropentane $SnFe_4$ skeleton (Figure 4). Thus, in contrast to the $SnFe_4(CO)_{16}$ structures **16S-1** and **16S-2**, the $SnFe_4$ skeleton in **15S-1** is distorted to bring Fe2 and Fe3 close enough to form a third iron-iron bond of length 2.747 Å which is bridged by one of the

CO groups. Thus there are three iron-iron bonds, four iron-tin bonds and one bridging CO group in **15S-1**. The four iron atoms and one tin atom in **15S-1** are nearly planar with equivalent Fe1-Fe2 and Fe3-Fe4 distances of 2.917 Å. For the iron-tin bonds the Sn-Fe2/Sn-Fe3 and Sn-Fe1/Sn-Fe4 distances are 2.543 Å and 2.442 Å, respectively. The Fe1-Fe2/Fe3-Fe4, Fe2-Fe3, Sn-Fe2/Sn-Fe3 and Sn-Fe1/Sn-Fe4 bond distances in **15S-1** coupled with their WBIs of 0.14, 0.19, 0.31 and 0.44, respectively, suggest formal single bonds in all cases, thereby giving each iron atom the favored 18-electron configuration. The ν(CO) frequency of 1834 $cm^{-1}$ for the bridging CO group in **15S-1** lies 244 $cm^{-1}$ below the lowest terminal ν(CO) frequency,

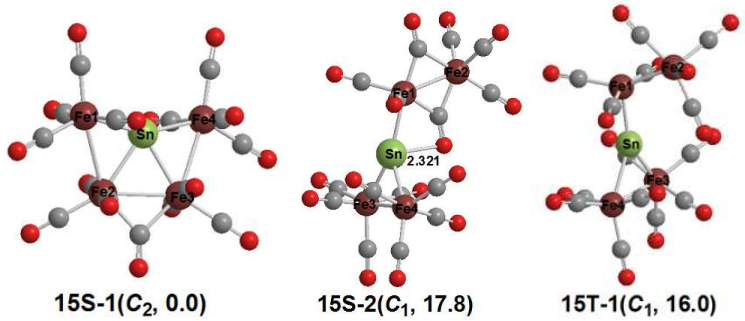


**Figure 4.** The optimized $SnFe_4(CO)_{15}$ structures.

The $SnFe_4(CO)_{15}$ structure **15S-2**, lying 17.8 kcal/mol above **15S-1**, is a $C_1$ singlet twisted spiropentane structure with two iron-iron bonds, three iron-tin bonds, and two bridging CO groups (Figure 4). Structure **15S-2** is a very unusual structure that can be dissected into a Sn(II) ligand of the type $:SnFe_2(CO)_8$ with a lone pair on the tin atom coordinating to an iron atom in an $Fe_2(CO)_7$ unit. The Sn→Fe dative bond in **15S-2** is of length 2.431 Å with a WBI value of 0.39. One of the bridging CO groups in the $Fe_2(CO)_7$ unit "bites back" to the Sn(II) atom by forming a dative O→Sn bond as noted above with a bonding distance of 2.321 Å. This CO group has an unusually low ν(CO) frequency of 1540 $cm^{-1}$ whereas the other bridging CO group in **15S-2** has a more typical bridging ν(CO) frequency of 1849 $cm^{-1}$. Thus the $:SnFe_2(CO)_8$ unit with exclusively terminal CO groups can be considered to be amphoteric by functioning as a Lewis base towards an $Fe_2(CO)_7$ unit but as a Lewis acid towards one of the bridging CO oxygen atoms of the $Fe_2(CO)_7$ unit. The Fe1=Fe2 distance of 2.431 Å in the $Fe_2(CO)_7$ unit combined with its WBI of 0.37 suggests the formal double bond required to give each iron atom in this $Fe_2(CO)_7$ unit the favored 18-electron configuration after considering the electron pair from the $:SnFe_2(CO)_8$ "ligand." The Fe3–Fe4 distance of 2.847 Å within the $:SnFe_2(CO)_8$ ligand is ~0.4 Å longer than the Fe1=Fe2 distance in the $Fe_2(CO)_7$ unit

and corresponds to a WBI of 0.19 which is approximately half that of the Fe1=Fe2 WBI. This indicates the formal Fe3–Fe4 single bond in the :$SnFe_2(CO)_8$ ligand required to give both iron atoms the favored 18-electron configuration.

