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Trinuclear Iron Carbonyl Thiocarbonyls: the Preference for Four- and Six-Electron Donor Bridging Thiocarbonyl Groups over Metal−Metal Multiple Bonding, while Satisfying the 18-Electron Rule

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Theoretical studies on $Fe_3(CS)_3(CO)_9$ show that the structure having an isosceles Fe_3 triangle with one edge bridged by two CS groups analogous to the $Fe_3(CO)_{10}(\mu\text{-}CO)_2$ structure of $Fe_3(CO)_{12}$ is energetically favored over structures of other types. However, the $Fe_3(CS)_3(CO)_9$ system is very highly fluxional with five distinct equilibrium structures lying within 6 kcal/mol of this global minimum. The lowest energy structures predicted for the unsaturated $Fe_3(CS)_3(CO)_n$ (n = 8, 7, 6) are very different from those previously predicted for the corresponding homoleptic carbonyls $Fe_3(CO)_{n+3}$. Thus $Fe_3(CS)_3(CO)_n$ (n = 8, 7, 6) structures with four- and six-electron donor thiocarbonyl groups and only formal Fe−Fe single bonds are energetically preferred over structures with some iron−iron multiple bonding. For $Fe_3(CS)_3(CO)_8$ the lowest energy structures have a unique four-electron donor thiocarbonyl group bridging all three iron atoms. Similarly, for $Fe_3(CS)_3(CO)_7$ the lowest energy structures have a unique six-electron donor thiocarbonyl group bridging all three iron atoms similar to the remarkable six-electron donor carbonyl group in the known stable $Cp_3Nb_3(CO)_6(\eta^2\text{-}\mu_3\text{-}CO)$. For the even more unsaturated $Fe_3(CS)_3(CO)_6$, the lowest energy structures have both a six-electron donor thiocarbonyl group bridging all three iron atoms and a four-electron donor thiocarbonyl group bridging one of the Fe−Fe edges. Thus all of these structures of the unsaturated derivatives $Fe_3(CS)_3(CO)_n$ (n = 8, 7, 6) require only formal Fe−Fe single bonds for each iron atom to have the favored 18-electron configuration. From the wide range of formal Fe−Fe single bonds found in these structures the lengths of doubly bridged single bonds are seen to be ~2.5 to 2.6 Å whereas unbridged single bonds are significantly longer at ~2.7 to 2.8 Å.

1. Introduction

Green-black solid "iron tetracarbonyl" was first prepared by Dewar and Jones[1] in 1907. However, its nature remained obscure for many years until Hieber and Becker[2,3] in 1930 showed that this "iron tetracarbonyl" is actually a trimer, $Fe_3(CO)_{12}$, by using cryoscopy in $Fe(CO)_5$ solution for a molecular weight determination. Subsequent elucidation of the nature of the metal−metal bonding framework and the arrangement of the 12 carbonyl groups in $Fe_3(CO)_{12}$ by X-ray diffraction followed a tortuous route[4] owing to disorder problems. Finally in 1966 Wei and Dahl[5] determined definitively the correct C_{2v} doubly bridged isosceles triangular structure of $Fe_3(CO)_{12}$ with two carbonyl groups bridging a single edge of the isosceles triangle, namely $Fe_3(CO)_{10}(\mu\text{-}CO)_2$ (Figure 1). More precise geometrical parameters for $Fe_3(CO)_{12}$ were subsequently obtained by Cotton and Troup.[6]

The structure of $Fe_3(CO)_{12}$ with two bridging carbonyl groups is not shared by the heavier congeners of iron, namely, ruthenium and osmium. Thus both $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ have been shown by X-ray diffraction[7−9] to have equilateral triangular structures containing only terminal carbonyl groups (Figure 1). A third alternative $M_3(CO)_{12}$ structure, namely, a D_{3h} triply bridged $M_3(CO)_9(\mu\text{-}CO)_3$ structure with a single carbonyl group bridging each edge of an equilateral M_3 triangle (Figure 1), is not known experimentally. Density functional theory (DFT) studies on

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(1) Dewar, J.; Jones, H. O. *Proc. Roy. Soc.* **1907**, *79A*, 66.
(2) Hieber, W.; Becker, E. *Chem. Ber.* **1930**, *63*, 1405.
(3) Hieber, W. *Z. Anorg. Allgem. Chem.* **1932**, *203*, 165.
(4) See the historical article by Desiderato, R.; Dobson, G. R. *J. Chem. Educ.* **1982**, *59*, 752.
(5) Wei, C. H.; Dahl, L. F. *J. Am. Chem. Soc.* **1966**, *88*, 1821.
(6) Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 4155.
(7) Mason, R.; Rae, A. I. M. *J. Chem. Soc. A* **1968**, 778.
(8) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.
(9) Corey, E. R.; Dahl, L. F. *J. Am. Chem. Soc.* **1961**, *83*, 2203.

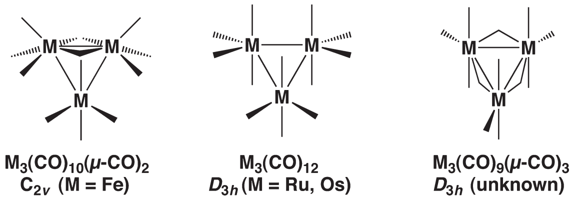

Figure 1. Three possible structures for the trinuclear derivatives $M_3(CO)_{12}$. Carbonyl groups are omitted for clarity.

$M_3(CO)_{12}$ for all three metals[10−12] predict this triply bridged structure to lie only a few kcal/mol higher than the other two structure types.

In addition to the saturated trinuclear metal carbonyls $M_3(CO)_{12}$ (M = Fe, Ru, Os) the unsaturated $M_3(CO)_n$ (n = 11, 10, 9) trinuclear metal carbonyls are of interest. The unsaturated $M_3(CO)_{11}$ (M = Ru, Os) derivatives have been generated by Bentsen and Wrighton[13,14] from the photolysis of $M_3(CO)_{12}$ in low-temperature matrices and characterized by their ν(CO) frequencies. The $Ru_3(CO)_{11}$ intermediate has also been observed in flash photolysis experiments[15] on $Ru_3(CO)_{12}$. Recently the series of saturated and unsaturated derivatives $M_3(CO)_n$ (n = 12, 11, 10, 9) has been systematically investigated for the three metals (M = Fe,[10] Ru,[11] Os[12]) using DFT methods.

A number of metal thiocarbonyl derivatives have been synthesized in which one or more carbonyl groups of a well-known homoleptic metal carbonyl have been replaced by a thiocarbonyl group.[16,17] These include $M(CS)(CO)_5$ (M = Cr, Mo, W),[18] isoelectronic with $M(CO)_6$, as well as $Fe(CS)(CO)_4$ (ref 19), isoelectronic with $Fe(CO)_5$. However, polynuclear metal derivatives containing only CO and CS ligands are still unknown. Because of the structural diversity in $M_3(CO)_{12}$ derivatives (Figure 1: M = Fe, Ru, Os), the corresponding trinuclear metal carbonyl thiocarbonyls $M_3(CS)_3(CO)_9$ are of particular interest. Furthermore, the chances of synthesizing the currently unknown $Fe_3(CS)_3(CO)_9$ are good since the known[19] $Fe(CS)(CO)_4$ is a likely potential precursor.

This paper describes DFT studies on the trinuclear $Fe_3(CS)_3(CO)_n$ (n = 9, 8, 7, 6) derivatives to explore their structures and energetics. Related DFT studies on mononuclear and binuclear iron carbonyl thiocarbonyls are described in a previous paper.[20] The unsaturated trinuclear $Fe_3(CS)_3(CO)_n$ derivatives were found to be particularly interesting, since four-electron donor edge-bridging η^2-μ-CS groups bridging edges or faces and six-electron donor face-bridging η^2-μ_3-CS groups (Figure 2) are prevalent in most of the predicted low energy structures. These results are totally different from the isoelectronic homoleptic $Fe_3(CO)_{n+3}$ derivatives,[10] where no examples of analogous four- and six-electron donor carbonyl groups were found in the predicted low energy structures. This is not because carbonyl groups cannot act as four- and six-electron donors. Thus a four-electron donor η^2-μ_3-CO group bridging two metal atoms is found in the stable compound $(Ph_2PCH_2PPh_2)_2Mn_2(CO)_4(\eta^2\text{-}\mu\text{-}CO)$, characterized by X-ray crystallography.[21,22] Similarly, a six-electron donor η^2-μ_3-CO group bridging three metal atoms is found in the stable compound $Cp_3Nb_3(CO)_6(\eta^2\text{-}\mu_3\text{-}CO)$, also characterized by X-ray crystallography.[23] A four-electron donor η^2-μ_3-CO group bridging three metal atoms is also conceptually possible (Figure 2), but so far has not been realized experimentally.

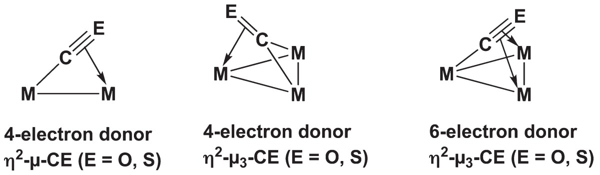

Figure 2. Four- and six-electron donor (thio)carbonyl groups.

