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Iron Carbonyl Thiocarbonyls: Effect of Substituting a Thiocarbonyl Group for a Carbonyl Group in Mononuclear and Binuclear Iron Carbonyl Derivatives

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Density functional theory (DFT) studies on $Fe(CS)(CO)_4$ using the B3LYP and BP86 methods show the axially and equatorially substituted trigonal bipyramidal structures to be essentially degenerate, in accord with the experimental observation of an equilibrium of these two isomers in $Fe(CS)(CO)_4$ synthesized from $Na_2Fe(CO)_4$ and $S{=}CCl_2$. Furthermore, the apically substituted square pyramidal structure of $Fe(CS)(CO)_4$ lies ~5 kcal/mol above the trigonal bipyramidal structures, implying a highly fluxional system. The lowest energy structures for the unsaturated $Fe(CS)(CO)_n$ ($n = 3, 2$) can be derived from the trigonal bipyramidal or square pyramidal structures of $Fe(CS)(CO)_4$ by removal of one or two carbonyl groups, respectively. For the binuclear $Fe_2(CS)_2(CO)_n$ ($n = 7, 6, 5, 4$) derivatives there is a clear energetic preference for bridging CS groups over bridging CO groups in most cases. Thus, the global minimum for $Fe_2(CS)_2(CO)_7$ is a triply bridged structure analogous to $Fe_2(CO)_9$ but with two bridging CS groups and one bridging CO group. The lowest energy structures for the unsaturated $Fe_2(CS)_2(CO)_n$ ($n = 6, 5, 4$) also contain two bridging CS groups, including at least one four-electron donor η^2-μ-CS group bonded to the iron atom not only through the carbon atom but also through the sulfur atom as indicated by relatively short Fe−S distances of ~2.6 Å. The Fe═Fe distances of ~2.4 Å in the highly unsaturated $Fe_2(CS)_2(CO)_n$ ($n = 5, 4$) derivatives with one or two four-electron donor bridging CS groups, respectively, suggest a formal bond order no higher than two, which is sufficient to give both iron atoms the favored 18-electron configuration.

1. Introduction

Metal carbonyl chemistry dates back to the discovery of $[Pt(CO)Cl_2]_2$ in 1868[1] and then to the discovery of the binary metal carbonyl $Ni(CO)_4$ in 1890.[2] A critical factor in the subsequent development of metal carbonyl chemistry as a major area of organometallic and coordination chemistry has been the ready availability and high stability of carbon monoxide. For this reason carbon monoxide can often be used to introduce carbonyl groups into a variety of transition metal complexes, often by reactions at elevated pressures.

Analogous methods cannot be used to synthesize metal thiocarbonyl complexes since carbon monosulfide, CS, is unstable at temperatures above −100 °C and is primarily observed in experiments at low temperatures (e.g., −190 °C).[3,4] Thus indirect methods must be used to introduce thiocarbonyl groups into transition metal complexes with compounds like carbon disulfide (CS_2) or thiophosgene ($S{=}CCl_2$) being common sources of CS groups.[5−9] Using this approach the first metal thiocarbonyl derivative, $(Ph_3P)_2Rh(CS)Cl$, was synthesized in 1966 by Baird and

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Wilkinson[10] by the reaction between $(Ph_3P)_3RhCl$ and CS_2, with elimination of Ph_3PS. The metal thiocarbonyls $Fe(CO)_4(CS)$[11] and $Cr(CO)_5(CS)$[12] closely related to $Fe(CO)_5$ and $Cr(CO)_6$ and with similar physical properties have been synthesized using $S{=}CCl_2$ as the source of the thiocarbonyl groups.

The chemistry of homoleptic iron carbonyls is by no means limited to mononuclear $Fe(CO)_5$. Thus the stable binuclear derivative $Fe_2(CO)_9$ has been prepared,[13−15] and the coordinatively unsaturated $Fe_2(CO)_8$ has been observed in low temperature matrices.[16−18] In addition the trinuclear $Fe_3(CO)_{12}$ is a stable compound.[13,19,20] A characteristic structural feature of these homoleptic polynuclear iron carbonyls is the presence of bridging carbonyl groups. Thus the structures of $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ are $Fe_2(CO)_6(\mu\text{-}CO)_3$ and $Fe_3(CO)_{10}(\mu\text{-}CO)_2$ with three and two bridging carbonyl groups, respectively.

Binuclear and trinuclear iron carbonyl thiocarbonyl derivatives analogous to $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ are not known even though they in principle should be obtainable from the known $Fe(CS)(CO)_4$ by methods related to the conversion of $Fe(CO)_5$ to $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$. This paper uses density functional theory (DFT) to explore possible binuclear $Fe_2(CS)_2(CO)_n$ ($n = 7, 6, 5, 4$) derivatives. Derivatives with one CS group per iron atom are chosen since they are the most likely compounds to be obtained from $Fe(CS)(CO)_4$. In addition the structures of unsaturated mononuclear decarbonylation products $Fe(CS)(CO)_n$ ($n = 3, 2$) are also explored. Questions of interest include the relative bridging tendencies of carbonyl and thiocarbonyl groups, as well as the possibility of preparing iron carbonyl thiocarbonyls with four-electron donor terminal or bridging carbonyl or thiocarbonyl groups. Previous theoretical work by Frenking and co-workers[21] focused on $Fe(CS)(CO)_4$ as part of a general study on $LFe(CO)_4$ derivatives with a wide range of L ligands.

2. Theoretical Methods

Electron correlation effects were considered using DFT methods, which have evolved as a practical and effective computational tool, especially for organometallic compounds.[22−30] Two DFT methods were used in this study. The first functional is the popular B3LYP method, which is the hybrid HF/DFT method using a combination of the three-parameter Becke functional (B3) with the Lee−Yang−Parr (LYP) generalized gradient correlation functional.[31,32] The other DFT method used in the present paper is BP86, which combines Becke's 1988 exchange functional (B) with Perdew's 1986 gradient corrected correlation functional method (P86).[33,34] It has been noted elsewhere that the BP86 method may be somewhat more reliable than B3LYP for the type of organometallic systems considered in this paper.[35−37]

Basis sets have been chosen to provide continuity with a body of existing research on organometallic compounds. Fortunately, DFT methods are far 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.[38−40] The loosely contracted DZP basis set for iron is the Wachters primitive set[41] augmented by two sets of p functions and one set of d functions, contracted following Hood, Pitzer and Schaefer,[42] designated (14s11p6d/10s8p3d). For $Fe(CS)(CO)_4$, $Fe(CS)(CO)_3$, $Fe(CS)(CO)_2$, $Fe_2(CS)_2(CO)_7$, $Fe_2(CS)_2(CO)_6$, $Fe_2(CS)_2(CO)_5$, and $Fe_2(CS)_2(CO)_4$ there are 207, 177, 147, 384, 354, 324, and 294 contracted Gaussian functions, respectively.

The geometries of all structures were fully optimized using the DZP B3LYP and DZP BP86 methods. Vibrational frequencies were determined by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. The corresponding infrared intensities were also evaluated analytically. All of the computations were carried out with the Gaussian 03 program,[43] exercising the fine grid option (75 radial shells, 302 angular points) for evaluating integrals numerically,[44] while the tight (10^{-8} hartree) designation is the default for the self-consistent field (SCF) convergence.

In the search for minima using all currently implemented DFT methods, low magnitude imaginary vibrational frequencies are suspect because of significant limitations in the numerical integration procedures used in the DFT computations. Thus all imaginary vibrational frequencies with a magnitude less than 100i cm^{-1} are considered questionable and are given less weight in the analysis.[44−46] Therefore, we do not always follow such low imaginary vibrational frequencies.

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Table 1. Total Energies (E, in Hartree), Relative Energies (ΔE, in kcal/mol), and Number of Imaginary Frequencies (Nimag) for the Optimized $Fe(CS)(CO)_4$ Structures

		14-1 (C_{3v})	**14-2** (C_{2v})	**14-3** (C_{4v})	**14-4** (C_s)
B3LYP	E	−2153.49117	−2153.49042	−2153.48265	−2153.43724
	ΔE	0.0	0.5	5.4	33.8
	Nimag	0	0	1(71i)	0
BP86	E	−2153.77578	−2153.77448	−2153.76697	−2153.71753
	ΔE	0.0	0.8	5.5	36.6
	Nimag	0	0	1(69i)	0

Table 2. Total Energies (E, in Hartree), Relative Energies (ΔE, in kcal/mol), and Number of Imaginary Frequencies (Nimag) for the Optimized $Fe(CS)(CO)_3$ Structures

		13-1 (C_s)	**13-2** (C_{3v})	**13-3** (C_s)
B3LYP	E	−1926.70322	−2040.09324	−2040.06437
	ΔE	0.0	3.0	21.1
	Nimag	0	0	0
BP86	E	−1926.97047	−2040.36681	−2040.33606
	ΔE	0.0	3.7	23.0
	Nimag	0	0	0

Table 3. Total Energies (E, in Hartree), Relative Energies (ΔE, in kcal/mol), and Number of Imaginary Frequencies (Nimag) for the Optimized $Fe(CS)(CO)_2$ Structures

		12-1 (C_s)	**12-2** (C_{2v})	**12-3** (C_s)	**12-4** (C_s)
B3LYP	E	−1926.70322	−1926.69722	−1926.67847	−1926.67484
	ΔE	0.0	3.8	15.5	17.8
	Nimag	0	1(83i)	0	0
BP86	E	23 > 1926.97047	−1926.96166	−1926.94394	−1926.96750
	ΔE	0.0	5.5	16.6	1.9
	Nimag	0	1(129i)	0	0

The optimized structures are listed in Tables 1−8 and depicted in Figures 1−9. In these figures the top numbers refer to distances obtained by the B3LYP method and the bottom numbers refer to distances obtained by the BP86 method. A given $Fe_a(CS)_a(CO)_b$ structure is designated as **ab-c** where **a** is the number of iron atoms (the same as the number of CS groups), **b** is the number of CO groups, and **c** orders the structures according to their relative energies. Thus the lowest energy structure of $Fe_2(CS)_2(CO)_7$ is designated **27−1**.

3. Results

3.1. Mononuclear Derivatives. 3.1.1. $Fe(CS)(CO)_4$. Four different structures of $Fe(CS)(CO)_4$ are predicted (Figure 1 and Table 1). Structures **14-1**, **14-2**, and **14-4** are genuine minima without any imaginary frequencies. In the most stable $Fe(CS)(CO)_4$ structure, namely **14-1** with C_{3v} symmetry, the linear CS group is in an axial position of the trigonal bipyramid. The C_{2v} structure **14-2**, with the linear CS group in an equatorial position of the trigonal bipyramid, lies 0.5 kcal/mol (B3LYP) or 0.8 kcal/mol (BP86) above **14-1**. These results are consistent with previous work by Frenking and co-workers[21] using the B3LYP functional, a 6-31G basis set for C, O, and S, and a DZP basis set for iron. The very similar energies of the two trigonal bipyramidal structures **14-1** and **14-2** of $Fe(CS)(CO)_4$ imply a fluxional system in accord with the experimental data of Petz.[11] Thus two ν(CS) frequencies were reported for $Fe(CS)(CO)_4$ synthesized from $Na_2Fe(CO)_4$ and $S{=}CCl_2$, suggesting that the observed species is a mixture of **14-1** and **14-2**.