The triplet $SnFe_4(CO)_{15}$ structure **15T-1**, lying 16.0 kcal/mol above **15S-1**, is a $C_1$ triplet structure with two iron-iron bonds, three iron-tin bonds and all terminal CO groups (Figure 4). Structure **15T-1** has a twisted spiropentane skeleton, similar to the $SnFe_4$ skeleton of **15S-2**. However, **15T-1** lacks a dative bond from one of the bridging CO groups to the tin atom as indicated by exclusively non-bonding Sn···O distances. The Sn→Fe dative bond in **15T-1** of length 2.410 Å with a WBI of 0.57 is very similar to that in **15S-2** discussed above except with a higher WBI owing to the tin coordination number of three because of the lack of a Sn···O bond. The Fe1–Fe2 distance of 2.490 Å in **15T-1** is similar to the Fe1–Fe2 distance of 2.431 Å in **15S-2**. However, the WBI of 0.21 for the Fe1–Fe2 interaction in **15T-1** is much less than the WBI of 0.37 in **15S-2**. Interpreting the Fe1–Fe2 bond in **15T-1** as a formal single bond gives these iron atoms a 17-electron configuration thereby providing the two unpaired electrons for the triplet spin state.

*3.1.3. $SnFe_4(CO)_{14}$.* Three singlet structures and two low-energy triplet structures were found for $SnFe_4(CO)_{14}$ within 20 kcal/mol of the lowest energy structure **14S-1** (Figure 5). Structure **14S-1** is a singlet structure with four iron-iron bonds, four iron-tin bonds, and one bridging CO group connecting the Fe3 and Fe4 atoms. The tin atom in **14S-1** is bonded to four iron atoms, leading to a distorted triangular pyramidal skeleton (Figure 5). In **14S-1** the Fe1–Fe2, Fe3–Fe4, Fe2–Fe3, and Fe2–Fe4 distances of 2.973 Å, 2.691 Å, 2.805 Å, and 2.806 Å, respectively. with Wiberg bond indices (WBIs) ranging from 0.15 to 0.23, can be considered as formal single bonds forming an $Fe_3$ triangle with an externally bonded fourth iron atom. The Sn-Fe1/Sn-Fe4 distances in **14S-1** of 2.455 Å/ 2.443 Å are shorter than the Sn-Fe2/Sn-Fe3 distances in **14S-1** of 2.576 Å/2.495 Å consistent with their WBIs of 0.53/0.48 and 0.30/0.38, respectively. However, they can all be considered as single bonds to give each iron atom the favored 18-electron configuration. The single bridging CO group in **14S-1** exhibits a ν(CO) frequency at 1849 $cm^{-1}$, which lies 230 $cm^{-1}$ below the lowest terminal ν(CO) frequency in accord with expectation.

The singlet $SnFe_4(CO)_{14}$ structure **14S-2**, lying 8.9 kcal/mol in energy above **14S-1**, has two pairs of bonded $Fe_2$ units, four iron-tin bonds and two bridging CO groups connecting the Fe3 and Fe4 atoms (Figure 5). The spiropentane $SnFe_4$ skeleton of **14S-2** is similar to the $SnFe_4$ skeleton of **16S-1**. The central tin atom in **14S-2 is** bonded to an $Fe_2(CO)_8$ unit and an $Fe_2(CO)_6$ unit with the two bridging CO groups in the latter unit.

