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6/14

The Facile Coupling of Carbon Monochalcogenides to Ethenedichalcogenone Ligands in Binuclear Iron Carbonyl Derivatives: A Theoretical Study

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Abstract

The lowest energy $\text{Fe}_2(\text{CO})_n(\text{CE})_2$ structures ($E = \text{S, Se, Te}$; $n = 8, 7, 6$) do not have separate CE ligands but instead have coupled C_2E_2 ligands functioning as four to six electron donors to the pair of iron atoms. The exothermicity of such coupling reactions as a function of the chalcogen E increases in the sequence $\text{S} < \text{Se} < \text{Te}$. However, the monomers $\text{Fe}(\text{CO})_4(\text{CE})$ are stable species owing to the high activation energies for the coupling reactions. Thus, the thiocarbonyl $\text{Fe}(\text{CO})_4(\text{CS})$ is a stable experimentally known complex. However, the coupled $\text{Fe}_2(\text{CO})_7(\text{C}_2\text{E}_2)$ structures are preferred both thermodynamically and kinetically over isomeric $\text{Fe}_2(\text{CO})_7(\text{CE})_2$ structures with discrete CE ligands. For the CS ligand, the previously optimized lowest energy $\text{Fe}_2(\text{CO})_n(\text{CS})_2$ structures ($n = 7, 6$) with discrete CS ligands are now found to lie ~ 11 kcal/mol ($n = 7$) and ~ 30 kcal/mol ($n = 6$) in energy above the lowest energy isomeric $\text{Fe}_2(\text{CO})_n(\text{C}_2\text{S}_2)$ structures with coupled C_2E_2 ligands.

Keywords: Carbon Monochalcogenides • Coupling • Ethenedichalcogenone • Density Functional Theory

1. Introduction

The chemistry of binary transition metal carbonyls dates back to the discovery of $\text{Ni}(\text{CO})_4$ in 1890.¹ In addition to $\text{Ni}(\text{CO})_4$ the mononuclear $\text{Fe}(\text{CO})_5$ and $\text{Cr}(\text{CO})_6$ and the binuclear $\text{Fe}_2(\text{CO})_9$ and $\text{Co}_2(\text{CO})_8$ are well-known commercially available binary first row transition metal carbonyls, which often are useful as intermediates for the synthesis of other first row transition metal derivatives. The synthesis of these and other metal carbonyl derivatives is facilitated by the ready availability and stability of the free carbon monoxide ligand.² Although free carbon monoxide is absolutely stable with respect to coupling to give $(\text{CO})_x$ oligomers,^{3,4} reductive coupling of CO by organoactinides has been discovered in recent years.^{5,6,7,8,9}

The heavier carbon monochalcogenides, namely CS, CSe, and CTe, are more reactive in part owing to the larger atomic radii as well as the lower electrophilicities of the heavier chalcogens. They are therefore not available as reagents for the synthesis of their metal complexes, at least under normal conditions. Thus free carbon monosulfide is unstable above -100°C with respect to polymerization.^{10,11} The heavier congeners CSe and CTe are still both experimentally unknown. However, some transition metal complexes of the heavier carbon monochalcogenides can be synthesized by indirect methods.^{12,13,14} For example, stable carbon-sulfur derivatives such as carbon disulfide (CS_2) and thiophosgene ($\text{S}=\text{CCl}_2$) can serve as CS sources for the synthesis of a variety of stable metal thiocarbonyls.^{15,16,17,18} Similarly CSe₂ can be used as a CSe source for the synthesis of some metal selenocarbonyls.¹³ The synthesis of metal tellurocarbonyls is more difficult than the synthesis of metal thiocarbonyls and selenocarbonyls since neither CTe_2 nor $\text{Te}=\text{CCl}_2$ are available as CTe sources. The first metal tellurocarbonyl complex, $\text{OsCl}_2(\text{CO})(\text{CTe})(\text{PPh}_3)_2$, was synthesized by Roper and co-workers using a different approach involving reaction between the electrophilic dichlorocarbene compound $\text{OsCl}_2(\text{CCl}_2)(\text{CO})(\text{PPh}_3)_2$ and the nucleophile HTe^- .¹⁹ Such nucleophilic reactions also provided an alternative approach for the synthesis of some metal thiocarbonyls and selenocarbonyls.^{10,20}

Hundreds of metal thiocarbonyls and selenocarbonyls as well as a few metal tellurocarbonyls have been synthesized by the above methods. However, most of these MCE (E = S, Se, Te) complexes contain only one CE group owing to difficulties in introducing more than a single CE group from the available CE sources into metal complexes. The few transition metal complexes containing more than one heavier carbon monochalcogenide group include the stable thiocarbonyls $\text{CpMn}(\text{CO})_{3-n}(\text{CS})_n$ ($n = 1, 2, 3$),²¹ $[(\text{Ph}_3\text{P})_2\text{Ir}(\text{CS})_2\text{Cl}_2]^+$,²² $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\text{CS})_2$,²³ and the poorly characterized unstable

$\text{Ni}(\text{CS})_4$.²⁴ Species containing a selenocarbonyl ligand and at least one carbonyl group include $[\text{Rh}_2\{(\text{SeC})\text{Mo}(\text{CO})_2(\text{Tp}^*)\}_2(\eta^4\text{-cod})_2]$,²⁵ and the proposed reactive intermediate $[(\text{Tp}^*)(\text{CO})_2\text{Mo}(\text{CSe})\text{Ir}(\text{CO})(\text{PPh}_3)]_2$.²⁶

Theoretical work predicts the dimer of the thiocarbonyl group (ethenedithione) to have a linear triplet spin state $\text{S}=\text{C}=\text{C}=\text{S}$ structure.^{3,27} However, this molecule has never been observed experimentally.²⁸ Nevertheless, a few metal ethenedithione complexes were synthesized by Seidel and coworkers including the mononuclear $\text{TpW}(\text{CO})_2(\text{C}_2\text{S}_2)^-$ anion,²⁹ the neutral binuclear $[(\text{triphos})\text{Co}]_2(\text{SCCS})$,³⁰ and the trimetallic $[\text{TpW}(\text{CO})_2]_2\text{Ni}(\text{C}_2\text{S}_2)_2$ complex (Tp = tris(pyrazolyl)borate).³¹ In most of the binuclear complexes the C_2S_2 ligand bridges the pair of metal atoms by bonding to one metal through its carbon atoms and to the other metal through its sulfur atoms (II in Figure 1). However, in the triplet spin state $[(\text{triphos})\text{Co}]_2(\text{SCCS})$ complex, the C_2S_2 ligand is bonded to each metal through a $\text{C}=\text{S}$ double bond (I in Figure 1). This structure is stable but easily converted to an isomer with bonding mode II (Figure 1) in polar solvents.

