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Abiological Iron–Sulfur Clusters

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Contents

I. Introduction

Iron−sulfur clusters are important chemical species, forming a large class in metal cluster chemistry. A very large number of iron−sulfur clusters have been synthesized and structurally determined, and their properties have been investigated. Particularly, the iron−sulfur cubane cluster attracted the attention of a wide range of scientists because the cubic Fe_4S_4 core is found in biological systems as the active site of several non-heme iron proteins such as high-potential proteins and ferredoxins. Many iron−sulfur cubane clusters have been synthesized as model compounds and their electron-transfer ability has been investigated under various conditions. A recent topic of this sort of clusters is the long sought-for crystal structure determination of the iron−molybdenum−sulfur core of nitrogenase.[1] Most of these clusters have thiolates as supporting ligands and therefore can be classified as inorganic clusters. There is another large class of iron−sulfur clusters in which the cluster core is surrounded by soft organic ligands via iron−carbon bonds and can be classified as organometallic clusters. Early and typical examples are cyclopentadienyl cluster $Cp_4Fe_4S_4$[2,3] and carbonyl cluster $(OC)_9Fe_3S_2$.[4] The investigation of the former cluster demonstrated interesting structural changes accompanying its redox, and the latter made a beginning for the research of organometallic clusters containing chalcogen atoms.

In comparison with the extensive and systematic nature of the research on the inorganic iron−sulfur clusters, the research on the corresponding organometallic clusters has been fragmentary in most cases, although numerous examples have been reported to date. Some review articles briefly dealt with this type of clusters,[5] but no review article focusing on abiological iron−sulfur clusters has been published, probably because the enormous variety of the synthetic methods, structures, and properties makes the uniform discussion and interpretation difficult. Interestingly, this very reason turns out to be one of the motivations for studying organometallic iron−sulfur clusters and, more generally, transition-metal chalcogen clusters. This article reviews the research on organometallic iron−sulfur clusters. Considerations are restricted to those in which the iron−sulfur core carries organic ligands such as cyclopentadienyl and substituted cyclopentadienyl and/or π-acidic ligands. Those having only inorganic ligands such as thiolates or halides are excluded.

Abbreviations used in this paper are as follows: Cp*, C_5Me_5; Cp′, general expression for substituted and nonsubstituted cyclopentadienyl ligands.

II. Synthesis of Iron–Sulfur Clusters

Iron−sulfur clusters can be prepared by various methods which can be classified into the following five types: (1) Reactions of iron−carbonyl complexes with sulfur-supplying agents (method A). This method has been mainly used for the synthesis of iron−sulfur clusters containing CO's as supporting ligands. (2) Reactions of bis(cyclopentadienyl)(tetracarbonyl)diiron and its derivatives with sulfur or sulfur-supplying agents (method B). For the synthesis of iron−sulfur clusters with cyclopentadienyl derivatives as ligands, which are thermally fairly robust in most cases, this method is frequently used. (3) Reactions of iron(II) salts and complexes with sulfides (method C). As in the preparation of thiolato-substituted iron−sulfur cubane clusters, these reactions also play important roles in the synthesis of organometallic clusters. (4) Expansion of small iron−sulfur clusters to higher nuclearity clusters (method D). This is another important method, especially in connection with the development of logical ways for constructing transition-metal clusters. (5) Electrochemical or chemical redox of the iron−sulfur clus-

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Shinji Inomata was born in 1964 in Hiratsuka, Japan. He received his B.Sc. in 1986, M.Sc. in 1989, and Ph.D. in 1992 from Tohoku University under the supervision of Professor Hiroshi Ogino. He continued his research as a research associate in the University. In 1996 he joined the Professor Rauchfuss' group at University of Illinois as a visiting scholar under the auspices of Japan Society for the Promotion of Science (JSPS), where he worked for a 10-month period on reactivity of rhenium sulfides toward olefins and alkynes. He moved to Fukushima University as an associate professor in 1997. His research interest is in the area of transition metal chalcogen cluster compounds.

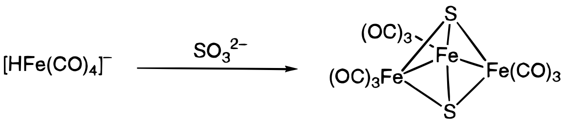
Hiromi Tobita was born in 1954 in Hitachinaka, Ibaraki, Japan. He received his Ph.D. degree in 1982 from Tohoku University for the work on tetrasilylethylene under the supervision of Professor Hideki Sakurai. In the same year, he joined Professor Satoru Masamune's group in Massachusetts Institute of Technology as a postdoctoral research associate. In 1984, he moved to Professor Masamune's group in Institute for Fundamental Research, Kao Corporation. In 1985, he joined Professor Hiroshi Ogino's group in Tohoku University as a research associate and started to work on transition metal chemistry. Since 1992 he has been an associate professor in the same place. His main interests involve synthesis and reactivity of organo transition metal compounds: silylene and germylene complexes, phosphido-bridged dinuclear complexes, cationic metallocene derivatives of groups 7 and 8 elements, and polynuclear metal-chalcogen complexes. He obtained the Chemical Society of Japan Award for Young Chemists in 1988.

ters (method E). Since iron–sulfur clusters usually have multiple oxidation states, this must be mentioned as the most widely used synthetic method. Iron–sulfur clusters which are classified by the five synthetic methods are summarized in Table 1.

A. Reactions of Iron–Carbonyl Complexes with Sulfur-Supplying Agents (Method A)

Iron carbonyl anions are excellent precursors for iron–sulfur clusters having carbonyl ligands, because the reactions of these anions with various sulfur-containing species proceed under relatively mild conditions and further dissociation of carbonyl ligands from the product can be avoided. $[HFe(CO)_4]^-$ and $[HFe_3(CO)_{11}]^-$ are usually used as iron carbonyl anions, which can be generated by treatment of $Fe(CO)_5$ with base.[6]

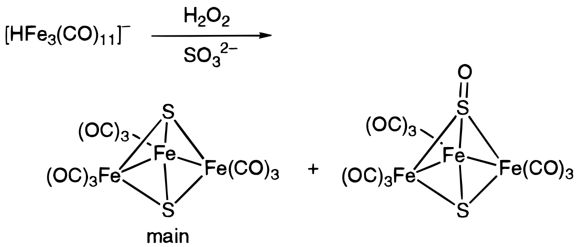
The anion $[HFe(CO)_4]^-$ reacts with sulfite ion to give Fe_3S_2-type cluster $(OC)_9Fe_3S_2$ (eq 1).[4,7] This



(1)

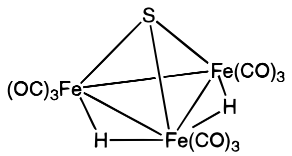
reaction was found by Hieber and Beck in 1958[4] and this discovery prompted the later prosperity of the chemistry of carbonyliron–chalcogen clusters. For instance, application of this method toward EO_3^{2-} (E = Se, Te) yields iron–selenium and –tellurium analogues $(OC)_9Fe_3E_2$, while mixing of two different EO_3^{2-} ions produces mixed-chalcogen clusters $(OC)_9Fe_3EE'$ (E, E′ = S, Se, Te).[8,9]

When the reaction of eq 1, with $[HFe_3(CO)_{11}]^-$ instead of $[HFe(CO)_4]^-$, is performed in the presence of hydrogen peroxide, a novel cluster involving a sulfur monoxide ligand (μ_3-SO) is formed besides $(OC)_9Fe_3S_2$ (eq 2).[10]

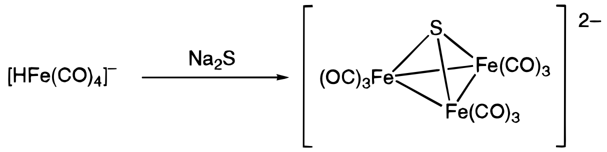


(2)

Chart 1



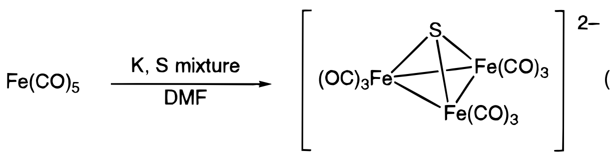
Employment of sulfide ion for the reaction with $[HFe(CO)_4]^-$ results in the formation of an anionic cluster with only one μ_3-sulfide ligand (eq 3).[11]



(3)

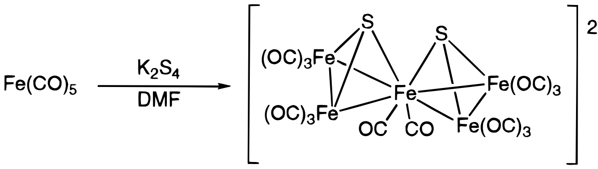
Usage of thiometalate ion $[MoS_4]^{2-}$ instead of Na_2S gives the same product.[12] Treatment of the anionic product of eq 3 with hydrochloric acid forms bis(μ-hydrido) cluster $H_2(OC)_9Fe_3S$ (Chart 1).[11] The crystal structure of this cluster has not been determined, but the large high-field shift of the ^1H NMR signal of hydrido ligands (−24.6 ppm) strongly supports a structure with bridging hydrido ligands.

The above-mentioned $[(OC)_9Fe_3S]^{2-}$ can also be synthesized by the reaction of $Fe(CO)_5$ with potassium polysulfide in DMF (eq 4).[13]

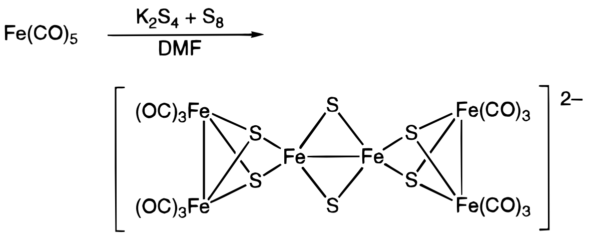


(4)

When $Fe(CO)_5$ is present in large excess, $[(OC)_9Fe_3S]^{2-}$ is formed in an excellent yield. As the ratio and chain length of polysulfide are increased, higher clusters with formulas $[(OC)_{14}Fe_5S_2]^{2-}$ and $[(OC)_{12}Fe_6S_6]^{2-}$ are formed successively (eqs 5 and 6).[14]



(5)



(6)

$[Fe_3(CO)_{11}]^{2-}$ reacts with sulfur dichloride SCl_2 to give the same products as those in eqs 4−6 (eqs 7 and 8).

$$[Fe_3(CO)_{11}]^{2-} \xrightarrow[CH_3CN]{SCl_2} [(OC)_9Fe_3S]^{2-} \qquad (7)$$

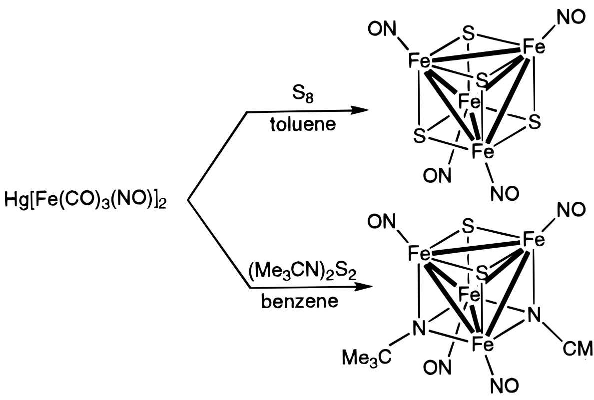
$$[Fe_3(CO)_{11}]^{2-} \xrightarrow[THF]{SCl_2} [(OC)_{14}Fe_5S_2]^{2-} + [(OC)_{12}Fe_6S_6]^{2-} \qquad (8)$$

When a small excess of $[Fe_3(CO)_{11}]^{2-}$ is used for SCl_2, $[(OC)_9Fe_3S]^{2-}$ is formed in good yield (eq 7). When the ratio of SCl_2 (a sulfur-supplying agent) is increased, higher clusters are formed (eq 8). This is a tendency analogous to that found in eqs 4−6. $[(OC)_{14}Fe_5S_2]^{2-}$ can also be obtained by the reaction of $[Fe_4(CO)_{13}]^{2-}$ with SCl_2 (eq 9) or by the oxidative condensation of $[(OC)_9Fe_3S]^{2-}$ induced by Ag(I) or tropylium salt (eq 10).[14]

$$[Fe_4(CO)_{13}]^{2-} \xrightarrow[THF]{SCl_2} [(OC)_{14}Fe_5S_2]^{2-} \qquad (9)$$

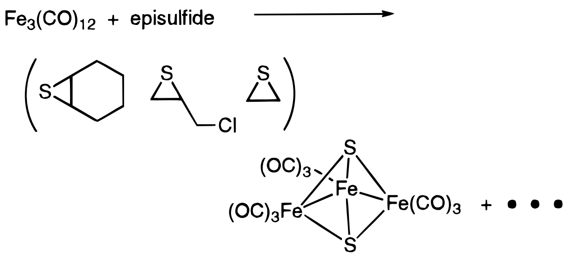
$$[(OC)_9Fe_3S]^{2-} \xrightarrow[(C_7H_7)BF_4]{AgBF_4\ \text{or}} [(OC)_{14}Fe_5S_2]^{2-} \qquad (10)$$

Anionic nitrosyl(tricarbonyl)iron complex $[Fe(CO)_3(NO)]^-$ is a useful starting material to synthesize iron−sulfur clusters containing nitrosyl ligands. As shown in eq 11, reactions of $[Fe(CO)_3(NO)]^-$ with S_8 or $(Me_3CN)_2S_2$ give cubane-type iron−sulfur clusters containing nitrosyl ligands.[15,16]



(11)

$Fe_3(CO)_{12}$ reacts with episulfides to give several iron−sulfur clusters in which $(OC)_9Fe_3S_2$ is found as a common product irrespective of the nature of episulfides (eq 12).[7,17,18]



(12)

When reaction of $Fe_3(CO)_{12}$ with sulfur is carried out in the presence of 1,3-cyclohexadiene, two sulfur-containing triiron complexes, $(OC)_9Fe_3S_2$ as well as $(\eta^4\text{-}C_6H_8)(OC)_8Fe_3S$, are obtained (eq 13).[19]

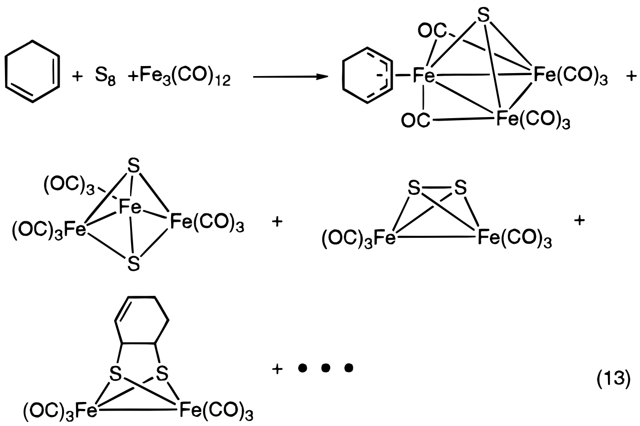
Table 1. Syntheses of Iron−Sulfur Clusters

