Supporting Information

Coupling Reactions of Carbon Monochalcogenide Ligands on an Iron Carbonyl Site: Effect of the Chalcogen

Zhong Zhang,*[a] Liang Pu,[a] and R. Bruce King*[b]

[a] College of Science, Northwest A&F University, Yangling, Shanxi 712100, P. R. China

[b] Department of Chemistry and Center for Computational Chemistry, University of Georgia, Athens, Georgia 30602, USA

Supporting Information:

Theoretical Methods

$Fe(CO)_4(CE)_2$

$Fe(CO)_3(CE)_2$

$Fe(CO)_2(CE)_2$

Thermochemistry

Orbital Interactions

Supporting Information

1. 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.[1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16] The popular B3LYP method, hich 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,[17,18] 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 $\alpha_d(C) = 0.75$, $\alpha_d(O) = 0.85$, and $\alpha_d(S) = 0.70$ to the standard Huzinaga-Dunning contracted DZ sets.[19,20,21] The Ahlrichs' DZP basis set[22] for Se atom was designated (14s10p5d/8s6p3d). The loosely contracted DZP basis set for iron is the Wachters primitive set[23] augmented by two sets of p functions and one set of d functions, contracted following Hood, Pitzer and Schaefer,[24] and designated (14s11p6d/10s8p3d). The effective core potential (ECP) basis sets Lanl2DZ[25,26] has been used for Te atom as designated (3s3p/2s2p) for 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,[27] exercising the fine grid option (75 radial shells, 302 angular points) for evaluating integrals numerically,[28] while the tight (10^{-8} hartree) designation is the default for the self-consistent field (SCF) convergence.

The optimized structures are depicted in Figures S1 to S3. Each $Fe(CE)_2(CO)_n$ (E= S, Se, Te; n= 4, 3, 2) structure is designated as **nE-x** where **n** is the number of CO groups, **E** is the chalcogen $(C_2E_2)/(CE)_2$ molecule(s), and **x** represents the binding mode in Scheme 2. Triplet structures are indicated by **T**. Thus the singlet η^2-E-C bonded structure of $Fe(CS)_2(CO)_4$ is designated **4S-a**.

Supporting Information
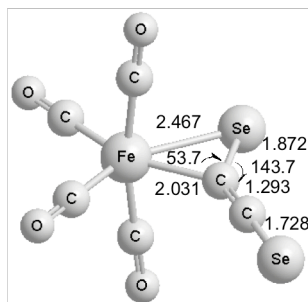
2. Results

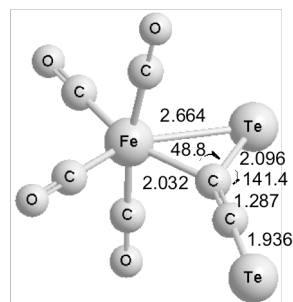### 2.1 Fe(CO)$_4$(CE)$_2$
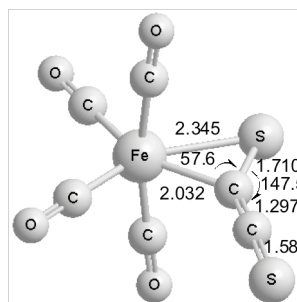
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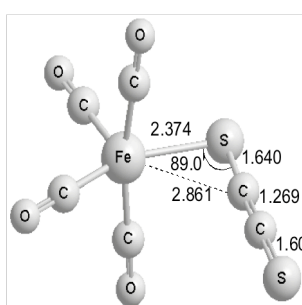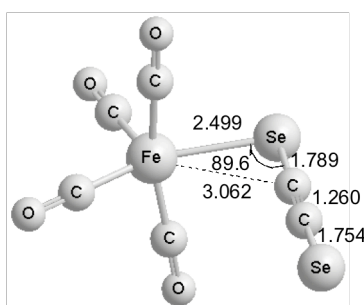
4S-aT(C_s, 10.2)   **4Se-aT**(C_s, 10.1)   **4Te-aT**(C_s, 11.4)
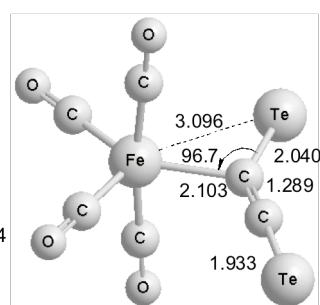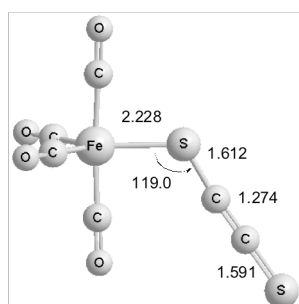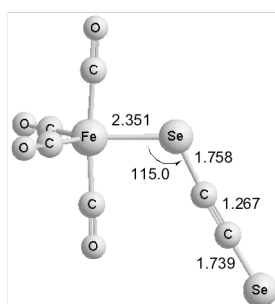
4S-b(C_s, 13.5)   **4Se-b**(C_s, 14.0)   **4Te-b**(C_s, 13.5)
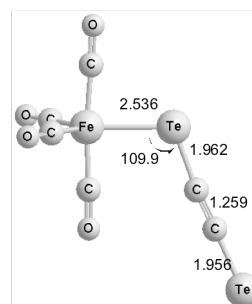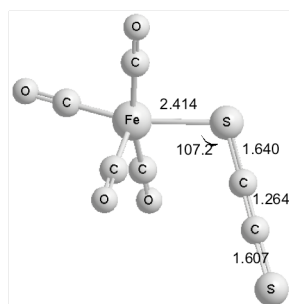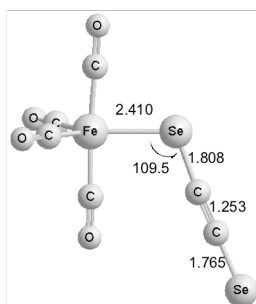
4S-bT(C_1, 12.9)   **4Se-dT**(C_s, 14.2)   **4Te-d**(C_s, 13.5)
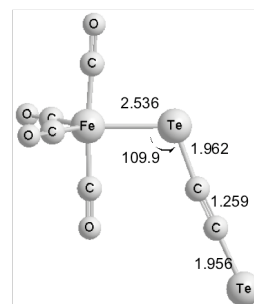
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4S-c(C_{2v}, 14.6)   **4Se-c**(C_{2v}, 18.2)   **4Te-c**(C_{2v}, 19.0)