The Fe1–Fe2 distance of 2.817 Å in the $Fe_2(CO)_8$ unit of **14S-2** with a corresponding WBI of 0.19 is very similar to the Fe–Fe distances in the $SnFe_4(CO)_{16}$ structure **16S-1**. This Fe1–Fe2 interaction can thus be considered as a formal single bond thereby giving each iron atom the favored 18-electron configuration. The Fe3=Fe4 distance of 2.352 Å in the $Fe_2(CO)_6$ unit of **14S-2** is at least 0.058 Å shorter than the formal iron-iron double bonds in **15S-2** and **15T-1**. However, its WBI of only 0.32 in **14S-2** is smaller than the WBIs of 0.37 and 0.57 for the Fe=Fe double bonds in **15S-2** and **15T-1**, respectively. Considering the Fe3≡Fe4 interaction in the $Fe_2(CO)_6$ unit of **14S-2** as a formal triple bond gives these iron atoms the favored 18-electron configuration. However, the Fe3–Fe4 interaction in the $Fe_2(CO)_6$ unit of **14S-2** as only a single bond can give each iron atom only a 16-electron configuration. The actual situation in **14S-2** could be a resonance hybrid between these two possibilities. The two bridging ν(CO) frequencies in **14S-2** of 1899 and 1903 $cm^{-1}$ are ~170 $cm^{-1}$ below the lowest terminal ν(CO) frequency in accord with expectation.

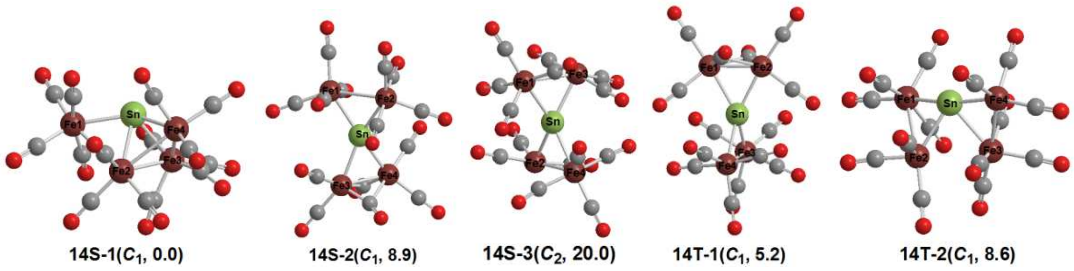


**Figure 5.** Optimized $SnFe_4(CO)_{14}$ structures.

The $SnFe_4(CO)_{14}$ structure **14S-3**, lying 20.0 kcal/mol in energy above **14S-1**, is an $Sn[Fe_2(CO)_7]_2$ structure with an $SnFe_4$ spiropentane skeleton and exclusively terminal CO groups (Figure 5). The iron-iron distances of 2.736 Å in **14S-3** with WBIs of 0.20 can be interpreted as formal single bonds, This provides Fe1 and Fe4 bearing four CO groups with the favored 18-electron configuration. However, Fe2 and Fe3, each bearing only three CO groups have only 16-electron configurations. The $Fe(CO)_3$ units with iron atoms Fe2 and Fe3 each have a gap in the coordination sphere corresponding to their 16-electron configurations. The $Sn[Fe_2(CO)_7]_2$ structure **14S-3** can be derived from the $Sn[Fe_2(CO)_8]_2$ structure **16S-1** by removal of a terminal CO group from each $Fe_2(CO)_8$ unit.

The $C_1$ triplet $SnFe_4(CO)_{14}$ structure **14T-1**, lying 5.2 kcal/mol in energy above **14S-1**, is a spiropentane $Sn[Fe_2(CO)_8][Fe_2(CO)_6]$ structure with two semibridging carbonyl groups connecting the Fe1 and Fe2 atoms in the $Fe_2(CO)_8$ unit with short Fe-C