The C_{4v} structure of $Fe(CS)(CO)_4$, namely **14-3** with a linear CS group in the apical position of a square pyramid,

Table 4. Total Energies (E, in Hartree), Relative Energies (ΔE, in kcal/mol), Number of Imaginary Frequencies (Nimag), and the Fe−Fe Bond Distances in Å for the 11 Optimized $Fe_2(CS)_2(CO)_7$ Structures with Two or Three Bridging Groups

		27-1 (C_{2v})	**27-2** (C_s)	**27-3** (C_2)	**27-4** (C_{2v})	**27-5** (C_{2v})	**27-6** (C_{2v})	**27-7** (C_s)	**27-8** (C_s)	**27-9** (C_s)	**27-10** (C_{3v})	**27-11** (C_{3v})
B3LYP	E	−4193.62348	−4193.61322	−4193.61034	−4193.60301	−4193.61035	−4193.60599	−4193.57939	−4193.61017	−4194.17631	−4193.58623	−4193.58116
	ΔE	0	6.4	8.2	12.8	8.2	11	27.7	8.4	14.3	23.4	26.6
	Nimag	0	0	0	1(34i)	1(8i)	1(34i)	1(35i)	1(7i)	0	3(56i,56i,8i)	3(65i,65i,8i)
	Fe−Fe	2.494	2.512	2.733	2.531	2.776	2.775	2.705	3.852	4.734	>3.200	>3.200
BP86	E	−4194.19911	−4194.19191	−4194.18469	−4194.18478	−4194.18182	−4194.17641	−4194.14953	−4193.60543	−4194.17264	−4194.1504	−4194.14445
	ΔE	0	4.5	9.1	9.0	10.9	14.2	31.1	11.3	16.6	30.6	34.3
	Nimag	0	0	0	0	1(10i)	1(20i)	1(29i)	1(9i)	0	3(91i,91i,9i)	3(108i,108i,9i)
	Fe−Fe	2.491	2.508	2.600	2.526	2.751	2.742	2.655	3.842	4.952	>3.200	>3.200

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Table 5. Total Energies (*E*, in Hartree), Relative Energies (Δ*E*, in kcal/mol), Number of Imaginary Frequencies (Nimag), and Fe−Fe Bond Distances in Å for the Optimized $Fe_2(CS)_2(CO)_6$ Structures with Three or Two Bridging Groups

		26-1 (C_1)	**26-2** (C_s)	**26-3** (C_{2v})	**26-4** (C_{2h})	**26-5** (C_{2v})	**26-6** (C_1)	**26-7** (C_{2h})	**26-8** (C_{2h})
B3LYP	*E*	−4080.25985	−4080.25274	−4080.24981	−4080.23955	−4080.23072	−4080.22982	−4080.24221	−4080.22990
	Δ*E*	0.0	4.6	6.4	12.9	18.4	19.0	11.2	18.9
	Nimag	0	0	0	2(47i,34i)	1(9i)	0	1(180i)	1(81i)
	Fe−Fe	2.615	2.503	2.407	2.463	2.469	2.629	2.617	2.592
BP86	*E*	−4080.82394	−4080.82336	−4080.82020	−4080.81093	−4080.80726	−4080.80049	−4080.81335	−4080.80123
	Δ*E*	0.0	0.4	2.3	8.2	11.5	14.7	6.6	14.2
	Nimag	0	0	0	2(55i,33i)	1(17i)	0	1(80i)	0
	Fe−Fe	2.584	2.462	2.413	2.449	2.472	2.591	2.587	2.570

Table 6. Total Energies (*E*, in Hartree), Relative Energies (Δ*E*, in kcal/mol), Number of Imaginary Frequencies (Nimag), and the Fe−Fe Bond Distances in Å for the Optimized $Fe_2(CS)_2(CO)_6$ Structures with One or No Bridging Groups

		26-9 (C_s)	**26-10** (C_{2v})	**26-11** (C_{2h})	**26-12** (C_{2v})	**26-13** (C_1)
B3LYP	*E*	−4080.25369	−4080.22569	−4080.21737	−4080.21263	−4080.21240
	Δ*E*	4.0	21.7	26.8	29.8	29.9
	Nimag	1(11i)	0	2(38i,28i)	3(46i,29i,16i)	3(52i,24i,15i)
	Fe−Fe	2.888	2.888	2.556	2.543	2.553
BP86	*E*	−4080.81341	−4080.78512	−4080.78755	−4080.78136	−4080.78117
	Δ*E*	6.6	24.4	22.8	26.7	26.8
	Nimag	1(17i)	1(23i)	2(60i,25i)	3(62i,24i,13i)	3(66i,23i,12i)
	Fe−Fe	2.829	2.822	2.564	2.551	2.562

Table 7. Total Energies (E, in Hartree), Relative Energies (Δ*E*, in kcal/mol), Number of Imaginary Frequencies (Nimag), and the Fe−Fe Bond Distances for the Optimized $Fe_2(CS)_2(CO)_5$ Structures

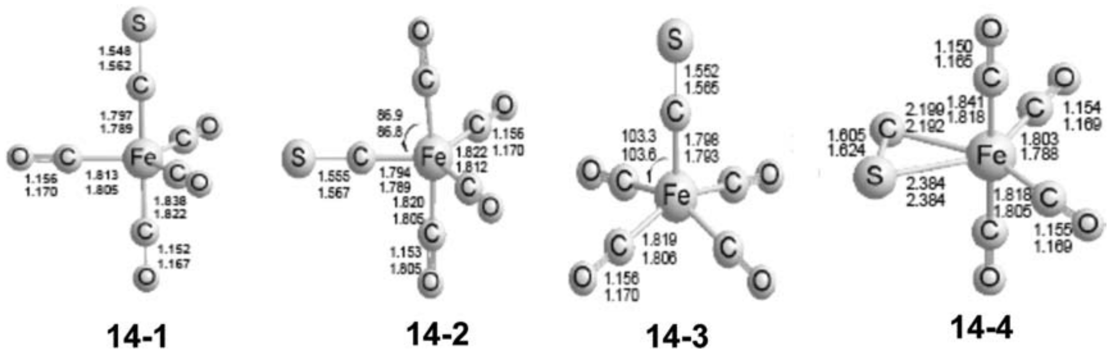
		25-1 (C_s)	**25-2** (C_1)	**25-3** (C_2)	**25-4** (C_{2v})	**25-5** (C_s)
B3LYP	*E*	−3966.90353	−3966.86591	−3966.86671	−3966.86074	−3966.85887
	Δ*E*	0.0	23.6	23.1	26.9	28.0
	Nimag	0	0	1(41i)	1(55i)	1 (54i)
	Fe−Fe	2.437	2.258	2.257	2.206	2.188
BP86	*E*	−3967.4627	(collapses to **25-1**)	−3967.43558	−3967.42826	−3967.42117
	Δ*E*	0.0		17.0	21.6	26.1
	Nimag	1(6i)		0	1(80i)	1(54i)
	Fe−Fe	2.419		2.272	2.215	2.202

Table 8. Total Energies (*E*, in Hartree), Relative Energies (Δ*E*, in kcal/mol), Number of Imaginary Frequencies (Nimag), and the Fe−Fe Bond Distances for the Optimized $Fe_2(CS)_2(CO)_4$ Structures

		24-1 (C_{2h})	**24-2** (C_{2v})	**24-3** (C_1)	**24-4** (C_1)	**24-5** (C_{2v})	**24-6** (C_1)
B3LYP	*E*	−3853.54373	−3853.51985	−3853.51602	−3853.51552	−3853.51179	−3853.49746
	Δ*E*	0.0	15.0	17.4	17.7	20.1	29.0
	Nimag	0	0	0	1(51i)	1(38i)	0
	Fe−Fe	2.408	2.451	2.441	2.450	2.394	2.425
BP86	*E*	−3854.0952	−3854.06861	−3854.07003	−3854.07003	−3854.06667	−3854.05623
	Δ*E*	0.0	16.7	15.8	15.8	17.9	24.5
	Nimag	0	0	0	0	1(59i)	0
	Fe−Fe	2.406	2.441	2.436	2.446	2.381	2.410

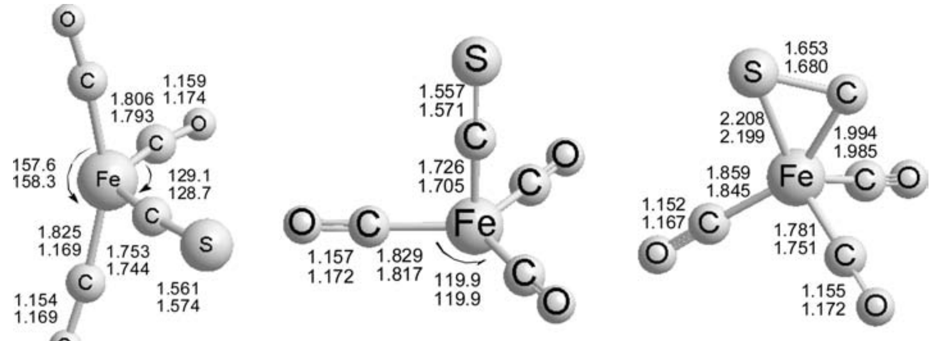
lies 5.4 kcal/mol (B3LYP) or 5.5 kcal/mol (BP86) above **14-1**and has an imaginary vibrational frequency of 71i (B3LYP) or 69i (BP86). Following the corresponding normal mode of **14-3** leads to **14-2**. The very high energy C_s $Fe(CS)(CO)_4$ structure, **14-4**, at 33.8 kcal/mol (B3LYP) or 36.6 kcal/mol (BP86) above **14-1**, has a nonlinear CS group in an equatorial position of the trigonal bipyramid bonded to the iron through both its carbon and sulfur atoms, as indicated by a relatively short Fe−S distance of 2.384 Å.

3.1.2. $Fe(CS)(CO)_3$. Three optimized structures for $Fe(CS)(CO)_3$ were found without imaginary vibrational frequencies (Figure 2 and Table 2). In the lowest lying



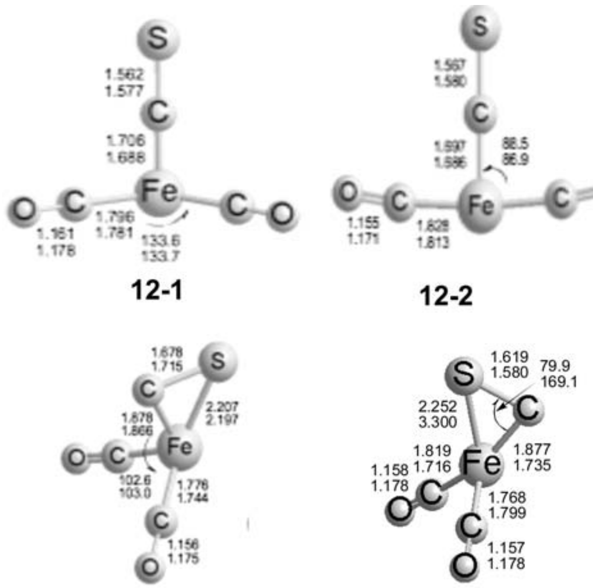
14-1 **14-2** **14-3** **14-4**

Figure 1. Four optimized structures of $Fe(CS)(CO)_4$. In these figures the top numbers refer to distances obtained by the B3LYP method, and the bottom numbers refer to distances obtained by the BP86 method.



13-1 **13-2** **13-3**

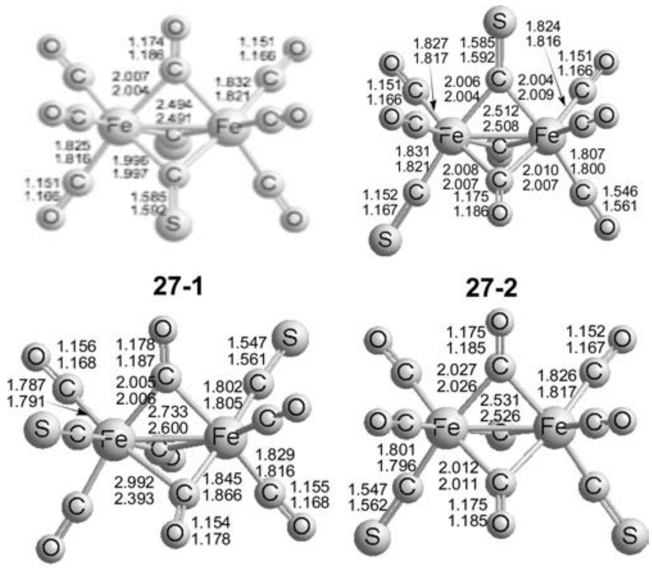
Figure 2. Three optimized structures of $Fe(CS)(CO)_3$.



12-1 **12-2**

12-3 **12-4**

Figure 3. Three optimized structures of $Fe(CS)(CO)_2$.



27-1 **27-2**

27-3 **27-4**

Figure 4. Optimized $Fe_2(CS)_2(CO)_7$ structures with three bridging groups.

structure **13-1** the coordination of the iron atom can be derived from a trigonal bipyramid by removal of an equatorial group with concurrent bending of the axial-Fe-axial angle from 180° to ~158°. The next $Fe(CS)(CO)_3$ structure in terms of energy is **13-2**, lying 3.0 kcal/mol (B3LYP) or 3.7 kcal/mol (BP86) above the global minimum **13-1**.