4S-cT(C_{2v}, 20.5)   **4Se-cT**(C_{2v}, 21.2)

4S-e(C_s, 46.5)   **4Se-e**(C_{2v}, 34.2)   **4Te-e**(C_{2v}, 22.3)
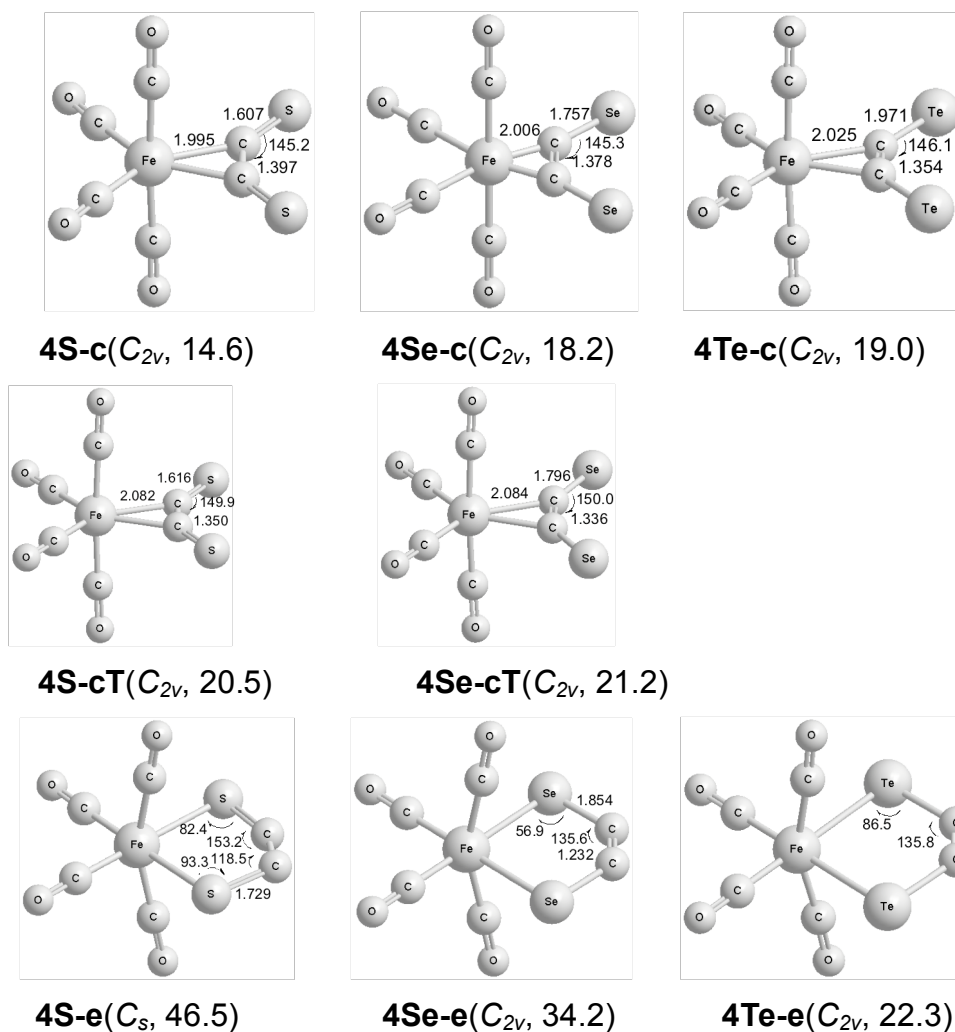
Figure S1. Twenty optimized $Fe(CO)_4(CE)_2$ (E = S, Se , Te). From Fig. S1 to Fig. S3, symmetry and relative energies (unit in kcal/mol) were given in parentheses. All of these structures were found to be genuine minima without any vibrational frequencies.