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.[24−32] 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 exchange functional (B3) with the Lee−Yang−Parr (LYP) generalized gradient correlation functional.[33,34] 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).[35,36] It has been noted elsewhere[10,37,38] that the BP86 method may be more reliable than B3LYP for the type of organometallic systems considered in this research.

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,

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(10) Wang, H.; Xie, Y.; King, R. B.; Schaefer, H. F. *J. Am. Chem. Soc.* **2006**, *128*, 11376.

(11) Peng, B.; Li, Q.-S.; Xie, Y.; King, R. B.; Schaefer, H. F. *Dalton Trans.* **2008**, 6977.

(12) Li, Q.-S; Xu, B.; Xie, Y.; King, R. B.; Schaefer, H. F. *Dalton Trans.* **2007**, 4312.

(13) Bentsen, J. G.; Wrighton, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 4518.

(14) Bentsen, J. G.; Wrighton, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 4530.

(15) DiBenedetto, J. A.; Ryba, D. W.; Ford, P. C. *Inorg. Chem.* **1988**, *28*, 3503.

(16) Broadhurst, P. V. *Polyhedron* **1985**, *4*, 1801.

(17) Petz, W. *Coord. Chem. Revs.* **2008**, *252*, 1689.

(18) Dombek, B. D.; Angelici, R. J. *J. Am. Chem. Soc.* **1978**, *95*, 7516.

(19) Petz, W. *J. Organomet. Chem.* **1978**, *146*, C23.

(20) Zhang, Z.; Li, Q.-S.; Xie, Y.; King, R. B.; Schaefer, H. F. *Inorg. Chem.* **2009**, *48*, 1974.

(21) Colton, R.; Commons, C. J. *Aust. J. Chem.* **1975**, *28*, 1673.

(22) Commons; Hoskins, C. J. *Aust. J. Chem.* **1975**, *28*, 1663.

(23) Herrmann, W. A.; Biersack, H.; Ziegler, M. L.; Weidenhammer, K.; Siegel, R.; Rehder, D. *J. Am. Chem. Soc.* **1981**, *103*, 1692.

(24) Ehlers, A. W.; Frenking, G. *J. Am. Chem. Soc.* **1994**, *116*, 1514.

(25) Delley, B.; Wrinn, M.; Luthi, H. P. *J. Chem. Phys.* **1994**, *100*, 5785.

(26) Li, J.; Schreckenbach, G.; Ziegler, T. *J. Am. Chem. Soc.* **1995**, *117*, 486.

(27) Jonas, V.; Thiel, W. *J. Chem. Phys.* **1995**, *102*, 8474.

(28) Barckholtz, T. A.; Bursten, B. E. *J. Am. Chem. Soc.* **1998**, *120*, 1926.

(29) Niu, S.; Hall, M. B. *Chem. Rev.* **2000**, *100*, 353.

(30) Macchi, P.; Sironi, A. *Coord. Chem. Rev.* **2003**, *238*, 383.

(31) Carreon, J.-L.; Harvey, J. N. *Phys. Chem. Chem. Phys.* **2006**, *8*, 93.

(32) Buhl, M.; Kabrede, H. *J. Chem. Theory Comput.* **2006**, *2*, 1282.

(33) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(34) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(35) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(36) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

(37) See especially Furche, F.; Perdew, J. P. *J. Chem. Phys.* **2006**, *124*, 044103.

(38) Wang, H. Y.; Xie, Y.; King, R. B.; Schaefer, H. F. *J. Am. Chem. Soc.* **2005**, *127*, 11646.

Table 1. Total Energies (*E*, in Hartree), Relative Energies (Δ*E*, in kcal/mol), Iron−Iron Bond Distances (*R*, in Å), and Numbers of Imaginary Vibrational Frequencies (*Nimag*) for the Optimized $Fe_3(CO)_9(CS)_3$ Structures

		39-1 (C_S)	**39-2** (C_S)	**39-3** (C_1)	**39-4** (C_1)	**39-5** (D_{3h})	**39-6** (C_S)	**39-7** (C_1)	**39-8** (C_{3h})	**39-9** (C_{3v})
B3LYP	$-E$	6120.39730	6120.39555	6120.38959	6120.38935	6120.38750	6120.38209	6120.38418	6120.37725	6120.36714
	ΔE	0.0	1.1	4.8	5.0	6.2	9.5	8.2	12.6	18.9
	$R_{Fe1-Fe2}$	2.546	2.545	2.572	2.567	2.705	2.721	2.599	2.777	2.789
	$R_{Fe1-Fe3}$	2.742	2.758	2.751	2.757	2.705	2.709	2.753	2.777	2.789
	$R_{Fe2-Fe3}$	2.742	2.758	2.734	2.754	2.705	2.784	2.751	2.777	2.789
	Nimag	0	0	0	0	0	0	0	1(16i)	1(20i)
BP86	$-E$	6121.25249	6121.25059	6121.24661	6121.24689	6121.24216	6121.24149	6121.24055	6121.23655	6121.22049
	ΔE	0.0	1.2	3.7	3.5	6.5	6.9	7.5	10.0	20.1
	$R_{Fe1-Fe2}$	2.537	2.534	2.558	2.552	2.686	2.663	2.576	2.722	2.760
	$R_{Fe1-Fe3}$	2.721	2.736	2.727	2.737	2.686	2.691	2.733	2.722	2.760
	$R_{Fe2-Fe3}$	2.721	2.736	2.714	2.731	2.686	2.729	2.729	2.722	2.760
	Nimag	0	0	0	0	0	0	0	0	4(22i, 10i, 9i, 9i)

Table 2. Total Energies (*E*, in Hartree), Relative Energies (Δ*E*, in kcal/mol), Iron−Iron Bond Distances (*R*, in Å), and Numbers of Imaginary Vibrational Frequencies (*Nimag*) for the Optimized $Fe_3(CS)_3(CO)_8$ Structures

		38-1(C_S)	**38-2**(C_1)	**38-3**(C_1)	**38-4**(C_1)	**38-5**(C_1)	**38-6**(C_1)	**38-7**(C_S)	**38-8**(C_S)	**38-9**(C_S)
B3LYP	$-E$	6007.04890	6007.04747	6007.04417	6007.04191	6007.03585	6007.03415	6007.02455	6007.01370	6007.00740
	ΔE	0.0	0.9	3.0	4.4	8.2	9.3	15.3	22.1	26.0
	$R_{Fe1-Fe2}$	2.664	2.667	2.650	2.661	2.701	2.671	2.382	2.579	2.768
	$R_{Fe1-Fe3}$	2.664	2.649	2.662	2.638	2.787	2.796	2.621	2.579	2.730
	$R_{Fe2-Fe3}$	2.584	2.588	2.614	2.624	2.681	2.650	2.675	2.502	2.805
	Nimag	0	0	0	0	0	0	0	1(25i)	0
BP86	$-E$	6007.90042	6007.90016	6007.89712	6007.89566	6007.88333	6007.88300	6007.87987	6007.87055	6007.86785
	ΔE	0.0	0.2	2.1	3.0	10.7	10.9	12.9	18.7	20.4
	$R_{Fe1-Fe2}$	2.642	2.652	2.631	2.655	2.663	2.652	2.358	2.564	2.563
	$R_{Fe1-Fe3}$	2.642	2.634	2.642	2.624	2.707	2.712	2.607	2.564	2.626
	$R_{Fe2-Fe3}$	2.574	2.580	2.596	2.607	2.589	2.563	2.632	2.485	2.709
	Nimag	0	0	0	0	0	0	0	1(20i)	0

$\alpha_d(O) = 0.85$, and $\alpha_d(S) = 0.70$ to the standard Huzinaga−Dunning contracted DZ sets.[39−41] The loosely contracted DZP basis set for iron is the Wachters primitive set[42] augmented by two sets of p functions and one set of d functions, contracted following Hood, Pitzer, and Schaefer,[43] designated (14s11p6d/10s8p3d). For $Fe_3(CS)_3(CO)_9$, $Fe_3(CS)_3(CO)_8$, $Fe_3(CS)_3(CO)_7$, and $Fe_3(CS)_3(CO)_6$ there are 531, 501, 471, and 441 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,[44] exercising the fine grid option (75 radial shells, 302 angular points) for evaluating integrals numerically,[45] 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.[45−47] Therefore, we do not always follow such low imaginary vibrational frequencies.

The infrared ν(CO) and ν(CS) frequencies are of particular interest since initial characterization of any $Fe_3(CS)_3(CO)_n$ derivatives is likely to depend on comparison of experimental and theoretical frequencies. The ν(CO) and ν(CS) frequencies discussed in the text were all obtained using the BP86 method without scaling. The BP86 method is generally found to be more reliable than the B3LYP method for predicting ν(CO) frequencies.[38] A complete list of the ν(CO) and ν(CS) frequencies for all of the structures discussed in this paper is found in the Supporting Information (Table S37).

The optimized structures are summarized in Tables 1 to 4 and depicted in Figures 3 to 6. 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 $Fe_3(CS)_3(CO)_9$ is designated **39-1**.