core	cluster	reactants	yield (%)	method	ref(s)
Fe_3S	$(Et_4N)_2[(OC)_9Fe_3S]$	$Fe(CO)_5 + NaOH + Na_2S$, HCl, Et_4NOH/pyridine	−	A	11
		$[Et_4N]_2[Fe_3(CO)_{11}] + SCl_2$	68	A	14
	$(Bu_4N)_2[(OC)_9Fe_3S]$	$[Bu_4N]_2[(PhS)_4Fe_4S_4]$ + 6 equiv of $LiBu^t$ THF/CO (1 atm)	5−10	D	47
	$(Bu_4N)_2[(OC)_9Fe_3S]$	$Fe(CO)_5 + (Bu_4N)_2MoS_4$ + NaOMe	−	A	12
	$(Ph_4P)_2[(OC)_9Fe_3S]$	$Fe(CO)_5$ + (K, S mixture)/DMF, Ph_4PBr	67	A	13
	$(\eta^4\text{-}C_6H_8)(OC)_6Fe_3S$	$Fe_3(CO)_{12} + S_8$ + cyclohexadiene	3	A	19
	$(OC)_9(\mu\text{-}OC)Fe_3S$	$Fe_3(CO)_{12}$ + NaOH/H_2O-MeOH, CO (i) Na_2SO_3/H_2O; (ii) HCl (excess)	5.6	A	57
	$(OC)_9(\mu\text{-}OC)Fe_3S$	$Fe_3(CO)_{12}$ + ethylene sulfide, hexane reflux	57	A	17
	$(OC)_9Fe_3S(\mu\text{-}SO)$	$Fe(CO)_5$/NaOH/H_2O−MeOH + $H_2O_2 + Na_2SO_3$	10	A	6
Fe_3S_2	$Cp^*_2(OC)_3Fe_3S_2$	$Cp^*_2Fe_2S_4 + Fe(CO)_5$ ($h\nu$ or Me_3NO), $Fe_2(CO)_9$, or $Fe_3(CO)_{12}$	15−37	D	44
	$(OC)_9Fe_3S_2$	$HFe(CO)_4^- + SO_3^{2-}$	−	A	4
		$Fe_3(CO)_{12}$ + cyclohexene sulfide	10	A	7
		$Fe_3(CO)_{12}$ + 3-chloropropylene sulfide	55	A	7
		$Fe_3(CO)_{12}$ + ethylene sulfide, hexane reflux	52	A	18
		$Fe_3(CO)_{12}$ + ethylene sulfide, hexane reflux	18	A	17
	$(OC)_8(NHMe_2)Fe_3S_2$	$(OC)_9Fe_3S_2 + NHMe_2$	66	D	18
	$\{(CF_3)_2C_2S_2\}_4Fe_3S_2$	$\{(CF_3)_2C_2S_2\}Fe_2(CO)_6 + S_8$	−	A	34
Fe_4S_2	$(OC)_{11}Fe_4S_2$	$(OC)_9Fe_3S_2 + Fe(CO)_5$	38	D	46
	$(ON)_4Fe_4S_2(\mu_3\text{-}NCMe_3)_2$	$Hg[Fe(CO)_3(NO)]_2 + (Me_3CN)_2S_2$	−	A	16,52
	$[PPN][(ON)_4Fe_4S_2(\mu_3\text{-}NCMe_3)_2]^b$	(i) $(ON)_4Fe_4S_2(\mu_3\text{-}NCMe_3)_2$ + Na/Hg; (ii) PPNCl	−	E	52
Fe_4S_3	$(Ph_4As)[(ON)_7Fe_4S_3]$	$(ON)_4Fe_4S_4$, Na, Ph_4AsCl	−	D	58
	$(NH_4)[(ON)_7Fe_4S_3]$	$FeSO_4 + NaNO_2 + (NH_4)_2S$	−	C	42
	$Na[(ON)_7Fe_4S_3]$	$(Et_4N)_2[\{C_6H_4(CH_2S)_2\}_2Fe_2S_2] + NaNO_2$	44	D	49
		$(Et_4N)_2[(RS)_4Fe_4S_4] + NaNO_2$	38	D	49
	$(Me_3S)[(ON)_7Fe_4S_3]$	$Na[(ON)_7Fe_4S_3] + (Me_3S)I$	64	E	59
	$(Me_3OS)[(ON)_7Fe_4S_3]$	$Na[(ON)_7Fe_4S_3] + (Me_3OS)I$	70	E	59
	$(Et_4N)[(ON)_7Fe_4S_3]$	$K[(ON)_7Fe_4S_3] + Et_4NBr$	70	E	60
	$(Et_4N)_2[(ON)_7Fe_4S_3]$	$(Et_4N)[(ON)_7Fe_4S_3]$ + sodium benzophenone ketyl	48[a]	E	60
	$[(ON)_7Fe_4S_3]^{3-}$ (unstable)	$[(ON)_7Fe_4S_3]^{2-}$ + sodium naphthalenide	−	E	60
Fe_4S_4	$Cp_4Fe_4S_4$	$Cp_2Fe_2(CO)_4 + {}^1/_2S_8$	62	B	3,20−22
		$Cp_2Fe_2(CO)_4$ + cyclohexene sulfide	−	B	2
	$[Cp_4Fe_4S_4](Br_3)$	$Cp_4Fe_4S_4 + Br_2$ (excess)	quantitative	E	51
	$[Cp_4Fe_4S_4](Br)$	$[Cp_4Fe_4S_4]^+(Br_3^-)$	quantitative	E	51
	$[Cp_4Fe_4S_4](I_4)$	$Cp_4Fe_4S_4 + 2I_2$	quantitative	E	51
	$[Cp_4Fe_4S_4](BF_4)$	$Cp_4Fe_4S_4 + AgBF_4$	quantitative	E	51
	$[Cp_4Fe_4S_4](PF_6)$	$Cp_4Fe_4S_4$ (electrolysis)	45	E	53
		$Cp_4Fe_4S_4$ (electrolysis)	60−70	E	54
		$Cp_4Fe_4S_4$ (electrolysis)	81	E	55
	$[Cp_4Fe_4S_4](PF_6)_2$	$Cp_4Fe_4S_4$ (electrolysis)	60	E	53
		$Cp_4Fe_4S_4$ (electrolysis)	60−70	E	54
		$[Cp_4Fe_4S_4](PF_6)$ (electrolysis)	82	E	55
	$[Cp_4Fe_4S_4](PF_6)_3$	$[Cp_4Fe_4S_4](PF_6)_2$	83	E	55
	$(MeC_5H_4)_4Fe_4S_4$	$[(MeC_5H_4)_4Fe_4S_4](PF_6) + NaBH_4$	30	E	23
	$[(MeC_5H_4)_4Fe_4S_4](PF_6)$	(i) $(MeC_5H_4)_2Fe_2(CO)_4 + S_8$; (ii) NH_4PF_6	17	B, E	23
	$[(MeC_5H_4)_4Fe_4S_4](PF_6)_2$	$[(MeC_5H_4)_4Fe_4S_4](PF_6) + [Cp_2Fe](PF_6)$	80	E	23
	$(ON)_4Fe_4S_4$	$Hg[Fe(CO)_3(NO)]_2 + S_8$	20	A	15,16
	$[Cp_2Co]^+[(ON)_4Fe_4S_4]^-$	$(ON)_4Fe_4S_4 + Cp_2Co$	−	E	15
	$(Ph_4As)[(ON)_4Fe_4S_4]$	(i) $(ON)_4Fe_4S_4$ + Na; (ii) Ph_4AsCl	−	E	15
	$[K(2,2,2\text{-crypt})][(ON)_4Fe_4S_4]$	(i) $(ON)_4Fe_4S_4$ + K; (ii) cryptand[2.2.2]	−	E	15
	$(OC)_{12}Fe_4S_4$	$(ON)_4Fe_4S_4$ + CO (3000 psi)	−	D	48
	$[(OC)_{12}Fe_4S_4](Br)$	$(OC)_{12}Fe_4S_4 + Br_2$ under CO (30 psi)	−	E	48
	$Cp^*_2(Ph_2C_2S_2)_2Fe_4S_4$	$Cp^*_2Fe_2(CO)_4 + S_8 + PhC{\equiv}CPh$	51	B	30
			41	B	31,32
	$Cp_2(Ph_2C_2S_2)_2Fe_4S_4$	$Cp_2Fe_2(CO)_4 + S_8 + PhC{\equiv}CPh$	32	B	30,32
	$Cp^*_2(Ph(Me)C_2S_2)_2Fe_4S_4$	$Cp^*_2Fe_2(CO)_4 + S_8 + PhC{\equiv}CMe$	10	B	32
	$Cp^*_2(Ph(Et)C_2S_2)_2Fe_4S_4$	$Cp^*_2Fe_2(CO)_4 + S_8 + PhC{\equiv}CEt$	15	B	32
	$Cp_2(Ph(Et)C_2S_2)_2Fe_4S_4$	$Cp_2Fe_2(CO)_4 + S_8 + PhC{\equiv}CEt$	18	B	32
	$Cp^*_2\{(MeO_2C)_2C_2S_2\}_2Fe_4S_4$	$Cp_2Fe_2(CO)_4 + S_8 + MeO_2CC{\equiv}CCO_2Me$	12	B	33
	$[Cp^*_2(Ph_2C_2S_2)_2Fe_4S_4](PF_6)$	$Cp^*_2(Ph_2C_2S_2)_2Fe_4S_4 + [Cp_2Fe](PF_6)$	92	E	61
		$Cp^*_2(Ph_2C_2S_2)_2Fe_4S_4$ (electrolysis)	92	E	30,61
	$\{(CF_3)_2C_2S_2\}_4Fe_4S_4$	$\{(CF_3)_2C_2S_2\}Fe_2(CO)_6 + S_8$	34[a]	A	34
	$(Ph_4As^+)_2[\{(CF_3)_2C_2S_2\}_4Fe_4S_4]^{2-}$	$\{(CF_3)_2C_2S_2\}_4Fe_4S_4 + Ph_4AsCl$	62[a]	E	34
	$(Bu_4N^+)_2[\{(CF_3)_2C_2S_2\}_4Fe_4S_4]^{2-}$	$\{(CF_3)_2C_2S_2\}_4Fe_4S_4 + Bu_4NCl$	−	E	34
	$(Ph_4As^+)[\{(CF_3)_2C_2S_2\}_4Fe_4S_4]^-$	$\{(CF_3)_2C_2S_2\}_4Fe_4S_4 + Ph_4As^+$ salts of the dianion	−	E	34
	$(Ph_4As^+)[(Ph_2C_2S_2)_4Fe_4S_4]^-$	$(Ph_2C_2S_2)_4Fe_4S_4 + H_2NNH_2 + Ph_4AsCl$	−	E	34
	$(Ph_2C_2S_2)_4Fe_4S_4$	$Fe(CO)_5 + S_8 + PhC{\equiv}CPh$	−	B	8
	$(Ph_4As)_2[(OC)_{12}Fe_4S_4]$	$Fe_2S_2(CO)_6$ + LiSR (R = Ph, $PhCH_2$, *i*Pr), Ph_4AsCl	40−60	D	62
		$Fe_2S_2(CO)_6 + LiEt_3BH$, Ph_4AsCl	75	D	63

Table 1 (Continued)

core	cluster	reactants	yield (%)	method	ref(s)
Fe_4S_4	$(Et_4N)_2[(OC)_{12}Fe_4S_4]$	$Fe_2S_2(CO)_6 + LiSPh$, Et_4NBr	40	D	62
	$(MeNC)_6Cl_2Fe_4S_4$	$(Ph_4P)_2[Cl_4Fe_4S_4] + MeNC$, THF	65	D	50
	$(t\text{BuNC})_6Br_2Fe_4S_4$	$(Et_4N)_2[Br_4Fe_4S_4] + t\text{BuNC}$, THF	60	D	50
	$(t\text{BuNC})_6(MeC_6H_4O)_2Fe_4S_4$	$(t\text{BuNC})_6Cl_2Fe_4S_4 + t\text{BuNC} + NaOC_6H_4Me$, toluene	84	D	50
	$(t\text{BuNC})_6(PhS)_2Fe_4S_4$	$(t\text{BuNC})_6Cl_2Fe_4S_4 + t\text{BuNC} + NaSPh$, toluene	45	D	50
		$(Ph_4P)_2[(PhS)_4Fe_4S_4] + t\text{BuNC} + (Et_3NH)(BPh_4)$, CH_3CN	68	D	50
	$(t\text{BuNC})_6(MeC_6H_4S)_2Fe_4S_4$	$(Et_4N)_2[(MeC_6H_4S)_4Fe_4S_4] + t\text{BuNC} + (Et_3NH)(ClO_4)$, CH_3CN	73	D	50
	$(t\text{BuNC})_6(t\text{BuS})_2Fe_4S_4$	$(t\text{BuNC})_6Cl_2Fe_4S_4 + t\text{BuNC} + LiSBu^t$, THF	64	D	50
		$(Et_4N)_2[(t\text{BuS})_4Fe_4S_4] + t\text{BuNC} + (Et_3NH)(ClO_4)$, CH_3CN	61	D	50
	$(t\text{BuNC})_6(EtS)_2Fe_4S_4$	$(t\text{BuNC})_6Cl_2Fe_4S_4 + NaSEt$, THF	66	D	50
		$(Ph_4P)_2[(EtS)_4Fe_4S_4] + t\text{BuNC} + (Et_3NH)(ClO_4)$, CH_3CN	83	D	50
Fe_4S_5	$Cp_4Fe_4S_5$	$[Cp_4Fe_4S_5](PF_6)_2 + NaBH_4$	83	E	20,22
	$[Cp_4Fe_4S_5]^+[MoOCl_4(thf)]^-$	$Cp_4Fe_4S_6 + 2Mo(O)Cl_3(thf)_2$	35	E	64
	$[Cp_4Fe_4S_5](PF_6)_2$	(i) $Cp_4Fe_4S_6 + O_2$; (ii) NH_4PF_6	75	E	20,22
	$[Cp_4Fe_4S_5](SbF_6)_2$	$Cp_4Fe_4S_6$ (electrolysis)	52	E	20
	$(MeC_5H_4)_4Fe_4S_5$	$[(MeC_5H_4)_4Fe_4S_5](PF_6)_2 + NaBH_4$	31	E	24
	$[(MeC_5H_4)_4Fe_4S_5](PF_6)$	$(MeC_5H_4)_4Fe_4S_5 + [(MeC_5H_4)_4Fe_4S_5](PF_6)_2$	43	E	24
	$[(MeC_5H_4)_4Fe_4S_5](PF_6)_2$	(i) $(MeC_5H_4)_2Fe_2(CO)_4 + S_8$; (ii) NH_4PF_6	27	B,E	24
	$((Me_3SiC_5H_4)_4Fe_4S_5$	$(Me_3SiC_5H_4)_2Fe_2(CO)_4 + S_8$	9	B	25
	$Cp^*{}_4Fe_4S_5$	$Cp^*{}_2Fe_2S_4 + PBu_3$	−	D	45
	$Cp^*{}_3(Ph_2C_2S_2)Fe_4S_5$	$Cp^*{}_2Fe_2(CO)_4 + S_8 + PhC{\equiv}CPh$	24	B	31,32
	$Cp^*{}_3\{(MeO_2C)_2C_2S_2\}Fe_4S_5$	$Cp_2Fe_2(CO)_4 + S_8 + MeO_2CC{\equiv}CCO_2Me$	11	B	33
	$[Cp^*{}_3(Ph_2C_2S_2)Fe_4S_5](PF_6)$	$Cp^*{}_3(Ph_2C_2S_2)Fe_4S_5 + [Cp_2Fe](PF_6)$	77	E	31
		$Cp^*{}_3(Ph_2C_2S_2)Fe_4S_5 + [(MeC_5H_4)_2Fe](PF_6)$	85	E	31
	$[Cp^*{}_3(Ph_2C_2S_2)Fe_4S_5](BF_4)$	$Cp^*{}_3(Ph_2C_2S_2)Fe_4S_5 + [(MeC_5H_4)_2Fe](BF_4)$	49	E	65
	$[Cp^*{}_3(Ph_2C_2S_2)Fe_4S_5](PF_6)_2$	$[Cp^*{}_3(Ph_2C_2S_2)Fe_4S_5](PF_6)$ (electrolysis)	81	E	61
Fe_4S_6	$Cp_4Fe_4S_6$ (mixture with $Cp_4Fe_4S_4$ and $Cp_4Fe_4S_5$)	$Cp_2Fe_2(CO)_4 + S_8$	25−35	B	20−22
		$Cp_2Fe_2(CO)_2(SR)_2 + S_8$ (R = Me, Et, Bz)	−	B	20,21
		$Cp_2Fe_2(CO)_4 + Et_2S_x$ (x = 3,4)	−	B	20,21
		$Cp_4Fe_4S_6{\cdot}2SO_2$	−	B	20−22
	$(MeC_5H_4)_4Fe_4S_6$	$(MeC_5H_4)_2Fe_2(CO)_4 + S_8$ (excess)	50	B	24
	$(Me_3SiC_5H_4)_4Fe_4S_6$	$(Me_3SiC_5H_4)_2Fe_2(CO)_4 + S_8$ (90 °C in toluene)	42	B	25
		$(Me_3SiC_5H_4)_2Fe_2(CO)_4 + S_8$ (100 °C in toluene)	26	B	25
	$\{Me_2Si(C_5H_4)_2\}_2Fe_4S_6$	$\{Me_2Si(C_5H_4)_2\}Fe_2(CO)_4 + S_8$, toluene reflux	47	B	36
	$\{Me_2Si(C_5H_4)_2\}_2Fe_4S_6(CO)$	$\{Me_2Si(C_5H_4)_2\}Fe_2(CO)_4 + S_8$, $h\nu$	40	B	36
Fe_5S_2	$(Et_4N)_2[(OC)_{14}Fe_5S_2]$	$Fe(CO)_5 + K_2S_4$, Bu_4NBr	36	A	13
		$(Et_4N)_2[(OC)_9Fe_3S] + AgBF_4$	40	D	14
	$(Bu_4N)_2[(OC)_{14}Fe_5S_2]$	$(Bu_4N)_2[Fe_4(CO)_{13}] + SCl_2$	12	A	14
	$[Me_3(PhCH_2)N]_2[(OC)_{14}Fe_5S_2]$	$[Me_3(PhCH_2)N]_2[Fe_3(CO)_{11}] + SCl_2$	−	A	14
	$[Me_3(PhCH_2)N][HFe_5S_2(CO)_{14}]$	$[Me_3(PhCH_2)N]_2[(OC)_{14}Fe_5S_2] + H_2SO_4$	40[a]	D	14
Fe_5S_{12}	$[\{Me_2Si(C_5H_4)_2\}_2Fe_5S_{12}]^+(FeCl_4)^-$	$\{Me_2Si(C_5H_4)_2\}Fe_2(CO)_4 + S_8$	−	B	36
	$\{Me_2Si(C_5H_4)_2\}_2Fe_5S_{12}$	$\{Me_2Si(C_5H_4)_2\}Fe_2(CO)_4 + S_8$, toluene reflux	47	B	36
Fe_6S_6	$[BzEt_3N]_2[(OC)_{12}Fe_6S_6]$	$(OC)_6Fe_2S_2$ + "[o-xyl-S_2]$_2$"[c]	29	D	66
	$[Et_4N]_2[(OC)_{12}Fe_6S_6]$	$(OC)_6Fe_2(SH)_2 + [Et_4N][Fe_2S_2Cl_2] + Et_3N$	ca. 70	D	66
		$Fe(CO)_5 + K_2S_4 + S_8$, Et_4NBr	22	A	13
	$[Me_3(PhCH_2)N]_2[(OC)_{12}Fe_6S_6]$	$[Me_3(PhCH_2)N]_2[Fe_3(CO)_{11}] + SCl_2$	−	A	14
	$(PhS)_2(Et_3P)_4Fe_6S_6$	$Fe(PEt_3)_2(SPh)_2 + (Bu_4N)_2[(PhS)_4Fe_4S_4]$	65	D	37,67
		$Fe(PEt_3)_2(SPh)_2 + (Me_3Si)_2S$	70	C	37,67
	$(p\text{-}BrC_6H_4S)_2(Et_3P)_4Fe_6S_6$	$Cl_2(Et_3P)_4Fe_6S_6 + 2NaS(p\text{-}BrC_6H_4)$	49	D	37
	$Cl_2(Et_3P)_4Fe_6S_6$	$Fe(PEt_3)_2Cl_2 + (Bu_4N)_2[Cl_4Fe_4S_4]$	70	C	67,68
		$Fe(PEt_3)_2Cl_2 + (Et_4N)_3[Cl_6Fe_6S_6]$	70	C	67,68
		$Fe(PEt_3)_2Cl_2 + Li_2S$	54	C	68
		$Fe(PEt_3)_2Cl_2 + (Me_3Si)_2S$	64	C	67
		$Fe(PEt_3)_2Cl_2 + (Me_3Si)_2S$	62	C	68
	$Br_2(Et_3P)_4Fe_6S_6$	$Fe(PEt_3)_2Br_2 + (Me_3Si)_2S$	16	C	68
		$Fe(PEt_3)_2Br_2 + (Et_4N)_2[Br_4Fe_4S_4]$	57	C	68
		$Fe(PEt_3)_2Br_2 + (Et_4N)_3[Br_6Fe_6S_6]$	65	C	68
	$I_2(Et_3P)_4Fe_6S_6$	$Fe(PEt_3)_2I_2 + (Me_3Si)_2S$ or Li_2S	14	C	68
		$Fe(PEt_3)_2I_2 + [I_4Fe_4S_4]^{2-}$ or $[I_6Fe_6S_6]^{3-}$	65	C	68
	$Cl_2(Me_3P)_4Fe_6S_6$	$Fe(PMe_3)_2Cl_2 + (Me_3Si)_2S$ or Li_2S	60	C	68
	$Cl_2(Bu_3P)_4Fe_6S_6$	$Fe(PBu_3)_2Cl_2 + (Me_3Si)_2S$ or Li_2S	unoptimized	C	68
	$[(Et_3P)_6Fe_6S_6](BF_4)$	$[Fe(OH_2)_6](BF_4)_2 + 4PEt_3 + Li_2S$	14	C	39
Fe_6S_8	$[(Et_3P)_6Fe_6S_8](BPh_4)_2$	(i) $[Fe(OH_2)_6](BF_4)_2 + PEt_3$ (excess) $+ H_2S$; (ii) $NaBPh_4$	20	C	40,69
	$[(Et_3P)_6Fe_6S_8](PF_6)$	(i) $[Fe(OH_2)_6]^+ + PEt_3$ (excess) $+ H_2S$; (ii) $TBAPF_6$	15	C	38
		$[(Et_3P)_6Fe_6S_8](PF_6)_2$ (electrolysis)	not isolated	E	38
Fe_7S_6	$Cl_3(Et_3P)_4Fe_7S_6$	$FeCl_2 + PEt_3 + (Me_3Si)_2S$	61	C	41

[a] Calculated by the present authors. [b] PPN: bis(triphenylphosphine)iminium. [c] "[o-xyl-S_2]$_2$": thiolate-disulfide mixture arising from reaction of o-xyl$(SH)_2$, n-BuLi, and I_2.