Table S1. The total energies (*E*, in Hartree), relative energies (ΔE, in kcal/mol), and spin contamination ($<S>^2$) for the optimized $Fe(CO)_4(CS)_2$ structures.

	4S-a	4S-aT	4S-b	4S-bT	4S-c	4S-cT	4S-d
-*E*	2589.7642	2589.7480	2589.7428	2589.7436	2589.7409	2589.7316	2589.6901
ΔE	0.0	10.2	13.5	12.9	14.6	20.5	46.5
$<S>^2$	0.00	2.04	0.00	2.00	0.00	2.02	0.00

Table S2. The total energies (*E*, in Hartree), relative energies (ΔE, in kcal/mol), and spin contamination ($<S>^2$) for the optimized $Fe(CO)_4(CSe)_2$ structures.

	4Se-a	4Se-aT	4Se-b	4Se-bT	4Se-c	4Se-cT	4Se-d
-*E*	6596.4546	6596.4386	6596.4323	6596.4320	6596.4256	6596.4208	6596.4001
ΔE	0.0	10.1	14.0	14.2	18.2	21.2	34.2
$<S>^2$	0.00	2.03	0.00	2.05	0.00	2.02	0.00

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Table S3. The total energies (E, in Hartree), relative energies (ΔE, in kcal/mol), and spin contamination ($<S>^2$) for the optimized $Fe(CO)_4(CTe)_2$ structures.
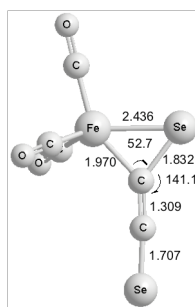
CTe	4Te-a	4Te-aT	4Te-b	4Te-bT	4Te-c	4Te-cT	4Te-d
E	1809.4805	1809.4623	1809.4651	1809.4589	1809.4502	1809.4483	1809.4449
ΔE	0.0	11.4	9.6	13.5	19.0	CTe-TseT	22.3
$<S>^2$	0.00	2.04	2.04	0.00	0.00	2.01	0.00

2.2 Fe(CO)₃(CE)₂
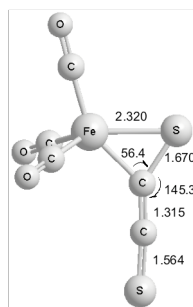
3S-aT(C_s, 0.0)   **3Se-aT**(C_s, 0.0)   **3Te-aT**(C_s, 0.0)
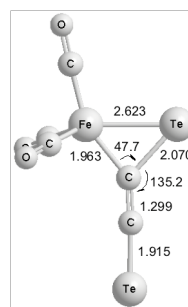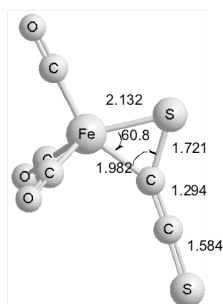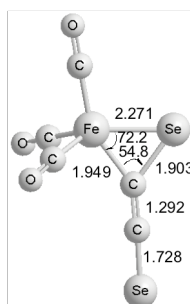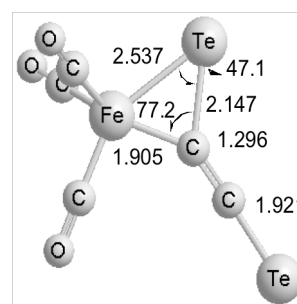
3S-a(C_s, 4.9)   **3Se-a**(C_s, 3.5)   **3Te-a**(C_s, 3.0)
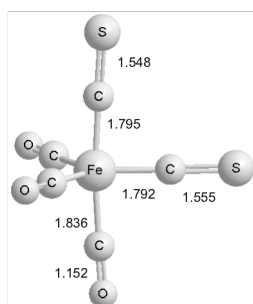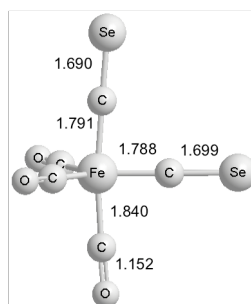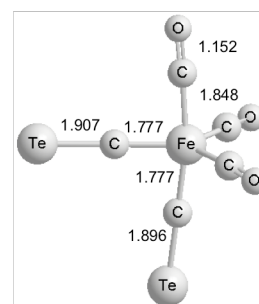
3S-f(C_s, 4.4)   **3Se-f**(C_s, 19.6)   **3Te-f**(C_s, 38.0)
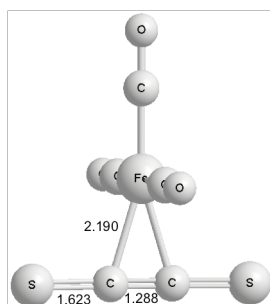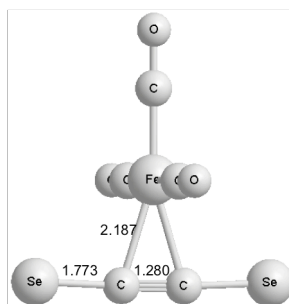
3S-cT(C_{2v}, 15.6)   **3Se-cT**(C_{2v}, 13.4)   **3Te-cT**(C_s, 8.1)
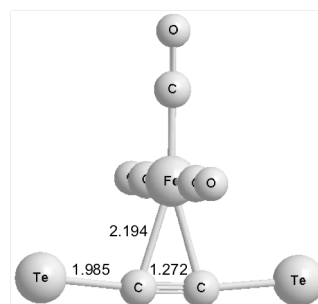
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3Se-c(C_s, 25.8)   **3Te-c**(C_s, 26.5)