3. Results

3.1. Coordinately Saturated $Fe_3(CS)_3(CO)_9$ Structures Isoelectronic with $Fe_3(CO)_{12}$.

The nine optimized $Fe_3(CS)_3(CO)_9$ structures include five doubly bridged, three triply bridged, and one unbridged structure (Figure 3 and Table 1). Seven of these structures lie within ~8 kcal/mol of the global minimum suggesting a highly fluxional system.

The lowest energy predicted structure of $Fe_3(CS)_3(CO)_9$, namely **39-1** (Figure 3 and Table 1), has two bridging CS groups and is a genuine minimum with no imaginary frequencies. This structure can be derived from the doubly bridged $Fe_3(CO)_{12}$ structure (Figure 1) by replacing the two CO groups bridging an Fe−Fe edge and one terminal equatorial CO group on the third iron atom with CS groups. Thus the terminal CS group in **39-1** is approximately coplanar with the Fe_3 triangle.

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(39) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823.

(40) Dunning, T. H.; Hay, P. J. Methods of Electronic Structure Theory; Schaefer, H. F., Ed.; Plenum: New York, 1977; pp 1−27.

(41) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.

(42) Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033.

(43) Hood, D. M.; Pitzer, R. M.; Schaefer, H. F. *J. Chem. Phys.* **1979**, *71*, 705.

(44) Frisch, M. J. et al. *Gaussian 03*, Revision C 02; Gaussian, Inc.: Wallingford, CT, 2004 (see Supporting Information for details).

(45) Papas, B. N.; Schaefer, H. F. *J. Mol. Struct.* **2006**, *768*, 175.

(46) Jacobsen, H.; Ziegler, T. *J. Am. Chem. Soc.* **1996**, *118*, 4631.

(47) Martin, J. M. L.; Bauschlicher, C. W.; Ricca, A. *Comput. Phys. Commun.* **2001**, *133*, 189.

Table 3. Total Energies (E, in Hartree), Relative Energies (ΔE, in kcal/mol), Iron–Iron Bond Distances (R, in Å), and Numbers of Imaginary Vibrational Frequencies (*Nimag*) for the Optimized $Fe_3(CS)_3(CO)_7$ Structures

		37-1 (C_1)	**37-2** (C_1)	**37-3** (C_s)	**37-4** (C_s)	**37-5** (C_s)
B3LYP	$-E$	5893.70406	5893.70391	5893.69527	5893.69401	5893.69084
	ΔE	0.0	0.1	5.5	6.3	8.3
	$R_{Fe1-Fe2}$	2.804	2.795	2.840	2.854	2.847
	$R_{Fe1-Fe3}$	2.779	2.812	2.840	2.854	2.847
	$R_{Fe2-Fe3}$	2.543	2.526	2.520	2.516	2.368
	Nimag	0	0	1(39i)	1(38i)	1(43i)
BP86	$-E$	5894.54317	5894.54236	5894.53479	5894.53395	5894.53164
	ΔE	0.0	0.5	5.3	5.8	7.2
	$R_{Fe1-Fe2}$	2.765	2.732	2.786	2.798	2.789
	$R_{Fe1-Fe3}$	2.719	2.774	2.786	2.798	2.789
	$R_{Fe2-Fe3}$	2.540	2.525	2.530	2.528	2.363
	Nimag	0	0	1(36i)	1(36i)	1(40i)

Table 4. Total Energies (E, in Hartree), Relative Energies (ΔE, in kcal/mol), Iron–Iron Bond Distances (R, in Å), and Number of Imaginary Vibrational Frequencies (*Nimag*) for the Optimized $Fe_3(CS)_3(CO)_6$ Structures

		36-1(C_1)	**36-2**(C_1)	**36-3**(C_1)	**36-4**(C_1)	**36-5**(C_1)	**36-6**(C_S)	**36-7**(C_1)	**36-8**(C_1)	**36-9**(C_S)
B3LYP	$-E$	5780.33913	5780.33910	5780.33847	5780.33259	5780.33138	5780.32489	5780.32329	5780.32064	5780.31930
	ΔE	0.0	0.0	0.4	4.1	4.9	8.9	9.9	11.6	12.4
	$R_{Fe1-Fe2}$	2.851	2.855	2.859	2.720	2.720	2.720	2.744	2.568	2.484
	$R_{Fe1-Fe3}$	2.530	2.531	2.528	2.724	2.748	2.720	2.717	2.917	2.484
	$R_{Fe2-Fe3}$	2.587	2.570	2.589	2.596	2.596	2.623	2.624	2.428	2.966
	Nimag	0	0	0	0	0	0	0	0	0
BP86	$-E$	5781.17254	5781.17260	5781.17120	5781.16652	5781.16480	5781.16150	5781.15964	5781.16129	5781.15360
	ΔE	0.0	0.0	0.9	4.0	5.2	7.4	8.7	7.6	12.7
	$R_{Fe1-Fe2}$	2.792	2.821	2.804	2.679	2.674	2.676	2.704	2.536	2.463
	$R_{Fe1-Fe3}$	2.513	2.513	2.512	2.673	2.700	2.676	2.670	2.793	2.463
	$R_{Fe2-Fe3}$	2.584	2.569	2.588	2.543	2.544	2.576	2.576	2.433	2.855
	Nimag	0	0	0	0	0	0	0	0	0

A second $Fe_3(CS)_3(CO)_9$ structure **39-2** (Figure 3 and Table 1) also has two CS ligands bridging an Fe–Fe edge. However, the third CS ligand on the third iron atom is in an axial position approximately perpendicular to the Fe_3 plane. Structure **39-2** is predicted to lie only 1.1 kcal/mol (B3LYP) or 1.2 kcal/mol (BP86) above **39-1** energetically.

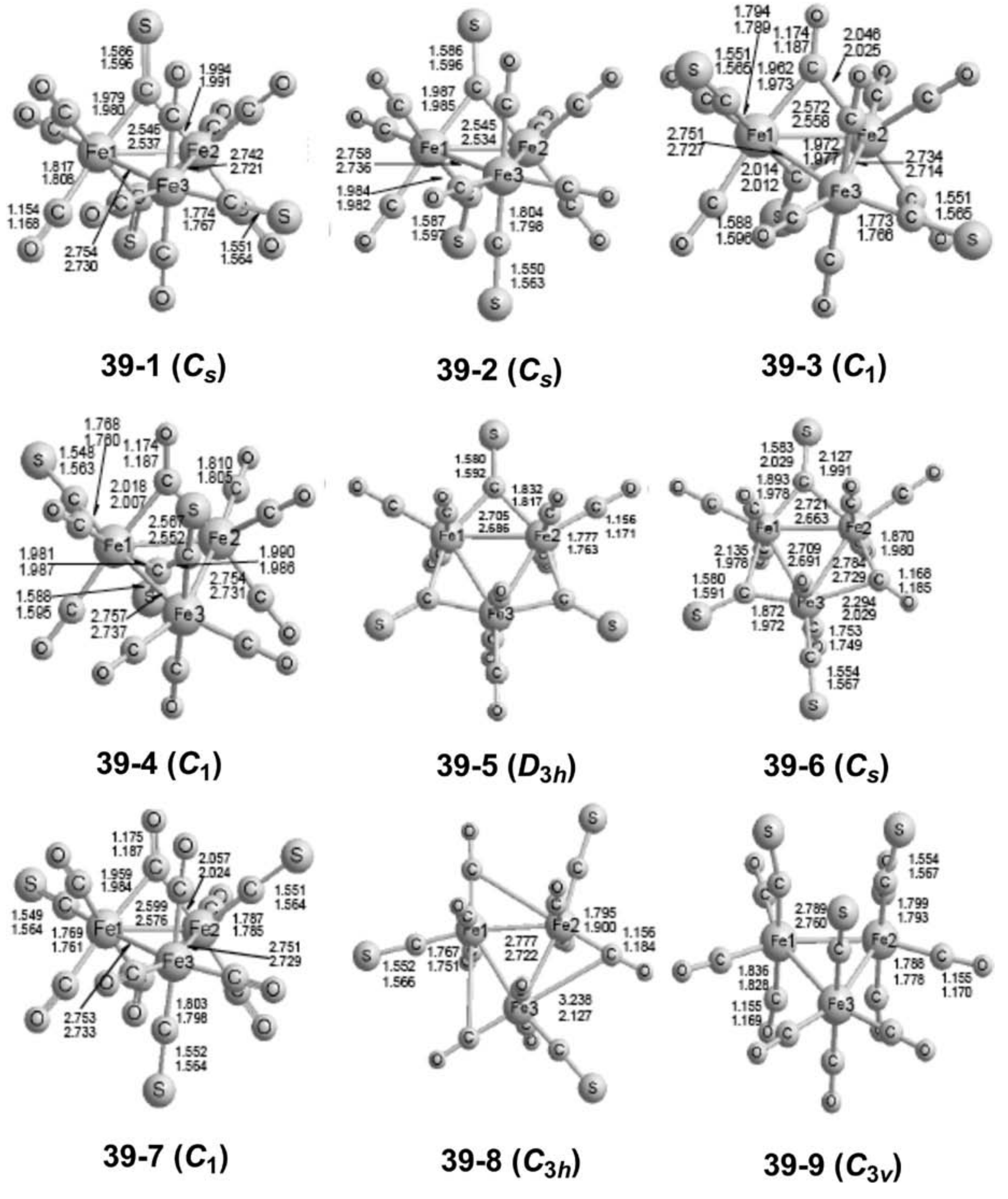
The $Fe_3(CS)_3(CO)_9$ structures **39-3** and **39-4** (Figure 3 and Table 1) both have one Fe–Fe edge bridged by both a CS group and a CO group. The difference between **39-3** and **39-4** mainly arises from the different position of the third CS group on the third Fe atom. Structures **39-3** and **39-4** lie 4.8 and 5.0 kcal/mol (B3LYP) or 3.7 and 3.5 kcal/mol (BP86) higher in energy, respectively, than **39-1** and have no imaginary vibrational frequencies.