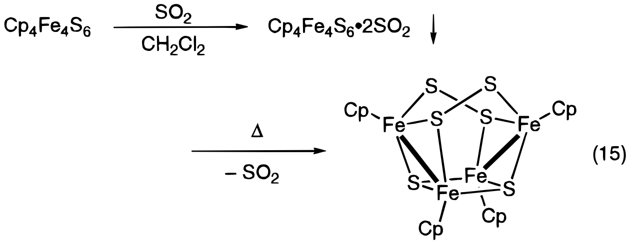

(13)

B. Reactions of Bis(cyclopentadienyl)(tetracarbonyl)diiron and Its Derivatives with Sulfur or Sulfur-Supplying Agents (Method B)

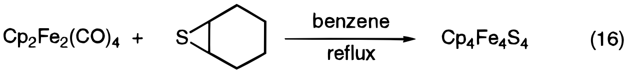
Heating $Cp_2Fe_2(CO)_4$ with elemental sulfur in high boiling point solvents gives tetrairon−sulfur clusters $Cp_4Fe_4S_4$, $Cp_4Fe_4S_5$ containing a disulfide ligand, and $Cp_4Fe_4S_6$ containing two disulfide ligands (eq 14).[3,20,21]

$$Cp_2Fe_2(CO)_4 + S_8 \xrightarrow[\text{reflux}]{\text{toluene}} Cp_4Fe_4S_4 + Cp_4Fe_4S_5 + Cp_4Fe_4S_6 \qquad (14)$$

Product ratio of the clusters is strongly dependent on the amount of sulfur for $Cp_2Fe_2(CO)_4$. $Cp_4Fe_4S_4$ can be obtained in moderate yield by treatment of $Cp_2Fe_2(CO)_4$ with a small excess of sulfur.[3] Both $Cp_4Fe_4S_5$ and $Cp_4Fe_4S_6$ are thermally unstable and can be converted to $Cp_4Fe_4S_4$ in refluxing bromobenzene in 15 min by loss of sulfur.[21] When excess sulfur is used, $Cp_4Fe_4S_6$ becomes the main product. Disulfide ligands in $Cp_4Fe_4S_6$ can act as a base, so that when a dichloromethane solution of $Cp_4Fe_4S_6$ is saturated with SO_2 gas, a crystalline precipitate of $Cp_4Fe_4S_6{\bullet}2SO_2{\bullet}{}^1/_4CH_2Cl_2$ deposits. SO_2 in the precipitate can be easily removed. Therefore, the SO_2 adduct formation of $Cp_4Fe_4S_6$ was used to isolate pure $Cp_4Fe_4S_6$ from the reaction mixture of eq 14 (eq 15).[20,22]


(15)

$Cp_4Fe_4S_5$ is a minor product among the products of eq 14. However, the cluster can be conveniently synthesized from $Cp_4Fe_4S_6$: Air oxidation of $Cp_4Fe_4S_6$ in CH_3CN solution containing NH_4PF_6 affords a dication $[Cp_4Fe_4S_5]^{2+}$. Reduction of the isolated salt $[Cp_4Fe_4S_5](PF_6)_2{\bullet}CH_3CN$ with $NaBH_4$ gives $Cp_4Fe_4S_5$.[20,22] $Cp_4Fe_4S_4$ can be synthesized selectively if a stoichiometric amount of cyclohexene sulfide is used (eq 16).[2]


(16)

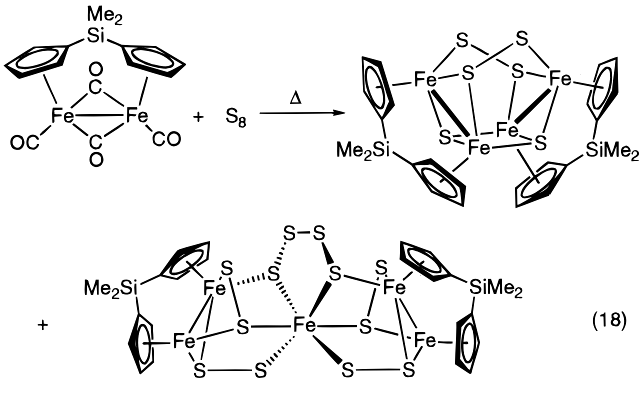
By use of $Cp'_2Fe_2(CO)_4$ complexes, containing substituted cyclopentadienyl ligands instead of $Cp_2Fe_2(CO)_4$, various tetrairon−sulfur clusters $(MeC_5H_4)_4Fe_4S_4$,[23] $(MeC_5H_4)_4Fe_4S_5$,[24] $(MeC_5H_4)_4Fe_4S_6$,[24] and $(Me_3SiC_5H_4)_4Fe_4S_6$[25] have been synthesized. However, when $Cp^*_2Fe_2(CO)_4$ and $\{1,3\text{-}C_5H_3(SiMe_3)_2\}_2Fe_2(CO)_4$ containing bulkier Cp derivatives are used, formation of tetrairon−sulfur clusters is retarded and $Cp^*_2Fe_2S_4$[26] and $\{1,3\text{-}C_5H_3(SiMe_3)_2\}_2Fe_2S_4$ containing two disulfide ligands[25] are formed, respectively.

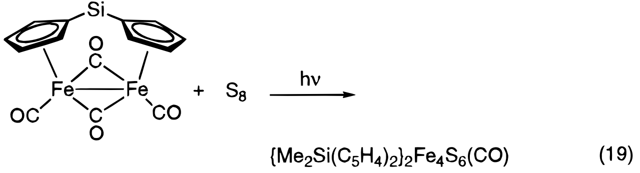
Reactions of transition metal carbonyl complexes with a mixture of elemental sulfur and alkynes have been found to give dithiolene complexes.[27−29] Reactions of $Cp'_2Fe_2(CO)_4$ with sulfur in the presence of alkynes result in the formation of tetrairon clusters containing both, dithiolene $(R_2C_2S_2)$ and Cp′ ligands (eq 17).[30−33] When reaction of $Fe(CO)_5$ with sulfur in the presence of an alkyne was carried out, $(R_2C_2S_2)_4Fe_4S_4$ was formed, which has been considered to be a cubane type cluster.[34,35]

$$Cp'_2Fe_2(CO)_4 + S_8 + R^1C{\equiv}CR^2 \xrightarrow[\text{reflux}]{\text{mesitylene or xylene}} Cp'_2(Ph_2C_2S_2)_2Fe_4S_4 + Cp^*_3(Ph_2C_2S_2)Fe_4S_5 \qquad (17)$$

Cp′ = Cp, Cp*;
R^1 = Ph, R^2 = Ph, Me, Et
$R^1 = R^2 = CO_2Me$

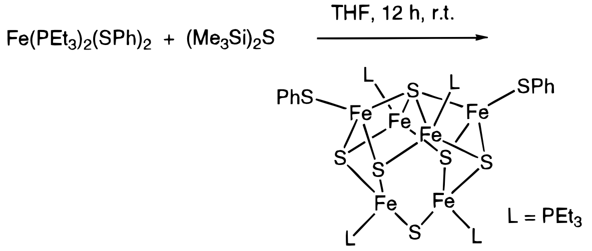
Reaction of $\{Me_2Si(C_5H_4)_2\}Fe_2(CO)_4$ containing a silylene-bridged bis(cyclopentadienyl) ligand with sulfur gives two clusters, $\{Me_2Si(C_5H_4)_2\}_2Fe_4S_6$ having a structure very similar to $Cp_4Fe_4S_6$ (see eq 15) and $\{Me_2Si(C_5H_4)_2\}_2Fe_5S_{12}$ (eq 18).[36] Photochemical reaction of $\{Me_2Si(C_5H_4)_2\}Fe_2(CO)_4$ with sulfur generates the Fe_4S_6 cluster with one terminal CO ligand (eq 19). This cluster loses the CO on heating in refluxing toluene to give $\{Me_2Si(C_5H_4)_2\}Fe_4S_6$ quantitatively.[36]


(18)


(19)

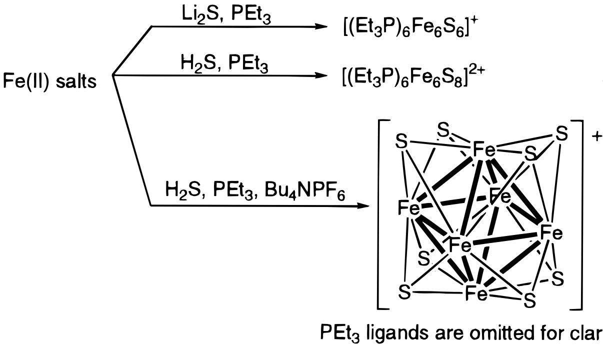
C. Reactions of Iron(II) Salts and Complexes with Sulfides (Method C)

$Fe(PEt_3)_2(SPh)_2$ reacts with $(Me_3Si)_2S$ to give $(PhS)_2(Et_3P)_4Fe_6S_6$ (eq 20).[37]



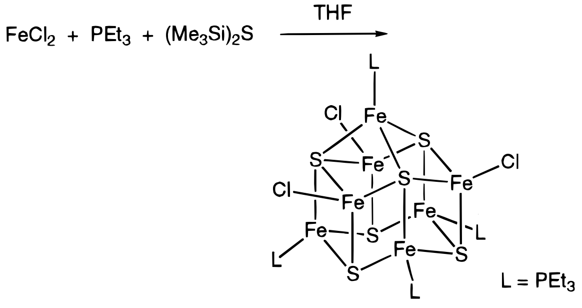
(20)

Reaction of $[Fe(H_2O)_6]^{2+}$ salts with PEt_3 and Li_2S affords $[(Et_3P)_6Fe_6S_6]^+$ salts having an Fe_6S_6 skeleton.[38] When reaction of $[Fe(H_2O)_6]^{2+}$ salts with PEt_3 and H_2S is performed in the presence of Bu_4NPF_6, a monocationic cluster $[(Et_3P)_6Fe_6S_8]^+$ having an Fe_6S_8 skeleton is obtained.[39] Treatment of $Fe(BF_4)_2$ with PEt_3 and H_2S gives a dicationic cluster $[(PEt_3)_6Fe_6S_8]^{2+}$ (eq 21).[40]



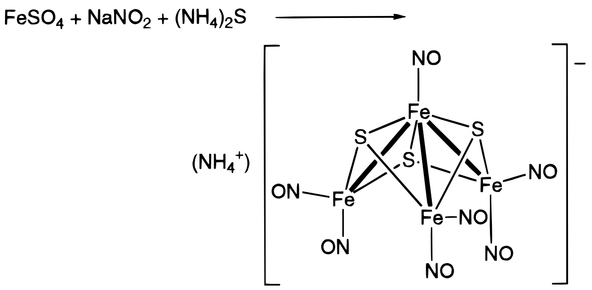
(21)

Reaction of $FeCl_2$ with $(Me_3Si)_2S$ in the presence of excess PEt_3 gives a cluster containing an Fe_7S_6 skeleton (eq 22).[41]



(22)

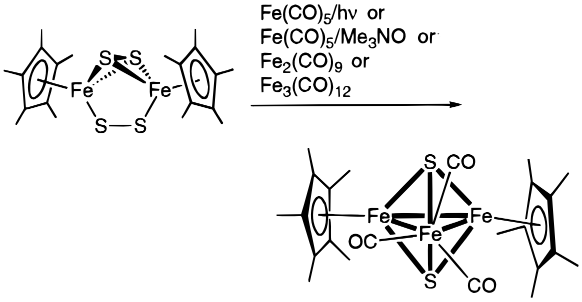
Roussin's salt, which was prepared as early as in 1858, can be easily prepared from reaction of $FeSO_4$ with $NaNO_2$ and $(NH_4)_2S$ (eq 23).[42,43]



(23)

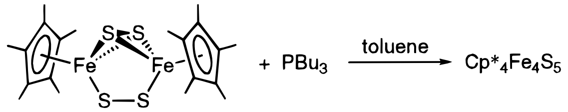
D. Expansion of Small Iron–Sulfur Clusters to Higher Nuclearity Clusters (Method D)

$Cp^*_2Fe_2S_4$[26] is a good precursor for the synthesis of some iron–sulfur clusters. Sulfur abstraction from $Cp^*_2Fe_2S_4$ by iron carbonyls under various conditions gives a trinuclear cluster $Cp^*_2(OC)_3Fe_3S_2$ having a *closo*-Fe_3S_2 skeleton (eq 24).[44]



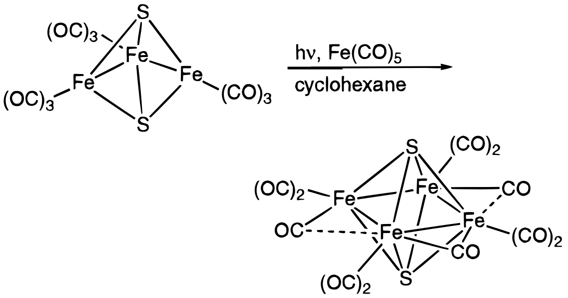
(24)

On the other hand, sulfur abstraction from $Cp^*_2Fe_2S_4$ by PBu_3 gives a tetrairon–sulfur cluster (eq 25).[45]



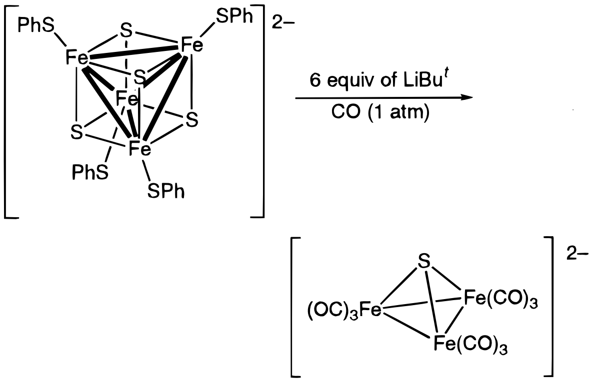
(25)

Photolysis of $Fe(CO)_5$ in the presence of $(OC)_9Fe_3S_2$ affords a tetrairon cluster $(OC)_{11}Fe_4S_2$ (eq 26).[46]



(26)

Treatment of $(Bu_4N)_2[(PhS)_4Fe_4S_4]$ with Li^tBu under a CO atmosphere gives a cluster with decreased nuclearity $[(OC)_9Fe_3S]^{2-}$ (eq 27).[47]



(27)

A cubane-type cluster supported by carbonyl ligands $(OC)_{12}Fe_4S_4$ was derived from cubane-type nitrosyl cluster $(ON)_4Fe_4S_4$ by ligand substitution reaction.[48] The same nitrosyl cluster gives the classical Roussin monoanion $[(ON)_4Fe_4S_3]^-$ by a sodium amalgam reduction (eq 28). Roussin's monoanion can also be

Table 2. Structural Data of Iron−Sulfur Clusters[a]