3S-e(C_{2v}, 15.1)   **3Se-e**(C_{2v}, 7.5)   **3Te-e**(C_{2v}, 0.3)
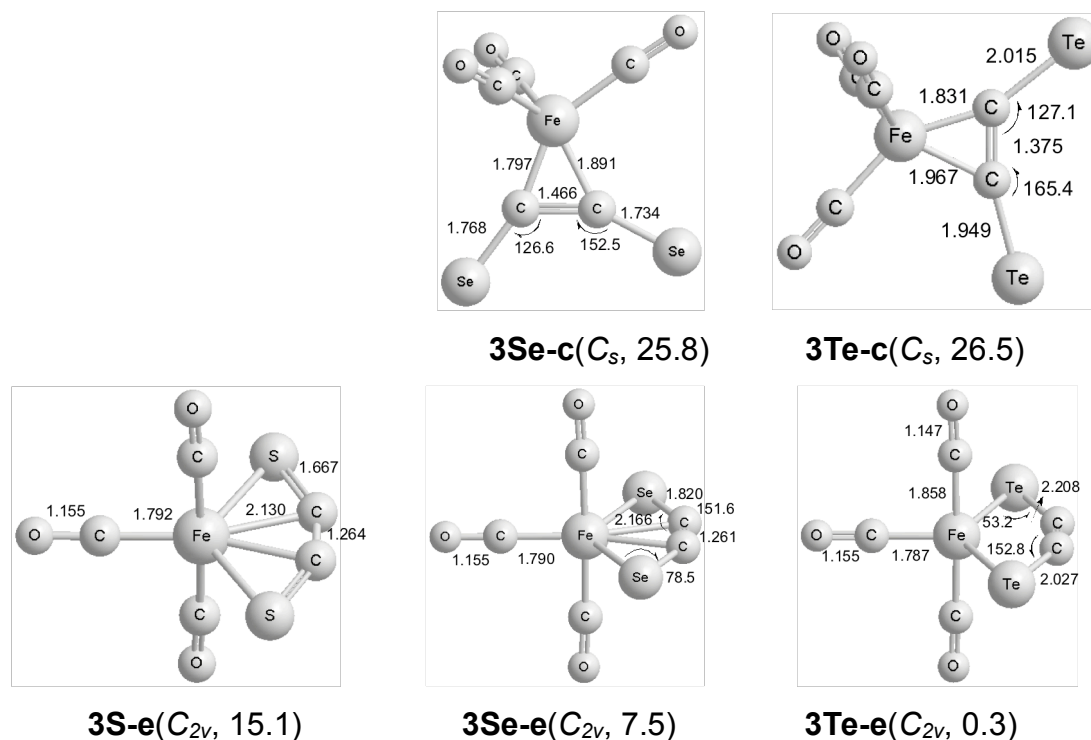
Figure S2. Optimized $Fe(CO)_3(CE)_2$ (E= S, Se, Te) structures.