The D_{3h} structure **39-5** of $Fe_3(CS)_3(CO)_9$ (Figure 3 and Table 1) has a bridging CS group on each Fe–Fe edge of the Fe_3 triangle. Structure **39-5** is a genuine minimum with all real vibrational frequencies predicted by both methods and lies 6.2 kcal/mol (B3LYP) or 6.5 kcal/mol (BP86) above **39-1**. The C_s triply bridged structure **39-6** of $Fe_3(CS)_3(CO)_9$ lying 9.5 kcal/mol (B3LYP) or 6.9 kcal/mol (BP86) above **39-1** with no imaginary vibrational frequencies, is derived from **39-5** by substituting a bridging CO group for one of the bridging CS group in **39-5**.

The $Fe_3(CS)_3(CO)_9$ structure **39-7** (Figure 3 and Table 1) has an Fe–Fe edge bridged by two CO groups. Structure **39-7** is a genuine minimum and lies energetically 8.2 kcal/mol (B3LYP) or 6.5 kcal/mol (BP86) above **39-1**. The C_{3h} $Fe_3(CS)_3(CO)_9$ structure **39-8** is predicted by B3LYP to have all terminal CS and CO groups with a small imaginary frequency of 16i cm^{-1}. However, the BP86 method predicts **39-8** to be a triply bridged structure with all real harmonic vibrational frequencies. Structure **39-8** lies 12.6 kcal/mol (B3LYP) or 10.0 kcal/mol (BP86) above **39-1**. The highest energy structure of $Fe_3(CS)_3(CO)_9$ in Figure 3 and Table 1, namely the C_{3v} structure **39-9** with all terminal CS and CO groups, has a small imaginary frequency (B3LYP) or four small imaginary frequencies (BP86). Structure **39-9** is predicted to lie 18.9 kcal/mol (B3LYP) or 20.1 kcal/mol (BP86) above the global minimum **39-1**.

The lengths of the doubly bridged Fe1–Fe2 edges in the $Fe_3(CS)_3(CO)_9$ structures **39-1** and **39-2** are predicted to be 2.545 Å (B3LYP) or 2.535 Å (BP86), which are ~0.05 Å shorter than the corresponding doubly bridged Fe–Fe edge in $Fe_3(CO)_{12}$. The lengths of the Fe1–Fe2 edges in the $Fe_3(CS)_3(CO)_9$ structures **39-3** and **39-4** bridged by one CS and one CO group increase to ~2.570 Å (B3LYP) or ~2.555 Å (BP86). The length of the Fe–Fe edge in **39-7** bridged by two CO groups increases to 2.599 Å (B3LYP) or 2.576 Å (BP86). Thus the replacement of bridging CS groups by bridging CO groups lengthens slightly the doubly bridged Fe–Fe edges in these structures. Furthermore, the unbridged Fe–Fe bond lengths in these doubly bridged structures increase slightly upon replacement of bridging CS by bridging CO groups elsewhere in the structure. The lengths of the singly bridged Fe–Fe edges in the triply bridging $Fe_3(CS)_3(CO)_9$ structures **39-5** and **39-6** are ~2.71 Å. All of these edge lengths are consistent with the Fe–Fe single bonds required to give all iron atoms the favored 18-electron configuration.

The ν(CO) frequencies predicted for the $Fe_3(CS)_3(CO)_9$ structures fall in the ranges 1970 to 2070 cm^{-1} for terminal carbonyl groups and 1850 to 1900 cm^{-1} for bridging carbonyl groups (see Table S37 in the Supporting Information). Similarly, the ν(CS) frequencies



39-1 (C_s) **39-2** (C_s) **39-3** (C_1)

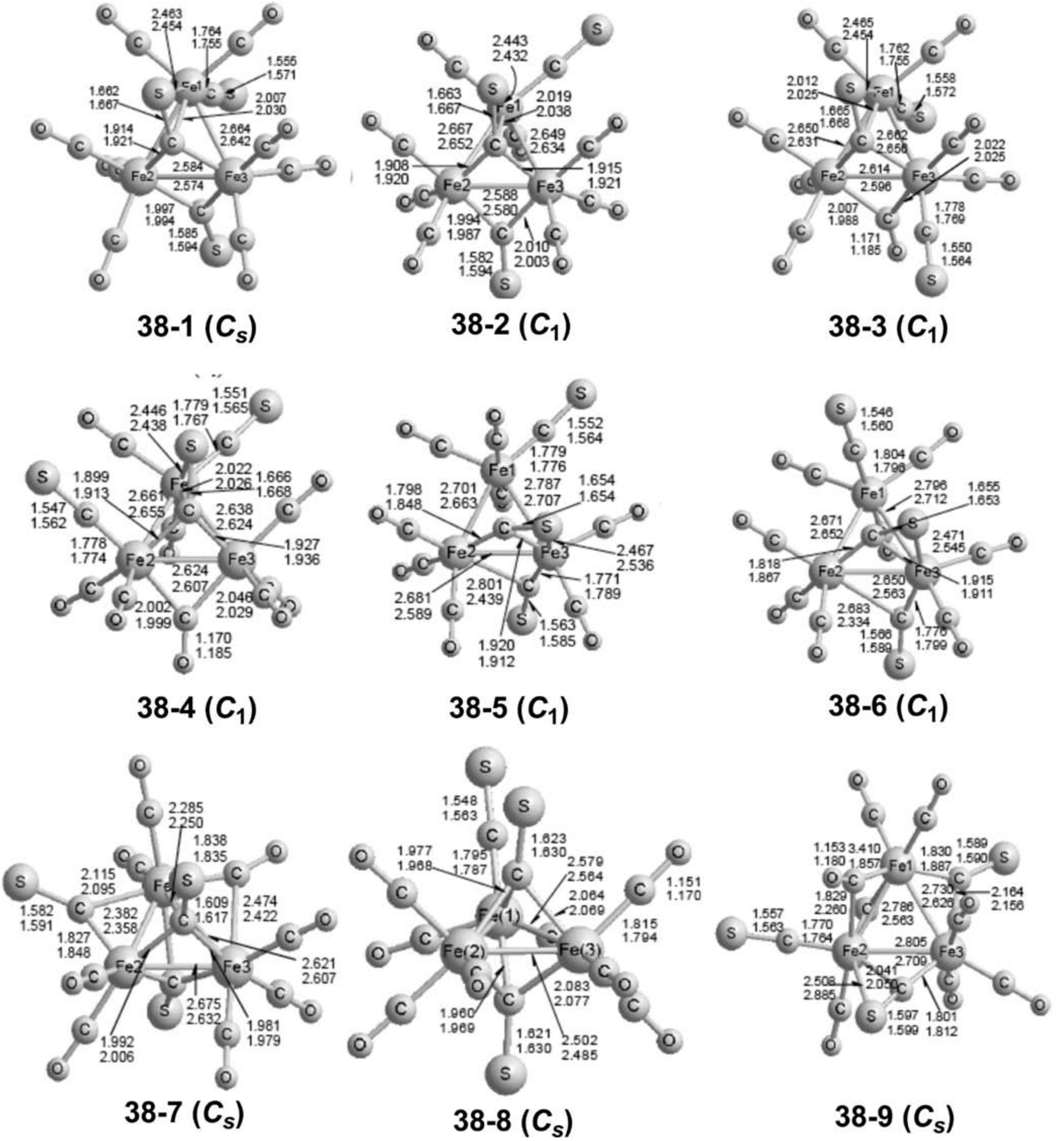
39-4 (C_1) **39-5** (D_{3h}) **39-6** (C_s)

39-7 (C_1) **39-8** (C_{3h}) **39-9** (C_{3v})

Figure 3. Nine optimized structures of $Fe_3(CS)_3(CO)_9$. In Figures 3 to 6 the upper distances are obtained by the B3LYP method and the lower distances by the BP86 method.

predicted for the $Fe_3(CS)_3(CO)_9$ structures fall in the ranges 1300 to 1340 cm^{-1} for terminal thiocarbonyl groups and 1145 to 1185 cm^{-1} for bridging thiocarbonyl groups. This is consistent with previous observations[17] on the ν(CE) frequencies (E = O, S) of terminal CE relative to bridging CE groups and reflects a lower formal C−E bond order of a bridging CE group relative to a terminal CE group.