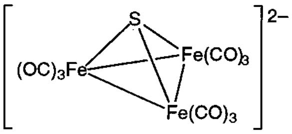
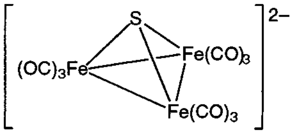
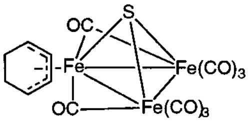
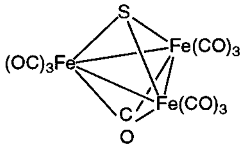
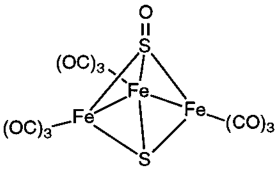
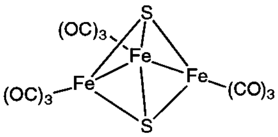
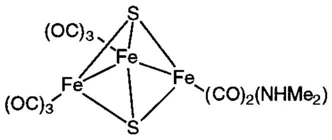
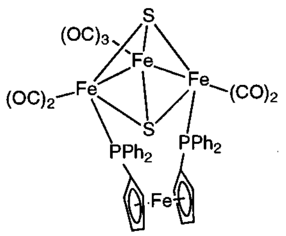
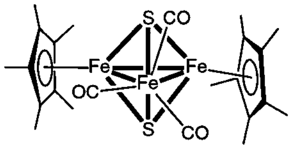
Cluster	Structure	Distance (Å)			ref
		Fe-Fe	Fe-S	others	
$(Ph_4P)_2[(OC)_9Fe_3S]$		2.574(1) | 2.595(1)	2.184(1) | 2.198(1)		47
$(Bu_4N)_2[(OC)_9Fe_3S]$		2.594(4) 2.605(4) 2.578(3)	2.185(7) 2.201(3) 2.199(5)		12
$(\eta^4\text{-}C_6H_8)(OC)_8Fe_3S$		2.597(1) 2.637(1) 2.634(1)	2.170(1) 2.186(1) 2.203(1)		19
$(OC)_9(\mu\text{-}OC)Fe_3S$		2.61±1[3]	2.21±1[3]		57
$(OC)_9Fe_3S(SO)$		2.623(1) 2.647(1)	2.140(1) 2.269(1) 2.222(1) 2.230(1) 2.139(1) 2.263(1)	S-O 1.471(2)	6
$(OC)_9Fe_3S_2$		2.582(9) 2.609(10) 3.371(10)	2.228(9)[2] 2.225(9)[2] 2.233(9)[2]		70
$(OC)_8(Me_2HN)Fe_3S_2$		2.570(2) 2.645(2)	2.237(3) 2.251(2) 2.250(2) 2.263(2) 2.214(2) 2.221(2)	Fe-N 2.088(6)	18
$(dppf)(OC)_7Fe_3S_2$[b]		2.575(2) 2.574(2)	2.272(2) 2.283(2) 2.260(2) 2.251(2) 2.261(2) 2.250(2)	Fe-P 2.220(2) 2.233(3)	72
$Cp^*_2(OC)_3Fe_3S_2$		2.704(1) 2.648(1) 2.601(1)	2.139(2) 2.139(1) 2.136(1) 2.133(2) 2.290(1) 2.285(1)		44

Table 2 (Continued)

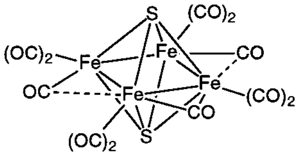
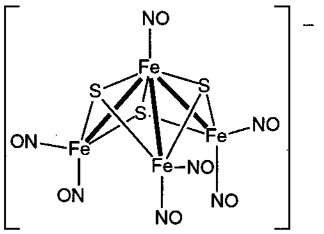
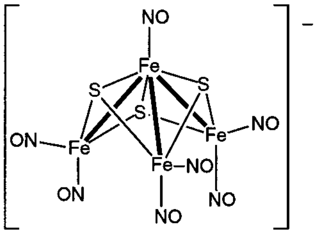
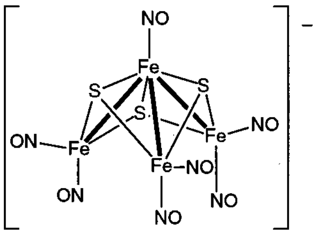
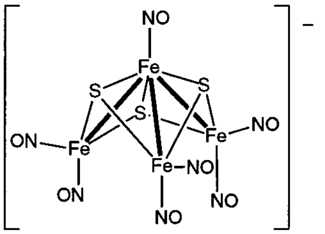
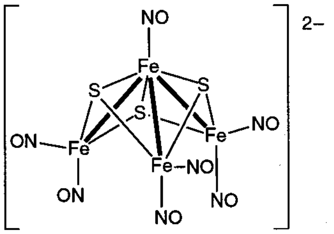
Cluster	Structure	Distance (Å)			ref
		Fe-Fe	Fe-S	others	
$(OC)_{11}Fe_4S_2$		2.489(3) 2.532(2)[2] 2.605(2)	2.332(2)[2] 2.347(2)[2] 2.278(8)[2] 2.294(2)[2]		46
$Cs[(ON)_7Fe_4S_3]$		2.736 2.691 2.702 3.558 3.567 3.594 esd 0.01	2.192 2.236 2.157 2.289 2.247 2.197 2.226 2.258 2.274 esd 0.04		75,76
$(Ph_4As)[(ON)_7Fe_4S_3]$		2.708(2) 2.708(2) 2.683(2) 3.628(2) 3.564(2) 3.519(2)	2.209(3) 2.205(3) 2.205(3) 2.255(3) 2.254(3) 2.251(3) 2.274(3) 2.257(3) 2.258(3)		58
$(Me_3S)[(ON)_7Fe_4S_3]$		2.695(4) 2.704(4) 2.703(4) 3.575(5) 3.589(5) 3.588(5)	2.212(4) 2.257(4) 2.253(4) 2.261(4) 2.203(4) 2.213(4) 2.256(4) 2.251(4) 2.249(4)		59
$(Et_4N)[(ON)_7Fe_4S_3]$		2.695(1) 2.704(1) 2.696(1) 3.564(1) 3.590(1) 3.566(1)	2.209(1) 2.207(1) 2.213(1) 2.251(1) 2.254(1) 2.248(1) 2.265(1) 2.254(1) 2.262(1)		60
$(Et_4N)_2[(ON)_7Fe_4S_3]$		2.781(1) 2.757(1) 2.753(1) 3.584(1) 3.683(1) 3.609(1)	2.216(2) 2.233(2) 2.230(2) 2.267(2) 2.277(2) 2.269(2) 2.284(2) 2.266(2) 2.271(2)		60

Table 2 (Continued)

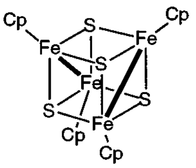
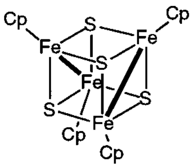
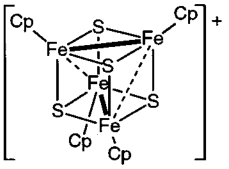
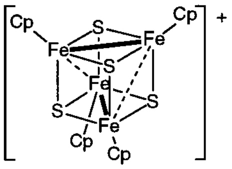
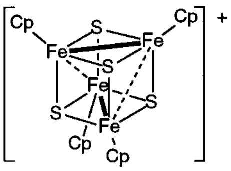
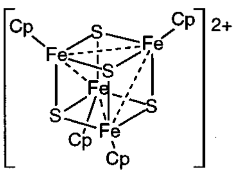
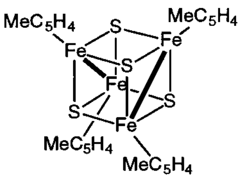
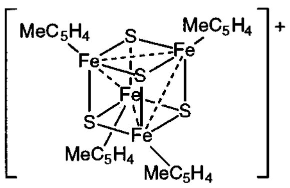
Cluster	Structure	Distance (Å)			ref
		Fe-Fe	Fe-S	others	
$Cp_4Fe_4S_4$		2.618 2.644 3.368[2] 3.365[2] (±0.002)	2.257 2.261 2.252[2] (±0.003) 2.205[2] 2.205[2] 2.209[2] 2.207[2] (±0.002)		3
$Cp_4Fe_4S_4$		2.650(6)[2] 3.355(16) 3.362(9)[2] 3.372(9)	2.201(9)[2] 2.202(8)[2] 2.198(8)[2] 2.215(9)[2] 2.248(10)[2] 2.252(11)[2]		2
$[Cp_4Fe_4S_4]Br$		2.661(5) 2.643(4) 3.188(3)[2] 3.319(3)[2]	2.245(5)[2] 2.186(5)[2] 2.214(5)[2] 2.183(5)[2] 2.246(5)[2] 2.210(5)[2]		51
$[Cp_4Fe_4S_4](PF_6)$		3.308(4) 3.297(2) 3.188(2)[2] 2.656(2)[2]	2.187(2)[2] 2.191(2)[2] 2.203(3)[2] 2.207(2)[2] 2.240(3)[2] 2.239(3)[2]		80
$[Cp_4Fe_4S_4](PF_6)$		3.302(6)[2] 3.213(4)[2] 2.631(4)[2]	2.178(6)[2] 2.147(6)[2] 2.238(6)[2] 2.211(6)[2] 2.278(6)[2] 2.227(7)[2]		80
$[Cp_4Fe_4S_4](PF_6)_2$		2.834(1)[4] 3.254(3)[2]	2.156(3)[4] 2.212(4)[4] 2.204(4)[4]		53
$(MeC_5H_4)_4Fe_4S_4$		2.612(3) 2.612(3) 3.364(2)[2] 3.388(2)[2]	2.188(2)[2] 2.204(3)[2] 2.194(3)[2] 2.204(3)[2] 2.246(2)[2] 2.240(3) 2.279(3)		23
$[(MeC_5H_4)_4Fe_4S_4](PF_6)$		2.898(3)[4] 3.304(3)[2]	2.193(5)[4] 2.234(5)[4] 2.138(4)[4]		23

Table 2 (Continued)

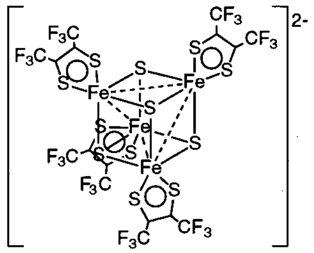
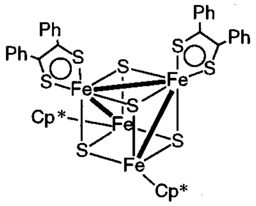
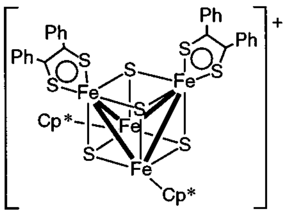
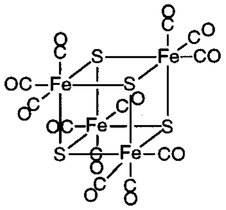
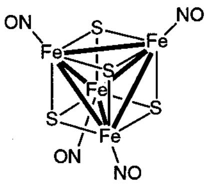
Cluster	Structure	Distance (Å)			ref
		Fe-Fe	Fe-S	others	
$(Ph_4As)_2[\{(CF_3)_2C_2S_2\}_4Fe_4S_4]$		3.225(7) 2.731(7) 2.713(7) 2.738(7) 2.737(7) 3.222(7)	2.246(10) 2.257(10) 2.249(10) 2.251(10) 2.245(10) 2.246(10) 2.235(10) 2.246(10) 2.153(11) 2.155(10) 2.153(11) 2.150(11)	Fe-S dithiolene 2.182(10) 2.150(10) 2.176(11) 2.174(10) 2.186(10) 2.180(10) 2.181(11) 2.155(10)	79
$Cp^*_2(Ph_2C_2S_2)_2Fe_4S_4$		3.400(1) 2.711(1) 3.255(1) 3.270(1) 2.717(1) 2.789(1)	2.185(2) 2.204(2) 2.197(2) 2.262(2) 2.273(2) 2.260(2) 2.250(2) 2.183(2) 2.254(2) 2.153(2) 2.155(2) 2.280(2)	Fe-S dithiolene 2.149(2) 2.187(2) 2.182(2) 2.158(2)	30,32
$[Cp^*_2(Ph_2C_2S_2)_2Fe_4S_4](PF_6)$		3.255(2) 2.772(1) 2.849(2) 2.774(1) 2.768(1) 3.222(1)	2.190(3) 2.238(2) 2.229(2) 2.172(2) 2.231(2) 2.228(2) 2.252(2) 2.268(2) 2.137(2) 2.241(2) 2.150(3) 2.267(2)	Fe-S dithiolene 2.161(2) 2.167(2) 2.157(2) 2.175(2)	61
$(OC)_{12}Fe_4S_4$		3.477(2) 3.477(2) 3.443(2)[4]	2.326(3)[4] 2.329(2)[2] 2.324(2)[2] 2.328(3)[4]		48
$(ON)_4Fe_4S_4$		2.641(1) 2.658(1) 2.657(1) 2.650(1) 2.659(1) 2.640(1)	2.213(2) 2.219(2) 2.220(2) 2.224(2) 2.221(2) 2.214(2) 2.208(1) 2.214(2) 2.219(2) 2.223(2) 2.215(2) 2.217(2)		15,16

Table 2 (Continued)

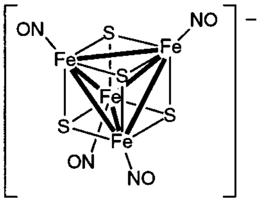
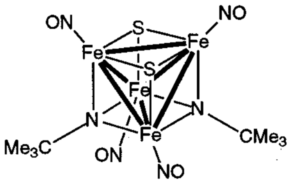
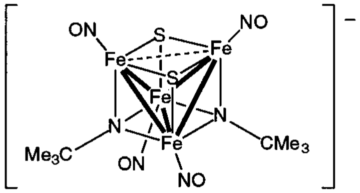
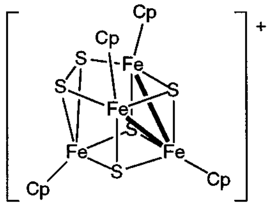
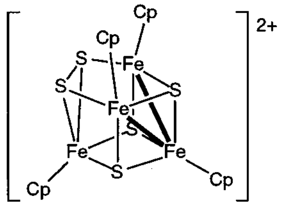
Cluster	Structure	Distance (Å)			ref
		Fe-Fe	Fe-S	others	
$[K(cryptand[2.2.2])][(ON)_4Fe_4S_4]$		2.703(1) 2.682(1) 2.690(1) 2.695(1) 2.684(1) 2.704(1)	2.230(2) 2.227(2) 2.239(2) 2.221(2) 2.224(2) 2.234(2) 2.233(2) 2.239(2) 2.231(2) 2.235(2) 2.234(2) 2.224(2)		15
$(ON)_4Fe_4S_2(\mu_3\text{-}NCMe_3)_2$		2.642(1) 2.559(1)[2] 2.565(1)[2] 2.496(1)	2.217(2) 2.227(2) 2.228(2)[2] 2.221(2)[2]	Fe-NCMe3 1.914(3)[2] 1.912(3)[2] 1.905(3)[2]	16,52
$(PPN)[(ON)_4Fe_4S_2(\mu_3\text{-}NCMe_3)_2]$		2.701(6) 2.552(6) 2.576(6) 2.573(6) 2.570(6) 2.576(6)	2.254(9) 2.265(8) 2.256(9) 2.244(9) 2.252(9) 2.244(10)	Fe-NCMe3 1.869(20) 1.845(20) 1.889(21) 1.898(21) 1.891(19) 1.888(21)	52
$[Cp_4Fe_4S_5][MoOCl_4(thf)]$		2.723(3) 2.866(3) 3.369(3) 3.721(3) 3.420(3) 3.402(3)	2.189(5) 2.218(3) 2.186(4) 2.240(4) 2.188(4) 2.208(5) 2.284(4) 2.276(5) 2.277(3) 2.271(4) 2.210(5) 2.194(4) 2.200(4)	S-S 2.067(4)	64
$[Cp_4Fe_4S_5](PF_6)_2$		2.661(1) 2.650(1) 3.392(1) 3.641(1) 3.414(1) 3.377(1)	2.185(2) 2.205(2) 2.169(2) 2.211(2) 2.217(2) 2.181(2) 2.258(2) 2.265(2) 2.272(2) 2.265(2) 2.186(2) 2.206(2) 2.169(2)	S-S 2.056(3)	77

Table 2 (Continued)

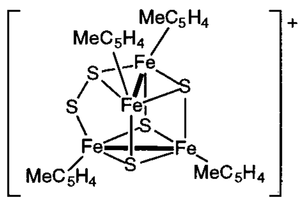
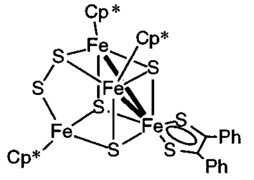
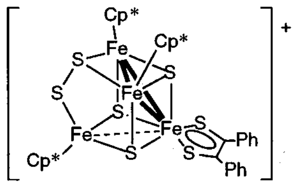
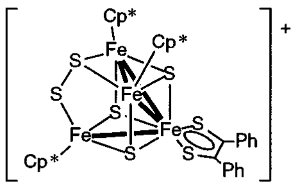
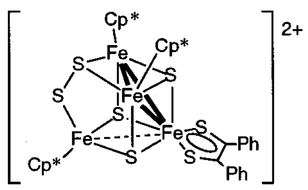
Cluster	Structure	Distance (Å)			ref
		Fe-Fe	Fe-S	others	
$[(MeC_5H_4)_4Fe_4S_5](PF_6)$		2.660(1) 2.665(1) 3.344(1) 3.783(1) 3.001(1) 3.698(1)	2.174(2) 2.182(2) 2.219(2) 2.223(2) 2.175(2) 2.290(2) 2.159(2) 2.231(2) 2.201(2) 2.211(2) 2.272(2) 2.209(2)	S-S 2.020(2)	24
$Cp^*_3(Ph_2C_2S_2)Fe_4S_5$		3.300(1) 3.769(1) 2.716(1) 3.760(2) 2.725(1) 3.307(2)	2.189(2) 2.202(2) 2.252(2) 2.188(2) 2.191(2) 2.250(2) 2.206(2) 2.219(2) 2.183(2) 2.267(2) 2.274(2) 2.151(2)	S-S 2.079(2) Fe-S dithiolene 2.180(2) 2.176(2)	31,32
$[Cp^*_3(Ph_2C_2S_2)Fe_4S_5](PF_6)$		2.736(2) 3.760(2) 2.783(1) 3.765(2) 2.767(2) 3.047(2)	2.249(2) 2.170(2) 2.245(2) 2.254(2) 2.179(2) 2.247(2) 2.175(2) 2.175(2) 2.186(2) 2.240(2) 2.237(2) 2.139(2)	S-S 2.034(2) Fe-S dithiolene 2.204(2) 2.200(2)	31,61
$[Cp^*_3(Ph_2C_2S_2)Fe_4S_5](BF_4)$		2.732(2) 2.887(2) 2.780(2) 2.866(2) 3.745(2) 3.728(2)	2.254(3) 2.173(4) 2.230(3) 2.253(3) 2.174(3) 2.239(3) 2.166(3) 2.173(3) 2.202(3) 2.214(3) 2.227(3) 2.179(3)	S-S 2.024(4) Fe-S dithiolene 2.226(3) 2.237(4)	65
$[Cp^*_3(Ph_2C_2S_2)Fe_4S_5](PF_4)_2$		2.710(1) 3.728(1) 2.701(1) 3.713(1) 2.705(1) 2.969(1)	2.245(2) 2.170(2) 2.243(2) 2.243(1) 2.166(2) 2.245(2) 2.169(2) 2.177(2) 2.183(2) 2.245(2) 2.236(2) 2.143(2)	S-S 2.021(2) Fe-S dithiolene 2.192(2) 2.188(2)	61