Table S4. The total energies (E, in Hartree), relative energies (ΔE, in kcal/mol), and spin contamination ($<S>^2$) for the optimized $Fe(CO)_3(CS)_2$ structures.

	3S-aT	3S-f	3S-a	3S-e	3S-cT
-E	2476.4069	2476.3999	2476.3990	2476.3829	2476.3725
ΔE	0.0	4.4	4.9	15.1	21.6
$<S>^2$	2.04	0.00	0.00	0.00	2.05

Table S5. The total energies (E, in Hartree), relative energies (ΔE, in kcal/mol), and spin contamination ($<S>^2$) for the optimized $Fe(CO)_3(CSe)_2$ structures.

	3Se-aT	3Se-a	3S-e	3S-eT	3Se-f	3Se-cT	3Se-c
-E	6483.0951	6483.0895	6483.0832	6483.0737	6483.0639	6483.0631	6483.0540
ΔE	0.0	3.5	7.5	13.4	19.6	20.1	25.8
$<S>^2$	2.04	0.00	0.00	2.04	0.00	2.03	0.00

Table S6. The total energies (E, in Hartree), relative energies (ΔE, in kcal/mol), and spin contamination ($<S>^2$) for the optimized $Fe(CO)_3(CTe)_2$ structures.

	3Te-aT	3Te-e	3Te-a	3Te-eT	3Te-cT	3Te-c	3Te-f
-E	1696.1194	1696.1190	1696.1146	1696.1061	1696.0959	1696.0772	1696.0589
ΔE	0.0	0.3	3.0	8.1	14.5	26.5	38.0
$<S>^2$	2.04	0.00	0.00	2.04	2.03	0.00	0.00

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2.3 Fe(CO)$_2$(CE)$_2$
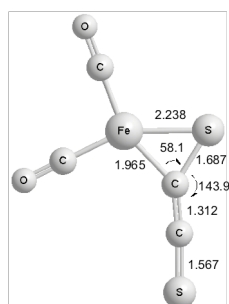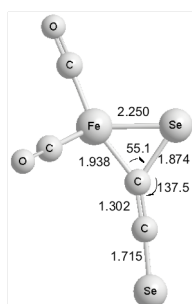
2S-aT(C_1, 0.0)   **2Se-aT**(C_1, 0.0)   **2Te-aT**(C_1, 1.3)
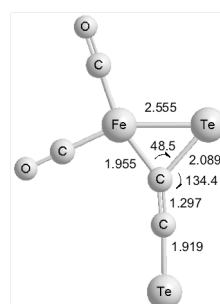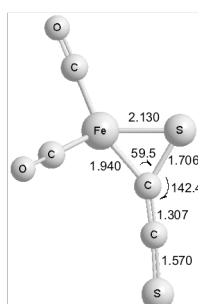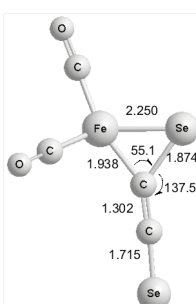
2S-a(C_1, 21.0)   **2Se-a**(C_1, 20.5)   **2Te-a**(C_1, 48.8)
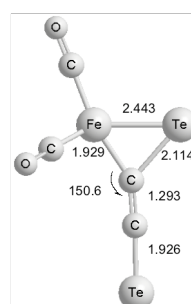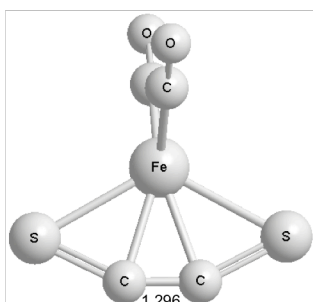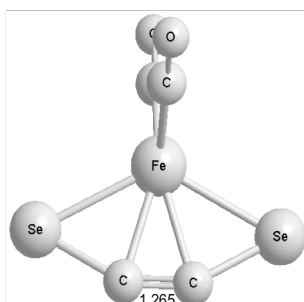
2S-eT(C_s, 12.6)   **2Se-eT**(C_s, 5.0)   **2Te-eT**(C_s, 0.0)
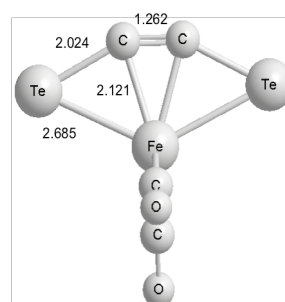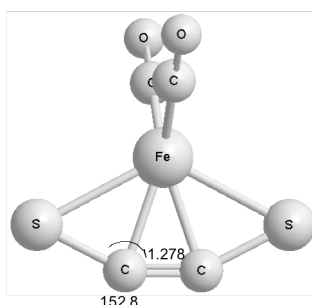
2S-e(C_{2v}, 14.5)   **2Se-e**(C_{2v}, 7.0)   **2Te-e**(C_s, 1.1)