3.2. Coordinately Unsaturated $Fe_3(CS)_3(CO)_n$ (n = 8, 7, 6) Derivatives. 3.2.1. $Fe_3(CS)_3(CO)_8$. The nine structures found for $Fe_3(CS)_3(CO)_8$ within 25 kcal/mol of the global minimum (Figure 4 and Table 2) are all predicted to have only real vibrational frequencies except for structure **38-8** with a very small imaginary vibrational frequency of $25i$ cm^{-1} (B3LYP) or $20i$ cm^{-1} (BP86). The four lowest-energy $Fe_3(CS)_3(CO)_8$ structures all have a four-electron donor η^2-μ_3-CS group bridging all three iron atoms with C−S distances of ~1.66 Å (see Figure 2). These η^2-μ_3-CS distances are significantly longer than the typical ~1.59 Å C−S distances for two-electron donor edge-bridging μ-CS groups. We tried to optimize $Fe_3(CS)_3(CO)_8$ structures with a four-electron donor η^2-μ_3-CO group but such optimizations led to structures > 30 kcal/mol in energy above the global minimum. This indicates that four-electron donor η^2-μ_3-CS groups are



38-1 (*C*$_s$) **38-2 (*C*$_1$)** **38-3 (*C*$_1$)**

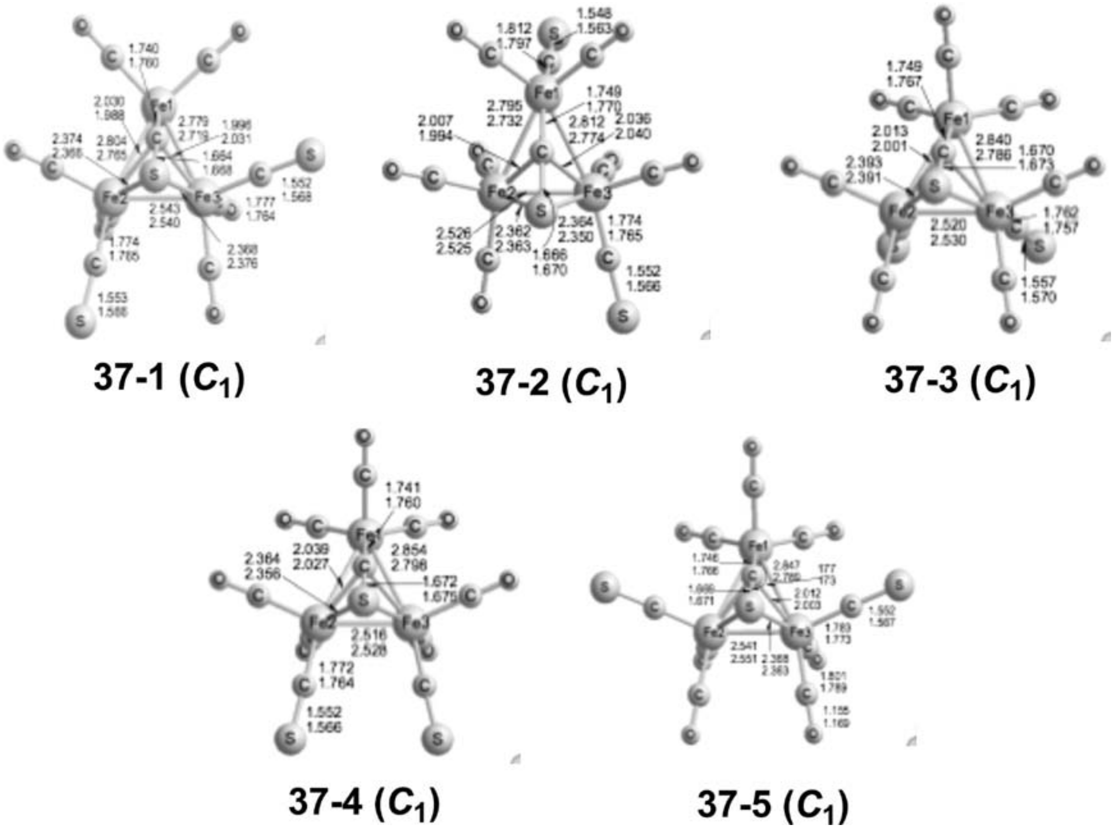
38-4 (*C*$_1$) **38-5 (*C*$_1$)** **38-6 (*C*$_1$)**

38-7 (*C*$_s$) **38-8 (*C*$_s$)** **38-9 (*C*$_s$)**

Figure 4. Nine optimized $Fe_3(CS)_3(CO)_8$ structures within 25 kcal/mol of the global minimum.

much more favorable than the analogous four-electron donor η^2-μ_3-CO groups. The ν(CS) frequencies predicted for the four-electron donor η^2-μ_3-CS groups fall in the very narrow range 1005 ± 2 cm^{-1} and thus are much lower than the normal two-electron donor bridging CS groups at 1145 to 1185 cm^{-1} (see Table S37 in the Supporting Information)

In the two lowest lying $Fe_3(CS)_3(CO)_8$ structures, namely **38-1** and **38-2** (Figure 4 and Table 2), the four-electron donor η^2-μ_3-CS group is supplemented by a two-electron donor CS group bridging an Fe−Fe edge. These edge-bridging CS groups exhibit ν(CS) frequencies in the narrow range 1172 ± 2 cm^{-1}. Structure **38-1** is the global minimum of $Fe_3(CS)_3(CO)_8$ and can be derived from the $Fe_3(CS)_3(CO)_9$ structure **39-2** (Figure 3) by converting a two-electron donor μ-CS bridge to a four-electron donor η^2-μ_3-CS bridge with loss of a carbonyl group. The unique Fe2−Fe3 distance in **38-1**, namely, 2.584 Å (B3LYP) or 2.574 Å (BP86), is ~0.04 Å longer than that in **39-1** whereas the two equivalent Fe−Fe bond distances in **38-1**, namely, 2.664 Å (B3LYP) or 2.642 Å (BP86), are ~0.09 Å shorter than those in **39-1**. The $Fe_3(CS)_3(CO)_8$ structure **38-2** is similar to **38-1** but with an equatorial terminal CS group on Fe1. Structure



37-1 (C_1) **37-2 (C_1)** **37-3 (C_1)**

37-4 (C_1) **37-5 (C_1)**

Figure 5. Five optimized $Fe_3(CS)_3(CO)_7$ structures within 20 kcal/mol of the global minimum.

38-2 lies only 0.9 kcal/mol (B3LYP) or 0.2 kcal/mol (BP86) above **38-1** so that these two $Fe_3(CS)_3(CO)_8$ structures can be considered as nearly degenerate in energy.

The next two $Fe_3(CS)_3(CO)_8$ structures **38-3** and **38-4** (Figure 4 and Table 2), lying ~3 kcal/mol above **38-1**, are similar to structures **38-1** and **38-2** except that the two-electron donor bridging group is a CO group rather than a CS group. In the next two $Fe_3(CS)_3(CO)_8$ structures **38-5** and **38-6** (Figure 4 and Table 2) at ~9 kcal/mol above **38-1**, there is a bridging thiocarbonyl group donating four electrons but bridging an Fe−Fe edge,that is, a η^2-μ-CS group, rather than the entire Fe_3 triangle as in the four lowest energy $Fe_3(CS)_3(CO)_8$ structures. Such a four-electron donor thiocarbonyl group bridging an edge rather than entire Fe_3 triangle in structures **38-5** and **38-6** is predicted to exhibit a ν(CS) frequency in the range 1039 ± 6 cm^{-1}. A second CS group in **38-5** and **38-6** is a two-electron donor semibridging CS group, predicted to exhibit a ν(CS) frequency in the range 1227 ± 8 cm^{-1}. This semibridging ν(CS) frequency lies between the ν(CS) frequencies of terminal CS groups at 1300 to 1340 cm^{-1} and normal two-electron donor bridging CS groups at 1145 to 1184 cm^{-1}. The Fe−Fe distances in all six of these lowest lying $Fe_3(CS)_3(CO)_8$ structures (**38-1** to **38-6**) correspond to the formal single bonds required to give all three iron atoms the favored 18-electron configuration.

Unlike the six lower-energy structures, the $Fe_3(CS)_3(CO)_8$ structure **38-7** (Figure 4 and Table 2) at 15.3 kcal/mol (B3LYP) or 12.9 kcal/mol (BP86) kcal/mol above **38-1** has only two-electron donor CS and CO groups. Structure **38-7** is unusual since it has four bridging groups. The two μ_3-CS groups bridge all three iron atoms, thereby forming an Fe_3C_2 trigonal bipyramid, and are predicted to exhibit ν(CS) frequencies at 1068 and 1106 cm^{-1}. In addition, one Fe−Fe edge in **38-7** is semibridged by the third CS group with very unequal Fe−C distances (Figure 4) and a second Fe−Fe edge is bridged by a CO group. The semibridging CS group is predicted to exhibit a ν(CS) frequency of 1210 cm^{-1}. The Fe1═Fe2 edge bridged by the μ-CS group is abnormally short, namely 2.382 Å (B3LYP) or 2.358 Å (BP86), suggesting the formal double bond required to give all three iron atoms in $Fe_3(CS)_3(CO)_8$ the favored 18-electron configuration with only two-electron donor CS and CO groups. In the next $Fe_3(CS)_3(CO)_8$ structure **38-8**, at 22.1 kcal/mol (B3LYP) or 18.7 kcal/mol (BP86) above **38-1**, the only bridging groups are two-electron donor μ_3-CS groups bridging the entire Fe_3 triangle, again forming an Fe_3C_2 trigonal bipyramid, as in **38-7**. These μ_3-CS groups in **38-8** are predicted to exhibit ν(CS) frequencies at 1068 and 1031 cm^{-1}. The Fe−C distances to the μ_3-CS groups in **38-8** are predicted to be ~2.0 Å, similar to the ~1.92 Å corresponding Ni−C distances found experimentally by X-ray crystallography in the known compound[48] $Cp_3Ni_3(\mu_3\text{-}CS)_2$. Similarly the predicted C−S distances in the μ_3-CS groups of **38-8** of 1.62 ± 0.01 Å are close to the experimental[48] C−S distances of 1.60 Å in $Cp_3Ni_3(\mu_3\text{-}CS)_2$. An analogous $Fe_3(CO)_9(\mu_3\text{-}CO)_2$ structure was predicted to be the global minimum for $Fe_3(CO)_{11}$ in a previous DFT study.[10]

The final $Fe_3(CS)_3(CO)_8$ structure **38-9**, within 30 kcal/mol of the global minimum **38-1**, lies 26.0 kcal/mol

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[48] North, T. E.; Thoden, J. B.; Spencer, B.; Byarnason, A.; Dahl, L. F. *Organometallics* **1992**, *11*, 4326.