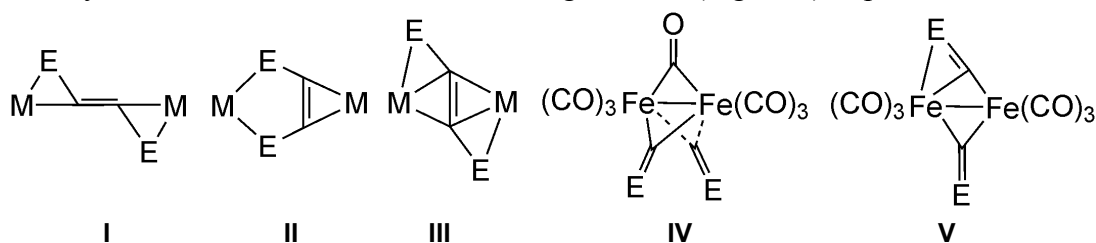


Figure 1. Coordination modes of C_2E_2 ligands ($\text{E} = \text{S}, \text{Se}, \text{Te}$) in binuclear transition metal systems.

The difficulties to date in synthesizing compounds containing more than one chalcocarbonyl group attached to a metal atom make theoretical studies in this area of interest. For example, are the binary species $\text{Cr}(\text{CE})_6$, $\text{Fe}(\text{CE})_5$, and $\text{Ni}(\text{CE})_4$ ($\text{E} = \text{S}, \text{Se}, \text{Te}$) unknown only because no suitable synthetic method has been found to circumvent the instabilities of the free ligands? Our recent Communication³² shows that coupled $\text{Fe}(\eta^2\text{-ECCE})$ ethenedichalcogenone structures are energetically preferred for singlet $\text{Fe}(\text{CO})_4(\text{C}_2\text{E}_2)$ and triplet $\text{Fe}(\text{CO})_3(\text{C}_2\text{E}_2)$ over $\text{Fe}(\text{CE})_2$ structures with two discrete CE ligands. The preference for coupled ethenedichalcogenone structures was found to increase in the series $\text{S} < \text{Se} < \text{Te}$. An ethenedithione structure (Figure 1, mode III) was also predicted for the highly unsaturated $\text{Cp}_2\text{Mn}_2(\text{CS})_2$.³³

Our 2009 theoretical study on $\text{Fe}_2(\text{CO})_n(\text{CS})_2$ ($n = 7, 6$) led only to structures with two separate CS groups.³⁴ No low energy structures were found in which the two CS groups couple to form a C_2S_2 ligand. This initial theoretical study suggested that CS groups prefer bridging over terminal positions in $\text{Fe}_2(\text{CO})_n(\text{CS})_2$. In $\text{Fe}_2(\text{CO})_7(\text{CS})_2$ the

lowest energy structures were found to have two-electron donor μ -CS bridges (Figure 1, mode IV). However, in the lowest energy unsaturated $\text{Fe}_2(\text{CO})_6(\text{CS})_2$ structure the bridging CS group is a four-electron donor η^2 - μ -CS group (Figure 1, mode V).

Recently we sought to extend our study on metal thiocarbonyls to binuclear iron carbonyl tellurocarbonyl derivatives of the type $\text{Fe}_2(\text{CO})_n(\text{CTe})_2$. We wanted to see what effect substituting the heavier and more electropositive chalcogen tellurium for sulfur in the CE ligands would have on the preferred structures. We immediately found that in all of the low energy $\text{Fe}_2(\text{CO})_n(\text{CTe})_2$ structures, the two CTe ligands coupled to form a C_2Te_2 ligand. This led to a reinvestigation of the $\text{Fe}_2(\text{CO})_n(\text{CS})_2$ systems reported in our 2009 paper³⁴ using starting structures closely related to the low energy $\text{Fe}_2(\text{CO})_n(\text{CTe})_2$ structures. Optimizing these structures led to some new coupled $\text{Fe}_2(\text{CO})_n(\text{C}_2\text{S}_2)$ isomers of lower energies than our previously reported³⁴ “lowest energy” isomeric $\text{Fe}_2(\text{CO})_n(\text{CS})_2$ structures with separate CS groups. Missing these coupled $\text{Fe}_2(\text{CO})_n(\text{C}_2\text{S}_2)$ isomers in our earlier work more generally illustrates the difficulty in finding suitable starting structures for density functional theory optimizations leading to the most favorable lowest energy structures for a given stoichiometry.

We have now expanded this study to the complete series of binuclear $\text{Fe}_2(\text{CO})_n(\text{CE})_2$ systems ($\text{E} = \text{S}, \text{Se}, \text{Te}$; $n = 8, 7, 6$) and report the results in this paper. Our previous communication³² on $\text{Fe}(\text{CO})_n(\text{CE})_2$ ($n = 4, 3$) was the initial report of coupling of two CE ligands to a C_2E_2 ligand in less complicated mononuclear iron carbonyl derivatives.

2. Theoretical Methods

Electron correlation effects were considered using density functional theory (DFT) methods, which have evolved as a practical and effective computational tool, especially for organometallic compounds.^{35,36,37,38,39,40,41} The popular B3LYP method, which is the hybrid HF/DFT method using a combination of the three-parameter Becke exchange functional (B3) with the Lee-Yang-Parr (LYP) generalized gradient correlation functional,^{42,43} was used in this study.

Basis sets have been chosen to provide continuity with a body of existing research on organometallic compounds. Fortunately, DFT methods are less basis set sensitive than higher-level methods such as coupled cluster theory. In this work all computations were performed using double- ζ plus polarization (DZP) basis sets. The DZP basis sets used for carbon, oxygen, and sulfur add one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(\text{C}) = 0.75$, $\alpha_d(\text{O}) = 0.85$, and $\alpha_d(\text{S}) = 0.70$

to the standard Huzinaga-Dunning contracted DZ sets.^{44,45,46} The Ahlrichs DZP basis set⁴⁷ for selenium is designated (14s10p5d/8s6p3d). The loosely contracted DZP basis set for iron is the Wachters primitive set⁴⁸ augmented by two sets of p functions and one set of d functions, contracted following Hood, Pitzer and Schaefer,⁴⁹ and designated (14s11p6d/10s8p3d). The effective core potential (ECP) basis sets Lanl2DZ^{50,51} was used for tellurium and designated (3s3p/2s2p) for the valence orbitals.