distances of ~ 1.8 Å and long Fe-C distances of ~ 2.2 Å. The Fe1=Fe2 distance of 2.427Å in the $Fe_2(CO)_6$ unit of **14T-1** is similar to the formal iron-iron double bonds in **15S-2** and **15T-1** although its WBI is rather low at 0.22. The Fe3–Fe4 bond length of 2.850 Å with a WBI of 0.18 in the $Fe_2(CO)_8$ unit of **14T-1** is similar to both Fe–Fe bonds in the $Sn[Fe_2(CO)_8]_2$ structure **16S-1** and thus can be interpreted as a formal single bond. Considering the Fe1=Fe2 bond in **14T-1** as a formal double bond and the Fe3–Fe4 bond as a formal single bond gives Fe3 and Fe4 the favored 18-electron configuration but Fe1 and Fe2 only 17 electron configurations. The latter two iron atoms in **14T-1** thus provide the two unpaired electrons for the triplet spin state. The two semibridging CO groups in **14T-1** exhibits ν(CO) frequencies at 1885 and 1897 $cm^{-1}$, which are approximately 180 $cm^{-1}$ below the lowest terminal ν(CO) frequency in accord with expectation.

The triplet $SnFe_4$ structure **14T-2**, lying 8.6 kcal/mol in energy above **14S-1**, is a distorted spiropentane $Sn[Fe_2(CO)_7]_2$ structure with all terminal carbonyl groups (Figure 5). The distortion brings the $Fe(CO)_3$ portions of the $Fe_2(CO)_7$ units closer together with an Fe2 and Fe3 bonding distance of 3.004 Å. Interpreting the three Fe–Fe interactions in **14S-1** as formal single bonds gives the iron atoms of the two $Fe(CO)_4$ units the favored 18-electron configuration. However, each iron atom in the two $Fe(CO)_3$ units has a 17-electron configuration thereby providing the two unpaired electrons for the triplet spin state of **14T-2**.

*3.1.4. $SnFe_4(CO)_{13}$.* The singlet $SnFe_4(CO)_{13}$ structure **13S-1** is a very favorable structure since it lies 19.6 kcal/mol in energy below the next lowest energy structure, namely the triplet structure **13T-1**. Structure **13S-1** has a butterfly skeleton (Figure 2) with five iron-iron bonds, four tin-iron bonds, and one bridging carbonyl group (Figure 6). Each iron atom bears three terminal CO groups. The thirteenth CO group in **13S-1** bridges the unique Fe–Fe bond corresponding to the body of the butterfly. This bridging CO group exhibits a ν(CO) frequency at 1874 $cm^{-1}$, which lies 190 $cm^{-1}$ below the lowest terminal ν(CO) frequency in accord with expectation. The four unbridged Fe–Fe bonds from the butterfly body to a wingtip have lengths of ~2.7 Å with WBIs of 0.22. The single CO-bridged Fe–Fe bond within the butterfly body is ~0.1 Å shorter at ~2.6 Å but has a slightly lower WBI of 0.18, probably related to some delocalization involving the bridging CO group. Considering all the iron-iron and tin-iron bonds in **13S-1** as formal single bonds gives the four iron atoms the favorable 18-electron configuration provided that the two wingtip iron atoms with two Fe–Fe bonds bear formal negative charges and the two body iron atoms with three Fe–Fe bonds bear formal positive charges. Replacing

the tin atom in the $SnFe_4(CO)_{13}$ structure **13S-1** with a carbide carbon atom gives the experimentally known[8] iron carbonyl carbide structure $CFe_4(CO)_{13}$.