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2S-f(C_2, 20.3)   **2Se-f**(C_1, 33.2)   **2Te-f**(C_s, 22.0)

2Se-hT(C_{2v}, 3.3)   **2Te-hT**(C_1, 1.3)

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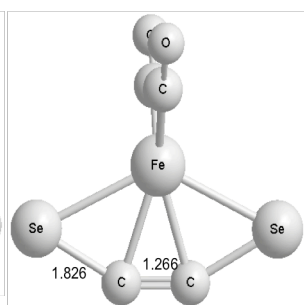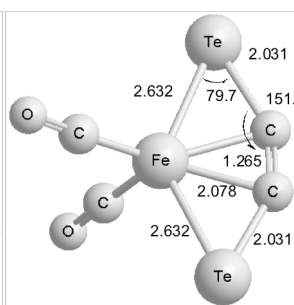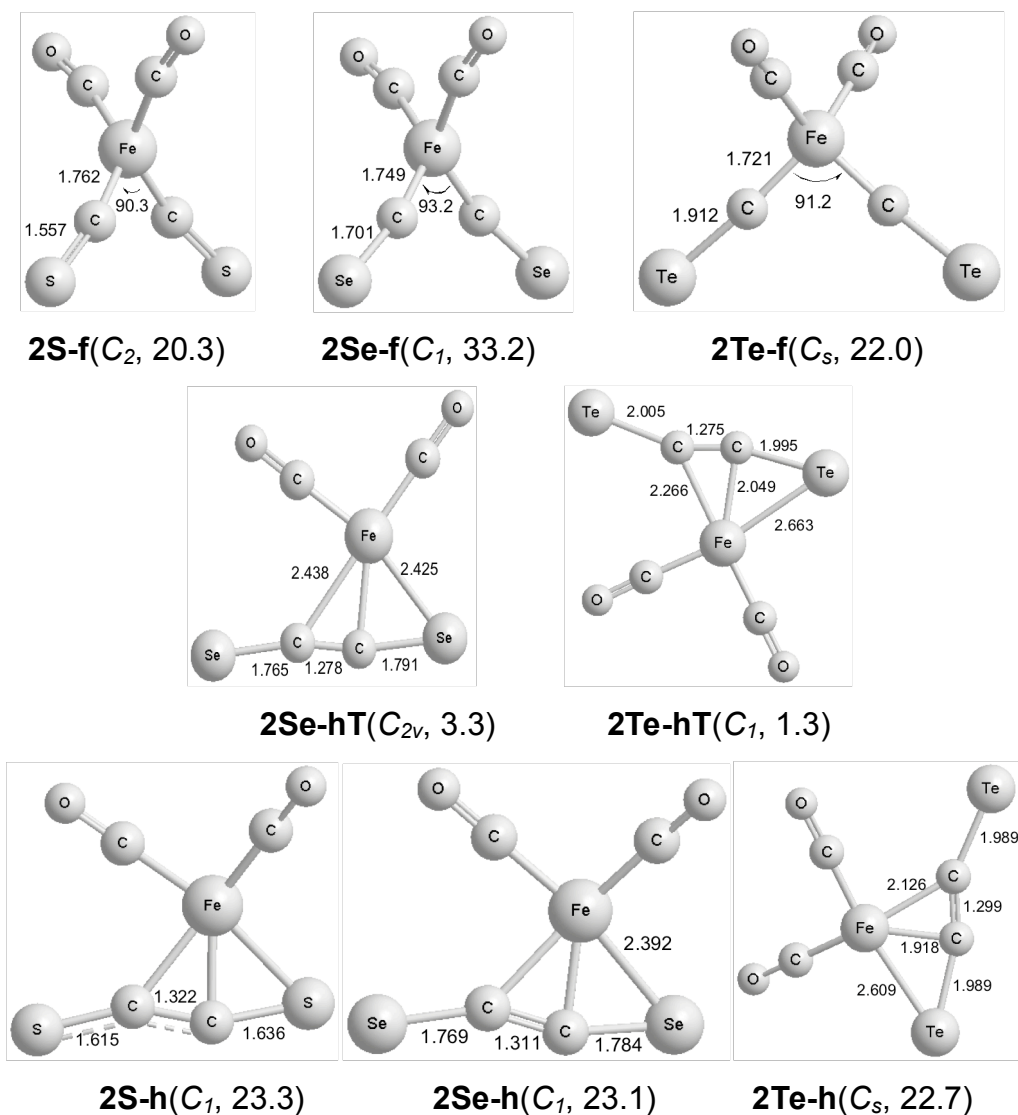
Figure S3. Optimized $Fe(CO)_2(CE)_2$ (E= S, Se, Te) structures.