The geometries of all structures were fully optimized using the B3LYP/DZP method. Vibrational frequencies were determined by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. All of the computations were carried out with the Gaussian 09 program,⁵² exercising the fine grid option (75 radial shells, 302 angular points) for evaluating integrals numerically,⁵³ while the tight (10^{-8} hartree) designation is the default for the self-consistent field (SCF) convergence.

The optimized structures are depicted in Figures 2 to 4. Each $\text{Fe}_2(\text{CO})_n(\text{CE})_2$ ($\text{E} = \text{S, Se, Te}$; $n = 8, 7, 6$) structure is designated as **nE-x** where **n** is the number of CO groups, **E** is the chalcogen atom (S, Se, Te), and **x** represents the binding mode in Figure 1. Triplet spin state structures are indicated by **T**. All of the structures reported in Figures 2 to 4 are local minima with no imaginary vibrational frequencies.

3. Results

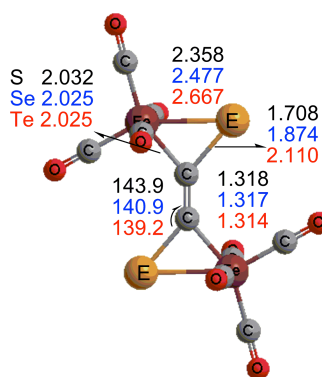
3.1 $\text{Fe}_2(\text{CO})_8(\text{CE})_2$ ($\text{E} = \text{S, Se, Te}$)

Five $\text{Fe}_2(\text{CO})_8(\text{CE})_2$ structures with coupled EC_2E ligands were found for each chalcogen (Figure S1 in the SI). However, these coupled structures were found to be kinetically inaccessible from the dimerization of $\text{Fe}(\text{CO})_4(\text{CE})$ with activation energies of 43.1, 52.4, and 67.6 kcal/mol for $\text{E} = \text{S, Se, and Te}$, respectively. (Figure S2 in the SI) so only the lowest energy such structures are discussed here.

The lowest energy $\text{Fe}_2(\text{CO})_8(\text{CE})_2$ structures **8E-I** (Figure 2) are found to have a EC_2E ligand bridging two $\text{Fe}(\text{CO})_4$ fragments through a dihapto $\eta^2\text{-(EC)CE-Fe}$ bond to each iron atom. The Fe-C distances are predicted to be ~ 2.03 Å and the Fe-E distances are predicted to be 2.358 Å for Fe-S, 2.477 Å for Fe-Se, and 2.667 Å for Fe-Te, respectively. Therefore, these bridging $\eta^2, \eta^2\text{-EC}_2\text{E}$ ligands function as two-electron donors to each iron atom thereby giving each iron atom the favored 18-electron configuration. The central C=C distances of the ECCE ligands in the **8E-I** structures are ~ 1.32 Å consistent with formal double bonds.

Dissociation of the $\text{Fe}_2(\text{CO})_8(\text{CE})_2$ structures **8E-I** into two isolated $\text{Fe}(\text{CE})(\text{CO})_4$ molecules is predicted to be endothermic by 15.1 kcal/mol (**8S-I**), 35.7 kcal/mol (**8Se-I**), and 55.3 kcal/mol (**8Te-I**) (Table S1 in the SI). This suggests that the **8E-I** structures are

viable with respect to dissociation into monomeric $\text{Fe}(\text{CE})(\text{CO})_4$. However, monomeric $\text{Fe}(\text{CS})(\text{CO})_4$ has been synthesized as a stable molecule,⁵⁴ owing to the high activation energy for the dimerization of this complex in which the iron has the favored 18-electron configuration (Figure S2 in the SI). Furthermore, dimerizations of $\text{Fe}(\text{CE})(\text{CO})_4$ (E = Se, Te) are also kinetically disfavored owing to the high activation energies of more than 35.0 kcal/mol. Thus the synthesis of monomeric $\text{Fe}(\text{CO})_4(\text{CSe})$ and $\text{Fe}(\text{CO})_4(\text{CTe})$ appear to be possible even though dimerization of these monomers into coupled C_2E_2 structures are exothermic processes.



8E-I (C_{2h} , 0.0, 0.0, 0.0)

Figure 2. Optimized lowest energy $\text{Fe}_2(\text{CO})_8(\text{CE})_2$ structures using the B3LYP method. From Figure 2 to 4, the black, blue, and red parameters represent those for the S, Se, and Te derivatives, respectively. Symmetry point groups and relative energies (in kcal/mol) are given in parentheses. The first, second, and third relative energies listed are for E = S, Se, and Te, respectively.

3.2 $\text{Fe}_2(\text{CO})_7(\text{CE})_2$

Several different $\text{Fe}_2(\text{CO})_7(\text{CE})_2$ structures were investigated. These include three possible coupled $\text{Fe}_2(\text{CO})_7(\text{C}_2\text{E}_2)$ structures in both singlet and triplet spin states as well as the uncoupled $\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-CE})_2$ structure corresponding to the lowest energy thiocarbonyl structure $\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-CS})_2$ found in the previous DFT study (Figure S1 in the Supporting Information).³⁴ The latter structure was designated as **27-1** in the 2009 paper and, for consistency, is designated here as **7S-IV** (Figure 3). Note that the coupled $\text{Fe}_2(\text{CO})_7(\text{C}_2\text{S}_2)$ structure **7S-I** is predicted to lie 10.9 kcal/mol in energy below the lowest energy uncoupled $\text{Fe}_2(\text{CO})_7(\text{CS})_2$ structure **7S-IV** found in the previous DFT study.³⁴ In addition two other singlet coupled $\text{Fe}_2(\text{CO})_7(\text{C}_2\text{S}_2)$ structures **7E-II** and **7E-VI** are found to lie in energy below the uncoupled structure **7E-IV**. The triplet $\text{Fe}_2(\text{CO})_7(\text{CE})_2$ structures of a given type are found consistently to have higher relative

energies than the corresponding singlet structures. Thus, only four representative singlet structures are discussed in this paper for each chalcogen (Figure 3).