Structure **13-2** has C_{3v} symmetry with the linear FeCS group on the C_3 axis and distorted tetrahedral coordination for the iron atom. A higher energy $Fe(CS)(CO)_3$ structure, namely **13-3** at 21.1 kcal/mol (B3LYP) or 23.0 kcal/mol (BP86) above **13-1**, has the CS group bonded to the iron atom through both the carbon and sulfur as indicated by Fe−S distances of 2.208 Å (B3LYP) or 2.199 Å (BP86). This CS group in **13-3** thus functions as a formal four-electron donor to give the iron the favored 18-electron configuration.

3.1.3. $Fe(CS)(CO)_2$. Four structures were optimized for $Fe(CS)(CO)_2$ (Figure 3 and Table 3). The global minimum **12-1** by both B3LYP and BP86 methods is a nonplanar T-shaped C_s structure with a C(O)−Fe-C(S)−C(O) dihedral angle of 133.7°. This structure can be derived from the global minimum **13-1** for $Fe(CS)(CO)_3$ (Figure 2) by removal of the carbonyl group cis to the CS group. The next higher lying structure for $Fe(CS)(CO)_2$, namely a planar structure **12-2** at 3.8 kcal/mol (B3LYP) or 5.5 kcal/mol (BP86) above **12-1**, has a significant imaginary vibrational frequency at 83i (B3LYP) or 129i (BP86). Following the corresponding normal mode leads to **12-1**.

In addition to structures **12-1** and **12-2** two additional structures for $Fe(CS)(CO)_2$ were found with a four-electron donor π-bonded CS ligand. Structures **12-3** and **12-4** differ in the relative orientations of the η^2-CS ligand to the carbonyl groups. Structure **12-3** for $Fe(CS)(CO)_2$ is a genuine local minimum lying 15.5 kcal/mol (B3LYP) or 16.6 kcal/mol (BP86) above the global minimum **12-1**. Structure **12-4** is predicted to lie above **12-1** by 17.8 kcal/mol (B3LYP) or 1.9 kcal/mol (BP86). We notice that the two methods give different geometries and energies for **12-4** as indicated by an Fe−S distance of 2.252 Å for the B3LYP structure but 3.300 Å for the BP86 structure. This may relate to the different origins of the two functionals, namely, parameter fitting to experiments for B3LYP and satisfying the uniform electron gas limit for BP86. Thus, for a complicated energy surface these two functionals could behave differently.

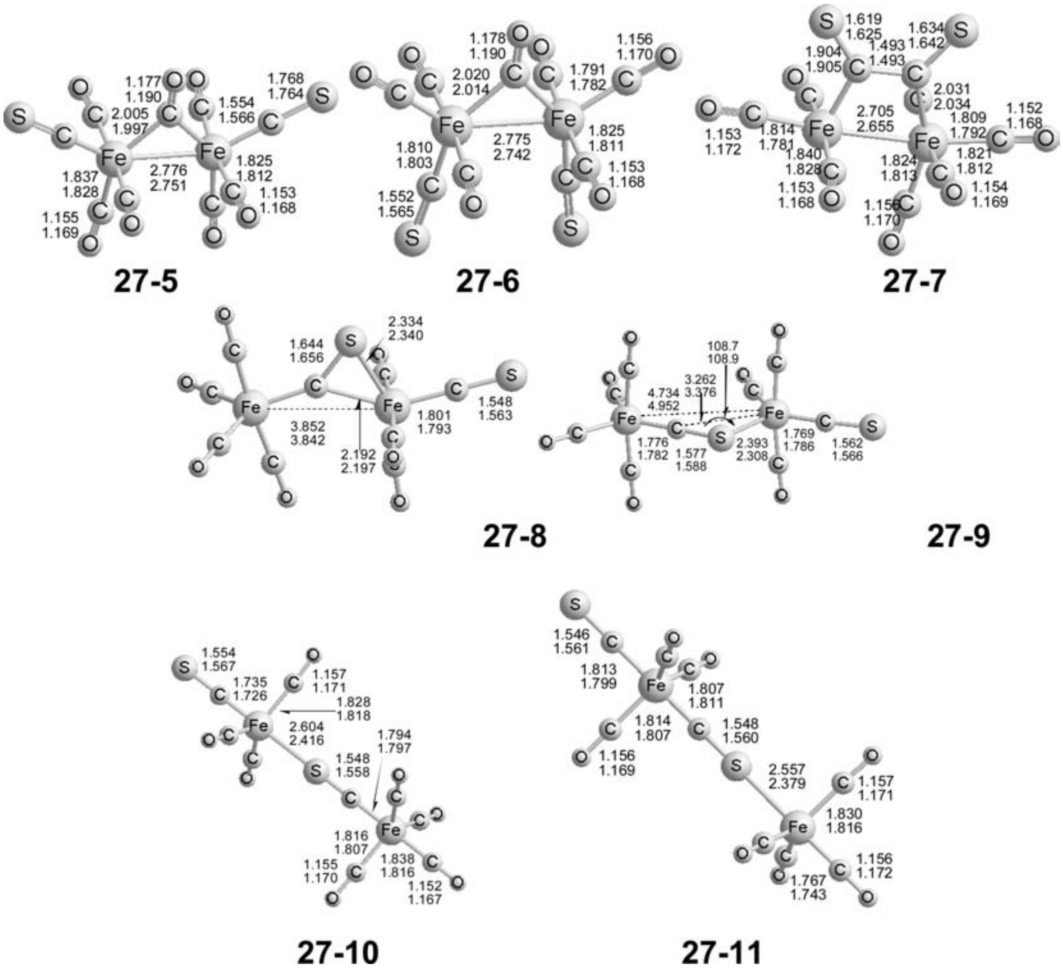


Figure 5. Structures of $Fe_2(CS)_2(CO)_7$ with one bridging group.

3.2. Binuclear Derivatives. 3.2.1. $Fe_2(CS)_2(CO)_7$. Eleven $Fe_2(CS)_2(CO)_7$ structures were optimized in this work. Four of these structures (Figure 4 and Table 4) have three bridging groups, either CO or CS groups. Two of the remaining structures, namely, **27-5** and **27-6** (Figure 5 and Table 4), have a single bridging carbonyl group. One of the structures, namely, **27-7**, has a single unusual bridging C_2S_2 (dithiooxalyl) group. Four of the structures (**27-8**, **27-9**, **27-10**, and **27-11**) have a single four-electron donor bridging CS group bonded to the iron atoms through both the carbon and sulfur atoms.

The lowest energy $Fe_2(CS)_2(CO)_7$ structure **27-1** (Figure 4) has two bridging CS groups and one bridging CO group. This structure is predicted to be a genuine minimum by both the B3LYP and BP86 methods. The Fe−Fe bond distance is predicted to be 2.494 Å (B3LYP) or 2.491 Å (BP86). This compares with the Fe−Fe distance of 2.523 Å determined by X-ray diffraction[15] for the carbonyl analogue $Fe_2(CO)_9$ (= $Fe_2(CO)_6(\mu\text{-}CO)_3$). Our second triply bridged structure **27-2** of $Fe_2(CS)_2(CO)_7$ has one bridging CS group and two bridging CO groups. Structure **27-2** is a genuine minimum, lying 6.4 kcal/mol (B3LYP) or 4.5 kcal/mol (BP86) higher in energy than **27-1**. The Fe−Fe bond distance of 2.512 Å (B3LYP) or 2.508 Å (BP86) in **27-2** is slightly longer than that in **27-1**.

The final two triply bridging $Fe_2(CS)_2(CO)_7$ structures are **27-3** and **27-4** with three bridging CO groups and two terminal CS groups in addition to four terminal CO groups (Figure 4 and Table 4). These two structures differ in the relative positions of the terminal CS groups. Structure **27-3** is a genuine minimum by both B3LYP or BP86 and is predicted to lie 8.2 kcal/mol (B3LYP) or 9.1 kcal/mol (BP86) higher in energy than the global minimum **27-1**. The Fe−Fe bond distance of 2.733 Å (B3LYP) or 2.600 Å (BP86) in **27-3** is significantly longer than that in **27-1** and **27-2**. Structure **27-4** is predicted to lie 12.8 kcal/mol (B3LYP) or 9.0 kcal/mol (BP86) higher in energy than **27-1**. Structure **27-4** is a genuine minimum by BP86 but has a small imaginary vibrational frequency of 31i by B3LYP. The Fe−Fe bond distance in **27-4** is 2.531 Å (B3LYP) or 2.526 Å (BP86).

Two structures for $Fe_2(CS)_2(CO)_7$ were found with a single bridging carbonyl group and both thiocarbonyl groups as terminal groups (Figure 5 and Table 4). Structure **27-5** lies 8.2 kcal/mol (B3LYP) or 10.9 kcal/mol (BP86) higher in energy than the **27-1** global minimum. However, it has a small imaginary vibrational frequency of 8i (B3LYP) or 10i (BP86). Structure **27-6** for $Fe_2(CS)_2(CO)_7$ is predicted to lie 11.0 kcal/mol (B3LYP) or 14.2 kcal/mol (BP86) higher in energy than **27-1**, with a small imaginary vibrational

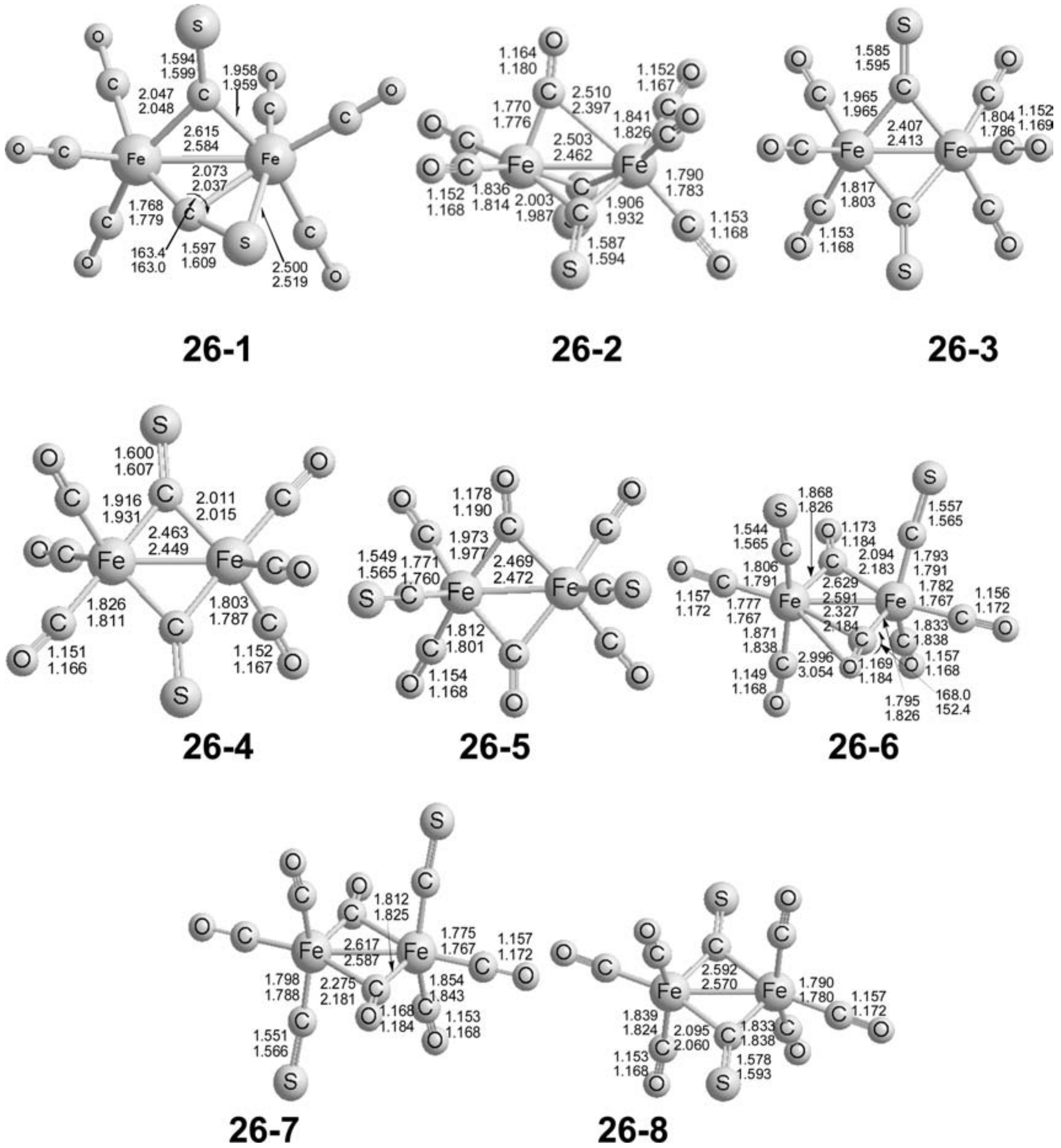


Figure 6. Eight optimized structures of $Fe_2(CS)_2(CO)_6$ with two or three bridging groups.

frequency of 34i (B3LYP) or 20i (BP86). The Fe−Fe bond distances in the singly bridged structures **27-5** and **27-6** of 2.76 ± 0.02 Å are significantly longer than the Fe−Fe distances of 2.49 ± 0.02 Å in the triply bridged structures **27-1**, **27-2**, and **27-4** even though in all of these $Fe_2(CS)_2(CO)_7$ structures the iron−iron bonds are necessarily single bonds. Attempted optimization of an $Os_2(CO)_9$-like structure with a single bridging CS group led to a relatively high energy structure **27-7** of $Fe_2(CS)_2(CO)_7$ (Figure 5), in which the two CS ligands couple to form a C−C bond to give a bridging μ-SCCS (dithiooxalyl) group.