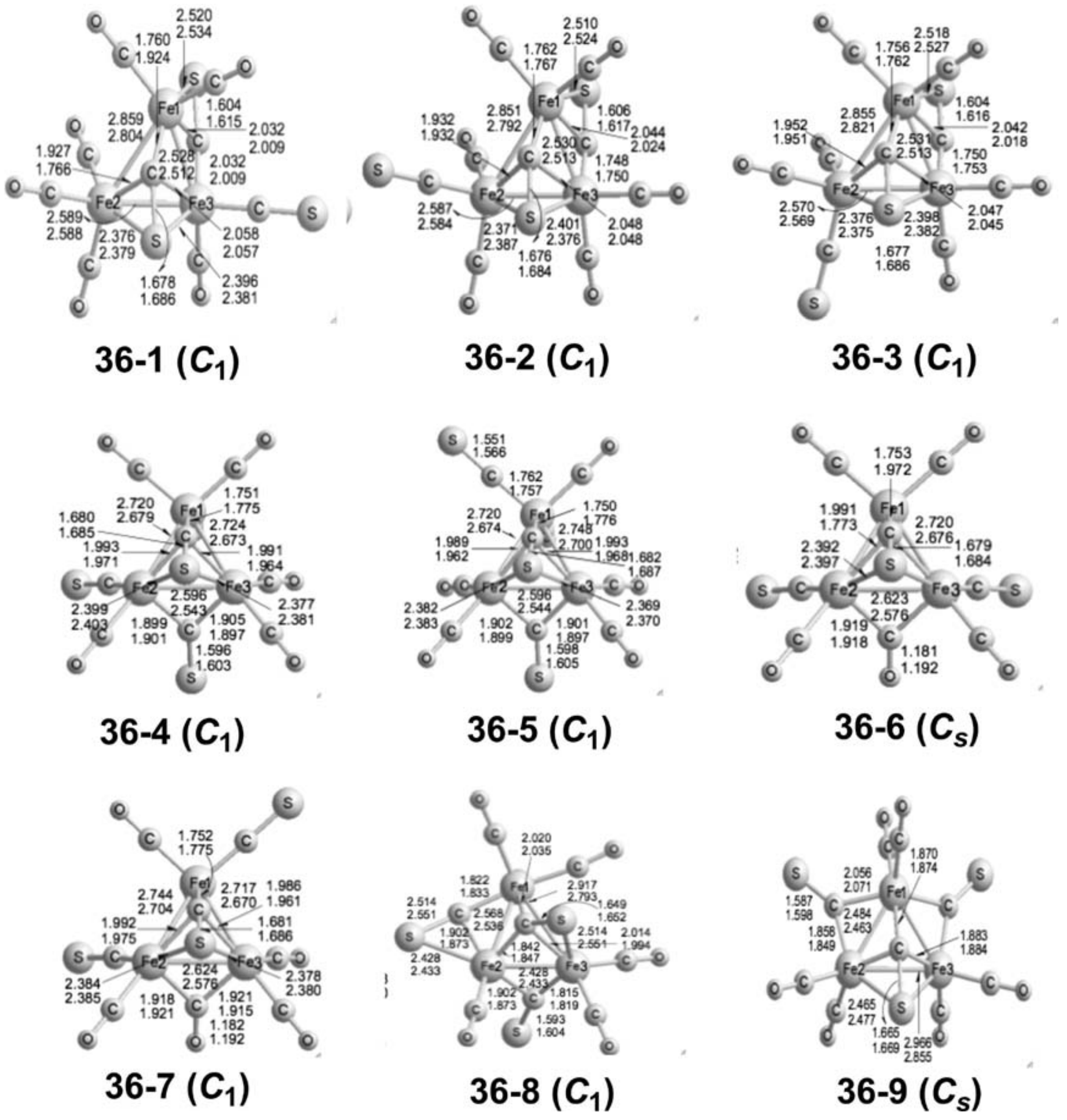

Figure 6. Nine optimized $Fe_3(CS)_3(CO)_6$ structures within 13 kcal/mol of the global minimum.

(B3LYP) or 20.4 kcal/mol (BP86) higher in energy than **38-1.** Structure **38-9** has four bridging groups, namely, a four-electron donor edge-bridging η^2-μ-CS group, as well as one μ-CS and two μ-CO groups, which donate two electrons each. The Fe−Fe bond distances of **38-9** suggest formal Fe−Fe single bonds leading to the favored 18-electron configuration for all three iron atoms.

3.2.2. $Fe_3(CS)_3(CO)_7$. Each of the five $Fe_3(CS)_3(CO)_7$ structures within 20 kcal/mol of the global minimum **37-1** has a six-electron donor η^2-μ_3-CS group bridging all three iron atoms (Figure 5 and Table 3). No other bridging groups are present in any of these five $Fe_3(CS)_3(CO)_7$ structures, which differ in the arrangement of the two terminal CS groups on the (η^2-μ_3-CS)Fe_3 framework. The unique six-electron donor η^2-μ_3-CS groups in these $Fe_3(CS)_3(CO)_7$ structures are predicted to exhibit ν(CS) frequencies in the narrow range 1109 ± 9 cm^{-1}. These ν(CS) frequencies are significantly higher than the 1005 ± 2 cm^{-1} ν(CS) frequencies predicted for the four-electron donor face-bridging η^2-μ_3-CS groups in several $Fe_3(CS)_3(CO)_8$ structures (see above).

The essentially degenerate structures **37-1** and **37-2** of $Fe_3(CS)_3(CO)_7$ (Figure 5 and Table 3) are both genuine minima with no imaginary vibrational frequencies by either method. However, structures **37-3**, **37-4**, and **37-5** all exhibit a small imaginary vibrational frequency $< 50i$ cm^{-1} by either method. The Fe−Fe distances in these five structures can be interpreted as formal single bonds, which, with the six-electron donor η^2-μ_3-CS group, gives each iron atom the favored 18-electron configuration.

3.2.3. $Fe_3(CS)_3(CO)_6$. Compared to $Fe_3(CS)_3(CO)_7$ the potential surface of $Fe_3(CS)_3(CO)_6$ is very complicated, with 13 structures within 20 kcal/mol of the global minimum. Only the nine structures within 13 kcal/mol of the global minimum are discussed in this paper (Figure 6 and Table 4). These nine structures of $Fe_3(CS)_3(CO)_6$ are all genuine minima without any imaginary frequencies using either method.

The three lowest energy $Fe_3(CS)_3(CO)_6$ structures (Figure 6 and Table 4) all have one six-electron donor thiocarbonyl group and one four-electron donor thiocarbonyl group, so that formal Fe−Fe single bonds along

Table 5. Bond Dissociation Energies (kcal/mol) for Successive Removal of Carbonyl Groups from $Fe_3(CS)_3(CO)_n$ (n = 9, 8, 7) and Their Carbonyl Analogues $Fe_3(CO)_{n+3}$

	B3LYP	BP86
$Fe_3(CS)_3(CO)_9 \rightarrow Fe_3(CS)_3(CO)_8 + CO$	12.4	14.7
$Fe_3(CS)_3(CO)_8 \rightarrow Fe_3(CS)_3(CO)_7 + CO$	10.2	17.9
$Fe_3(CS)_3(CO)_7 \rightarrow Fe_3(CS)_3(CO)_6 + CO$	22.8	27.2
$Fe_3(CO)_{12} \rightarrow Fe_3(CO)_{11} + CO$	42.7	43.9
$Fe_3(CO)_{11} \rightarrow Fe_3(CO)_{10} + CO$	23.9	31.6
$Fe_3(CO)_{10} \rightarrow Fe_3(CO)_9 + CO$	30.5	37.9

Table 6. Iron−Iron Distances in the $Fe_3(CS)_3(CO)_9$ Structures (Å)[a]