Table 2 (Continued)

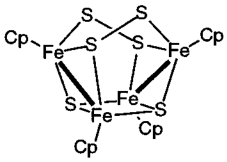
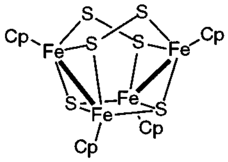
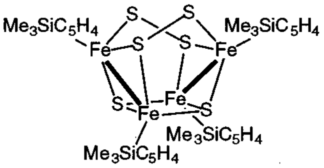
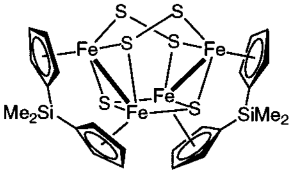
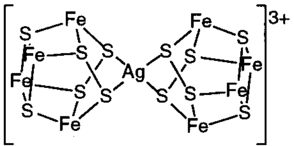
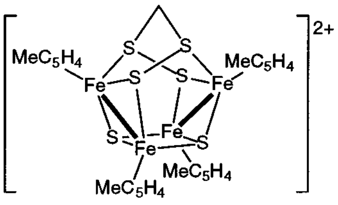
Cluster	Structure	Distance (Å)			ref
		Fe-Fe	Fe-S	others	
$Cp_4Fe_4S_6$		2.638(2)[2] 3.405(2) 4.342(3)	2.203(3) 2.247(3)	S-S 2.037(4)[2]	20,21
$Cp_4Fe_4S_6$		2.637(2)[2]	2.198(2)[2] 2.213(3)[2] 2.240(3)[2] 2.201(2)[2] 2.182(3)[2] 2.255(2)[2]	S-S 2.039(3)[2]	78
$(Me_3SiC_5H_4)_4Fe_4S_6$		2.653(2) 2.667(2) 3.448(2) 3.845(2) 3.849(2) 4.365(2)	2.206(3) 2.213(2) 2.252(2) 2.213(2) 2.182(3) 2.270(3) 2.206(2) 2.207(2) 2.247(3) 2.257(2) 2.203(3) 2.188(3)	S-S 2.029(2) 2.029(4)	25
$\{Me_2Si(C_5H_4)_2\}_2Fe_4S_6$		2.6210(9) 2.6251(9) 3.431(1) 4.368(1)	2.2167(13) 2.2158(14) 2.2658(13) 2.2409(13) 2.1816(13) 2.186(2) 2.2021(13) 2.2009(14) 2.2194(13) 2.2132(14) 2.2393(14) 2.2389(13)	S-S 2.034(2) 2.035(2)	36
$[(Cp_4Fe_4S_6)_2Ag](SbF_6)_3$	 Cp ligands are omitted.	2.658(4)[2] 2.999(5) 4.382(4)	2.183(3) 2.237(4)	S-S 2.048(7)	21
$[(MeC_5H_4)_4Fe_4(S)_2(S_2CH_2S_2)](FeCl_4)$		2.650(2) 2.643(2)	2.197(2) 2.201(3) 2.203(2) 2.242(3) 2.138(2) 2.203(2) 2.196(2) 2.201(3) 2.189(2) 2.204(3) 2.134(3) 2.239(3)	S-S 2.193(3) 2.186(3) S-C 1.796(8) 1.812(7)	84

Table 2 (Continued)

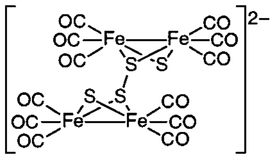
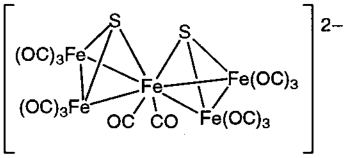
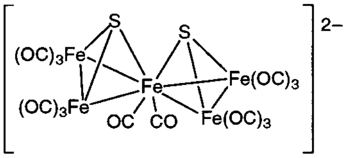
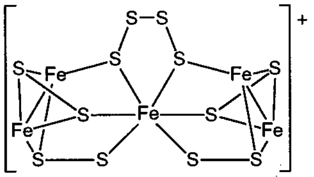
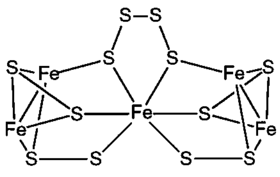
Cluster	Structure	Distance (Å)			ref
		Fe-Fe	Fe-S	others	
$(\mathrm{Ph_4As})_2[(\mathrm{OC})_{12}\mathrm{Fe_4S_4}]$		2.518(1)[2]	2.297(1)[2]	S-S	63
			2.285(1)[2]	2.164(2)	
			2.245(1)[2]		
			2.245(1)[2]		
$[\mathrm{Bu_4N}]_2[(\mathrm{OC})_{14}\mathrm{Fe_5S_2}]$		molecule 1			
		2.617(6)	2.209(8)		13
		2.621(6)	2.208(9)		
		2.628(6)	2.169(9)		
		2.626(6)	2.163(9)		
		2.555(6)	2.173(9)		
		2.566(6)	2.182(9)		
		molecule 2			
		2.613(6)	2.185(10)		
		2.618(7)	2.207(9)		
		2.632(7)	2.172(10)		
		2.616(6)	2.144(10)		
		2.550(7)	2.159(10)		
		2.564(7)	2.189(9)		
$[(\mathrm{Ph_3P})_2\mathrm{N}]_2[(\mathrm{OC})_{14}\mathrm{Fe_5S_2}]$		2.556(1)	2.186(2)		14
		2.628(1)	2.180(1)		
		2.634(1)	2.209(2)		
		2.626(1)	2.218(1)		
		2.643(1)	2.174(2)		
		2.564(1)	2.191(2)		
$[\{\mathrm{Me_2Si(C_5H_4)_2}\}_2\mathrm{Fe_5S_{12}}](\mathrm{FeCl_4})$	 Me2Si(C5H4)2 ligands are omitted.	2.561(2)	2.215(2)	S-S	36
		2.581(2)	2.305(3)	2.067(3)	
			2.300(2)	2.068(3)	
			2.186(2)	2.058(3)	
			2.299(3)	2.067(3)	
			2.321(2)	2.068(3)	
			2.251(2)	2.073(3)	
			2.181(3)	2.041(4)	
			2.240(2)		
			2.165(3)		
			2.286(3)		
			2.175(3)		
			2.169(3)		
			2.274(2)		
			2.180(2)		
			2.241(2)		
			2.184(3)		
			2.256(3)		
$\{\mathrm{Me_2Si(C_5H_4)_2}\}_2\mathrm{Fe_5S_{12}}$	 Me2Si(C5H4)2 ligands are omitted.	2.550(3)[2]	2.226(5)[2]	S-S	36
			2.275(5)[2]	2.067(7)[2]	
			2.278(5)[2]	2.065(6)[2]	
			2.193(5)[2]	2.100(6)[2]	
			2.243(6)[2]	2.019(9)	
			2.245(5)[2]		
			2.170(5)[2]		
			2.175(5)[2]		
			2.291(6)[2]		

Table 2 (Continued)

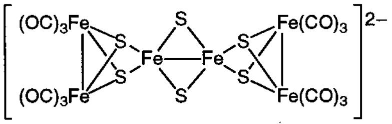
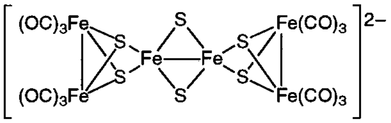
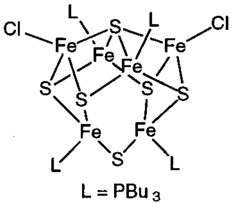
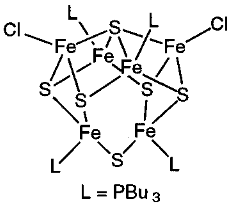
Cluster	Structure	Distance (Å)			ref
		Fe-Fe	Fe-S	others	
$(BzEt_2MeN)_2[(OC)_{12}Fe_6S_6]$		2.499(1)[2] 2.693(1)	2.315(2)[2] 2.318(2)[2] 2.330(2)[2] 2.337(2)[2] 2.323(2)[2] 2.287(1)[2] 2.197(1)[2] 2.203(1)[2]		66
$[(Ph_3P)_2N]_2[(OC)_{12}Fe_6S_6]$		2.506(1)[2] 2.675(2)	2.308(2)[2] 2.295(2)[2] 2.298(2)[2] 2.304(2)[2] 2.197(2)[2] 2.199(2)[2] 2.310(2)[2] 2.300(2)[2]		14
$Cl_2(Bu_3P)_4Fe_6S_6$		2.670 | 2.702 2.643 | 2.679 2.689 2.696 2.835 2.655 esd 0.005 | 0.007	2.177 | 2.197 2.203 | 2.233 2.241 | 2.281 2.154 2.182 2.203 2.215 2.331 2.345 esd 0.010 | 0.012	Fe-Cl 2.186 2.200 Fe-P 2.289 2.316 2.324 2.306	67
$Cl_2(Bu_3P)_4Fe_6S_6$		2.678(5) 2.648(7) 2.702(6) 2.670(6) 2.696(7) 2.689(7) 2.643(6) 2.645(6) 2.679(5) 2.650(7) 2.835(6) 2.655(7)	2.197(10) 2.180(10) 2.177(10) 2.195(10) 2.233(12) 2.213(10) 2.203(10) 2.218(10) 2.281(11) 2.255(11) 2.261(11) 2.241(11) 2.154(11) 2.182(10) 2.331(10) 2.345(10) 2.215(10) 2.203(10)	Fe-Cl 2.200(11) 2.186(12) Fe-P 2.289(11) 2.342(11) 2.316(11) 2.306(11)	68

Table 2 (Continued)

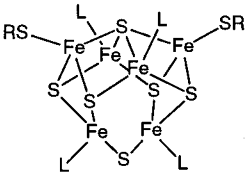
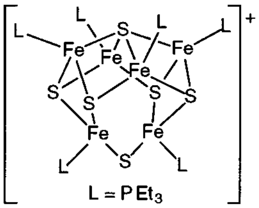
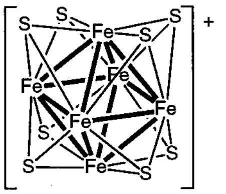
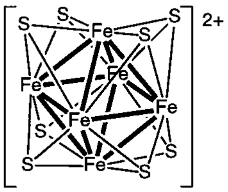
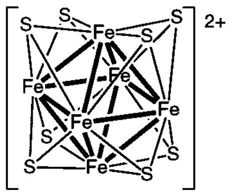
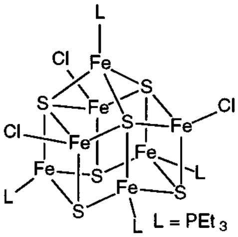
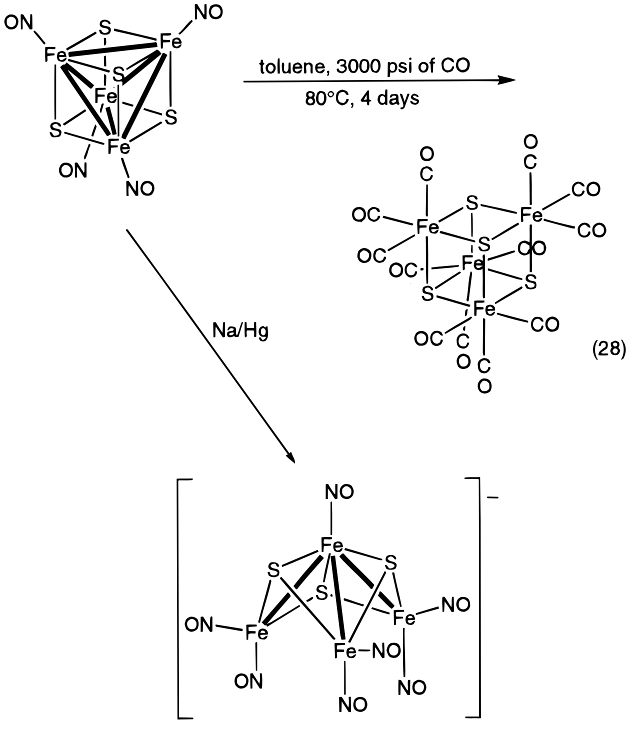
Cluster	Structure	Distance (Å)			ref
		Fe-Fe	Fe-S	others	
$(p\text{-BrC}_6\text{H}_4\text{S})_2(\text{Et}_3\text{P})_4\text{Fe}_6\text{S}_6$	 L = PEt$_3$, R = p-BrC$_6$H$_4$	2.675(4) 2.656(4) 2.694(5) 2.650(4) 2.619(4) 2.657(4) 2.647(4) 2.635(4) 2.700(4) 2.665(4) 2.856(4) 2.602(4)	2.194(6) 2.187(6) 2.204(6) 2.185(7) 2.249(7) 2.220(6) 2.221(7) 2.233(6) 2.250(7) 2.241(7) 2.234(7) 2.244(6) 2.164(7) 2.158(7) 2.309(6) 2.329(6) 2.220(6) 2.226(6)	Fe-S thiolate 2.251(7) 2.259(7) Fe-P 2.301(7) 2.293(6) 2.287(7) 2.283(8)	37
$[(\text{Et}_3\text{P})_6\text{Fe}_6\text{S}_6](\text{BF}_4)$	 L = PEt$_3$	2.665(3) 2.651(2)[2] 2.654(3) 2.627(3) 2.716(2)[2] 2.629(2)[2] 2.719(2)[2] 2.969(3)	2.224(3)[2] 2.217(3)[2] 2.216(3)[2] 2.229(3)[2] 2.198(3)[2] 2.192(3)[2] 2.299(4) 2.279(4) 2.231(3)[2] 2.153(4) 2.153(4)	Fe-P 2.381(5) 2.271(4) 2.363(5) 2.293(4) 2.281(4)[2]	39
$[(\text{Et}_3\text{P})_6\text{Fe}_6\text{S}_8](\text{PF}_6)$	 A Et$_3$P ligand on each Fe atom is omitted.	2.636(2)[6] 2.636(2)[6]	2.256(3)[6] 2.255(3)[6] 2.250(3)[6] 2.243(3)[6]	Fe-P 2.263(3)[6]	38
$[(\text{Et}_3\text{P})_6\text{Fe}_6\text{S}_8](\text{BPh}_4)_2$	 A Et$_3$P ligand on each Fe atom is omitted.	2.633(3)[2] 2.602(3)[2] 2.612(3)[2] 2.611(3)[2] 2.638(3)[2] 2.606(3)[2]	2.253(4)[2] 2.241(4)[2] 2.250(4)[2] 2.241(3)[2] 2.246(3)[2] 2.246(3)[2] 2.249(3)[2] 2.254(3)[2] 2.239(3)[2] 2.248(3)[2] 2.245(4)[2] 2.251(4)[2]	Fe-P 2.286(3)[2] 2.305(4)[2] 2.289(4)[2]	40
$[(\text{Et}_3\text{P})_6\text{Fe}_6\text{S}_8](\text{BPh}_4)_2$	 A Et$_3$P ligand on each Fe atom is omitted.	2.638(8)[2] 2.610(9)[2] 2.620(7)[2] 2.613(8)[2] 2.655(6)[2] 2.605(7)[2]	2.264(8)[2] 2.258(9)[2] 2.265(10)[2] 2.248(10)[2] 2.263(12)[2] 2.248(13)[2] 2.247(10)[2] 2.249(11)[2] 2.253(11)[2] 2.263(11)[2] 2.275(11)[2] 2.249(10)[2]	Fe-P 2.288(14)[2] 2.300(8)[2] 2.301(11)[2]	69

Table 2 (Continued)

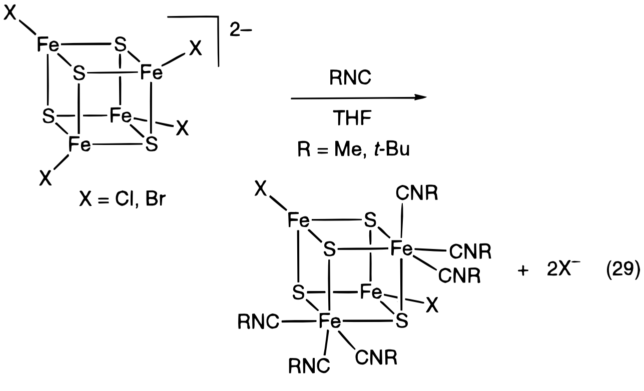
Cluster	Structure	Distance (Å) Fe-Fe	 Fe-S	 others	ref
$Cl_3(Et_3P)_4Fe_7S_6$		2.986(2)[3] 2.584(2)[3] 2.746(3)[3] 2.626(2)[6] 4.148(2)[3]	2.193(2)[3] 2.179(3)[6] 2.231(3)[3] 2.276(3)[3] 2.366(3)[6]	Fe-P 2.298(5) 2.289(3)[3] Fe-Cl 2.189(3)[3]	41

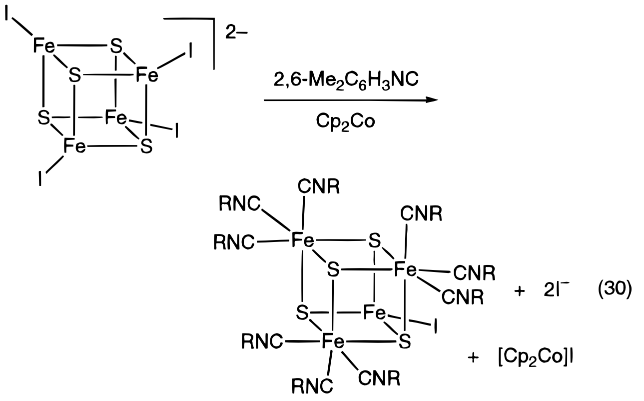
[a] Numbers in square brackets indicate the multiplicity of the distance. [b] dppf = 1,1'-bis(diphenylphosphino)ferrocene.

prepared by nitrosylation of Fe_2S_2 and Fe_4S_4 complexes with thiolate ligands.[49]

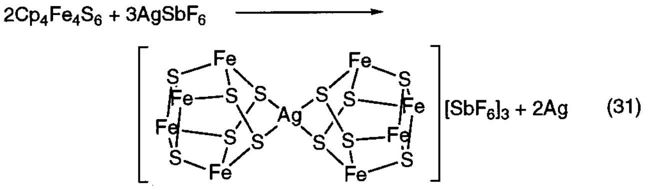


Cubane-type clusters with isonitrile ligands are conveniently prepared by reactions of $[Fe_4S_4X_4]^{2-}$ (X = Cl, Br, I) with isonitriles (eqs 29 and 30). The remaining halide ligands on the Fe_4S_4 can be further substituted by thiolate groups by treatment with metal thiolates.[50]





By utilizing the basicity of the disulfide ligands in $Cp_4Fe_4S_6$, silver-bridged iron–sulfur cluster is obtained (eq 31).[20,22] During the course of the reaction each tetrairon cluster is oxidized to the monocation.