Table S7. The total energies (E, in Hartree), relative energies (ΔE, in kcal/mol), and spin contamination ($<S>^2$) for the optimized $Fe(CO)_2(CS)_2$ structures.

	2S-aT	2S-eT	2S-e	2S-f	2S-a	2S-h
-E	2363.0425	2363.0225	2363.0194	2363.0101	2363.0091	2363.0053
ΔE	0.0	12.6	14.5	20.3	21.0	23.3
$<S>^2$	2.07	2.22	0.00	0.00	0.00	0.00

Table S8. The total energies (E, in Hartree), relative energies (ΔE, in kcal/mol), and spin contamination ($<S>^2$) for the optimized $Fe(CO)_2(CSe)_2$ structures.

	2Se-aT	2Se-hT	2Se-eT	2Se-e	2Se-a	2Se-h	2Se-f
-E	6369.7301	6369.7249	6369.7221	6369.7189	6369.6975	6369.6932	6369.6771
ΔE	0.0	3.3	5.0	7.0	20.5	23.1	33.2
$<S>^2$	2.07	2.06	2.20	0.00	0.00	0.00	0.00

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Table S9. The total energies (E, in Hartree), relative energies (ΔE, in kcal/mol), and spin contamination ($<S>^2$) for the optimized $Fe(CO)_2(CTe)_2$ structures.

	2Te-aT	2Te-a	2Te-hT	2Te-aT	2Te-f	2Te-h
-E	1582.7544	1582.7527	1582.7524	1582.7523	1582.7193	1582.7182
ΔE	0.0	1.1	1.3	1.3	22.0	22.7
$<S>^2$	2.23	0	2.05	2.07	0	0

2.4 Thermochemistry

Table S10. Energies (units in kcal/mol) for dissociation of the mononuclear complexes $Fe(CE)_2(CO)_n$ into two mononuclear $Fe(CO)_n$ or C_2E_2, for dissociation of one CO group from $Fe(CE)_2(CO)_n$, and for coupling two free CE molecules into C_2E_2.

Reactions	Energy
$Fe(CO)_4(C_2S_2) \rightarrow Fe(CO)_4 + C_2S_2$ (S)	48.6
$Fe(CO)_4(C_2S_2) \rightarrow Fe(CO)_4 + C_2S_2$ (T)	33.6
$Fe(CO)_4(C_2Se_2) \rightarrow Fe(CO)_4 + C_2Se_2$ (S)	50.6
$Fe(CO)_4(C_2Se_2) \rightarrow Fe(CO)_4 + C_2Se_2$ (T)	36.5
$Fe(CO)_4(C_2Te_2) \rightarrow Fe(CO)_4 + C_2Te_2$ (S)	50.0
$Fe(CO)_4(C_2Te_2) \rightarrow Fe(CO)_4 + C_2Te_2$ (T)	36.9
$Fe(CO)_3(C_2S_2) \rightarrow Fe(CO)_3 + C_2S_2$ (S)	74.7
$Fe(CO)_3(C_2S_2) \rightarrow Fe(CO)_3 + C_2S_2$ (T)	59.7
$Fe(CO)_3(C_2Se_2) \rightarrow Fe(CO)_3 + C_2Se_2$ (S)	75.3
$Fe(CO)_3(C_2Se_2) \rightarrow Fe(CO)_3 + C_2Se_2$ (T)	61.2
$Fe(CO)_3(C_2Te_2) \rightarrow Fe(CO)_3 + C_2Te_2$ (S)	73.8
$Fe(CO)_3(C_2Te_2) \rightarrow Fe(CO)_3 + C_2Te_2$ (T)	60.7
$Fe(CO)_4(C_2S_2) \rightarrow Fe(CO)_3(C_2S_2) + CO$	9.1
$Fe(CO)_4(C_2Se_2) \rightarrow Fe(CO)_3(C_2Se_2) + CO$	10.5
$Fe(CO)_4(C_2Te_2) \rightarrow Fe(CO)_3(C_2Te_2) + CO$	11.4
$Fe(CO)_3(C_2S_2) \rightarrow Fe(CO)_2(C_2S_2) + CO$	13.6
$Fe(CO)_3(C_2Se_2) \rightarrow Fe(CO)_2(C_2Se_2) + CO$	13.9
$Fe(CO)_3(C_2Te_2) \rightarrow Fe(CO)_2(C_2Te_2) + CO$	13.9
$2CS \rightarrow C_2S_2$(S)	-46.4
$2CS \rightarrow C_2S_2$(T)	-61.4
$2CSe \rightarrow C_2Se_2$(S)	-64.3
$2CSe \rightarrow C_2Se_2$(T)	-78.4
$2CTe \rightarrow C_2Te_2$(S)	-99.6
$2CTe \rightarrow C_2Te_2$(T)	-112.7