The lowest energy $\text{Fe}_2(\text{CO})_7(\text{CE})_2$ structures **7E-I** are derived from **8E-I** by loss of a terminal CO group (Figure 3). This leads to shortening of the Fe-C distances to $\sim 1.94 \pm 0.01 \text{ \AA}$ and the Fe-E distances to 2.154 \AA (E = S), 2.278 \AA (E = Se), and 2.472 \AA (E = Te) for the bonding of the ECCE ligand to the $\text{Fe}(\text{CO})_3$ unit. The shortening of the Fe-E distances by $\sim 0.2 \text{ \AA}$ in going from the $\text{Fe}(\text{CO})_4$ unit in **8E-I** to the $\text{Fe}(\text{CO})_3$ unit in **7E-1** suggests Fe=E double bonds to the $\text{Fe}(\text{CO})_3$ iron atom using one electron from the iron atom and three electrons from the chalcogen (including the two electrons of one of the lone pairs in **8E-1**). The interpretation of the Fe=S bond to the $\text{Fe}(\text{CO})_3$ group in **7E-1** as a formal double bond is supported by the large Wiberg bond index (WBI) of 1.19 for the S=Fe bond to the $\text{Fe}(\text{CO})_3$ unit in **7E-I** relative to the WBI of 0.70 for the S-Fe bonds to the $\text{Fe}(\text{CO})_4$ units in **8S-1**. Thus in **7E-1** the dihapto η^2, η^2 -ECCE ligand acts as a six-electron donor to the pair of iron atoms, thereby giving each iron atom the favored 18-electron rare gas configuration. The η^2 -EC(CE)-Fe bond dissociation energies from the $\text{Fe}(\text{CO})_3$ iron atom in **7E-1** are relatively high at $58.5 \pm 2.0 \text{ kcal/mol}$, which is roughly 20 kcal/mol greater than those in **8E-I** (Table S1 in SI) and supports this interpretation of the bonding of the η^2, η^2 -ECCE ligand to the $\text{Fe}(\text{CO})_3$ group in **7E-1**.

The second lowest energy $\text{Fe}_2(\text{CO})_7(\text{CE})_2$ structures **7E-II** (Figure 3), lying 4.1 kcal/mol (**7S-II**), 3.3 kcal/mol (**7Se-II**), and 1.3 kcal/mol (**7Te-II**) above the global minima **7S-I**, have a different type of bridging ECCE ligand, which can be formally derived from the acetylenedithiolate dianion $[\text{SC}\equiv\text{CS}]^{2-}$ (Figure 3). The $\text{C}\equiv\text{C}$ triple bond of this dianion is π -bonded to the $\text{Fe}(\text{CO})_4$ iron thereby giving that iron atom the favored 18-electron configuration (See Figure S6 in the Supporting Information). Such coordination of the $\text{C}\equiv\text{C}$ triple bond bends the originally linear SCCS unit in the metal-free linear acetylenedithiolate into the *cis* configuration in **7E-II**. The two sulfur atoms of the acetylenedithiolate can then form a bidentate five-membered chelate ring with the $\text{Fe}(\text{CO})_3$ iron. The resulting S \rightarrow Fe bonds in the five-membered $\text{C}_2\text{S}_2\text{Fe}$ chelate ring involve three bonding orbitals, namely a three-center S-Fe-S π bond (HOMO in Figure S6), an occupied $(\text{SC}_2\text{S})\text{Fe}(\text{CO})_4$ back bonding orbital (HOMO-3 in Figure S6), and a three-center S-Fe-S σ bond (HOMO-1 in Figure S6). The three-center S-Fe-S σ and π bonds correspond to the pair of sulfur atoms functioning as an effective net four-electron donor to the $\text{Fe}(\text{CO})_3$ iron atom. The average Fe-S bond order appears to be 1.5, which is consistent with an intermediate Fe-S distance of 2.287 \AA in the chelate $\text{C}_2\text{S}_2\text{Fe}$ ring between the singly bonded Fe-S distance of 2.358 \AA in **8S-I** and the doubly bonded Fe=S distance of 2.154 \AA in **7S-I**. This interpretation of the bonding in **7E-II**

gives the $\text{Fe}(\text{CO})_3$ iron atom as well as the $\text{Fe}(\text{CO})_4$ iron atom the favored 18-electron configuration. The small energy separations between the $\text{Fe}_2(\text{CO})_7(\text{CE})_2$ structures **7E-I** and **7E-II** suggest fluxional systems. In this connection the bridging SCCS ligand in the somewhat related cobalt complex $\text{TpCo}(\text{SCCS})\text{CoTp}$ (Tp = tris(pyrazolyl)borate) has been characterized to exhibit bonding mode **I** in nonpolar solvents but bonding mode **II** in polar solvents.³⁰

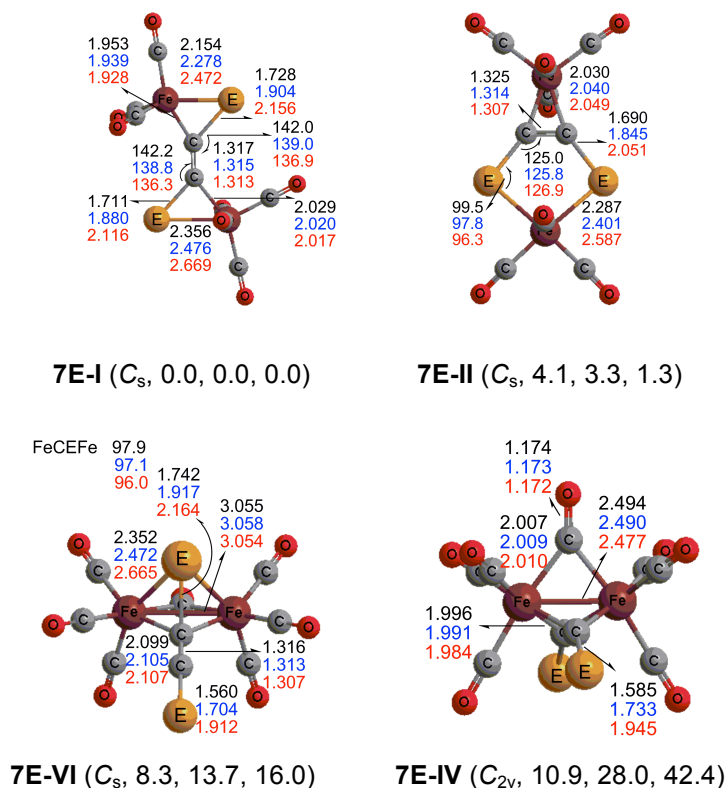


Figure 3. Representative optimized $\text{Fe}_2(\text{CO})_7(\text{CE})_2$ structures. Symmetry point groups and relative energies (in kcal/mol) are given in parentheses. The first, second, and third relative energies listed are for $E = \text{S}$, Se , and Te , respectively.