Four singly bridged structures with formally four-electron donor bridging CS groups were found, namely **27-8**, **27-9**, **27-10**, and **27-11** (Figure 5 and Table 4). A four-electron donor bridging carbonyl group of a type similar to that predicted for structures **27-8** and **27-9** is found in the heterobinuclear molybdenum−tungsten complex HB-$(pz)_3(OC)_2W(\mu\text{-CS})Mo(CO)_2(\eta^5\text{-}C_9H_7)$, which has been characterized by X-ray diffraction.[47] Structure **27-8** lies in energy above **27-1** by 8.4 kcal/mol (B3LYP) or 11.3 kcal/mol (BP86). Both methods predict a negligible imaginary frequency, namely 7i (B3LYP) or 9i (BP86). Structure **27-8** is derived from an equatorial CS structure of $Fe(CO)_4(CS)$, namely **14-2** in Figure 1, bonding to a $Fe(CO)_3(CS)$ unit through the thiocarbonyl group of the former, which now becomes an four-electron donor η^2-μ-CS group. The very long Fe···Fe distance in **27-8** is 3.852 Å (B3LYP) or 3.842 Å (B3LYP) and indicates no direct bonding between the iron atoms. However, since the bridging thiocarbonyl group in **27-8** is a four-electron donor, each Fe atom has the favorable 18-electron configuration. Structure **27-9**, which is similar to **27-8**, but with an internal rotation, lies energetically higher than **27-1** by 14.3 kcal/mol (B3LYP) or 16.6 kcal/mol (BP86). The Fe···Fe distance is even longer in **27-9** at 4.734 Å (B3LYP) or 4.952 Å (BP86).

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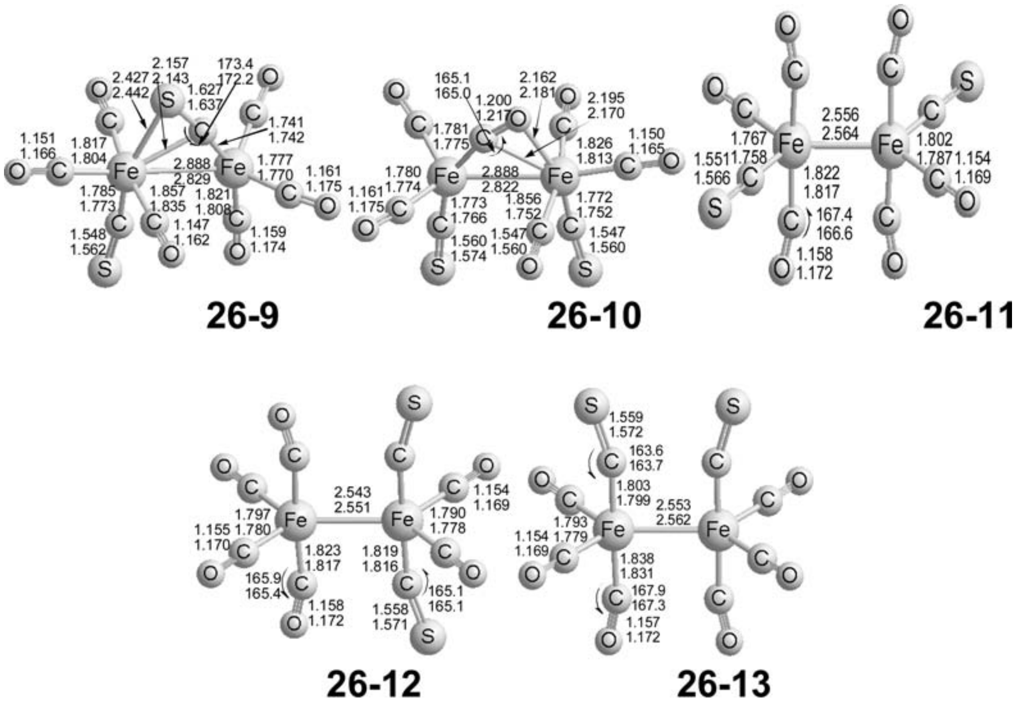
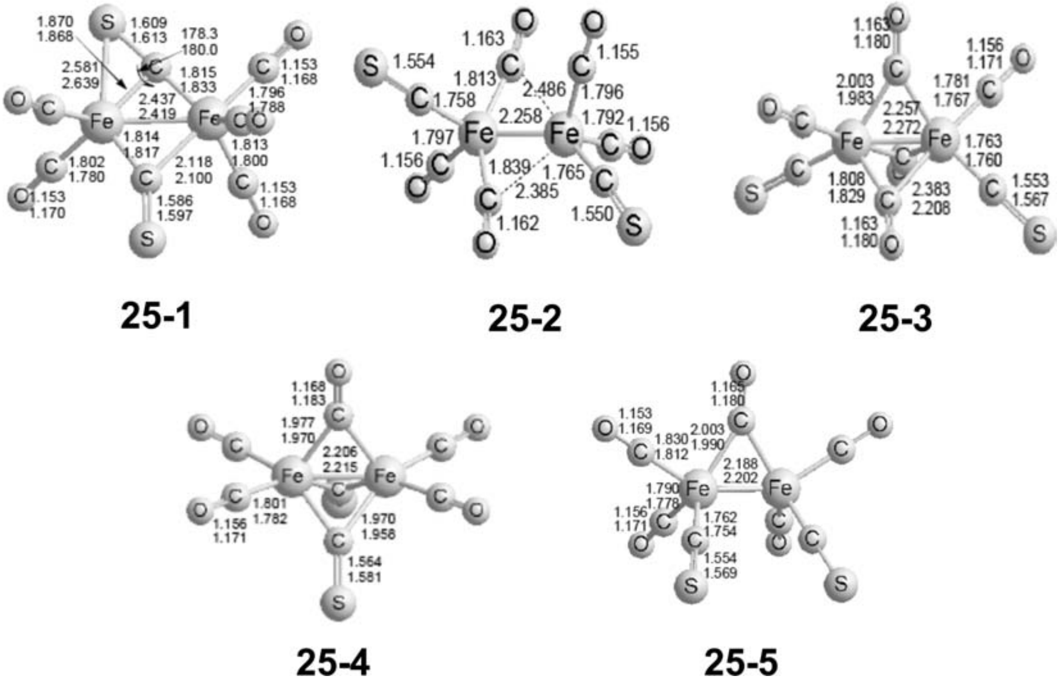
(47) Doyle, R. A.; Daniels, L. M.; Angelici, R. J.; Stone, F. G. A. *J. Am. Chem. Soc.* **1989**, *111*, 4995.



26-9 **26-10** **26-11**

26-12 **26-13**

Figure 7. Six optimized structures of $Fe_2(CS)_2(CO)_6$ with one or no bridging groups.



25-1 **25-2** **25-3**

25-4 **25-5**

Figure 8. Five optimized structures of $Fe_2(CS)_2(CO)_5$ within 30 kcal/mol of the global minimum.

The structures **27-10** and **27-11** of $Fe_2(CS)_2(CO)_7$ both have an unusual linear bridging thiocarbonyl group bonded to one iron atom only through its carbon atom and bonded to the other iron atom only through its sulfur atom. Thus the bridging thiocarbonyl group in **27-10** and **27-11**, although a formal four-electron donor, is of a very different type than the four-electron donor bridging thiocarbonyl groups in **27-8** and **27-9**. The difference between structures **27-10** and **27-11** is that the bridging CS ligand is bonded to the iron atom bearing the terminal CS group through the sulfur atom in **27-10** but through the carbon atom in **27-11**. Structure **27-10** lies at a relatively high energy, namely, 23.4 kcal/mol (B3LYP) or 30.6 kcal/mol (BP86) above the global minimum **27-1**. Structure **27-11** lies at an even higher energy, namely 26.6 kcal/mol (B3LYP) or 34.3 kcal/mol (BP86) above **27-1**. Both structures **27-10** and **27-11** have three small imaginary frequencies. Each Fe atom in **27-10** and **27-11** has the favorable 18-electron configuration. A CS ligand bridging a pair of metal atoms by bonding through one metal atom through the carbon atom and to the other metal atom

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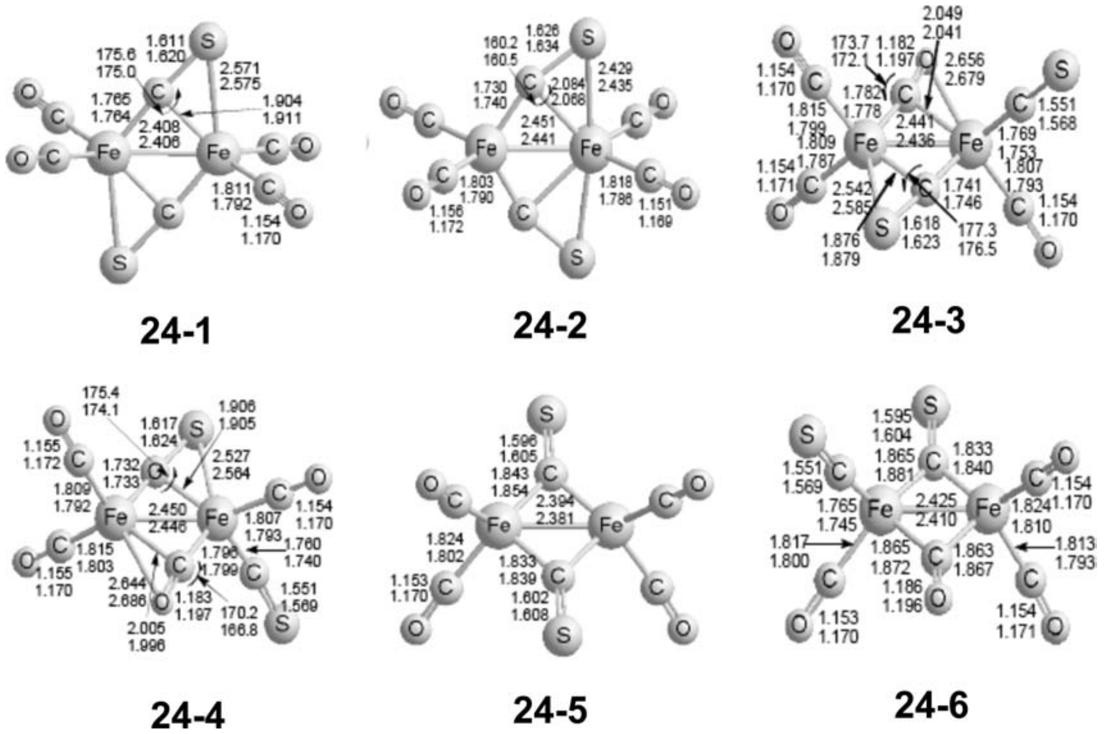
(48) Lotz, S.; Pille, R. R.; Van Rooyen, P. H. *Inorg. Chem.* **1986**, *25*, 3053.