$Fe_3(CS)_3(CO)_9$ structure	doubly bridged Fe−Fe distances	singly bridged Fe−Fe distances	unbridged Fe−Fe distances
39-1	2.54		2.73 (2)
39-2	2.54		2.75 (2)
39-3	2.56		2.74, 2.72
39-4	2.56		2.74, 2.74
39-5		2.70 (3)	
39-6		2.75, 2.71, 2.68	
39-7	2.59		2.74, 2.74
39-8		2.74 (3)	
39-9			2.77 (3)

[a] Average of the B3LYP and BP86 results.

each edge of the Fe_3 triangle are sufficient to give each iron atom the favored 18-electron configuration. Structures **36-1** and **36-2** are degenerate to within 0.05 kcal/mol. The Fe1−Fe2 distances in **36-1** and **36-2** are ~2.8 Å, consistent with an unbridged single bond. The Fe1−Fe3 bond distances (~2.53 Å) are predicted to be very close to that of the doubly bridged Fe−Fe single bond (~2.54 Å) of **39-1**. Moreover, the distances between the carbon atom of the six-electron donor η^2-μ_3-CS group and the iron atoms are predicted to be 1.760 Å (B3LYP) or 1.740 Å (BP86) for Fe1−C, 1.927 Å (B3LYP) or 1.924 Å (BP86) for Fe2−C, and 2.058 Å (B3LYP) or 2.057 Å (BP86) for Fe3−C, respectively, which are slightly shorter than the corresponding Fe−C distances in **37-1** (Figure 5). The Fe2−Fe3 edge bridged by the four-electron donor η^2-μ-CS ligand in **36-1** and **36-2** is predicted to be 2.59 Å. The $Fe_3(CS)_3(CO)_6$ structure **36-3** lies 0.4 kcal/mol (B3LYP) or 0.9 kcal/mol (BP86) kcal/mol above **36-1** or **36-2** energetically, and differs from **36-2** by the location of the terminal CS group. The six-electron donor η^2-μ_3-CS groups and four-electron donor η^2-μ-CS groups in **36-1**, **36-2**, and **36-3** are predicted to exhibit ν(CS) frequencies at 1058 ± 1 cm^{-1} and 1182 ± 2 cm^{-1}, respectively.

The $Fe_3(CS)_3(CO)_6$ structures **36-4** and **36-5** (Figure 6 and Table 4) also have a six-electron donor η^2-μ_3-CS ligand. However, their additional bridging CS ligand is only a formal two-electron donor with no direct Fe−S interaction rather than the four-electron donor η^2-μ-CS ligand found in **36-1**, **36-2**, and **36-3**. The ν(CS) frequencies of the six-electron donor η^2-μ_3-CS groups in **36-4** and **36-5** at 1066 ± 1 cm^{-1} are close to the corresponding ν(CS) frequencies in **36-1**, **36-2**, and **36-3**. The ν(CS) frequencies of the edge-bridging CS groups in **36-4** and **36-5** are predicted to be 1160 ± 1 cm^{-1}. The energies of **36-4** and **36-5** are predicted to lie 4.6 ± 0.6 kcal/mol above **36-1** or **36-2**. The $Fe_3(CS)_3(CO)_6$ structures **36-6** and **36-7** are similar to **36-4** and **36-5** but substitute μ-CO groups for the μ-CS groups. These two structures lie 9.0 ± 0.9 kcal/mol above the global minimum **36-1** of $Fe_3(CS)_3(CO)_6$, again indicating that bridging carbonyl groups are less favorable energetically than bridging thiocarbonyl groups. The bridging ν(CO) frequencies in **36-6** and **36-7** are predicted to fall in the range 1850 ± 2 cm^{-1}, which is a typical region for edge-bridging carbonyl groups in homoleptic metal carbonyl derivatives.

The $Fe_3(CS)_3(CO)_6$ structure **36-8** (Figure 6 and Table 4) at 11.6 kcal/mol (B3LYP) or 7.6 kcal/mol (BP86) above **36-1** is of interest since all three of its CS groups are four-electron donor bridging CS groups. One of these CS groups is a η^2-μ_3-CS group bridging all three iron atoms and exhibiting a ν(CS) frequency at 1045 cm^{-1}. The remaining two CS groups are η^2-μ-CS groups bridging Fe−Fe edges and are predicted to exhibit ν(CS) frequencies at 1165 and 1198 cm^{-1}. The $Fe_3(CS)_3(CO)_6$ structure **36-9** at 12.4 kcal/mol (B3LYP) or 12.7 kcal/mol (BP86) has one six-electron donor η^2-μ_3-CS group and two two-electron donor μ-CS groups exhibiting ν(CS) frequencies at 1020 cm^{-1} and 1189 and 1174 cm^{-1}, respectively.

3.3. Dissociation Energies. Table 5 compares the bond dissociation energies (BDEs) of single carbonyl dissociation steps (eqs 1a and 1b) for the corresponding $Fe_3(CS)_3(CO)_n$ and $Fe_3(CO)_{n+3}$ derivatives according to the following equations:

$$Fe_3(CS)_3(CO)_n \rightarrow Fe_3(CS)_3(CO)_{n-1} + CO \qquad (1a)$$

$$Fe_3(CO)_{n+3} \rightarrow Fe_3(CO)_{n+2} + CO(n = 9, 8, 7) \qquad (1b)$$

In this connection the BDEs for loss of CO from the trinuclear $Fe_3(CS)_3(CO)_n$ derivatives (n = 9, 8) are predicted to be substantially lower than those of the corresponding $Fe_3(CO)_{n+3}$ derivatives. The CO dissociation energy of $Fe_3(CS)_3(CO)_7$ to $Fe_3(CS)_3(CO)_6$ is also less than the corresponding CO dissociation energy of $Fe_3(CO)_{10}$ to $Fe_3(CO)_9$, although the difference is much less dramatic. The much lower CO dissociation energies of the trinuclear $Fe_3(CS)_3(CO)_n$ derivatives relative to the corresponding $Fe_3(CO)_{n+3}$ structures is probably a consequence of the much greater tendency of thiocarbonyl groups than carbonyl groups to function as formal four- and six-electron donor ligands, as indicated consistently by the DFT results reported here. This also suggests that the stable trinuclear photolysis product of $Fe(CS)(CO)_4$, for example, might not be $Fe_3(CS)_3(CO)_9$ but instead $Fe_3(CS)_3(CO)_8$ or $Fe_3(CS)_3(CO)_7$, containing one four-electron donor or six-electron donor thiocarbonyl group, respectively. This indicates a possible major difference between the chemistry of metal carbonyls and metal thiocarbonyls.

4. Discussion

The results obtained in this research show clearly that the lowest energy structures for the unsaturated $Fe_3(CS)_3(CO)_n$ derivatives (n = 8, 7, 6) have four- and six-electron donor bridging thiocarbonyl groups (Figure 2) in preference to iron−iron multiple bonds. Thus the lowest energy structures for $Fe_3(CS)_3(CO)_8$ have one four-electron donor bridging thiocarbonyl group, those for $Fe_3(CS)_3(CO)_7$ have one six-electron donor bridging thiocarbonyl group, and those for $Fe_3(CS)_3(CO)_6$ have one six-electron donor and one four-electron donor bridging thiocarbonyl group. In all of these cases three formal Fe−Fe single bonds in the Fe_3 triangles are sufficient to give each iron atom the favored 18-electron configuration. Also note that no low energy $Fe_3(CS)_3(CO)_n$ structures (n = 8, 7, 6) were found containing six- and/or four-electron donor carbonyl rather than thiocarbonyl groups. This supports further the energetic preference for bridging thiocarbonyl groups relative to bridging carbonyl groups.

Because of the prevalence of formal Fe−Fe single bonds with a variety of bridging carbonyl and thiocarbonyl groups, the $Fe_3(CS)_3(CO)_n$ derivatives (n = 9, 8, 7, 6) are good systems for studying the effects on metal−metal bond lengths, as the number and nature of the bridging groups are changed while keeping constant the formal metal−metal bond order. For the saturated $Fe_3(CS)_3(CO)_9$ the only types of possible bridging groups in principle are two-electron donor carbonyl and thiocarbonyl groups, which may either bridge an edge (μ-CE) (E = O, S) of the Fe_3 triangle or the entire Fe_3 triangle (μ_3-CE). However, no energetically competitive $Fe_3(CS)_3(CO)_9$ structures were found containing face-bridging μ_3-CE thiocarbonyl or carbonyl groups so only edge-bridging thiocarbonyl and carbonyl groups need to be considered.

The predicted Fe−Fe edge lengths in the Fe_3 triangles of the nine optimized $Fe_3(CS)_3(CO)_9$ structures (Figure 3 and Table 1), which necessarily correspond to formal single bonds, indicate clearly a shortening of the Fe−Fe edge as the number of bridges is increased (Table 6). Thus in the four lowest energy $Fe_3(CS)_3(CO)_9$ structures **39-1**, **39-2**, **39-3**, and **39-4** the doubly bridged edges are 2.55 ± 0.01 Å whereas the unbridged edges are significantly longer at 2.74 ± 0.02 Å. Singly bridged Fe−Fe edges are found in some of the higher energy $Fe_3(CS)_3(CO)_9$ structures (**39-5**, **39-6**, and **39-8**). Their lengths of 2.72 ± 0.03 Å are only slightly shorter than the unbridged Fe−Fe edges in the $Fe_3(CS)_3(CO)_9$ structures.