The $\text{Fe}_2(\text{CO})_7(\text{CE})_2$ structures **7E-III** (Figure 3) are predicted to lie 8.3 kcal/mol (**7S-III**), 13.7 kcal/mol (**7Se-III**), and 16.0 kcal/mol (**7Te-III**) above the corresponding global minima **7E-I** (Figure 3). In the **7E-III** structures the Fe_2 unit is bridged symmetrically both by a CO group and by one of the CE subunits of the $\eta^2\text{-}\mu\text{-ECCE}$ ligand. For the bridging $\eta^2\text{-}\mu\text{-ECCE}$ ligands, the Fe-C distances are ~ 2.01 Å and the Fe-E distances are 2.352 Å (**7S-III**), 2.472 Å (**7Se-III**), and 2.665 Å (**7Te-III**), which are comparable with the Fe-C and Fe-E distances in **8E-I** (Figure 2). The Fe-C-E-Fe dihedral angles in **7E-III** are predicted to be $97 \pm 1^\circ$ suggesting possible donation of electron pairs

from orthogonal π orbitals of the $C\equiv E$ multiple bond to each iron atom. In addition, a chalcogen lone pair from this $C\equiv E$ multiple bond can become involved in the bonding of the η^2 - μ -ECCE ligand to the metal atom making this ligand a six-electron donor to the central Fe_2 unit. However, the predicted $Fe\cdots Fe$ distances of ~ 3.05 Å are too long to interpret as formal single bonds, consistent with the very small WBIs of 0.10. This interpretation of the bonding in **7E-VI** gives each iron atom the favored 18-electron configuration.

The lowest energy uncoupled $Fe_2(CO)_7(CE)_2$ structures **7E-IV** lie 10.9 kcal/mol (**7S-IV**) 28.0 kcal/mol (**7Se-IV**), and 42.4 kcal/mol (**7Te-IV**) above **7E-I** (Figure 3). These increasing energies of the uncoupled structures **7E-IV** relative to the coupled structures **7E-1** from $Fe_2(CO)_7(CS)_2$ to $Fe_2(CO)_7(CTe)_2$ indicate the tendency for such coupling reactions to increase in the sequence $S < Se < Te$ similar to the previous work³² on the mononuclear derivatives $Fe(CO)_3(CE)_2$. In the previous DFT study³⁴ on $Fe_2(CS)_2(CO)_7$ complexes the structure **7S-IV** was assumed to be the global minimum since no lower energy structures were found at that time. We now realize that our choice of starting $Fe_2(CO)_7(CS)_2$ structures for the optimizations carried out at that time was too limited to lead to the lowest energy $Fe_2(CO)_7(C_2S_2)$ structures with coupled CS groups.

3.3 $Fe_2(CO)_6(CE)_2$

The lowest energy uncoupled $Fe_2(CO)_6(\mu-CE)(\eta^2-\mu-CE)$ structures³⁴ and several coupled $Fe_2(CO)_6(C_2E_2)$ structures in both singlet and triplet spin states were considered for $Fe_2(CO)_6(CE)_2$ (Figure 4). Six coupled $Fe_2(CO)_6(\mu-C_2E_2)$ structures and one unusual $Fe_2(CO)_6(\mu-CCE)(\mu-E)$ structure were found at lower energies than the lowest energy uncoupled $Fe_2(CO)_6(CE)_2$ structure **6E-V** with two separate CE ligands. This uncoupled $Fe_2(CO)_6(CS)_2$ structure **6S-V** was designated **26-1** in the previous DFT study.³⁴ At that time structure **6S-V** was assumed to be the lowest energy $Fe_2(CO)_6(CS)_2$ structure since no coupled $Fe_2(CO)_6(C_2S_2)$ structures of any type were found. We now know, however, that the previously discovered uncoupled $Fe_2(CO)_6(CS)_2$ structure **6S-V** lies ~ 30 kcal/mol above the lowest energy coupled $Fe_2(CO)_6(C_2S_2)$ structure **6S-VI**. For selenium and tellurium the corresponding lowest energy uncoupled $Fe_2(CO)_6(CE)_2$ structures **6E-V** lie even further in energy above the lowest energy coupled $Fe_2(CO)_6(C_2E_2)$ structures **6E-VI** at 38.6 kcal/mol ($E = Se$) and 46.4 kcal/mol ($E = Te$).