24-1 24-2 24-3

24-4 24-5 24-6

Figure 9. Optimized structures of $Fe_2(CS)_2(CO)_4$ within 30 kcal/mol of the global minimum.

through the sulfur atom is found in the experimentally known[48] (η^6-MePh)$Cr(CO)_2{-}C{\equiv}S{-}Cr(CO)_5$. However, the C−S−Cr angle in this complex is found by X-ray diffraction to be bent to 110°. This contrasts with the predicted structures **27-10** and **27-11** for $Fe_2(CS)_2(CO)_7$ (Figure 5) in which the C−S−Fe angle is linear (180°).

3.2.2. $Fe_2(CS)_2(CO)_6$. A total of 16 structures were found for $Fe_2(CS)_2(CO)_6$ including four unbridged, two singly bridged, seven doubly bridged, one triply bridged, and two quadruply bridged structures (Figures 6 and 7 and Tables 5 and 6). These structures have been optimized, indicating a very complicated potential energy surface. Among this plethora of $Fe_2(CS)_2(CO)_6$ structures only those within 30 kcal/mol of the global minimum **26-1** and with no imaginary vibrational frequencies above 100i are discussed in this paper. Both of the quadruply bridged structures for $Fe_2(CS)_2(CO)_6$ were found to have high energies and large imaginary vibrational frequencies clearly indicating that they are not viable structures. Therefore the quadruply bridged structures of $Fe_2(CS)_2(CO)_6$ are not discussed in this paper.

The $Fe_2(\eta^2\text{-}\mu\text{-}CS)(\mu\text{-}CS)(CO)_6$ structure (**26-1**), with C_1 symmetry, is predicted to be the global minimum by both BP86 and B3LYP methods. Structure **26-1** is derived from the global minimum **27-1** of $Fe_2(CS)_2(CO)_7$ (Figure 4) by loss of a bridging CO group with concurrent conversion a two-electron donor bridging CS group into a four-electron donor bridge. The iron−iron bond distance of **26-1** is predicted to be 2.615 Å (B3LYP) or 2.584 Å (BP86), which is ∼0.1 Å longer than that in **27-1** but still consistent with a Fe−Fe single bond leading to a favorable 18-electon configuration for each iron atom.

The lowest lying triply bridged structure of $Fe_2(CS)_2(CO)_6$, namely **26-2**, lies above the global minimum **26-1** by 4.6 kcal/mol (B3LYP) or 0.4 kcal/mol (BP86). Structure **26-2** is a genuine minimum with both BP86 and B3LYP methods. Structure **26-2** can be regarded to be derived from the global minimum **27-1** by removal of a terminal CO group with concurrent conversion of the bridging carbonyl group into a semibridging carbonyl group. The iron−iron bond distance changes relatively little in going from **27-1** to **26-2**. This suggests a formal Fe−Fe single bond in **26-2** leading to a 16-electron configuration for the iron atom bearing only two terminal carbonyl groups.

Six other doubly bridged $Fe_2(CS)_2(CO)_6$ structures were found (Figure 6 and Table 5). The C_{2v} structure **26-3** with two bridging CS groups is a genuine minimum lying 6.4 kcal/mol (B3LYP) or 2.3 kcal/mol (BP86) above **26-1**. The Fe=Fe bond distance of 2.407 Å (B3LYP) or 2.413 Å (BP86) in **26-3** may be interpreted to be the formal double bond needed to give both iron atoms the favored 18-electron configuration. The C_{2h} structure **26-4** for $Fe_2(CS)_2(CO)_6$ with two CS bridges and two small imaginary vibrational frequencies is closely related to **26-2** and lies 12.9 kcal/mol (B3LYP) or 8.2 kcal/mol (BP86) above **26-1**. The Fe=Fe bond distance in **26-4** is 2.463 Å (B3LYP) or 2.449 Å (BP86) consistent with the double bond required to give both iron atoms the favored 18-electron configuration. A C_{2v} structure **26-5** of $Fe_2(CS)_2(CO)_6$ with two bridging CO groups is of higher energy than the structures with two bridging CS groups. Thus structure **26-5** lies 18.4 kcal/mol (B3LYP) or 11.5 kcal/mol (BP86) above the global minimum **26-1** and has a small imaginary vibrational frequency at 9i (B3LYP) or 17i (BP86). The Fe=Fe bond distance in **26-5** is 2.469 Å (B3LYP) or 2.472 Å (BP86), consistent with the formal double bond required for the favored 18-electron iron configuration. A second $Fe_2(CS)_2(CO)_6$ structure with two bridging carbonyl groups, namely **26-6** at 19.0 kcal/mol (B3LYP) or 14.7 kcal/mol (BP86), has a significantly longer Fe−Fe bond distance of 2.629 Å (B3LYP) or 2.591 Å (BP86), suggesting a single bond.

The final two doubly bridged structures for $Fe_2(CS)_2(CO)_6$ (Figure 6 and Table 5) are **26-7** with two bridging CO groups at 11.2 kcal/mol (B3LYP) or 6.4 kcal/mol (BP86) above **26-1** and **26-8** with two bridging CS groups at 18.9 kcal/mol (B3LYP) or 14.2 kcal/mol (BP86) above **26-1**. Structure **26-7** has a relatively large imaginary frequency at 180i (B3LYP) or 80i (BP86). The Fe−Fe distances in both **26-7** and **26-8** are around 2.6 Å, suggesting single rather than double bonds. This suggests that one of the iron atoms in **26-7** and **26-8** has only a 16-electron configuration rather than the favored 18-electron configuration.

Two singly bridged structures for $Fe_2(CS)_2(CO)_6$ were optimized (Figure 7 and Table 6). Structure **26-9** with a bridging η^2-μ-CS group is predicted to be higher in energy than **26-1** by 4.0 kcal/mol (B3LYP) or 6.6 kcal/mol (BP86). Structure **26-9** has a small imaginary vibrational frequency of 11i (B3LYP) or 17i (BP86). We reoptimized the BP86 geometry of **26-9** using the Ultrafine (99, 590) numerical integration grid. The geometry was nearly unchanged, and the new imaginary vibrational frequency became 16i. The bridging CS group in **26-9** is a formal four-electron donor similar to that found experimentally[47] in $[HB(pz)_3](CO)_2W(\mu$-$CS)Mo(CO)_2(\eta^5$-$C_9H_7)$. In **26-9**, as depicted in Figure 7, the bridging CS ligand is a σ-donor of two electrons to the "right" iron atom and π-donor of two more electrons through the CS multiple bond to the "left" iron atom. The involvement of the sulfur atom, as well as the carbon atom of this bridging η^2-μ-CS group, is supported by the relatively short Fe−S distance of 2.427 Å (B3LYP) or 2.442 Å (BP86). The C−S bond distance in this η^2-μ-CS group, namely 1.627 Å (B3LYP) or 1.637 Å (BP86), is longer than the C−S bond distances in typical terminal CS groups.

The singly bridged $Fe_2(CS)_2(CO)_6$ structure **26-10** is similar to **26-9** except that the four-electron donor bridge is a CO rather than a CS group (Figure 7 and Table 6). Structure **26-9** is predicted to be a genuine minimum by B3LYP, but it has a small imaginary frequency of 23i by BP86. Structure **26-10** lies significantly higher in energy than **26-9**, at 21.7 kcal/mol (B3LYP) or 24.4 kcal/mol (BP86) above the global minimum **26-1**. The C−O bond distance in this four-electron donor bridging η^2-μ-CO group of 1.200 Å (B3LYP) or 1.217 Å (BP86) is longer than the C−O bond distances in terminal CO groups (close to 1.160 Å). The relatively short Fe−O distance of 2.162 Å (B3LYP) or 2.181 Å (BP86) to this η^2-μ-CO group suggests involvement of the oxygen atom, as well as the carbon atom, in the metal−ligand bonding. The ν(CO) frequency for this four-electron donor η^2-μ-CO group at 1713 cm^{-1} (BP86) is significantly lower than those of terminal CO groups or the usual two-electron donor bridging CO groups in similar compounds. The Fe−Fe bond lengths of ~2.8 Å are almost identical for **26-9** and **26-10** and are consistent with the Fe−Fe single bonds needed to give both atoms the favored 18-electron configurations.

Three unbridged structures were found for $Fe_2(CS)_2(CO)_6$ (Figure 7 and Table 6) but all at relatively high energies. Among these three unbridged structures the C_{2h} structure **26-11** has the lowest energy, but it lies 26.8 kcal/mol (B3LYP) or 22.8 kcal/mol (BP86) above the most stable $Fe_2(CS)_2(CO)_6$ structure **26-1**. Two additional unbridged $Fe_2(CS)_2(CO)_6$ structures **26-12** and **26-13**, both with C_{2v} symmetry, were found at still higher energies. The Fe═Fe distances in these structures fall in the range 2.54 to 2.57 Å, consistent with the unbridged double bond required to give both iron atoms the favored 18-electron configuration.

3.2.3. $Fe_2(CS)_2(CO)_5$. The global minimum structure for $Fe_2(CS)_2(CO)_5$ is **25-1** with two bridging CS groups (Figure 8 and Table 7). This structure is predicted to be a genuine minimum by B3LYP but to have a small imaginary vibrational frequency of 6i by BP86. However, using the finer (99,590) integration grid in the BP86 calculation removed this imaginary vibrational frequency. One of the CS groups in **25-1** is a four-electron donor η^2-μ-CS group, as indicated by the relatively short Fe−S distance of 2.581 Å (B3LYP) or 2.639 Å (BP86). The other bridging CS group in **26-1** is a normal two-electron donor. The Fe═Fe distance is 2.437 Å (B3LYP) or 2.419 Å (BP86) consistent with the formal double bond required to give both metal atoms the favored 18-electron configuration with the single four-electron donor η^2-μ-CS group.

All of the other optimized structures for $Fe_2(CS)_2(CO)_5$ were found to lie more than 17 kcal/mol above the global minimum **25-1**. Four additional such structures were found within 30 kcal/mol of the global minimum (Figure 8 and Table 7). Structures **25-3** and **25-4** both have three bridging groups. In structure **25-3**, at 23.1 kcal/mol (B3LYP) or 17.0 kcal/mol (BP86) above **25-1**, all three bridging groups are CO groups. Structure **25-4** at 26.9 kcal/mol (B3LYP) or 21.6 kcal/mol (BP86) above **25-1** has two bridging CS groups and one bridging CO group. In the two triply bridged structures **25-3** and **25-4** the Fe≡Fe distances fall in the range 2.20 Å to 2.27 Å, consistent with the formal triple bonds required to give both iron atoms the favored 18-electron configurations.

The B3LYP method also predicts a structure **25-2** for $Fe_2(CS)_2(CO)_5$ with two semibridging CO groups and only terminal CS groups at 23.6 kcal/mol above **25-1**. The Fe≡Fe distance of 2.258 Å in **25-2** is consistent with the formal triple bond needed to give both iron atoms the favored 18-electron configuration. The BP86 method predicts that structure **25-2** is not a stationary point but dissociated into **25-1**.

A singly bridged $Fe_2(CS)_2(CO)_5$ structure **25-5** was also found at 28.0 kcal/mol (B3LYP) or 26.1 kcal/mol (BP86) above the global minimum **25-1**. This structure has a single bridging CO group and a short Fe≡Fe distance of 2.188 Å (B3LYP) or 2.202 Å (BP86), consistent with the formal triple bond necessary to give both iron atoms the favored 18-electron configurations.

3.2.4. $Fe_2(CS)_2(CO)_4$. Six structures were found for $Fe_2(CS)_2(CO)_4$ within 30 kcal/mol of the global minimum (Figure 9 and Table 8). The global minimum **24-1** is a C_{2h}

structure with no imaginary vibrational frequencies. The two bridging CS groups in **24-1** are seen to be four-electron donor η^2-μ-CS groups, as indicated by the relatively short Fe−S distances of 2.571 Å (B3LYP) or 2.575 Å (BP86). The Fe═Fe distance in **24-1** is 2.408 Å (B3LYP) or 2.406 Å (BP86), consistent with the double bond needed to give both iron atoms the favored 18-electron configuration with the two four-electron donor bridging CS groups.