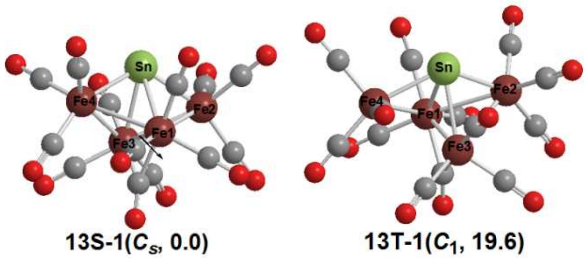


**Figure 6.** The optimized $SnFe_4(CO)_{13}$ structures.

The Fe–Sn–Fe angle of 120.9° in the $SnFe_4(CO)_{13}$ structure **13S-1** deviates considerably from linearity in contrast to the nearly linear Fe–C–Fe angle of 176.1° (B3LYP/DZP) or 174.7° (BP86/DZP) in its carbide analogue $CFe_4(CO)_{13}$. Therefore **13S-1** is best interpreted as a trigonal bipyramidal $SnFe_4$ cluster with an equatorial tin atom. Because of the significantly bent Fe–Sn–Fe angle the tin atom has a formal external lone pair and thus is a donor of two skeletal electrons. This makes **13S-1** a 12 skeletal electron system after adding the two skeletal electrons provided by each $Fe(CO)_3$ unit and two more skeletal electrons from the "extra" carbonyl group to the two skeletal electrons provided by the tin vertex. Thus **13S-1** is a $2n + 2$ (for $n = 5$) skeletal electron system consistent with its deltahedral structure by the Wade-Mingos rules[20,21,22] and with a similar skeletal electron count to the experimentally known[23] trigonal bipyramidal carborane $C_2B_3H_5$.

The triplet $SnFe_4(CO)_{13}$ **13T-1**, lying 19.6 kcal/mol in energy above **13S-1**, can be derived from the butterfly structure **13S-1** by stretching one of the four Fe–Fe bonds beyond bonding distance (Figure 6). The two iron atoms at the ends of the stretched Fe–Fe bond thus attain a 17-electron configuration thereby providing the two unpaired electrons for the triplet spin state of **13T-1**. The bridging CO group in **13T-1** exhibits a ν(CO) frequency of 1858 $cm^{-1}$, which lies ~200 $cm^{-1}$ below the lowest terminal ν(CO) frequency in accord with expectation.

*3.1.5. $SnFe_4(CO)_{12}$.* Two singlet low-energy structures **12S-1** and **12S-2** and one low-energy triplet structure **12T-1** for $SnFe_4(CO)_{12}$ lie within 10 kcal/mol of the lowest energy structure (Figure 7). The lowest energy $SnFe_4(CO)_{12}$ structure **12T-1** is a singly CO-bridged triplet spin state structure with an $SnFe_4$ butterfly skeleton having five Fe–Fe bonds and four Sn–Fe bonds. The semibridging CO groups in **12T-1** have short Fe-C distances of ~ 1.8 Å and long Fe-C distances of ranging from ~2.1 to ~2.4 Å. These

semibridging CO groups exhibit ν(CO) frequencies at 1841. 1867, and 1924 $cm^{-1}$ which are all well below the lowest terminal ν(CO) frequency in accord with expectation. The Fe1-Fe3 and Fe2-Fe3 edges bridged by CO groups of lengths 2.395 and 2.435 Å in **12T-1** are significantly shorter than the unbridged Fe1-Fe3, Fe2-Fe4, and Fe1-Fe4 edges of lengths 2.622, 2.686, and 2.703 Å, respectively. The two short Fe–Fe edges have WBIs of 0.27 and 0.30 whereas the three longer Fe–Fe edges have smaller WBIs ranging from 0.16 to 0.18. Considering all of these five Fe–Fe interactions in **12T-1** as formal single bonds gives two of the four iron atoms the favored 18-electron configuration. However, the other two iron atoms in **12T-1** have only 17-electron configurations accounting for the triplet spin state of **12T-1**.