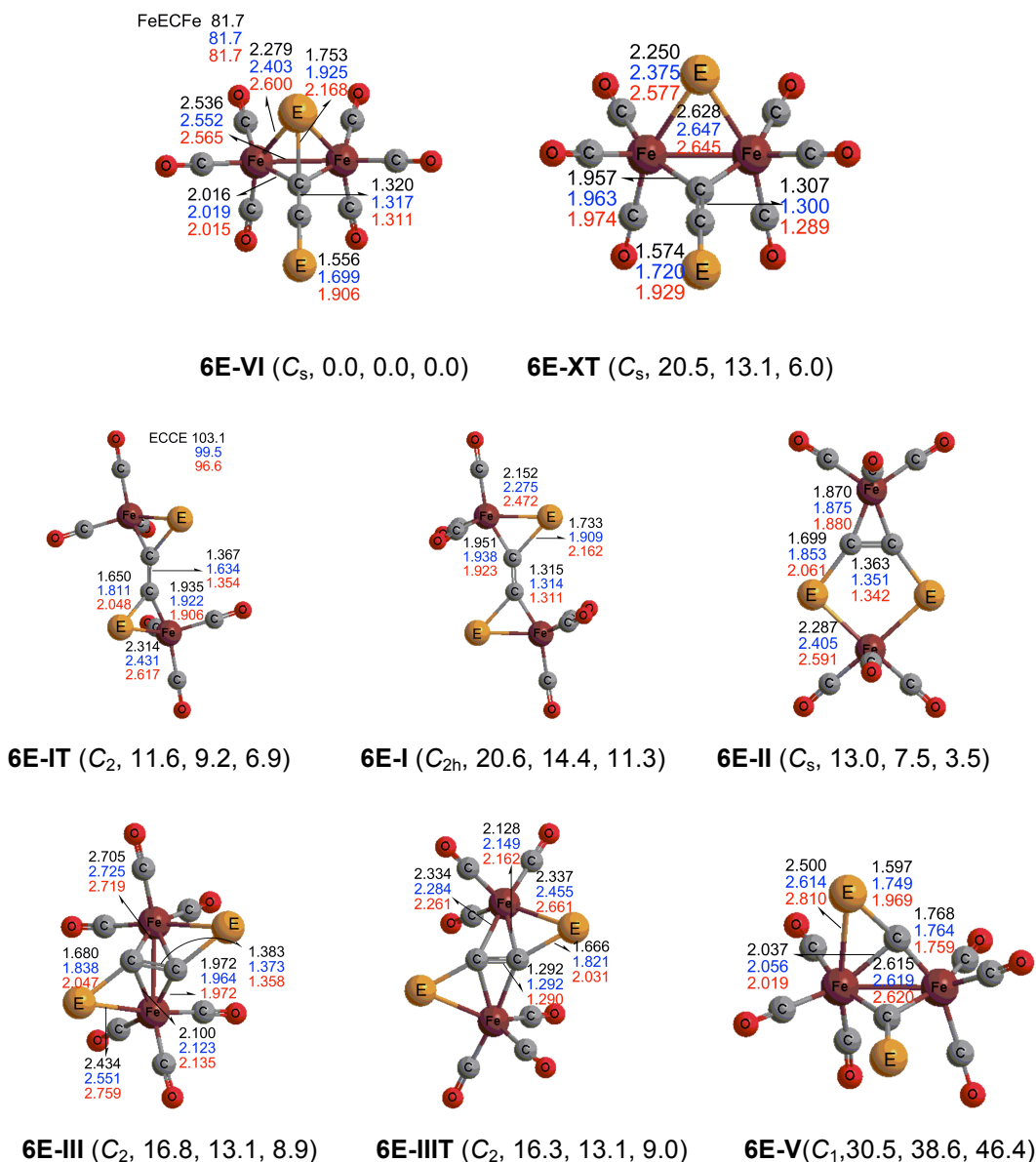


Figure 4. Optimized $Fe_2(CO)_6(CE)_2$ structures. Symmetry point groups and relative energies (in kcal/mol) are given in parentheses. The first, second, and third relative energies listed are for E = S, Se, and Te, respectively.

The lowest energy $Fe_2(CO)_6(C_2E_2)$ structures **6E-VI** (Figure 4) have the ECCE ligand bridging two iron atoms through a C=E double bond leaving an uncomplexed C=E double bond. These structures are derived from **7E-VI** by loss of the bridging CO group. The slightly shortened Fe-C distances to the ECCE ligand in **6E-VI** relative to **7E-VI** are ~ 2.016 Å and the Fe-E distances in **6E-VI** are 2.279 Å for Fe-S, 2.403 Å for Fe-Se, and 2.600 Å for Fe-Te. Furthermore, the Fe-Fe distances in **6E-VI** are predicted to be 2.550 ± 0.015 Å, consistent with bridged Fe-Fe single bonds in **7E-VI**. Such Fe-Fe single bonds

combined with the six-electron donor C_2E_2 groups give each iron atom in **6E-VI** the favored 18-electron configuration.

Attempted optimization of a **6E-VI** structure in the triplet spin state led to cleavage of a C-E bond in the ECCE ligand to give a triplet spin state $Fe_2(CO)_6(\mu-CCE)(\mu-E)$ structure **6E-XT** having a bridging $E=C=C$ carbenoid ligand and a bridging chalcogen atom (Figure 4). The **6E-XT** structures lie 20.5 kcal/mol (E = S), 13.1 kcal/mol (E = Se), and 6.0 kcal/mol (E = Te) above **6E-VI** and thus become increasingly more favorable in the sequence $S < Se < Te$. The bridging $E=C=C$ carbenoid ligand and the bridging chalcogen atom in the **6E-XT** structures each are two-electron donors to the pair of iron atoms. The predicted Fe-Fe distances in **6E-XT** of $2.635 \pm 0.012 \text{ \AA}$ are $\sim 0.1 \text{ \AA}$ longer than those in **6E-VI** and can be interpreted as formal single bonds. This gives each Fe atom in **6E-XT** a 17-electron configuration consistent with a binuclear triplet.

A second type of triplet $Fe_2(CO)_6(C_2E_2)$ structure **6E-IT**, lying 11.6 kcal/mol (E = S), 9.2 kcal/mol (E = Se), and 6.9 kcal/mol (E = Te) above **6E-VI**, can be generated from the **7E-I** structures by loss of a terminal CO group from the $Fe(CO)_4$ unit with concurrent distortion of the ECCE dihedrals from planar to $100 \pm 4^\circ$ (Figure 4). The singlet structures **6E-I** were also found, but are predicted to have higher energies than the corresponding triplet structures, namely 20.6 kcal/mol (E = S), 14.4 kcal/mol (E = Se), and 11.3 kcal/mol (E = Te) above **6E-VI** (Figure 4).

The $Fe_2(CO)_6(C_2E_2)$ structures **6E-II**, lying 13.0 kcal/mol (E = S), 7.5 kcal/mol (E = Se), and 3.5 kcal/mol (E = Te) in energy above **6E-VI**, may be derived from **7E-II** by loss of a CO group from the $Fe(CO)_4$ unit. The six-electron donor bridging ECCE ligand in **7E-II** is retained in **6E-II** with the C-C multiple bond coordinated to one of the $Fe(CO)_3$ groups and the chalcogen atoms forming a chelate with the other $Fe(CO)_3$ group.

The singlet $Fe_2(CO)_6(C_2E_2)$ structure **6E-III** and corresponding triplet structure **6E-IIIT** are nearly degenerate in energy lying 16.5 ± 0.3 kcal/mol (E = S), 13.1 kcal/mol (E = Se), and 9.0 kcal/mol (E = Te) above **6E-VI** (Figure 4). Structures **6E-III** and **6E-IIIT** contain bridging acetylenedithiolate $\eta^4-\mu$ -SCCS ligands similar to those found in two previously reported $Cp_2Mn_2(CS)_2$ structures.³³ This type of bridging acetylenedithiolate ligand donates three electrons to each metal atom when considered formally as a neutral ligand. In the singlet structures **6E-III** the Fe-Fe distances of $2.715 \pm 0.015 \text{ \AA}$ correspond to formal single bonds giving each iron atom the favored 18-electron configuration. However, in the triplet structures **6E-IIIT** the much longer Fe-Fe distances exceeding 3.73 \AA indicate the lack of an iron-iron bond, thereby giving each iron atom the 17-electron configuration for a binuclear triplet.