Cp ligands are omitted.

E. Electrochemical or Chemical Redox of the Iron–Sulfur Clusters (Method E)

Since many of the organometallic iron–sulfur clusters show several one-electron redox waves in their cyclic voltammograms (see Section IV), redox reactions of iron–sulfur clusters provide another versatile method for the synthesis of novel clusters. Both chemical redox method and bulk electrolysis are frequently used and, in the former method, typical oxidizing agents are oxygen, halogen, $AgBF_4$, ferrocenium salt, etc. and reducing agents are cobaltocene, alkaline metal, sodium naphthalenide, hydrazine, sodium tetrahydroborate, etc. (eqs 32–36).

$$Cp_4Fe_4S_4 \xrightarrow[CH_2Cl_2]{Br_2 \text{ or } AgBF_4} [Cp_4Fe_4S_4]X \quad (32)^{51}$$

X = Br_3 or BF_4

$$[(MeC_5H_4)_4Fe_4S_4](PF_6) \xrightarrow[CH_3CN]{[Cp_2Fe](PF_6)} [(MeC_5H_4)_4Fe_4S_4](PF_6)_2 \tag{33}$$
[23]

$$(ON)_4Fe_4S_4 \xrightarrow[toluene]{Cp_2Co} [Cp_2Co][(ON)_4Fe_4S_4] \tag{34}$$
[15]

$$(ON)_4Fe_4S_2(\mu_3\text{-}NCMe_3)_2 \xrightarrow[\text{2) } (Ph_3P)_2NCl,\ \text{acetone}]{\text{1) Na/Hg, THF}} [(Ph_3P)_2N][(ON)_4Fe_4S_2(\mu_3\text{-}NCMe_3)_2] \tag{35}$$
[52]

$$[Cp_4Fe_4S_5](PF_6)_2 \xrightarrow[CH_3CN]{NaBH_4} Cp_4Fe_4S_5 \tag{36}$$
[22]

Comproportionation reaction between a cluster system with different oxidation states is useful to prepare a cluster with an intermediate oxidation state which is not easily accessible (eq 37).[24]

$$(MeC_5H_4)_4Fe_4S_5 + [(MeC_5H_4)_4Fe_4S_5](PF_6)_2 \xrightarrow[CH_3CN]{} [(MeC_5H_4)_4Fe_4S_5](PF_6) \tag{37}$$

The oxidation states of products depend on not only the stoichiometry of the agents but also their redox power, so that selection of appropriate agent is sometimes critical. On the other hand, bulk electrolysis in controlled potential techniques allows us to freely set the electrode potential and is, therefore, favorable for the synthesis of individual oxidation states of iron−sulfur clusters having multiple-oxidation states. Typical examples of the electrochemical syntheses of clusters in different oxidation states are those of $[Cp_4Fe_4S_4]^{n+}$ ($n = 0-3$)[53−55] and their selenium analogues.[56] Each of the cyclic voltammograms of these cluster systems shows four redox waves, indicating the existence of five oxidation states (see Table 3 for $Cp_4Fe_4S_4$). These oxidation states had been first erroneously assigned to $n = 1-$, 0, 1+, 2+, and 3+, but the assignment was corrected later to $n = 0$, 1+, 2+, 3+, and 4+ on the basis of the DC polarograms and X-ray crystal structure analysis of some products obtained by controlled potential electrolysis.[55,56] On the basis of the corrected redox potential data, $[Cp_4Fe_4S_4]^{n+}$ (n = 1+, 2+, 3+) were obtained in high yields by electrolysis at + 0.17, +0.5, and + 0.95 V vs SCE, respectively (eqs 38−40).[55] The tricationic iron−selenium cubane cluster $[Cp_4Fe_4Se_4]^{3+}(PF_6^-)_3$ was also synthesized by electrolysis at +1.0 V vs SCE and crystallographically characterized (eq 41).[56]

$$Cp_4Fe_4S_4 \xrightarrow[0.1\ M\ NH_4PF_6\text{-}CH_3CN]{+0.17\ V\ vs.\ SCE} [Cp_4Fe_4S_4]^+ \tag{38}$$

$$[Cp_4Fe_4S_4]^+ \xrightarrow[0.1\ M\ NH_4PF_6\text{-}CH_3CN]{+0.5\ V\ vs.\ SCE} [Cp_4Fe_4S_4]^{2+} \tag{39}$$

$$[Cp_4Fe_4S_4]^{2+} \xrightarrow[0.1\ M\ NH_4PF_6\text{-}CH_3CN]{+0.95\ V\ vs.\ SCE} [Cp_4Fe_4S_4]^{3+} \tag{40}$$

$$[Cp_4Fe_4Se_4]^{2+} \xrightarrow[0.1\ M\ NH_4PF_6\text{-}CH_3CN]{+1.0\ V\ vs.\ SCE} [Cp_4Fe_4Se_4]^{3+} \tag{41}$$

A drawback of bulk electrolysis is that we have to remove a large amount of electrolytes from the reaction mixture after electrolysis, and this process sometimes disturbs the isolation of products, especially when the products are unstable.

The compositions of clusters are preserved in most redox reactions, but there are some exceptions (eq 42).[20,22]

$$Cp_4Fe_4S_6 + 1/2O_2 + 2NH_4PF_6 \xrightarrow[CH_3CN]{r.t.} [Cp_4Fe_4S_5](PF_6)_2 + 1/8S_8 + 2NH_3 + H_2O \tag{42}$$

III. Structures of Iron–Sulfur Clusters

Structurally determined iron−sulfur clusters having organic supporting ligands contain three to seven iron atoms in the cluster core. In this chapter, we classify the iron−sulfur clusters by the number of iron atoms and consider the structures of each of them. Some important structural data are summarized in Table 2.

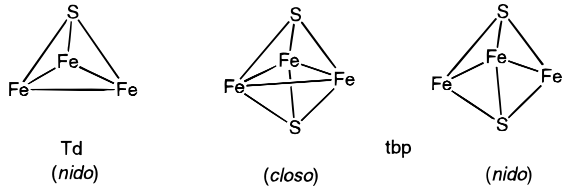
A. Triiron Clusters

In triiron−sulfur clusters, three iron atoms take triangular arrangements, and either one or two sulfur atoms cap one or both sides of the triangle to form tetrahedral (Td) or trigonal-bipyramidal (tbp) structures. The latter type of clusters can be further classified by the presence of iron−iron bonds into two types: *closo* and *nido* (Scheme 1).

Known clusters with a tetrahedral Fe_3S core are $[(OC)_9Fe_3S]^{2-}$, $(\eta^4\text{-}C_6H_8)(\mu\text{-}OC)_2(OC)_6Fe_3S$, and $(OC)_9(\mu_3\text{-}OC)Fe_3S$. The only example of the *closo*-Fe_3S_2-type cluster is $Cp^*_2(OC)_3Fe_3S_2$. Two of the *nido*-Fe_3S_2-type clusters, namely $(OC)_9Fe_3S_2$ and its derivative $(OC)_8(Me_2HN)Fe_3S_2$, have been crystallographically analyzed. There are also the derivatives of this type of clusters in which the carbonyl ligands are partly substituted by phosphines, arsines, phosphites, etc. These derivatives are considered to have also the *nido*-Fe_3S_2 cluster core.[71,72]

All of these clusters nicely obey cluster electron counting rules such as Wade's rule[73] and PSEPT.[74] Thus, all of the Fe_3S-type clusters have 12 cluster electrons which corresponds to the *nido* structure with four vertexes ($[(OC)_9Fe_3S]^{2-}$ and $(\eta^4\text{-}C_6H_8)(\mu\text{-}OC)_2(OC)_6Fe_3S$) or the *closo* structure with five vertexes ($(OC)_9(\mu_3\text{-}OC)Fe_3S$). In the Fe_3S_2-type clusters, $Cp^*_2(OC)_3Fe_3S_2$ and $(OC)_9Fe_3S_2$ have 12 and 14clus-

Scheme 1. Structural Types of Triiron Clusters



example

$[(OC)_9Fe_3S]^{2-}$ [11,12]	$Cp^*_2(OC)_3Fe_3S_2$ [44]	$(OC)_9Fe_3S_2$ [70]
$(\eta_4\text{-}C_6H_8)(OC)_8Fe_3S$ [19]		$(OC)_8(NHMe_2)Fe_3S_2$ [18]
$(OC)_9(\mu_3\text{-}OC)Fe_3S$ [57]		$(OC)_9Fe_3S(SO)$ [6]

Table 3. Redox Properties of Iron−Sulfur Clusters

cluster	redox								condition	ref(s)
$Cp_4Fe_4S_6$				1−/0	0/1+	1+/2+	2+/3+[a]			
				−1.325	+0.06	+0.367			0.1 M $TBASbF_6-CH_2Cl_2$, vs SCE	20,21
				−1.71	−0.49	−0.175	+0.855		0.1 M $TBAPF_6$−PhCN, vs Fc/Fc^+ [b]	87
				−1.72	−0.45	−0.14			0.1 M $TBAPF_6-CH_2Cl_2$, vs Fc/Fc^+	87
$Cp_4Fe_4S_5$			2−/1−[a]	1−/0	0/1+	1+/2+	2+/3+			
			−2.19	−1.72	−0.64	−0.335	+0.785		0.1 M $TBAPF_6$−PhCN, vs Fc/Fc^+	87
			−1.77	−1.33	−0.23	+0.07	+1.19		0.1 M $TBAPF_6-CH_3CN$, vs SCE	88
				−1.76	−0.61	−0.30			0.1 M $TBAPF_6-CH_2Cl_2$, vs Fc/Fc^+	87
$[Cp_4Fe_4S_5](PF_6)_2$					0/1+	1+/2+				
					−0.23	+0.07			0.1 M $TBAPF_6-CH_3CN$, vs SCE	86
					−0.27	−0.13			0.1 M $TBAPF_6$-aqueous Triton X-100, pH 7	86
$Cp_4Fe_4S_4$				1−/0[a]	0/1+	1+/2+	2+/3+	3+/4+		
					−0.33	+0.33	+0.88	+1.41	0.1 M $TBAPF_6-CH_3CN$, vs SSCE	53,54
				−2.075	−0.74	−0.11	+0.425	+0.915	0.1 M $TBAPF_6$−PhCN, vs Fc/Fc^+	87
				−2.1	−0.73	−0.10	+0.43	+0.94	0.1 M $TBAPF_6-CH_3CN$, vs Fc/Fc^+	87
					−0.73	−0.05			0.1 M $TBAPF_6-CH_2Cl_2$, vs Fc/Fc^+	87
$(MeC_5H_4)_4Fe_4S_4$				1−/0[a]	0/1+	1+/2+	2+/3+	3+/4+		
				−2.1	−0.82	−0.16	+0.40	+0.92	0.1 M $TBAPF_6-CH_3CN$, vs Fc/Fc^+	24
$(MeC_5H_4)_4Fe_4S_5$			2−/1−[a]	1−/0	0/1+	1+/2+	2+/3+			
			−2.3	−1.77	−0.71	−0.38	+0.72		0.1 M $TBAPF_6-CH_3CN$, vs Fc/Fc^+	24
$(MeC_5H_4)_4Fe_4S_6$				1−/0	0/1+	1+/2+	2+/3+[a]			
				−1.89	−0.57	−0.24	+0.86		0.1 M $TBAPF_6-CH_2Cl_2$, vs Fc/Fc^+	24
$(Me_3SiC_5H_4)_4Fe_4S_6$				2−/0	0/1+	1+/2+				
				−1.31	−0.08	+0.26			0.1 M TBAB−CH_3CN, vs SCE	25
$\{Me_2Si(C_5H_4)_2\}_2Fe_4S_6$				1−/0	0/1+	1+/2+	2+/3+[a]	3+/4+[a]		
				−1.75	−0.45	+0.14	+0.80	+1.02	0.1 M $TBAPF_6-CH_2Cl_2$, vs Fc/Fc^+	36
$\{Me_2Si(C_5H_4)_2\}_2Fe_4S_6(CO)$				1−/0	0/1+	1+/2+	2+/3+[a]			
				−1.62	−0.38	−0.01	+0.80		0.1 M $TBAPF_6-CH_2Cl_2$, vs Fc/Fc^+	36
$\{(CF_3)_2C_2S_2\}_4Fe_4S_4$	4−/3−	3−/2−	2−/1−	1−/0					0.1 M $TBAPF_6-CH_2Cl_2$, vs AgI/0.42 M $TBAPF_6$−0.5 M Bu_4NI/CH_2Cl_2	34
	−0.7	−0.10	+0.54	+0.98						
$(Ph_4As)[L_4Fe_4S_4]$	4−/3−	3−/2−	2−/1−	1−/0					0.1 M $TBAPF_6-CH_2Cl_2$, vs AgI/0.42 M $TBAPF_6$−0.5 M Bu_4NI/CH_2Cl_2	
L = $(CF_3)_2C_2S_2$	−0.61	−0.08	+0.54	+1.00						34
$(Bu_4N)_2[L_4Fe_4S_4]$	4−/3−	3−/2−	2−/1−	1−/0					0.1 M $TBAPF_6-CH_2Cl_2$, vs AgI/0.42 M $TBAPF_6$−0.5 M Bu_4NI/CH_2Cl_2	
L = $(CF_3)_2C_2S_2$	−0.60	−0.05	+0.57	+1.02						34
$(Ph_2C_2S_2)_4Fe_4S_4$		3−/2−	2−/1−	1−/0					0.1 M $TBAPF_6-CH_2Cl_2$, vs AgI/0.42 M $TBAPF_6$−0.5 M Bu_4NI/CH_2Cl_2	
		−0.76	−0.16	+0.13						34
$(Ph_4As)[(Ph_2C_2S_2)_4Fe_4S_4]$		3−/2−	2−/1−	1−/0					0.1 M $TBAPF_6-CH_2Cl_2$, vs AgI/0.42 M $TBAPF_6$−0.5 M Bu_4NI/CH_2Cl_2	
		−0.71	−0.15	+0.15						34
$Cp^*_2(Ph_2C_2S_2)_2Fe_4S_4$			2−/1−	1−/0	0/1+	1+/2+				
			−1.13	−0.55	+0.20	+0.64			0.1 M TBAB−CH_2Cl_2, vs SCE	30,61
$Cp^*_3(Ph_2C_2S_2)Fe_4S_5$				1−/0	0/1+	1+/2+	2+/3+			
				−0.90	−0.14	+0.58	+1.19		0.1 M TBAB−CH_2Cl_2, vs SCE	31,61
$(ON)_4Fe_4S_4$			2−/1−	1−/0						
			−0.65	+0.13					0.1 M $TBAPF_6-CH_2Cl_2$, vs SCE	15,16