The next higher lying $Fe_2(CS)_2(CO)_4$ structure is the C_{2v} structure **24-2** lying 15.0 kcal/mol (B3LYP) or 16.7 kcal/mol (BP86) above the global minimum **24-1** with no imaginary vibrational frequencies. There are two four-electron donor bridging η^2-μ-CS groups in **24-2** as there are in **24-1**, as indicated by Fe−S distances of 2.429 Å (B3LYP) or 2.435 Å (BP86) in **24-2**. However, in **24-2** both Fe−S bonds are to the same iron atom (the "right" iron atom in Figure 9), whereas in **24-1** there is one Fe−S bond to each iron atom. The Fe═Fe distance of 2.451 Å (B3LYP) or 2.441 Å (BP86) in **24-2** is ~0.04 Å longer than that in **24-1**. However, it is still within the range of the formal double bond needed to give both metal atoms the favored 18-electron configuration.

Two doubly bridged $Fe_2(CS)_2(CO)_4$ structures **24-3** and **24-4** (Figure 9 and Table 8) are found with one four-electron donor η^2-μ-CS group and one four-electron donor η^2-μ-CO group lying energetically higher than **24-1**, by 17.4 and 17.7 kcal/mol (B3LYP) or 15.8 and 15.8 kcal/mol (BP86), respectively. The four-electron donor CS and CO groups are indicated by Fe−S and Fe−O distances of 2.55 ± 0.03 Å and 2.66 ± 0.03 Å, respectively. The Fe═Fe bonds in **24-3** and **24-4** fall in the range 2.41 ± 0.04 Å, consistent with the double bonds needed to give both iron atoms the favored 18-electron configurations. In **24-3** the terminal CS group is approximately *trans* to the Fe−C bond to the bridging CS group, whereas in **24-4** the terminal CS group is approximately *trans* to the Fe−S bond to the bridging CS group.

The next higher lying $Fe_2(CS)_2(CO)_4$ structure **24-5** has two bridging CS groups and lies 20.1 kcal/mol (B3LYP) or 17.9 kcal/mol (BP86) higher than **24-1** (Figure 9 and Table 8). Structure **24-5** has a small imaginary frequency with both B3LYP and BP86 methods, namely 38i or 59i respectively. The final $Fe_2(CS)_2(CO)_4$ structure within 30 kcal/mol of the global minimum is **24-6** at 29.0 kcal/mol (B3LYP) or 24.5 kcal/mol (BP86) above **24-1**.

Structure **24-6** is similar to **24-5** except that it has one bridging CS group and one bridging CO group. The Fe═Fe distances for **24-5** and **24-6** fall in the range 2.40 ± 0.02 Å, consistent with formal double bonds. Since all of the CS and CO groups in **24-5** and **24-6** are two-electron donors, the iron atoms in **24-5** and **24-6** both have 16-electron configurations rather than the favored 18-electron configurations.

3.3. Dissociation Energies. Table 9 reports the bond dissociation energies (BDEs) in terms of the single carbonyl dissociation steps:

$$Fe(CS)(CO)_m \rightarrow Fe(CS)(CO)_{m-1} + CO \ (m = 4, 3) \quad (1)$$

$$Fe_2(CS)_2(CO)_n \rightarrow Fe_2(CS)_2(CO)_{n-1} + CO \ (n = 7, 6, 5) \quad (2)$$

The BDEs for the loss of CO from the mononuclear $Fe(CS)(CO)_m$ derivatives (m = 4, 3) are somewhat higher than the experimental BDEs[49] of 27 kcal/mol, 41 kcal/mol, and 37 kcal/mol for $Ni(CO)_4$, $Fe(CO)_5$, and $Cr(CO)_6$, respectively. The BDEs for loss of CO from the binuclear $Fe_2(CS)_2(CO)_n$ derivatives (n = 7, 6, 5) are somewhat lower than those for the mononuclear $Fe(CS)(CO)_m$ derivatives. Furthermore, the BDE for loss of CO from $Fe_2(CS)_2(CO)_7$ is within 1 kcal/mol of that for loss of CO from the closely related $Fe_2(CO)_9$ (Table 9).

Table 10 reports the energies of the dissociation of the binuclear $Fe_2(CS)_2(CO)_n$ into mononuclear fragments by the reactions:

$$Fe_2(CS)_2(CO)_n \rightarrow Fe(CS)(CO)_x + Fe(CS)(CO)_y \ (n = x + y) \quad (3)$$

In general the dissociation energies are seen to increase as the number of carbonyl groups is decreased. The energies for the symmetrical dissociation of $Fe_2(CS)_2(CO)_6$ into $2Fe(CS)(CO)_3$ are very similar (within 1.1 kcal/mol) to that for the unsymmetrical dissociation of $Fe_2(CS)_2(CO)_6$ into $Fe(CS)(CO)_4 + Fe(CS)(CO)_2$. The dissociation energies are particularly high (>70 kcal/mol) for the binuclear structures bridged by a four-electron donor η^2-μ-CS group, such as **25-1** and **24-1**. Compared with the analogous complexes $Fe_2(CO)_{n+2}$, the corresponding dissociation energies for losing a carbonyl from $Fe_2(CS)_2(CO)_n$ are somewhat smaller (Table 9). The dissociation energies of binuclear $Fe_2(CS)_2(CO)_n$ into mononuclear complexes (Table 10) are much larger than those of their analogous complexes $Fe_2(CO)_{n+2}$.

3.4. Vibrational Frequencies. The harmonic vibrational frequencies and the infrared intensities for all of the structures have been evaluated by both the B3LYP and BP86 methods. These results were initially used to determine if a structure is a genuine minimum. The predicted ν(CO) and ν(CS) harmonic vibrational frequencies and IR intensities for the most stable structures of $Fe_2(CS)_2(CO)_n$ (n = 7, 6, 5, 4) are of particular interest, since any future experimental work to detect such species are likely to rely on relatively strong ν(CO) and ν(CS) vibrational frequencies for initial product characterization. The ν(CO) and ν(CS) stretching frequencies

Table 9. Bond Dissociation Energy (kcal/mol) for Successive Removal of Carbonyl Groups from $Fe(CS)(CO)_m$, $Fe_2(CS)_2(CO)_n$[a,b]

	B3LYP	BP86
$Fe(CS)(CO)_4 \rightarrow Fe(CS)(CO)_3 + CO$	46.9	55.1
$Fe(CS)(CO)_3 \rightarrow Fe(CS)(CO)_2 + CO$	48.6	54.5
$Fe_2(CS)_2(CO)_7 \rightarrow Fe_2(CS)_2(CO)_6 + CO$	30.6	35.2
$Fe_2(CS)_2(CO)_6 \rightarrow Fe_2(CS)_2(CO)_5 + CO$	14.9	24.3
$Fe_2(CS)_2(CO)_5 \rightarrow Fe_2(CS)_2(CO)_4 + CO$	22.6	29.2
$Fe_2(CO)_9 \rightarrow Fe_2(CO)_8 + CO$	29.4	35.1
$Fe_2(CO)_8 \rightarrow Fe_2(CO)_7 + CO$	25.4	37.6
$Fe_2(CO)_7 \rightarrow Fe_2(CO)_6 + CO$	32.6	33.9

[a] BDEs for $Fe_2(CO)_{n+2}$ are listed for comparison. All results reported here refer to the lowest-energy structures of $Fe_2(CS)_2(CO)_n$. [b] BDEs of $Fe_2(CO)_n$ are taken from Xie, Y.; Schaefer, H. F.; King, R. B. *J. Am. Chem. Soc.***2000**, *122*, 8746.

Table 10. Energies (in kcal/mol) for Dissociation of the Binuclear Complexes $Fe_2(CS)_2(CO)_n$ into Two Mononuclear $Fe(CS)(CO)_x$ or $Fe(CO)_{x+1}$ Fragments[a]

reaction	bridges in $Fe_2(CS)_2(CO)_n$	B3LYP		BP86	
		D_{Fe-Fe}	R_{Fe-Fe}	D_{Fe-Fe}	R_{Fe-Fe}
$Fe_2(CS)_2(CO)_7$ (27-1) → $Fe(CS)(CO)_4$ + $Fe(CS)(CO)_3$	di-μ-CS, μ-CO	24.9	2.494	36.8	2.491
$Fe_2(CS)_2(CO)_6$ (26-1) → $Fe(CS)(CO)_3$ + $Fe(CS)(CO)_3$	di-μ-CS, semi-μ-CO	44.9	2.503	57.1	2.462
$Fe_2(CS)_2(CO)_6$ (26-1) → $Fe(CS)(CO)_4$ + $Fe(CS)(CO)_2$		42.4		56.0	
$Fe_2(CS)_2(CO)_5$ (25-1) → $Fe(CS)(CO)_3$ + $Fe(CS)(CO)_2$	η^2-μ-CS, μ-CS	74.4	2.437	86.8	2.419
$Fe_2(CS)_2(CO)_4$ (24-1) → $Fe(CS)(CO)_2$ + $Fe(CS)(CO)_2$	di-η^2-μ-CS	99.7	2.408	112.1	2.406
$Fe_2(CO)_9$ → $Fe(CO)_5$ + $Fe(CO)_4$	tri-μ-CO	4.6	2.525	28.3	2.519
$Fe_2(CO)_8$ → $Fe(CO)_4$ + $Fe(CO)_4$	di-μ-CO	9.0	2.443	43.0	2.447
$Fe_2(CO)_8$ → $Fe(CO)_5$ + $Fe(CO)_3$		8.4		35.1	
$Fe_2(CO)_7$ → $Fe(CO)_4$ + $Fe(CO)_3$	disemi-μ-CO	16.8	2.231	47.3	2.235
$Fe_2(CO)_6$ → $Fe(CO)_3$ + $Fe(CO)_3$	di-η^2-μ-CO	17.4	2.435	55.3	2.434

[a] Dissociation energies for $Fe_2(CO)_n$ are listed for comparison. Dissociation energies of $Fe_2(CO)_n$ are taken from the results of Xie, Y.; Schaefer, H. F.; King, R. B. *J. Am. Chem. Soc.* **2000**, *122*, 8746.

are listed in Tables 11 and 12 for the mononuclear $Fe(CS)(CO)_n$ ($n = 4, 3, 2$) and binuclear $Fe_2(CS)_2(CO)_n$ ($n = 7, 6, 5, 4$) derivatives, respectively. These results were obtained with the BP86 method, which has been shown to be more reliable than the B3LYP method for such infrared frequencies.[50,51]

The data in Tables 11 and 12 indicate that terminal ν(CS) frequencies fall in the range 1280 to 1340 cm^{-1}. The somewhat lower ν(CS) frequencies in the range 1237 to 1255 cm^{-1} for the relatively high energy unbridged $Fe_2(CS)_2(CO)_6$ structures **26-12** and **26-13** relate to the fact that their Fe−C−S angles are slightly bent to 165 ± 2° (Figure 7).

As expected by analogy with the bridging carbonyl groups, bridging ν(CS) frequencies are predicted to be significantly lower, in the range 1130 to 1210 cm^{-1}. Unlike bridging CO groups, the ν(CS) frequencies of bridging CS groups appear to be insensitive as to whether they are formal two-electron donor μ-CS groups (bonding to the metals only through the carbon atom) or four-electron donor η^2-μ-CS groups (bonding to the metals through both the carbon and sulfur atoms). However, the bidentate CS groups bonding to a single metal through both the carbon and sulfur atoms in the relatively high energy mononuclear structures **14-4** (Figure 1) for $Fe(CS)(CO)_4$, **13-3** (Figure 2) for $Fe(CS)(CO)_3$, and **12-3** and **12-4** (Figure 3) for $Fe(CS)(CO)_2$ have abnormally low ν(CS) frequencies in the range 860 to 1020 cm^{-1}.