The uncoupled $\text{Fe}_2(\text{CO})_6(\text{CE})_2$ structures **6E-V** have one two-electron donor bridging μ -CE group and one four-electron donor η^2 - μ -CE group (Figure 4). They are high energy structures relative to the $\text{Fe}_2(\text{CO})_6(\text{C}_2\text{E}_2)$ structures with coupled ECCE ligands discussed above lying 30.5 kcal/mol (E = S), 38.6 kcal/mol (E = Se), and 46.4 kcal/mol (E = Te) in energy above the global minima structures **6E-VI**. These energies of the uncoupled **6E-V** structures relative to the lowest energy coupled **6E-VI** structures increase in the sequence $\text{S} < \text{Se} < \text{Te}$, which is the same as that discussed above for the $\text{Fe}_2(\text{CO})_7(\text{CE})_2$ structures. The Fe–Fe distances of 2.617 ± 0.003 Å in **6E-V** correspond to formal single bonds, thereby giving each iron atom the favored 18-electron configuration.

3.4 Coupling Mechanisms

The coupling of two coordinatively saturated $\text{Fe}(\text{CO})_4(\text{CE})$ molecules to give the $\text{Fe}_2(\text{CO})_8(\text{C}_2\text{E}_2)$ dimers should be rather difficult for kinetic reasons (See Figure S2 in SI), even though the coupled binuclear $\text{Fe}_2(\text{CO})_8(\text{C}_2\text{E}_2)$ are thermodynamically preferred. However, the reactive coordinatively unsaturated species $\text{Fe}(\text{CO})_3(\text{CE})$ with an active site can be generated from $\text{Fe}(\text{CO})_4(\text{CE})$ by pyrolysis or photolysis, and then further react with an additional $\text{Fe}(\text{CO})_4(\text{CE})$ molecule to give an $\text{Fe}_2(\text{CO})_7(\text{C}_2\text{E}_2)$ derivative. A reasonable mechanism was considered as shown in Figure 5. The $\text{Fe}_2(\text{CO})_7(\eta^2$ - μ -CE)(CE) intermediates, namely **Int₁**, are formed by an $\text{Fe}(\text{CO})_4(\text{CE})$ unit donating two π electrons of the CE ligand to the 16-electron species $\text{Fe}(\text{CO})_3(\text{CE})$. The **Int₁** structures were found to have energies of -14.9 (S), -18.2 (Se), and -20.3 (Te) kcal/mol lower than the corresponding free $\text{Fe}(\text{CO})_4(\text{CE})$ and $\text{Fe}(\text{CO})_3(\text{CE})$ fragments. This obviously indicates that the tendency of CE (E= S, Se, Te) to function as four electron donor groups increases in the sequence $\text{S} < \text{Se} < \text{Te}$, arising from the heavier E atoms with increasing atomic radius atoms as well as the reduced electronegativity. The two carbon atoms of CE groups in **Int₁** are not far away from each other (less than 2.73 Å), leading to facile formation of the transition states **TS**. The activation energies of these **TS** structures are predicted to be 12.3 (S), 7.5 (Se), and 3.3 (Te) kcal/mol, respectively. Therefore, kinetic coupling of two CE groups in **Int₁** also follows the sequence $\text{S} < \text{Se} < \text{Te}$. This should be reasonable since the distances of the iron atom to the heavier chalcogens are short enough to view as metal-carbon double bonds for further coupling (Figure S4 in SI). Following the corresponding imaginary vibrational frequencies as well as forward IRC calculations lead to the coupled intermediates **Int₂**, simultaneously releasing 27.5 (S), 33.1 (Se), and 42.1 kcal/mol (Te) from the corresponding **TS** structures. This obviously indicates that such coupling reactions

become increasingly exothermic in the sequence $S < Se < Te$. These **Int₂** structures can convert into **7E-VI** (Figure 3), maybe even **7E-I** (Figure 3). In short, our predicted $Fe_2(CO)_7(C_2E_2)$ structures should be reasonable synthetic targets from both thermodynamic and kinetic considerations. Note, however, that related coupling processes can become sterically difficult, especially for the formation of the intermediates **Int₁**, if one or more carbonyl groups are substituted by bulky ligands.

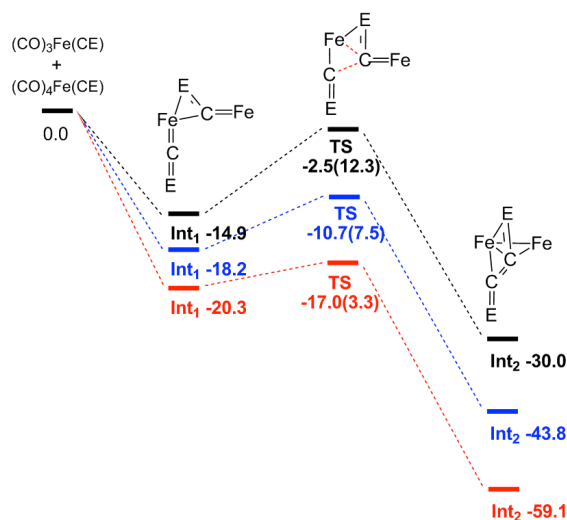


Figure 5. Proposed coupling processes for $Fe_2(CO)_7(CE)_2$ for $E = S$ (black), $E = Se$ (blue), and $E = Te$ (red). The energies are given in kcal/mol.

4. Discussion

Free carbon monoxide is a stable molecule forming diverse metal carbonyls including stable species (e.g., $Cr(CO)_6$) with six discrete CO groups bonded to a central metal atom. Coupling of CO groups to give C_nO_n ligands occurs mainly in actinide chemistry^{5,6,7,8,9} but not generally in d-block transition metal chemistry. The heavier carbon monochalcogenides CE ($E = S, Se, Te$) are not stable molecules in contrast to CO. For example, monomeric CS polymerizes even at low temperatures. However, a variety of stable metal thiocarbonyls, are known, including the iron pentacarbonyl analogue $Fe(CO)_4(CS)$.^{15,16,17,18} The results from this theoretical study suggest that the coordinatively saturated monomers $Fe(CO)_4(CE)$ are stable molecules for kinetic reasons, even though dimerization of these monomers to give the coupled dinuclear $Fe_2(CO)_8(C_2E_2)$ complexes is predicted to be exothermic.