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2.5 Orbital Interactions

4Se-a(HOMO-4)   **3Se-aT**(HOMO)   **3Se-aT**(HOMO-1)   **4Se-b**(HOMO)

4Se-c(HOMO)   **3Se-c**(HOMO)   **4Se-d**(HOMO-2)   **4Se-d**(HOMO-3)

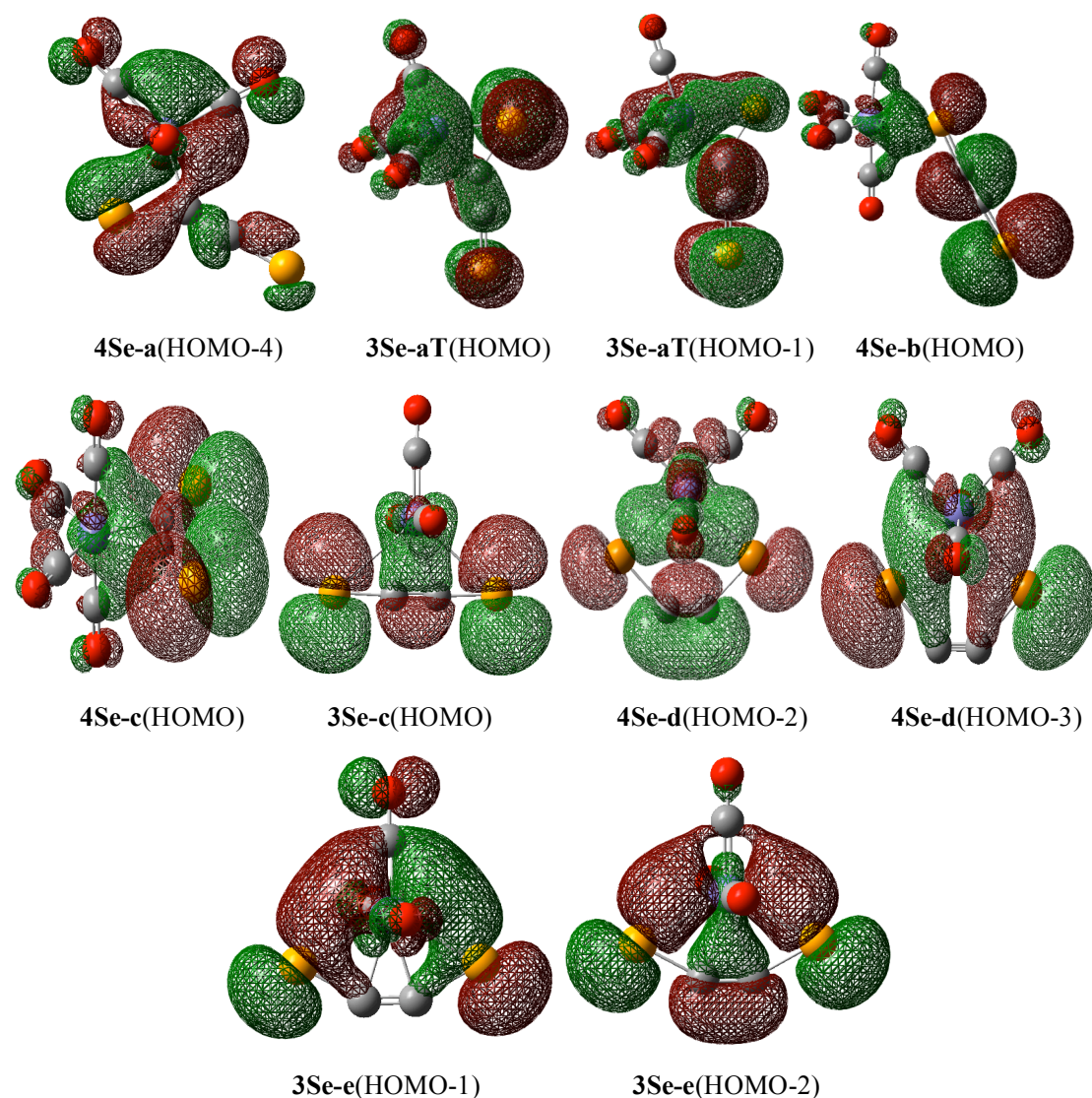**3Se-e**(HOMO-1)   **3Se-e**(HOMO-2)

Fig. S4. Selective orbitals for different modes of Se containing systems.

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