$(Et_4N^+)[(ON)_7Fe_4S_3]^-$		4−/3−	3−/2−	2−/1−							
		−1.75	−1.26	−0.68						0.2 M Et_4NClO_4−CH_3CN, vs SCE	60
		−1.9[a]	−1.33	−0.79						0.2 M $TBAClO_4$−CH_2Cl_2, vs SCE	60
		−1.81	−1.35	−0.77						0.2 M $TBAClO_4$−THF, vs SCE	60
Et_4N^+, Bu_4N^+, Me_3S^+, and Me_3SO^+		−2.14	−1.19	−1.31						0.2 M $TBAPF_6$−THF, vs Fc/Fc^+	89
$\{Me_2Si(C_5H_4)_2\}_2Fe_5S_{12}$					1−/0	0/1+	1+/2+[a]				
					−1.53	−0.41	+0.49			0.1 M $TBAPF_6$−CH_2Cl_2, vs Fc/Fc^+	36
$(RS)_2(Et_3P)_4Fe_6S_6$					1−/0[c]						
R = Ph					−0.87					0.1 M $TBAClO_4$−THF, vs SCE	37
					1−/0[c]						
R = *p*-C_6H_4Br					−0.60					0.1 M $TBAClO_4$−THF, vs SCE	37
$Cl_2(Et_3P)_4Fe_6S_6$					1−/0	0/1+	1+/2+				
					−0.78	+0.19	+0.98			0.2 M $TBAClO_4$−CH_2Cl_2, vs SCE	68
$[(Et_3P)_6Fe_6S_8]^{2+}$						0/1+	1+/2+	2+/3+	3+/4+		
						−1.05[a]	−0.06	+0.59	+1.25	0.1 M $TBAClO_4$−CH_3CN, vs SCE	38
						−1.03	+0.06	+0.80	+1.36	0.1 M $TBAClO_4$−CH_2Cl_2, vs SCE	38
$[(OC)_{12}Fe_6S_6]^{2-}$	*n*−/4−[a]	4−/3−	3−/2−	2−/*n*[a]							
	−2.02	−1.73	−1.13	−0.08						0.1 M $TBAClO_4$−CH_3CN, vs SCE	66
			−1.083							0.1 M $TBAPF_6$−CH_3CN, vs SCE	13
$[(OC)_9Fe_3S]^{2-}$			3−/2−								
			−0.21							0.1 M $TBAPF_6$−CH_3CN, vs SCE	13
$[(OC)_9Fe_3S]^{2-}$				2−/1−							
				−0.25						0.2 M Et_4NClO_4−CH_3CN, vs SCE	14
				−0.34						CH_2Cl_2, vs SCE	14
				−0.35						0.1 M $TBAClO_4$−1,2-dichloroethane vs Ag/AgCl	90
$[(OC)_{14}Fe_5S_2]^{2-}$		4−/3−	3−/2−								
		−1.60	+0.017							0.1 M $TBAPF_6$−CH_3CN, vs SCE	13
$(Et_4N)_2[(OC)_{14}Fe_5S_2]$			3−/2−	2−/1−	1−/0						
			−1.71	−0.18	+0.26					0.2 M $TBAClO_4$−CH_2Cl_2, vs SCE	14
			−1.53	−0.07	+0.41[a]					0.2 M Et_4NClO_4−CH_3CN, vs SCE	14
$(OC)_9Fe_3S_2$				2−/1−[a]	1−/0						
				−1.38	−0.43					PhCN, vs Ag/AgCl	91
$(OC)_9Fe_3(S)(CO)$					1−/0[a]	0/1+[a]					
					−0.26	+0.43				PhCN, vs Ag/AgCl	91
$(OC)_9Fe_3(S)(SO)$				2−/1−[a]	1−/0[a]						
				−1.0	−0.31					PhCN, vs Ag/AgCl	91

[a] Irreversible (peak potential was described). [b] Abbreviation Fc/Fc^+: ferrocene/ferricinium couple. [c] Number of the electron for the reduction was not mentioned. Another irreversible reduction and an oxidation were observed.

Scheme 2. Structural Types of Tetrairon Clusters

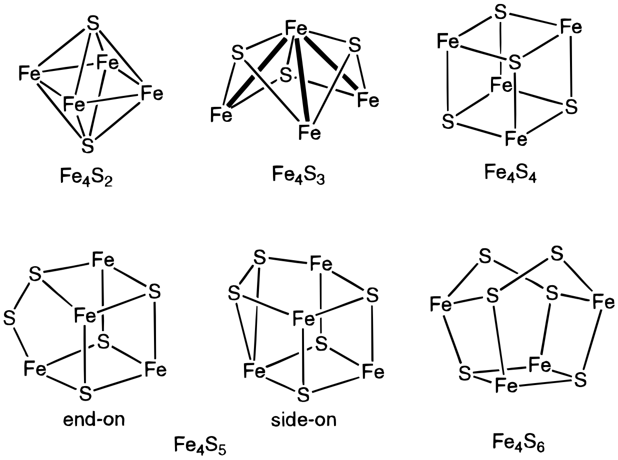
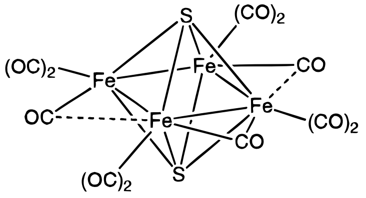


Chart 2



ter electrons and adopt *closo* and *nido* structures, respectively, in accord with the Wade's rule.

B. Tetrairon Clusters

Scheme 2 shows the core structures of different tetrairon−sulfur clusters. The number of sulfur atoms ranges from two to six. In the Fe_4S_2 cluster, four iron atoms take a square planar geometry, and two μ_4-sulfido ligands cap both sides of the square. In the Fe_4S_3 cluster, four iron atoms adopt a distorted tetrahedral arrangement, and μ_3-sulfido ligands cap three of the four triangular planes. This can be also viewed as a cubane cluster in which one of four μ_3-sulfido ligands is lost (vide infra). The Fe_4S_4 cluster is the so-called "cubane cluster" and has a distorted cubic structure. The iron−iron bond lengths subtly change according to the type of ligands and the total charge of the cluster. This cluster will be discussed later in detail. The Fe_4S_5 cluster has three μ_3-sulfido and one μ_3-disulfido ligands, and can be classified into two types according to the bridging mode of the μ_3-disulfido ligand: one has an end-on type μ_3-S_2 while the other has a side-on type μ_3-S_2 (see Scheme 2). Finally, the Fe_4S_6 cluster has two μ_3-sulfido and two end-on type μ_3-disulfido ligands.

The only example of an Fe_4S_2 cluster is $(OC)_{11}Fe_4S_2$ which was prepared by photolysis of $(OC)_9Fe_3S_2$ and $Fe(CO)_5$. The cluster core is surrounded by 11 carbonyl ligands; one bridging, two semi-bridging, and eight terminal ones (Chart 2).[46]

The Fe_4S_3-type clusters have a common structure $[(ON)_7Fe_4S_3]^{n-}$ ($n = 1$ and 2) and are called "Roussin's salts" (Chart 3). The apical iron atom has one nitrosyl ligand and each of three basal iron atoms has two nitrosyl ligands. The apical iron atom is bonded to three basal iron atoms but there is no bond between the basal iron atoms. The structures of the monoanion and the dianion are almost identical. So far, the structures of the salts of Cs^+,[75,76] $[Ph_4As]^+$,[58] $[Me_3S]^+$,[59] and $[Et_4N]^+$ [60] have been determined crystallographically.

Chart 3

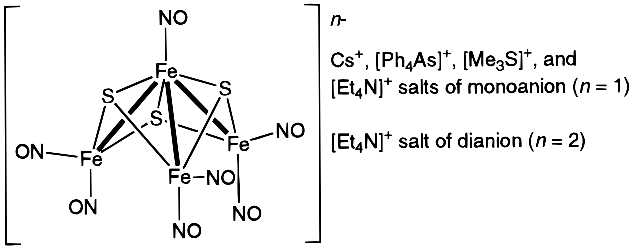


Chart 4

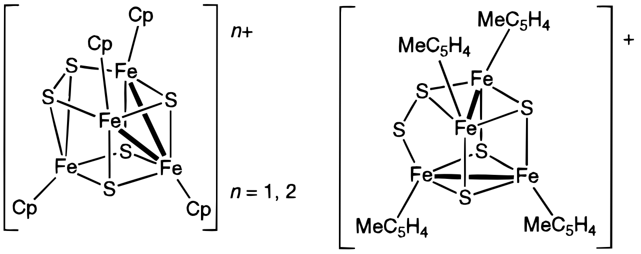
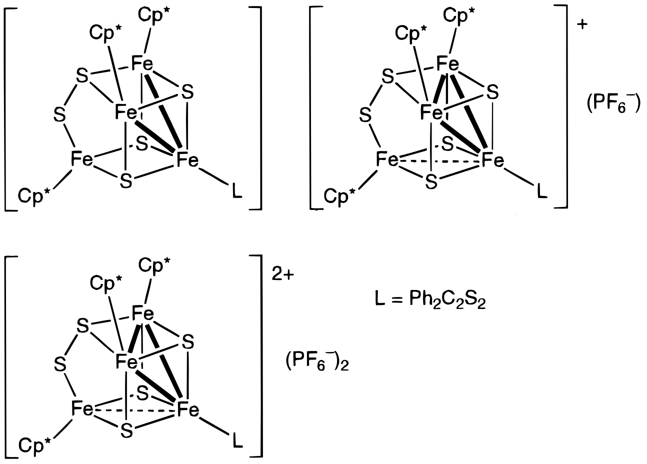


Chart 5

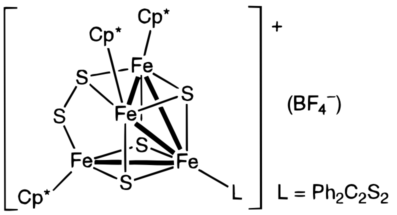


As to the Fe_4S_5-type clusters, the structures of $[Cp_4Fe_4S_5]^{n+}$ ($n = 1, 2$)[64,77] and $[(MeC_5H_4)_4Fe_4S_5]^+$ [24] have been determined by crystal structure analysis (Chart 4).

Interestingly, there are some differences in the structures of them: In the former, the disulfido ligand is side-on, whereas in the latter, it is end-on. In the former, two iron−iron bonds share an iron atom, while in the latter, they do not. These structural differences seem to originate from the difference of crystal packing in these complexes. All of the mixed-ligand clusters $[Cp^*_3(Ph_2C_2S_2)Fe_4S_5]^{n+}(PF_6^-)_n$ ($n = 0, 1, 2$)[32,61] have an end-on-type disulfido ligand, but the total iron−iron distance decreases with the increase of the positive charge of the clusters (Chart 5 and Table 2).

The core structure of the monocationic cluster was found to be significantly dependent on the counteranion: When the counteranion is PF_6^-, the Fe−Fe bond expressed by a dotted line is much longer (3.047(2) Å) than other three Fe−Fe bonds expressed

Chart 6



by bold lines (2.736−2.783 Å) (Chart 5), whereas when the counteranion is BF_4^-, this bond becomes comparable (2.866(2) Å) to other three Fe−Fe bonds (2.732−2.887 Å) (Chart 6).[65] These findings indicate that the Fe_4S_5 framework is quite flexible.

In contrast to the above observed differences for $Cp^*_2Fe_4S_5$-type clusters, substitution of Cp hydrogens by Me_3Si in $Cp_4Fe_4S_6$ clusters does not result in distinct structural differences between $Cp_4Fe_4S_6$[20,21,78] and $(Me_3SiC_5H_4)_4Fe_4S_6$.[25]

C. Cubane Clusters (Fe_4S_4 Clusters)

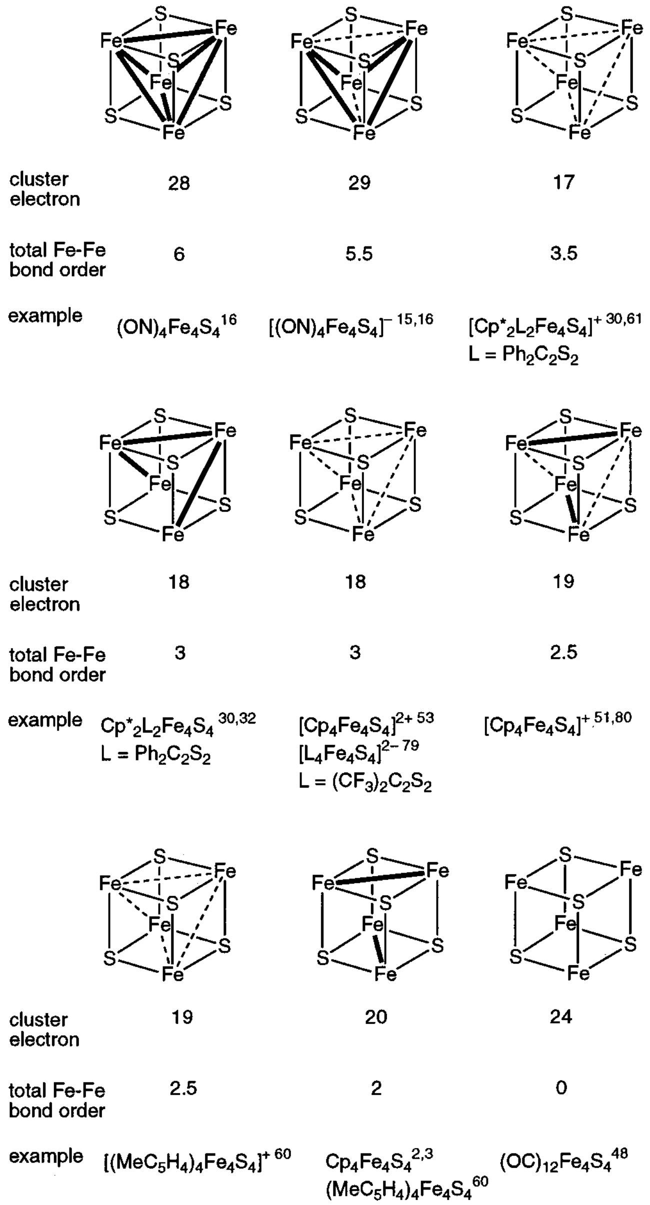
Cubane cluster is undoubtedly the most versatile and the most thoroughly investigated among iron−sulfur clusters. Numerous clusters of this type having various supporting ligands and oxidation states have been prepared and the crystal structures of most of them have been determined. The types of the core structures of known Fe_4S_4 clusters are classified and summarized in Scheme 3.

The iron−sulfur cores of all of these Fe_4S_4 possess distorted cubic structures, but the number of iron−iron bonds and the iron−iron distances change subtly according to the supporting ligands and charge of the clusters. In Scheme 3, an iron−iron bond (2.5−2.7 Å) is drawn by a solid line and two iron atoms with weak interaction (2.7−3.0 Å) are connected by a dotted line. For instance, $(ON)_4Fe_4S_4$ has all of six iron−iron bonds, while $(OC)_{12}Fe_4S_4$ has no iron−iron bond.

These structural differences can be rationalized by considering the cluster electron numbers and the MO of the Fe_4S_4 clusters. The cluster electron numbers in these clusters can be easily calculated by simply adding up the d electrons of iron atoms in the formal oxidation states. For example, the formal oxidation states of the iron atoms in $(ON)_4Fe_4S_4$, $(OC)_{12}Fe_4S_4$, and $Cp_4Fe_4S_4$ are Fe(I), Fe(II), and Fe(III), respectively. Therefore, the d electron numbers of these iron atoms, d^7, d^6, and d^5, give the cluster electron numbers, 28, 24, and 20, respectively.

Molecular orbital calculations for Fe_4S_4 clusters have been done by some researchers using various methods,[15,53,81,82] which gave almost identical results about the molecular orbitals concerning the iron−iron interactions. Scheme 4 shows the MO energy level scheme for $Cp_4M_4S_4$ derived by Dahl et al.[53] Among 20 metal-based cluster orbitals, $a_1 + e + t_2$, $t_1 + t_2$, and $e + t_1 + t_2$ are bonding, antibonding, and nonbonding with respect to the intermetallic interaction, respectively. The MO energy level scheme for $(OC)_{12}Fe_4S_4$ is analogous to this. As shown in Scheme 4, the nonbonding $e + t_1 + t_2$ level in these clusters is located *above* the antibonding $t_1 + t_2$ level. Therefore, in $Cp_4Fe_4S_4$, 20 cluster electrons fill the six bonding orbitals and four of the six antibonding orbitals to lead to the total Fe−Fe bond order of 2. In $(OC)_{12}Fe_4S_4$, 24 cluster electrons fill up all the bonding and antibonding orbitals, so that there is no Fe−Fe bond.