Binuclear iron carbonyl thiocarbonyls of the type $Fe_2(CO)_n(CS)_2$ ($n = 7, 6, 5$) were previously studied extensively by density functional methods leading to a variety of

interesting structures with discrete CS ligands.³⁴ In these structures the CS ligand was found to be more favorable than the CO ligand as a bridging group. Furthermore, four-electron donor η^2 - μ -CS groups were found to be more prevalent than four-electron donor η^2 - μ -CO groups. No $\text{Fe}_2(\text{CO})_n(\text{C}_2\text{S}_2)$ structures with coupled CS ligands were found in this earlier study.

We assumed that this earlier study³⁴ led to the lowest energy $\text{Fe}_2(\text{CO})_n(\text{CS})_2$ structures. However, when we tried to extend this work to the corresponding tellurocarbonyls $\text{Fe}_2(\text{CO})_n(\text{CTe})_2$ all of the low energy structures that we found had C_2Te_2 ligands formed by coupling the two CTe ligands through carbon-carbon bond formation. This led to a reinvestigation of the $\text{Fe}_2(\text{CO})_n(\text{CS})_2$ systems. In this connection, we reoptimized the low-energy $\text{Fe}_2(\text{CO})_n(\text{C}_2\text{Te}_2)$ structures after replacing the tellurium atoms with sulfur atoms. The lowest energy $\text{Fe}_2(\text{CO})_n(\text{C}_2\text{S}_2)$ structures with coupled C_2S_2 ligands were found to lie ~ 11 kcal/mol ($n = 7$) and ~ 30 kcal/mol ($n = 6$) below their lowest energy $\text{Fe}_2(\text{CO})_n(\text{CS})_2$ isomers with discrete CS ligands. Thus the numerous $\text{Fe}_2(\text{CO})_n(\text{CS})_2$ species with discrete CS ligands reported in the previous paper³⁴ all appear to be metastable species with respect to ligand dimerization to give lower energy isomeric $\text{Fe}_2(\text{CO})_n(\text{C}_2\text{S}_2)$ species. Furthermore, the tendency for ligand dimerization in $\text{Fe}_2(\text{CO})_n(\text{CE})_2$ species to give isomeric $\text{Fe}_2(\text{CO})_n(\text{C}_2\text{E}_2)$ species as a function of the chalcogen atom E clearly increases in the sequence $\text{O} < \text{S} < \text{Se} < \text{Te}$.

The scope of metal thiocarbonyl chemistry relative to the extensive scope of metal carbonyl chemistry has been assumed for many years to be limited mainly by the instability of free carbon monosulfide as a synthetic reagent rather than by the inherent instability of species with multiple CS ligands. The research on $\text{Fe}_2(\text{CO})_n(\text{CS})_2$ derivatives reported here suggests that many species with multiple discrete CS ligands might be energetically disfavored relative to isomeric species with coupled C_xS_x ligands.

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Supporting Information: Figure S1: All of the optimized $\text{Fe}_2(\text{CO})_8(\text{CE})_2$ structures; Figure S2: Proposed $\text{Fe}_2(\text{CO})_8(\text{CE})_2$ formation mechanisms; Figure S3: All of the optimized $\text{Fe}_2(\text{CO})_7(\text{CE})_2$ structures; Figure S4: The predicted intermediates and

transition states for coupling $\text{Fe}(\text{CO})_4(\text{CE})$ and $\text{Fe}(\text{CO})_3(\text{CE})$ units; Figure S5: Several important orbitals for **8S-I**, **7S-I**, and **6S-I**; Figure S6: Several important orbitals for **7S-II**; Figure S7: Several important orbitals for **7S-VI** and **6S-VI**; Figure S8: The predicted spin density for **6S-XT**; Table S1: $\text{Fe}_2(\text{CO})_n(\text{EC}_2\text{E})$ ($n = 8, 7, 6$; $\text{E} = \text{S, Se, Te}$) reaction energies; Tables S2 to S16: Total energies (E , in Hartree), relative energies (ΔE , in kcal/mol), spin contamination ($\langle S^2 \rangle$), and numbers of imaginary frequencies (N_{img}) for the optimized $\text{Fe}_2(\text{CO})_n(\text{EC}_2\text{E})$ ($n = 8, 7, 6$; $\text{E} = \text{S, Se, Te}$) structures; Table S17 to S37: the theoretical harmonic vibrational frequencies for $\text{Fe}_2(\text{CO})_8(\text{EC}_2\text{E})$ (4*3 isomers), $\text{Fe}_2(\text{CO})_7(\text{EC}_2\text{E})$ (4*3 isomers), $\text{Fe}_2(\text{CO})_6(\text{EC}_2\text{E})$ (8*3 isomers); Table S38 to S82: the theoretical Cartesian coordinates for $\text{Fe}_2(\text{CO})_8(\text{EC}_2\text{E})$ (18 isomers), $\text{Fe}_2(\text{CO})_7(\text{EC}_2\text{E})$ (21 isomers), $\text{Fe}_2(\text{CO})_6(\text{EC}_2\text{E})$ (24 isomers); Complete Gaussian 09 reference (Reference 52).

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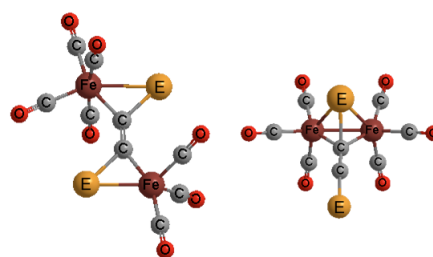
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Table of Contents Entry

The Facile Coupling of Carbon Monochalcogenides to Ethenedichalcogenone Ligands in Binuclear Iron Carbonyl Derivatives: A Theoretical Study

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The lowest energy $\text{Fe}_2(\text{CO})_n(\text{CE})_2$ structures ($\text{E} = \text{S}, \text{Se}, \text{Te}; n = 7, 6$) do not have separate CE ligands but instead have coupled C_2E_2 ligands functioning as four to six-electron donors to the pair of iron atoms. The exothermicity of such coupling reactions as a function of the chalcogen E increases in the sequence $\text{S} < \text{Se} < \text{Te}$.



$\text{Fe}_2(\text{CO})_7(\text{C}_2\text{E}_2)$

$\text{Fe}_2(\text{CO})_6(\text{C}_2\text{E}_2)$