The known compound $Fe(CS)(CO)_4$ is reported[11] to exhibit two ν(CS) frequencies at 1320 and 1305 cm^{-1} in Nujol, clearly suggesting a mixture of two structures. Since the two trigonal bipyramidal structures **14-1** and **14-2** (Figure 1) are predicted to be within less than 1 kcal/mol of each other in terms of energy (Table 1), it is reasonable for $Fe(CS)(CO)_4$ to exist under ambient conditions as a mixture of **14-1** and **14-2**. If this is the case, the experimental 1320 cm^{-1} band in $Fe(CS)(CO)_4$ can then correspond to the axially substituted structure **14-1** with a predicted ν(CS) frequency of 1336 cm^{-1}, and the experimental 1305 cm^{-1} band to the equatorially substituted structure **14-2** with a predicted ν(CS) frequency of 1315 cm^{-1}. The predicted strong infrared ν(CO) frequencies of 2063, 2010, and 1991 cm^{-1} for **14-1** and 2070, 2008, and 1990 cm^{-1} for **14-2** would be very difficult to resolve experimentally in a mixture of **14-1** and **14-2** since the maximum difference between these frequencies between the isomers is only 7 cm^{-1}. However, these calculated ν(CO) frequencies are reasonably close to the experimental[11] strong ν(CO) frequencies for $Fe(CS)(CO)_4$ at 2100, 2035, and 2000 cm^{-1}.

3.5. Iron−Iron Bond Lengths. The Fe−Fe single bond distances in binuclear iron carbonyl and thiocarbonyl derivatives correlate strongly with the number of bridging groups and become significantly shorter as the number of bridging groups is increased (Table 13). Thus formal Fe−Fe single bonds bridged by a total of three groups are predicted to have lengths in the narrow range 2.51 ± 0.02 Å close to the experimental Fe−Fe distance[15] of 2.52 Å found for $Fe_2(CO)_9$. For structures with only two bridging groups the formal

Table 11. ν(CO) and ν(CS) Stretching Frequencies Predicted for the Mononuclear $Fe(CS)(CO)_n$ ($n = 4, 3, 2$) Derivatives[a] and Their Vibrational Symmetries

	ν(CO)	ν(CS)
	$Fe(CS)(CO)_4$ Structures	
14-1 (C_{3v})	2063(a_1, 346), 2010(a_1, 367), 1991(e, 1067), 1991(e, 1067)	1336 (a_1, 635)
14-2 (C_{2v})	2070 (a_1, 191), 2008 (a_1, 331), 2008 (b_2, 1239), 1990 (b_1, 1047)	1315 (a_1, 652)
14-3 (C_{4v})	2067 (a_1, 284), 2000 (b_2, 0), 1992 (e, 1277), 1992 (e, 1277)	1315 (a_1, 674)
14-4 (C_s)	2078 (a′, 197), 2014 (a′, 287), 2009 (a″, 1198), 1997 (a′, 925)	1008 (a′, 64)
	$Fe(CS)(CO)_4$ expt.[11] 2100, 2035, 2000	1320, 1305
	$Fe(CS)(CO)_3$ Structures	
13-1 (C_s)	2044(a′, 222), 1976(a″, 1405), 1967(a′, 877)	1302 (a′, 572)
13-2 (C_{3v})	2025 (a_1, 122), 1963 (a_1, 1067), 1963 (e, 1067)	1334 (a_1, 492)
13-3 (C_s)	2045 (a′, 431), 1994 (a′, 839), 1981 (a″, 726)	910 (a′, 47)
	$Fe(CS)(CO)_2$ Structures	
12-1 (C_s)	1993(a′, 294), 1935(a″, 1330)	1327 (a′, 446)
12-2 (C_{2v})	2039 (a_1, 62), 1955 (b_2, 1775)	1324 (a_1, 454)
12-3 (C_s)	2011 (a′, 605), 1963 (a″, 797),	864 (a′, 33)
12-4 (C_s)	1985 (a′, 652), 1942 (a″, 803)	1019 (a′, 79)

[a] Infrared intensities are given in parentheses in km/mol.

Table 12. ν(CO) and ν(CS) Stretching Frequencies Predicted for the Binuclear $Fe_2(CS)_2(CO)_n$ ($n = 7, 6, 5, 4$) Derivatives[a]

	$Fe_2(CS)_2(CO)_7$ Structures	
27-1 (C_{2v})	2067(45), 2040(1600), 2016(a_1, 1215), 2014 (1170), 2012(10), 2009 (0), **1881 (457**)	**1202 (198), 1169 (677**)
27-2 (C_s)	2061 (230), 2032 (1334), 2014 (1253), 2009 (12), 2008 (606), **1891 (258), 1873 (669)**	1321 (603), **1181 (546)**
27-3 (C_{22})	2050 (180), 2024 (1566), 2004 (1074), 2001 (393), **1942 (54), 1929 (533), 1870 (490)**	1320 (183), 1315 (1158)
27-4 (C_{2v})	2053 (612), 2023 (1145), 2009 (1318), 2005 (0), **1900 (14), 1876 (656), 1872 (636)**	1327 (825), 1314 (535)
27-5 (C_{2v})	2066 (159), 2021 (203), 2011 (1959), 2011 (950) 1984 (116), 1983 (0), **1856 (483)**	1328 (264), 1320 (1133)
27-6 (C_{2v})	2068 (260), 2029 (908), 2010 (1967), 2001 (433), 1993 (453), 1981 (0), **1850 (387)**	1319 (941), 1284 (168)
27-7 (C_s)	2064 (320), 2023 (1286), 2002 (96), 2000 (1887), 1986 (384), 1981 (397), 1966 (67)	**1137 (140), 1025 (9)**
27-8 (C_s)	2072 (200), 2047 (438), 2016 (1218), 2008 (1130), 1996 (540), 1984 (273), 1980 (758)	1319 (831), **1035 (383)**
27-9 (C_s)	2074.9 (513), 2024 (616), 2016 (1230), 2016 (941), 2001 (655), 1985 (444), 1972 (912)	1318 (757), **1244 (738)**
27-10 (C_{3v})	2063 (716), 2029 (203), 2011 (254), 1993 (1244), 993 (1244), 1979 (708), 1979 (708),	1353 (271), **1337 (1579)**
27-11 (C_{3v})	2055(379), 2037(451), 1994(1205), 1994(1205), 1990(305), 1978(750), 1978(750)	1366(32), **1305 (1956)**
	$Fe_2(CS)_2(CO)_6$ Structures	
26-1 (C_1)	2057 (276), 2028 (1645), 2008 (727), 2001 (1230), 1993 (129), 1982 (109)	**1193 (265), 1157 (377)**
26-2 (C_s)	2056 (295), 2019 (1894), 2008 (754), 2004 (662) 1994 (401), **1933 (327)**	**1193 (245), 1161 (507)**
26-3 (C_{2v})	2054 (128), 2028 (1668), 2005 (1154), 1998 (1338), 1997 (0), 1990 (2)	**1187 (102), 1147 (639)**
26-4 (C_{2h})	2062 (0), 2036 (1766), 2014 (911), 2012 (0), 2006 (1460), 1994 (0)	**1161 (0), 1130 (846)**
26-5 (C_{2v})	2043 (788), 2011 (1203), 2004 (1342), 1999 (0), **1866 (144), 1838 (716)**	1328 (755), 1316 (455)
26-6 (C_1)	2038 (901), 2003 (2075), 1991 (333), 1978 (197) 1902 (827), 1897 (18)	1316 (795), 1284 (354)
26-7 (C_i)	2032 (0), 2008 (2305), 1988 (925), 1987 (0), 1900 (821), 1896 (0)	1300 (0), 1301 (1305)
26-8 (C_{2h})	2051 (0), 2008 (2124), 1995 (2065), 1987 (0), 1984 (655), 1968 (0)	**1201 (0), 1188 (566)**
26-9 (C_s)	2073(84), 2027(1094), 2024(463), 2008(1259), 1963(585), 1961(663)	1323(398), **1164 (254**)
26-10 (C_s)	2064 (293), 2023 (592), 2017 (1194), 1997 (957), 1962 (585), **1713 (293)**	1345 (592), 1291 (279)
26-11 (C_{2h})	2042 (0), 2006 (1823), 1992 (0), 1983 (1967), 1970 (218), 1949 (0)	1322 (0), 1316 (1498)
26-12 (C_{2v})	2046 (164), 2021 (1733), 1995 (1305), 1985 (289), 1981 (0), 1962 (865)	1301 (156), 1247 (948)
26-13 (C_{2v})	2049 (437), 2020 (1808), 1994 (1592), 1992 (741), 1988 (0), 1959 (45)	1296 (726), 1255 (182)
	$Fe_2(CS)_2(CO)_5$ Structures	
25-1 (C_s)	2050(406), 2015(1337), 2007(418), 1998(1156), 1983(362)	**1203(157), 1155 (442**)
25-3 (C_{22})	2019 (376), 2003 (1314), **1931 (180), 1925 (659), 1911 (696)**	1317 (257), 1310 (1217)
25-4 (C_{2v})	2026 (167), 2002 (2280), 1982 (1075), 1977 (0), **1905 (665)**	**1229 (335), 1219 (537)**
25-5 (C_s)	2031 (593), 2004 (1517), 1993 (1166), 1973 (0), **1907 (510)**	1322 (850), 1290 (201)
	$Fe_2(CS)_2(CO)_4$ Structures	
24-1 (C_{2h})	2027(0), 2005(1743), 1986(1599), 1977(0)	**1188(0), 1159 (499)**
24-2 (C_{2v})	2030 (55), 2005 (1650), 1988 (1256), 1973 (346)	**1134 (76), 1098 (344)**
24-3 (C_1)	2020 (556), 1995 (1557), 1979 (578), **1838 (430)**	1309 (586), **1179 (306)**
24-4 (C_1)	2018 (393), 1999 (1663), 1972 (752), **1831 (440)**	1319 (622), **1178 (230)**
24-5 (C_{2v})	2024 (75), 1996 (1753), 1978 (1717), 1968 (0)	**1176 (79), 1160 (537)**
24-6 (C_1)	2016 (667), 1990 (1624), 1969 (718), **1828 (290)**	1304 (614), **1161 (393)**

[a] Infrared intensities are given in parentheses in km/mol. Bridging ν(CO) and ν(CS) frequencies are in **bold** type.

Table 13. Some Iron−Iron Single Bond Lengths in Binuclear Iron Carbonyl and Thiocarbonyl Derivatives[a]

compound	bridges	Fe−Fe, Å
	Three Bridging Groups	
$Fe_2(CO)_9$	3 μ-CO	2.52[15]
$Fe_2(CS)_2(CO)_7$ (**27-1**)	2 μ-CS + μ-CO	2.49
$Fe_2(CS)_2(CO)_7$ (**27-2**)	μ-CS + 2 μ-CO	2.51
$Fe_2(CS)_2(CO)_7$ (**27-3**)	3 μ-CO	2.67
$Fe_2(CS)_2(CO)_7$ (**27-4**)	3 μ-CO	2.53
	Two Bridging Groups	
$Fe_2(CS)_2(CO)_6$ (**26-1**)	η^2-μ-CS + μ-CS	2.60
$Fe_2(CS)_2(CO)_6$ (**26-6**)	η^2-μ-CS + μ-CO	2.60
$Fe_2(CS)_2(CO)_6$ (**26-7**)	2 μ-CO	2.59
$Fe_2(CS)_2(CO)_6$ (**26-8**)	2 μ-CS	2.58
	One Bridging Group	
$Fe_2(CS)_2(CO)_7$ (**27-5**)	μ-CO	2.76
$Fe_2(CS)_2(CO)_7$ (**27-6**)	μ-CO	2.76
$Fe_2(CS)_2(CO)_6$ (**26-9**)	η^2-μ-CS	2.85
$Fe_2(CS)_2(CO)_6$ (**26-10**)	η^2-μ-CS	2.85

[a] Average of B3LYP and BP86 predictions.

Fe−Fe single bond distances increase to 2.59 ± 0.01 Å, and for structures with only a single bridging group the formal Fe−Fe single bond distances increase to 2.80 ± 0.05 Å (Table 13). These data show clearly that the number of bridging groups must be considered in attempts to relate metal−metal distance to formal metal−metal bond order.

A similar observation can be made regarding the correlation of formal Fe=Fe double bond distances to the number of bridging groups in binuclear iron carbonyl and thiocarbonyl derivatives (Table 14). In this case a total of 13 structures with two bridging groups and formal Fe=Fe double bonds are all seen to have iron−iron distances in the range 2.44 ± 0.05 Å. However, the five examples of unbridged formal Fe=Fe double bonds are significantly longer in the range 2.59 ± 0.03 Å.