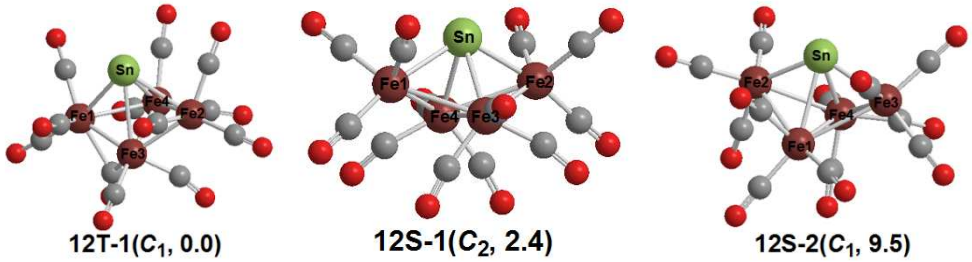


**Figure 7.** The optimized $SnFe_4(CO)_{12}$ structures.

The $C_2$ singlet $SnFe_4(CO)_{12}$ structure **12S-1**, lying only 2.4 kcal/mol in energy above **12T-1**, also has a butterfly skeleton with five iron-iron bonds and four tin-iron bonds and all terminal CO groups (Figure 7). All five Fe–Fe bonds in **12S-1** have lengths between 2.63 and 2.75 Å and WBIs between 0.15 to 0.23. None of these Fe–Fe distances and corresponding WBIs suggest formal double bonds. However, for all of the iron atoms in **12S-1** to have the favored 18-electron configuration there must be one double bond somewhere in the central $SnFe_4$ butterfly. Structure **12S-1** could be a resonance hybrid between canonical structures having a formal Fe=Fe bond for one of the butterfly edges and formal Fe–Fe single bonds for the four other butterfly edges.

The next singlet Sn $Fe_4(CO)_{12}$ structure **12S-2**, lying 9.5 kcal/mol above **12T-1**, has a similar $SnFe_4$ butterfly skeleton to **12S-1** but with two semibridging CO groups rather than all terminal CO groups (Figure 7). The semibridging CO groups in **12S-2** have short Fe-C distances of ~ 1.8 Å and long Fe-C distances of 2.3 Å (Figure 7).

**3.2. Thermochemistry.** The thermochemical predictions in Table 1 and 2 provide insights into the viability of the $SnFe_4(CO)_n$ ($n$ = 16 to 13) derivatives. Table 1 reports the dissociation energies for removing one CO group from the lowest energy $SnFe_4(CO)_n$ ($n$

= 16 to 13) structures according to the following equations:

$$SnFe_4(CO)_n \rightarrow SnFe_4(CO)_{n-1} + CO \ (n = 16 \text{ to } 13)$$

The CO dissociation energies of $SnFe_4(CO)_n$ ($n$ = 16 to 13) are all predicted to be at least 19.5 kcal/mol. However, the CO dissociation energy of $SnFe_4(CO)_{16}$ of 49.8 kcal/mol is much higher than those of $SnFe_4(CO)_n$ ($n$ = 15, 14) suggesting that $SnFe_4(CO)_{16}$ is very stable with respect to carbonyl dissociation. This agrees with experiment, since only $SnFe_4(CO)_{16}$ has been synthesized to date. The carbonyl dissociation energy of $SnFe_4(CO)_{13}$ is also high at 46.6 kcal/mol so that $SnFe_4(CO)_{13}$ analogous to the known[8] $CFe_4(CO)_{13}$ could be another synthesis target. These CO dissociation energies can be compared with the experimental CO dissociation energies of 27, 41, and 37 kcal/mol for $Ni(CO)_4$, $Fe(CO)_5$, and $Cr(CO)_6$, respectively.[24]

**Table 1.** Bond dissociation energies (kcal/mol) after zero-point energy corrections (kcal/mol) for successive removal of carbonyl groups from the lowest energy optimized $SnFe_4(CO)_n$ ($n$ = 16 to 13) structures by the M06-L method.

| | M06-L |
|---|---|
| $SnFe_4(CO)_{16}$ (**16S-1**) → $SnFe_4(CO)_{15}$ (**15S-1**) + CO | 49.8 |
| $SnFe_4(CO)_{15}$ (**15S-1**) → $SnFe_4(CO)_{14}$ (**14S-1**) + CO | 23.6 |
| $SnFe_4(CO)_{14}$ (**14S-1**) → $SnFe_4(CO)_{13}$ (**13S-1**) + CO | 19.8 |
| $SnFe_4(CO)_{13}$ (**13S-1**) → $SnFe_4(CO)_{12}$ (**12T-1**) + CO | 46.6 |