The six lowest energy $Fe_3(CS)_3(CO)_8$ structures (Figure 4 and Table 2) all have four-electron donor bridging thiocarbonyl groups, so that formal single bonds along each of the three edges of the Fe_3 triangles are sufficient to give each iron atom the favored 18-electron configuration. In the four lowest energy $Fe_3(CS)_3(CO)_8$ structures (**38-1**, **38-2**, **38-3**, and **38-4**) this four-electron donor thiocarbonyl group is a η^2-μ_3-CS group bridging all three iron atoms of the Fe_3 triangle (Figure 2). *This type of four-electron donor bridging thiocarbonyl group has not yet been found experimentally in a stable compound.* However, it can be derived from a normal two-electron donor edge-bridging μ-CS group by donation of the sulfur lone pair to a third metal atom. The next two $Fe_3(CS)_3(CO)_8$ structures in terms of energy (**38-5** and **38-6**) also have a four-electron donor thiocarbonyl group but one that bridges only one Fe−Fe edge rather than the entire Fe_3 triangle. Such an η^2-μ-CS bridging thiocarbonyl group is analogous to the η^2-μ-CO group found[21,22] in $(Ph_2PCH_2PPh_2)_2Mn_2(CO)_4(\eta^2$-$\mu$-CO) (Figure 2). All six of these $Fe_3(CS)_3(CO)_8$ structures thus need only single Fe−Fe bonds for each iron atom to achieve a formal 18-electron configuration.

Table 7. Iron−Iron Distances in the $Fe_3(CS)_3(CO)_8$ Structures (Å)[a]

$Fe_3(CS)_3$-$(CO)_8$ structure	4-electron donor group	doubly bridged Fe−Fe distances	singly bridged Fe−Fe distances	unbridged Fe−Fe distances	Fe=Fe distance
38-1	μ_3-CS	2.58	2.65 (2)		
38-2	μ_3-CS	2.58	2.66, 2.64		
38-3	μ_3-CS	2.60	2.65, 2.64		
38-4	μ_3-CS	2.62	2.66, 2.63		
38-5	μ-CS		2.64	2.75, 2.68	
38-6	μ-CS	2.61		2.75, 2.66	
38-7		2.65, 2.61			2.37
38-8		2.57 (2)			2.49

[a] Average of the B3LYP and BP86 results.

For these six lowest lying $Fe_3(CS)_3(CO)_8$ structures (Figure 4 and Table 2) the relationship of the Fe−Fe single bond distances to the number and nature of the bridging groups can be studied similar to the analysis of the Fe−Fe bond distances in the $Fe_3(CS)_3(CO)_9$ structures discussed above (Table 7). Thus in these six $Fe_3(CS)_3(CO)_8$ structures the doubly bridged Fe−Fe edges are 2.60 ± 0.02 Å, only slightly longer than the 2.55 ± 0.01 Å lengths of the doubly bridged Fe−Fe edges in the $Fe_3(CS)_3(CO)_9$ structures (Table 6). In the $Fe_3(CS)_3(CO)_8$ structures **38-1**, **38-2**, **38-3**, and **38-4** the lengths of the Fe−Fe edges bridged only by the four-electron donor thiocarbonyl group are 2.64 ± 0.02 Å, which is about 0.05 Å shorter than the singly bridged Fe−Fe edges in the $Fe_3(CS)_3(CO)_9$ structures discussed above. The lengths of the unbridged Fe−Fe edges in the $Fe_3(CS)_3(CO)_8$ structures containing edge-bridging rather than face-bridging four-electron donor thiocarbonyl groups (**38-5** and **38-6**) are 2.70 ± 0.05 Å, which are similar to the unbridged Fe−Fe edge lengths in the $Fe_3(CS)_3(CO)_9$ structures.

The remaining two (higher energy) $Fe_3(CS)_3(CO)_8$ structures, namely, **38-7** and **38-8** (Figure 4), contain only two-electron donor carbonyl and thiocarbonyl groups and thus require one formal Fe=Fe double bond in their Fe_3 triangles for each iron atom to have the favored 18-electron configuration. In both structures there is an abnormally short Fe=Fe distance in the Fe_3 triangle, which can correspond to this formal double bond. In **38-7** this abnormally short Fe=Fe distance is a singly bridged edge of length 2.37 Å, which is ~0.3 Å shorter than the length of a singly bridged formal Fe−Fe single bond. Furthermore, this predicted 2.37 Å formal Fe=Fe double bond distance in **38-7** is very similar to the 2.316 Å distance determined by X-ray diffraction[49] for the formal Fe=Fe double bond in $(Bu^t_2C_2)Fe_2(CO)_6$ bridged by a di-*tert*-butylacetylene unit. In **38-8** the shortened Fe=Fe double bond edge is 2.49 Å. These two iron atoms are apparently prevented from a closer approach by the two μ_3-CS face-bridging thiocarbonyl groups.

All five of the low-energy $Fe_3(CS)_3(CO)_7$ structures (Figure 5 and Table 3) have a six-electron donor η^2-μ_3-CS group as the only bridging group, so that the favored 18-electron configuration is achieved for all of the iron atoms with only Fe−Fe single bonds in the Fe_3 triangles. *This type of six-electron donor bridging thiocarbonyl group has not yet been found experimentally in a stable compound.*[17] The lengths of the unique edges of the Fe_3 triangles bridged by the sulfur atom in these $Fe_3(CS)_3(CO)_7$ structures are 2.53 ± 0.1 Å whereas the lengths of the remaining two Fe−Fe edges in each structure are 2.78 ± 0.04 Å.

The three lowest energy $Fe_3(CS)_3(CO)_6$ structures, namely **36-1**, **36-2**, and **36-3** (Figure 6 and Table 4), have both

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(49) Cotton, F. A.; Jamerson, J. D.; Stults, B. R. *J. Am. Chem. Soc.* **1976**, *98*, 1774.

Table 8. Iron–Iron Distances in the $Fe_3(CS)_3(CO)_6$ Structures (Å)[a]

$Fe_3(CS)_3(CO)_6$ structure	6- and 4-electron donor CS groups	S-bridged Fe–Fe distances	Doubly bridged Fe–Fe distances	Singly bridged Fe–Fe distances
36-1	6 + 4	2.59	2.52	2.83
36-2	6 + 4	2.59	2.52	2.82
36-3	6 + 4	2.57	2.52	2.84
36-4	6	2.57		2.69 (2)
36-5	6	2.57		2.72, 2.69
36-6	6	2.60		2.69 (2)
36-7	6	2.59		2.72, 2.69
36-9	6	2.91	2.47 (2)	

[a] Average of the B3LYP and BP86 results.

six-electron donor and four-electron donor thiocarbonyl groups and thus again require only formal Fe–Fe single bonds in the Fe_3 triangle to give all iron atoms the favored 18-electron configuration. The lengths of the edges bridged by the sulfur atom of the η^2-μ_3-CS group at 2.56 ± 0.03 Å (Table 8) are similar to those of the corresponding edges in the $Fe_3(CS)_3(CO)_7$ structures (Figure 5 and Table 3). The Fe–Fe edges bridged by both the six-electron donor η^2-μ_3-CS group and the four-electron donor η^2-μ-CS group are 2.52 Å, whereas the Fe–Fe edges bridged only by the η^2-μ_3-CS group are significantly longer at 2.83 ± 0.01 Å.

Five of the remaining $Fe_3(CS)_3(CO)_6$ structures (**36-4**, **36-5**, **36-6**, **36-7**, and **36-9**) have only the six-electron donor thiocarbonyl group with all of the other carbonyl and thiocarbonyl groups functioning as conventional two-electron donors (Figure 6). The resulting unsaturation is reflected in shortening the singly bridged Fe–Fe distances from 2.83 ± 0.01 Å in the saturated structures **36-1**, **36-2**, and **36-3** to 2.70 ± 0.02 Å in the unsaturated structures **36-4**, **36-5**, **36-6**, **36-7**, and **36-9** (Table 8). In the remaining relatively high energy $Fe_3(CS)_3(CO)_6$ structure **36-8** the unsymmetrical arrangement of the three four-electron donor bridging thiocarbonyl groups is so complicated that comparison of its Fe–Fe bond lengths with those in the other structures is of questionable significance.

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Supporting Information Available: Tables S1–S4: Theoretical harmonic vibrational frequencies for $Fe_3(CS)_3(CO)_9$ (9 structures), $Fe_3(CS)_3(CO)_8$ (9 structures), $Fe_3(CS)_3(CO)_7$ (5 structures), $Fe_3(CS)_3(CO)_6$ (9 structures) using the BP86 method; Tables S5–S36: Theoretical Cartesian coordinates for $Fe_3(CS)_3(CO)_9$ (9 structures), $Fe_3(CS)_3(CO)_8$ (9 structures), $Fe_3(CS)_3(CO)_7$ (5 structures), $Fe_3(CS)_3(CO)_6$ (9 structures) using the B3LYP method; Table S37: The ν(CO) and ν(CS) stretching frequencies and corresponding infrared intensities predicted for the $Fe_3(CS)_3(CO)_n$ (n = 9, 8, 7, 6) structures; complete Gaussian 03 reference (Reference 44). This material is available free of charge via the Internet at http://pubs.acs.org.