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Table 14. Some Iron−Iron Double Bond Lengths in Binuclear Iron Carbonyl and Thiocarbonyl Derivatives[a]

compound	bridges	Fe−Fe, Å
Fe═Fe Double Bonds, Two Bridging Groups		
$Fe_2(CO)_8$	2 μ-CO	2.45[52]
$Fe_2(CS)_2(CO)_6$ (**26-2**)	2 μ-CS	2.48
$Fe_2(CS)_2(CO)_6$ (**26-3**)	2 μ-CS	2.41
$Fe_2(CS)_2(CO)_6$ (**26-4**)	2 μ-CS	2.45
$Fe_2(CS)_2(CO)_6$ (**26-5**)	2 μ-CO	2.47
$Fe_2(CS)_2(CO)_5$ (**25-1**)	η^2-μ-CS + μ- CS	2.42
$Fe_2(CO)_6$	2 η^2-μ- CO	2.44[52]
$Fe_2(CS)_2(CO)_4$ (**24-1**)	2 η^2-μ-CS	2.41
$Fe_2(CS)_2(CO)_4$ (**24-2**)	2 η^2-μ-CS	2.44
$Fe_2(CS)_2(CO)_4$ (**24-3**)	η^2-μ-CS + η^2-μ-CO	2.44
$Fe_2(CS)_2(CO)_4$ (**24-4**)	η^2-μ-CS + η^2-μ-CO	2.45
$Fe_2(CS)_2(CO)_4$ (**24-5**)	2 μ-CS	2.39
$Fe_2(CS)_2(CO)_4$ (**24-6**)	μ-CS + μ-CO	2.45
Fe═Fe Double Bonds, No Bridging Groups		
$Fe_2(CO)_8$		2.61[52]
$Fe_2(CS)_2(CO)_6$ (**26-11**)		2.56
$Fe_2(CS)_2(CO)_6$ (**26-12**)		2.55
$Fe_2(CS)_2(CO)_6$ (**26-13**)		2.56

[a] Average of B3LYP and BP86 predictions.

Table 15. Some Iron−Iron Double Bond Lengths in Binuclear Iron Carbonyl and Thiocarbonyl Derivatives[a]

compound	bridges	Fe−Fe, Å
$Fe_2(CO)_7$	3 μ-CO	2.21[52]
$Fe_2(CS)_2(CO)_5$ (**25-2**)	2 μ-CO	2.26
$Fe_2(CS)_2(CO)_5$ (**25-3**)	3 μ-CO	2.26
$Fe_2(CS)_2(CO)_5$ (**25-4**)	2 μ-CS + μ-CO	2.21
$Fe_2(CS)_2(CO)_5$ (**25-5**)	1 μ-CO	2.19

[a] Average of B3LYP and BP86 predictions.

For the formal Fe≡Fe triple bonds the distances are consistently in the range 2.23 ± 0.04 Å regardless of whether there are one to three bridging groups (Table 15).

4. Discussion

4.1. Mononuclear Structures. Our conclusions with respect to $Fe(CS)(CO)_4$ are in essential agreement with the previous DFT studies of Chen, Hartmann, and Frenking[21] in indicating that the two trigonal bipyramidal structures, namely, **14-1** with axial CS substitution and **14-2** with equatorial CS substitution (Figure 1 and Table 1), have essentially the same energies. Furthermore, the apically substituted square pyramidal structure **14-3** lies only ~5.0 kcal/mol above the trigonal bipyramidal structures. This suggests that $Fe(CS)(CO)_4$ is a highly fluxional system. Furthermore, the experimental observation of two CS frequencies[11] in $Fe(CS)(CO)_4$ suggests that this product is a mixture of the two essentially degenerate trigonal bipyramidal isomers **14-1** and **14-2**. An alternative structure **14-4** for $Fe(CS)(CO)_4$ with a bidentate η^2-CS ligand bonded to the iron through both the carbon and sulfur atoms lies too high in energy to be competitive with the structures **14-1**, **14-2**, and **14-3** having monodentate CS ligands.

The lowest energy structures for the unsaturated $Fe(CS)(CO)_n$ (n = 3, 2) may be understood relative to the $Fe(CS)(CO)_4$ structures (Figure 1 and Table 1) by removal of CO ligands. Thus, the global minimum **13-1** for $Fe(CS)(CO)_3$ (Figure 2 and Table 2) can be derived from the trigonal bipyramidal $Fe(CS)(CO)_4$ structure **14-2** by removal of an equatorial carbonyl group. The next $Fe(CS)(CO)_3$ structure **13-2** can be derived from the global minimum of $Fe(CS)(CO)_4$ (**14-1**) by removal of the axial CO ligand opposite the axial CS ligand. The global minimum for the even more unsaturated $Fe(CS)(CO)_2$, namely, **12-1** (Figure 3 and Table 3), may be derived from the global minimum of $Fe(CS)(CO)_4$ (**14-1** in Figure 1) by removal of an axial and an equatorial CO group. Again the $Fe(CS)(CO)_n$ (n = 3, 2) structures with bidentate η^2-CS groups such as **13-3**, **12-3**, and **12-4** (Figures 2 and 3) lie at least 15 kcal/mol above the structures with monodentate CS groups and thus are not energetically competitive.

4.2. Binuclear Structures. A total of 35 structures (Figures 4 through 9) within 30 kcal/mol of the global minima were found for the $Fe_2(CS)_2(CO)_n$ (n = 7, 6, 5, 4) derivatives, indicating relatively complicated potential energy surfaces. However, the general pattern of the relative energies of this plethora of structures suggests the following trends:

(1) Bridging CS groups are energetically preferred over bridging CO groups, as has been previously noted in experimental studies on $(\eta^5\text{-}C_5H_5)_2Fe_2(CS)_n(CO)_{4\text{-}n}$ (n = 1, 2) derivatives.[53,54]

(2) In the highly unsaturated derivatives $Fe_2(CS)_2(CO)_n$ (n = 5, 4) four-electron donor bridging CS groups are energetically preferred over metal−metal bonds of order greater than two.

In addition, a comparison of Fe−C distances to equivalent types of terminal or bridging CO and CS groups indicates that the Fe−C distances are shorter to the CS group than to the corresponding CO group. This is consistent with previous observations[8,9] that CS is a better π-acceptor ligand than CO.

Comparison of the lowest energy structures of $Fe_2(CS)_2(CO)_n$ (n = 7, 6, 5, 4) with those of the corresponding homoleptic binuclear iron carbonyls[52] $Fe_2(CO)_{n+2}$ is instructive. The global minimum of $Fe_2(CS)_2(CO)_7$, namely **27-1** (Figure 4 and Table 4), is a triply bridged structure like the experimentally known[14,15] $Fe_2(CO)_9$. Two of the three bridging groups in **27-1** are the CS groups, indicative of the preference for bridging CS groups relative to bridging CO groups. The next three lowest lying $Fe_2(CS)_2(CO)_7$ structures **27-2**, **27-3**, and **27-4** (Figure 4 and Table 4) are also triply bridged structures with one, zero, and zero of the three bridges, respectively, being CS groups and the remainder CO groups. Two singly bridged structures (**27-5** and **27-6**) have comparable energies with **27-3** and **27-4**, and lie energetically above the global minimum **27-1** by about 10 kcal/mol (Table 4).

The lowest energy structure **26-1** for $Fe_2(CS)_2(CO)_6$ has a two-electron donor CS bridge and a four-electron donor CS bridge, which is different from the doubly bridged global minimum structure of $Fe_2(CO)_8$.[52] The relatively low energy structures **26-2** and **26-3** in the obviously complicated $Fe_2(CS)_2(CO)_6$ potential energy surface (Figure 6 and Table 5) both have two CS bridges. The difference between structures **26-2** and **26-3** is that **26-2** also has a semibridging

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(53) Choi, M. G.; Danield, L. M.; Angelici, R. J. *J. Organomet. Chem.* **1990**, *383*, 321.

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CO group whereas in **26-3** all of the CO groups are terminal. The lowest energy structure predicted for $Fe_2(CO)_8$ is a doubly bridged structure[52] very similar to structure **26-3** for $Fe_2(CS)_2(CO)_6$. The predicted Fe═Fe distances for the formal double bonds for the doubly bridged $Fe_2(CO)_8$ structure and the $Fe_2(CS)_2(CO)_6$ structure **26-3** (Figure 6 and Table 5) are very similar, namely 2.45 ± 0.01 Å.

Another relatively low energy structure for $Fe_2(CS)_2(CO)_6$ is **26-9**, which has a four-electron donor bridging η^2-μ-CS group. The Fe−Fe distance of 2.85 ± 0.04 Å in **26-9** is significantly longer than that in **26-1** or **26-2**, since only a formal single bond is required to give both iron atoms the favored 18-electron configuration. No corresponding structure for $Fe_2(CO)_8$ with a four-electron donor bridging η^2-μ-CO group was found in the earlier work.[52] This is consistent with the greater tendency of CS (relative to CO) to form four-electron donor bridging groups.

The lowest energy structure for $Fe_2(CO)_7$ predicted in our earlier work[52] is a relatively unsymmetrical structure with two semibridging CO groups and an Fe≡Fe distance of 2.23 ± 0.01 Å, suggesting the formal triple bond required to give both iron atoms the favored 18-electron configuration. An analogous structure **25-2** (Figure 8 and Table 7) was found for $Fe_2(CS)_2(CO)_5$ but only as a relatively high energy structure at 23.6 kcal/mol above the global minimum **25-1**. The Fe≡Fe bond distance of 2.258 Å in **25-2** is very similar to the predicted Fe≡Fe distance of 2.23 ± 0.01 Å in the corresponding global minimum of $Fe_2(CO)_7$.

The global minimum for $Fe_2(CS)_2(CO)_5$, namely **25-1** (Figure 8) with two bridging CS groups, lies >17 kcal/mol below any other $Fe_2(CS)_2(CO)_5$ structure found in this work and thus appears to be a highly preferred structure. However, no corresponding $Fe_2(CO)_7$ structure was found in the earlier work.[52] Structure **25-1** is interesting since one of its bridging CS groups is a four electron donor with a relatively short Fe−S distance of 2.61 ± 0.03 Å whereas its other bridging CS group is a normal two-electron donor with a clearly nonbonding long Fe−S distance. This configuration of the bridging CS groups means that a formal Fe═Fe double bond is sufficient to give both iron atoms the favored 18-electron configuration. In this connection, the Fe═Fe bond distance of 2.43 ± 0.01 Å in structure **25-1** for $Fe_2(CS)_2(CO)_5$ (Figure 8 and Table 7) is very similar to the Fe═Fe bond distance of 2.45 ± 0.01 Å in structure **26-2** of $Fe_2(CS)_2(CO)_6$ (Figure 6 and Table 5), which also requires a formal iron−iron double bond to give both iron atoms the favored 18-electron configuration.

The global minimum **24-1** (Figure 9 and Table 8) for $Fe_2(CS)_2(CO)_4$ of C_{2h} symmetry and two four-electron donor bridging η^2-μ-CS groups is closely related to the global minimum predicted[52] for $Fe_2(CO)_6$, which also has C_{2h} symmetry and two four-electron donor bridging η^2-μ-CO groups. The predicted Fe═Fe distance of 2.41 Å for **24-2** (Figure 9) is very close to the predicted 2.43 Å for the analogous $Fe_2(CO)_6$ global minimum and consistent with the formal double bonds needed to give both iron atoms the favored 18-electron configuration.

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Supporting Information Available: Tables S1−S7: Theoretical harmonic vibrational frequencies for $Fe(CS)(CO)_4$ (4 structures), $Fe(CS)(CO)_3$ (3 structures), $Fe(CS)(CO)_2$ (4 structures), $Fe_2(CS)_2(CO)_7$ (7 structures), $Fe_2(CS)_2(CO)_6$ (13 structures), $Fe_2(CS)_2(CO)_5$ (5 structures), $Fe_2(CS)_2(CO)_4$ (6 structures) using the BP86 method; Tables S8−S53: Theoretical Cartesian coordinates for $Fe(CS)(CO)_4$ (4 structures), $Fe(CS)(CO)_3$ (3 structures), $Fe(CS)(CO)_2$ (4 structures), $Fe_2(CS)_2(CO)_7$ (11 structures), $Fe_2(CS)_2(CO)_6$ (13 structures), $Fe_2(CS)_2(CO)_5$ (6 structures), $Fe_2(CS)_2(CO)_4$ (6 structures) using the B3LYP method; complete Gaussian 03 reference (ref 42). This material is available free of charge via the Internet at http://pubs.acs.org.

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