Table 2 reports the energies for the following disproportionation reactions:

$$2\ SnFe_4(CO)_n \rightarrow SnFe_4(CO)_{n+1} + SnFe_4\ (CO)_{n-1} \ (n = 15 \text{ to } 13)$$

The disproportionation of $SnFe_4CO)_{15}$ into $SnFe_4(CO)_{16}$ + $SnFe_4(CO)_{14}$ is an exothermic process by 26.2 kcal/mol, Similarly, the disproportionation of $SnFe_4(CO)_{14}$ into $SnFe_4(CO)_{15}$ + $SnFe_4(CO)_{13}$ is an exothermic process, albeit with a much lower energy release of only 3.8 kcal/mol. This suggests that neither $SnFe_4(CO)_{15}$ nor $SnFe_4(CO)_{14}$ are viable species. In contrast, the disproportionation of $SnFe_4(CO)_{13}$ into $SnFe_4(CO)_{14}$ and $SnFe_4(CO)_{12}$ is an endothermic process by 26.8 kcal $mol^{-1}$, suggesting that $SnFe_4(CO)_{13}$ might be a stable molecule.

**Table 2.** Disproportionation energies after zero-point energy corrections (kcal/mol) for the reactions $2SnFe_4(CO)_n \rightarrow SnFe_4(CO)_{n+1} + SnFe_4(CO)_{n-1}$ ($n$ = 15 to 13) with the lowest energy structures by the M06-L method.

| | M06-L |
|---|---|
| 2 $SnFe_4(CO)_{15}$(**15S-1**)→ $SnFe_4(CO)_{16}$ (**16S-1**) + $SnFe_4(CO)_{14}$ (**14S-1**) | –26.2 |
| 2 $SnFe_4(CO)_{14}$(**14S-1**)→ $SnFe_4(CO)_{15}$ (**15S-1**) + $SnFe_4(CO)_{13}$ (**13S-1**) | –3.8 |
| 2 $SnFe_4(CO)_{13}$(**13S-1**)→ $SnFe_4(CO)_{14}$ (**14S-1**) + $SnFe_4(CO)_{12}$ (**12T-1**) | 26.8 |

## 4. Conclusions

The lowest energy structures of the tetranuclear tin-iron carbonyls $SnFe_4(CO)_n$ ($n$ = 16, 15, 14, 13, 12) follow a similar pattern to those of the corresponding iron carbonyl carbides $CFe_4(CO)_n$. Thus for both systems the lowest energy $EFe_4(CO)_{16}$ structures are of the type $E[Fe_2(CO)_8]_2$ with a central $EFe_4$ spiropentane network and an iron-iron bond in each $Fe_2(CO)_8$ unit. The tin derivative $Sn[Fe_2(CO)_8]_2$ is thus formally a Sn(IV) derivative of the known $Fe_2(CO)_8^{2-}$ anion. The lowest energy structures for the $SnFe_4(CO)_n$ ($n$ = 15, 14, 13) species have 18–$n$ Fe–Fe bonds thereby providing each iron atom with the preferred 18-electron configuration. Thus for the $SnFe_4(CO)_{15}$ system the central $SnFe_4$ spiropentane unit is distorted to form a third Fe–Fe bond connecting the two $Fe_2(CO)_8$ units thereby leading to a bonded Fe–Fe–Fe–Fe chain. Further CO loss from $SnFe_4(CO)_{15}$ adds a fourth Fe–Fe bond in the lowest energy $SnFe_4(CO)_{14}$ structure. The lowest energy $SnFe_4(CO)_{13}$ structure is analogous to that of the experimentally known iron carbonyl carbide $CFe_4(CO)_{13}$ with a central $Fe_4$ butterfly having five Fe–Fe bonds. Further closure of the $Fe_4$ unit in the low-energy $SnFe_4(CO)_{12}$ structures does not occur by forming a sixth Fe–Fe bond thereby giving a central $Fe_4$ tetrahedron. Instead the central $Fe_4$ butterfly is maintained in low-energy singlet and triplet $SnFe_4(CO)_{12}$ structures.

The energetics of CO dissociation from the $EFe_4(CO)_n$ (E = C, Sn; $n$ = 16, 15, 14, 13) account for the experimentally observed differences between the systems with central tin and central carbon atoms. Thus for the tin systems the CO dissociation energy from $SnFe_4(CO)_{16}$ is relatively high at 49.8 kcal/mol consistent with its experimental observation as a stable species. The CO dissociation products $SnFe_4(CO)_n$ ($n$ = 15, 14) are not viable with respect to $SnFe_4(CO)_{16}$ + $SnFe_4(CO)_{13}$. However, $SnFe_4(CO)_{13}$ has a significant CO dissociation energy of 46.6 kcal/mol. This suggests the possibility of synthesizing $SnFe_4(CO)_{13}$ analogous to the known $CFe_4(CO)_{13}$. For the tetranuclear iron carbonyl carbides $CFe_4(CO)_n$ the CO dissociation energies of the species with more than 13 CO groups are all very small or even negative suggesting $CFe_4(CO)_{13}$ to be the carbonyl-richest viable iron tetracarbonyl carbide consistent with experiment.

This theoretical study also resulted in the identification of a higher energy $SnFe_4(CO)_{15}$ structure **15S-2** which can be dissected into a derivative of $Fe_2(CO)_8$ with a central Fe=Fe double bond in which one of the CO group has been replaced by a $:SnFe_2(CO)_8$ "ligand" containing a bivalent Sn(II) ligand with a lone pair on the tin atom. Although **15S-2** is a relatively high energy $SnFe_4(CO)_{15}$ structure, lying ~18 kcal/mol above its isomer **15S-1**, its observation suggests the possibility of other

transition metal systems where the lowest energy structure has such a bivalent tin :$SnFe_2(CO)_8$ ligand.

**Acknowledgement**

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**Supporting Information.** Tables S1 to S15: Theoretical Cartesian coordinates for the structures of $SnFe_4(CO)_n$ ($n$ = 16 to 12) using the M06-L/TZP and BP86/DZP methods; Tables S16 to S30: Theoretical harmonic vibrational frequencies for the structures of $SnFe_4(CO)_n$ ($n$=16 to 12) using the M06-L/TZP and BP86/DZP methods; Tables S31 to S34: Metal-metal distances, natural population analysis natural charges, metal electron configuration, formal metal-metal bond orders, and WBIs for the $SnFe_4(CO)_n$ ($n$ = 16 to 12) structures using the M06-L/TZP and BP86/DZP methods; Table S35. ν(CO) frequencies and infrared intensities (in km/mol) for the $SnFe_4(CO)_n$ ($n$ = 16 to 12) structures calculated by using the BP86/DZP method; Complete Gaussian09 reference (reference 15).

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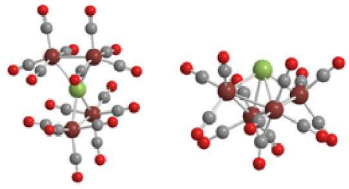
# Table of Contents Entry

## Tetranuclear Iron Carbonyl Complexes with a Central Tin Atom: Relationship to Iron Carbonyl Carbides

Xiaoli Gong, Liyao Zhu,* Jufeng Zhao, Guangmang Cui, Xinmiao Lu,[a] Yaoming Xie, and R. Bruce King,*

The energetics of CO dissociation from the lowest energy $EFe_4(CO)_n$ (E = C, Sn; $n$ = 16, 15, 14, 13) structures account for the experimentally observed differences between the systems with central tin and central carbon atoms.



$Sn[Fe_2(CO)_8]_2$ $SnFe_4(CO)_{13}$