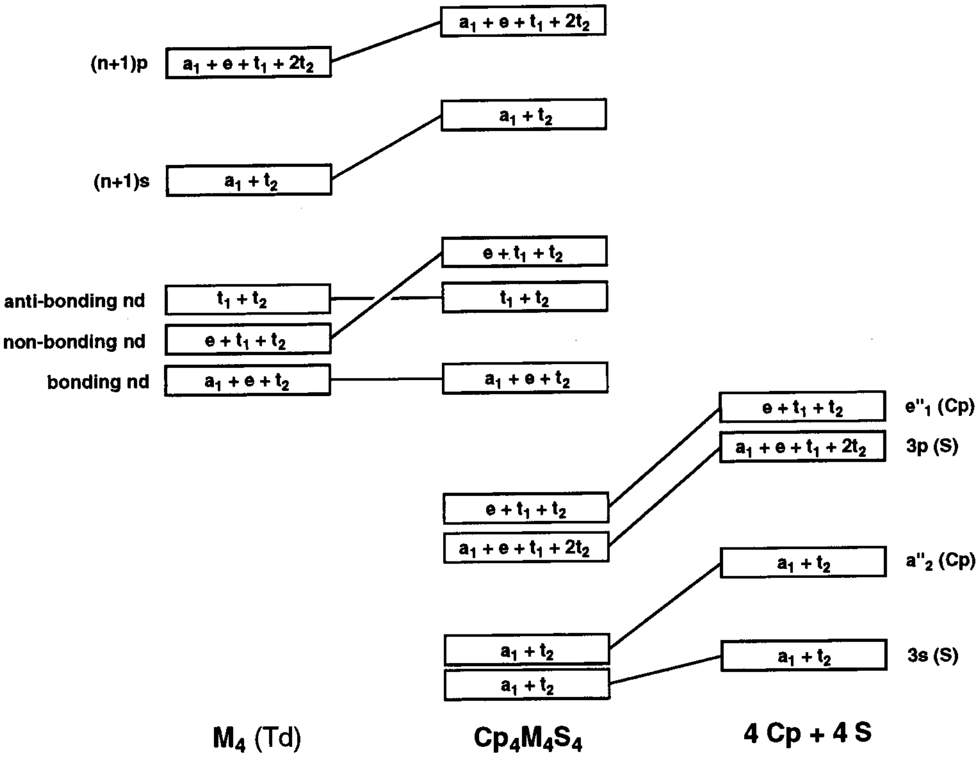
Scheme 3



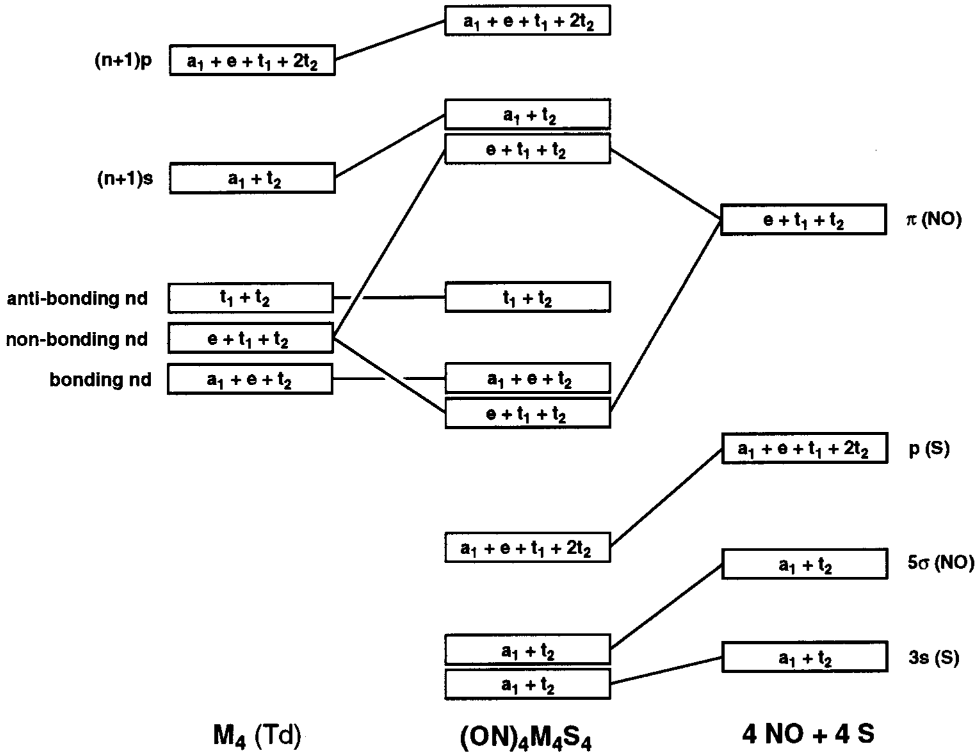
In contrast, the nonbonding $e + t_1 + t_2$ level of $(ON)_4Fe_4S_4$ is located *below* the bonding $a_1 + e + t_2$ level as shown in Scheme 5.[15] Thus, 28 cluster electrons fill first the eight nonbonding orbitals and then six bonding orbitals, and no electron occupies the antibonding orbitals. This electronic configuration results in the total iron−iron bond order of 6.

In these clusters, a one-electron oxidation or reduction causes an appreciable change of iron−iron distances, because such electronic changes involve the antibonding $t_1 + t_2$ or bonding $a_1 + e + t_2$ levels. This phenomenon is clearly demonstrated in $[Cp_4Fe_4S_4]^{n+}$ ($n = 0, 1, 2$), $[(ON)_4Fe_4S_4]^{n-}$ ($n = 0, 1$), $[(ON)_4Fe_4S_2(\mu_3\text{-}NCMe_3)_2]^{n-}$ ($n = 0, 1$), and $[Cp^*_2(Ph_2C_2S_2)_2Fe_4S_4]^{n+}$ ($n = 0, 1$).

Scheme 4



Scheme 5



The ordering of the bonding, nonbonding, and antibonding levels greatly depends on the coordination geometry of the metal sites and the supporting ligands.[82] Incidentally, a high-spin iron−sulfur cluster $[Fe_4(SR)_4S_4]^{2-}$ has its nonbonding $e + t_1 + t_2$ level between the bonding $a_1 + e + t_2$ and antibonding $t_1 + t_2$ levels. These orbitals are filled with 22 electrons coming from two d^6 Fe(II) and two d^5 Fe(III) atoms in this cluster to produce the ground-state configuration $(a_1 + e + t_2)^{12}(e + t_1 + t_2)^{10}(t_1 + t_2)^0$. In this type of cluster, a one- or two-electron oxidation or reduction is expected to occur by taking in and out of electrons in only nonbonding orbitals. This is consistent with the observation that the electron

Chart 7

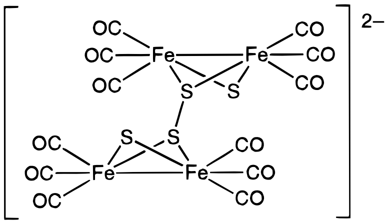
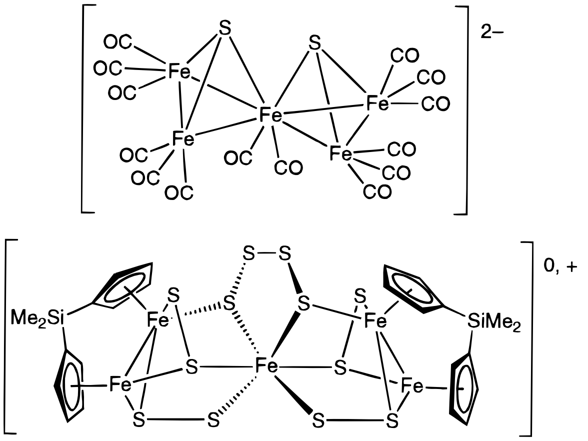


Chart 8



transfer on this cluster, and also on the electronically analogous active centers of the high-potential iron protein and of the bacterial ferredoxins, causes virtually no changes in the Fe−Fe distances in the Fe_4S_4 core.[15]

The only exceptional Fe_4S_4 cluster is $[(OC)_{12}Fe_4S_4]^{2-}$,[63,83] which does not have a cubane structure. This cluster consists of two $[(OC)_6Fe_2S_2]$ units bonding to each other through one of the bridging sulfido ligands in each unit (Chart 7). This compound was prepared by treating $[(OC)_6Fe_2S_2]$ with $LiBEt_3H$.

D. Pentairon and Higher Nuclearity Clusters

Pentanuclear or higher nuclearity clusters are rare in the iron−sulfur clusters having organic supporting ligands. This contrasts greatly with the situation of those bearing inorganic supporting ligands, especially thiolates, where the high nuclearity clusters are frequently encountered.

In the pentairon cluster $[(OC)_{14}Fe_5S_2]^{2-}$, the Fe_5S_2 core comprises two Fe_3S units sharing an iron atom.[13] Another example of a pentairon cluster is $[\{Me_2Si(C_5H_4)_2\}_2Fe_5S_{12}]^{0,+}$ in which two diiron units bridged by $Me_2Si(C_5H_4)_2$ ligands are connected with a central iron atom by two kinds of disulfido ligands and a tetrasulfido ligand (Chart 8).[36]

As to hexairon clusters, two kinds of Fe_6S_6 clusters with different core structures are known. $[Fe_6S_6(CO)_{12}]^{2-}$ [13,66] has a structure with two $(OC)_6Fe_2S_2$ units coordinated to the iron atoms of an Fe_2S_2 center. Another cluster $[Fe_6S_6(PEt_3)_6]^{+}$ [39] takes a basket-shaped core with one μ_4-S, four μ_3-S, and one μ_2-S (Chart 9).

An interesting heptairon cluster $Cl_3(Et_3P)_4Fe_7S_6$ has an Fe_7S_6 monocapped-prismane core (Chart 10).[41]

Chart 9

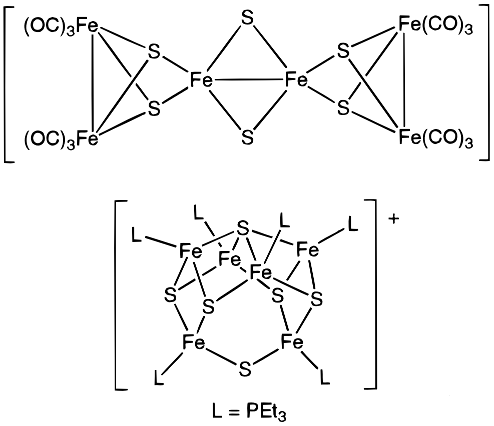
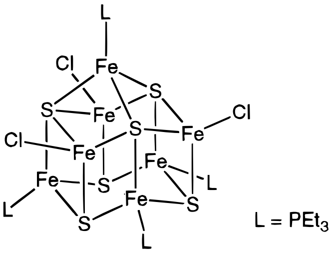


Chart 10



IV. Electrochemical Properties

Among the iron−sulfur clusters, the electrochemically most thoroughly investigated are those with Fe_4S_3, Fe_4S_4, Fe_4S_5, and Fe_4S_6 cores surrounded by organic ligands such as cyclopentadienyl and nitrosyl. Since the Fe_4S_4-type clusters have a core analogous to the iron−sulfur cores of the high-potential iron protein and of the bacterial ferredoxins that work as redox catalysts or mediators, scientists have been particularly interested in the electrochemical properties of these clusters. The electrochemical analysis provides basic data which not only is useful to understand the redox behavior of these clusters but also is required to perform bulk electrolysis or chemical redox reaction to prepare the clusters in different oxidation states. Comparison of their structures offers important information to clarify the relationship between the structure and the skeletal electron count.

Multiple-step redox waves with good reversibility feature the cyclic voltammograms of organometallic iron−sulfur clusters. A similar tendency is noticed in inorganic iron−sulfur clusters having Fe_4S_4 or Fe_6S_6 core,[85] but with fewer redox steps.

Aprotic solvents such as acetonitrile and dichloromethane are normally used as solvents for electrochemical measurements, but protic solvents or micelles are also sometimes used as exemplified by Jordanov's research on the redox behavior of $[Cp_4Fe_4S_5](PF_6)_2$.[86] Redox properties of various iron−sulfur clusters are summarized in Table 3.

Although the difference in the conditions of electrochemical measurements (supporting electrolyte, solvent, etc.) makes the comparison of redox potentials between these clusters difficult, we can find some trends in the electrochemical behavior of them.

Table 4. Data of Mössbauer Spectra of Iron−Sulfur Clusters

cluster	isomer shift (δ, mm s^{-1})	quadrupole splitting (ΔE_Q, mm s^{-1})	line width (Γ, mm s^{-1})	condition	ref(s)
$\{(CF_3)_2C_2S_2\}_4Fe_3S_2$	0.46	1.85	0.49, 0.49	77 K	34
$(NH_4)[(ON)_7FeS_3]$	0.243	0.889	−	78 K	93
	0.127	0.921	−		
$[K(cryptand[2.2.2])][(ON)_4Fe_4S_4]$	0.156	0.935	0.232	r.t.	15
$(ON)_4Fe_4S_4$	0.092	1.448	0.321	300 K	93
	0.117	1.461	0.316	195 K	
	0.150	1.473	0.334	78 K	
	−	1.461	−	4.2 K	
$(ON)_4Fe_4S_2(NCMe_3)_2$	0.039	1.307	0.285	300 K	93
	0.116	1.316	0.297	195 K	
	0.141	1.326	0.321	78 K	
	−	1.311	−	4.2 K	
$[L_4Fe_4S_4]$	0.32	1.68	0.30, 0.28	25 °C	34
$(Ph_4As)[L_4Fe_4S_4]$	0.35	1.62	0.26, 0.26	25 °C	34
$(Bu_4N)_2[L_4Fe_4S_4]$	0.39	1.64	0.29, 0.25	25 °C	34
$L = (CF_3)_2C_2S_2$					
$[L_4Fe_4S_4]$					
$L = Ph_2C_2S_2$	0.36	1.68	0.31, 0.30	25 °C	34
$(Ph_4As)_2[L_4Fe_4S_4]$	0.08	1.64		4.2 K, 0 kOe	94
$L = (CF_3)_2C_2S_2$	−[a]	ca. 1.64		4.2 K, 50 kOe	
$[L_4Fe_4S_4]$	0.06	1.67	0.35, 0.31	296 K	95
$L = (CF_3)_2C_2S_2$	0.13	1.67	0.35, 0.32	78 K	
	0.03	1.68	0.36, 0.33	4.2 K	
$(Ph_4As)[L_4Fe_4S_4]$	0.10	1.60	0.26, 0.27	296 K	95
$L = (CF_3)_2C_2S_2$	0.17	1.62	0.31, 0.30	78 K	
	0.06	1.63	0.31, 0.30	4.2 K	
$(Ph_4As)_2[L_4Fe_4S_4]$	0.14	1.62	0.37, 0.38	296 K	95
$L = (CF_3)_2C_2S_2$	0.19	1.66	0.27, 0.33	78 K	
	0.09	1.65	0.35, 0.32	4.2 K	
$[Cp_4Fe_4S_5][MoOCl_4(thf)]$	0.31−0.35	1.075	0.40	4.2 K	64
$[Cp_4Fe_4S_5]$	0.47	−1.30	0.34	1.8 K 40, 80 kOe	77
	0.47	0.98	0.32		
	0.25	1.17	0.32		
$[Cp_4Fe_4S_5](PF_6)$	0.42	−1.09	0.30[b]	1.8 K 40, 80 kOe	77
	0.44	1.21	0.30[b]		
	0.28	1.25	0.30[b]		
$[Cp_4Fe_4S_5](PF_6)_2$	0.37	1.00	0.28	1.8 K 40, 80 kOe	77
	0.43	0.60	0.32		
	0.24	−0.97	0.28		
$\{Me_2Si(C_5H_4)_2\}_2Fe_4S_6$	0.34	1.02	0.27	77 K	36
$\{Me_2Si(C_5H_4)_2\}_2Fe_5S_{12}$	0.25	1.10	0.34	77 K	36
	0.35	1.11	0.34		
	0.25	0.43	0.34		
$[(Et_3P)_6Fe_6S_6](BF_4)$	0.41	0.53	0.28	4.2 K	39
	0.41	0.88	0.24		
	0.38	1.25	0.30		
$[(Et_3P)_6Fe_6S_8](BPh_4)_2$	0.281	0.268		7 K	69
$Cl_3(Et_3P)_4Fe_7S_6$	0.67	0.51	c	4.2 K	92
	0.36	0.87			
	0.36	0.28			
$Cl_2(Et_3P)_4Fe_6S_6$	0.63	0.60	c	4.2 K	92
	0.34	0.87			
	0.32	1.10			
$Br_2(Et_3P)_4Fe_6S_6$	0.61	0.56	c	4.2 K	92
	0.33	0.79			
	0.29	1.04			
$I_2(Et_3P)_4Fe_6S_6$	0.60	0.53	c	4.2 K	92
	0.38	0.84			
	0.23	0.95			
$(PhS)_2(Et_3P)_4Fe_6S_6$	0.43	0.61	c	4.2 K	92
	0.39	0.86			
	0.37	1.15			
$[(Et_3P)_6Fe_6S_6](BPh_4)$	0.41	0.35	c	4.2 K	95
	0.41	0.88			
	0.38	1.25			
$(BzEt_3N)_2[(OC)_{12}Fe_6S_6]$	0.30	0.91	d	4.2 K	66
	0.07	0.80	d		

[a] Complicated. [b] Data without external field. [c] 0.25−0.34. [d] No description.

Starting from the neutral oxidation state, the clusters carrying π-acidic supporting ligands such as carbonyls, nitrosyls, or dithiolenes tend to be reduced, while those bearing electron-donating ligands such as cyclopentadienyl derivatives or phosphines tend to be oxidized. For example, $Cp_4Fe_4S_4$, $Cp^*_3(Ph_2C_2S_2)Fe_4S_5$, $Cp^*_2(Ph_2C_2S_2)_2Fe_4S_4$, and $\{(CF_3)_2C_2S_2\}_4Fe_4S_4$ exhibit oxidation waves and reduction waves which are equal to the number of Cp or Cp* ligands and dithiolene ligands, respectively. These trends can be explained by the usual effect of electron-withdrawing ligands that depress the vacant frontier orbitals and electron-donating ligands that elevate the occupied frontier orbitals.

In many iron–sulfur clusters, the cyclic voltammograms mostly consist of reversible one-electron redox waves, but the clusters containing carbonyl ligands frequently shows irreversible or quasireversible waves. This seems to be due to the weakening of metal–carbonyl bonds induced by the oxidation or reduction of the cluster core, which causes CO dissociation.

V. Mössbauer Spectroscopy

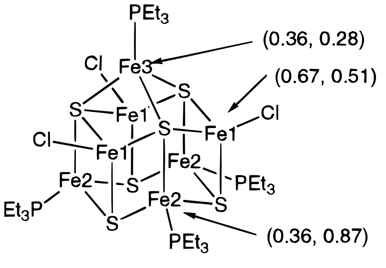
Mössbauer spectra have been measured for several iron–sulfur clusters. The data are summarized in Table 4. The general tendency of the data can be outlined as follows. The isomer shift (δ) ranges from 0 to 0.7 mm s^{-1}, which corresponds to the oxidation states of iron atoms ranging approximately from +4 to +2. Typical ranges of isomer shifts for some representative iron fragments in clusters are as follows: 0.2–0.5 for iron atoms with cyclopentadienyl ligands, 0–0.2 for those with NO, 0–0.4 for those with dithiolene ligands ($(CF_3)_2C_2S_2$), 0.3–0.5 for those with phosphine ligands, and 0.6–0.7 mm s^{-1} for those with halides. In general, the stronger the π-acidity of the ligand, the smaller the isomer shift, and thus the higher the effective oxidation state of the iron atom. The quadrupole splitting values (ΔE_Q) are in the range of 0.3–1.7 mm s^{-1}, but it seems difficult to find the general trends in them.

In a number of clusters, the signals of Mössbauer spectra have been assigned. Thus, the spectrum of $(Et_3P)_4Cl_3Fe_7S_6$ shows three sets of signals (Chart 11). The isomer shifts and quadrupole splittings (δ, ΔE_Q) of these signals are (0.67, 0.51), (0.36, 0.87), and (0.36, 0.28) and the intensity ratio is 3:3:1 in this order. These signals were therefore assigned to Fe1, Fe2, and Fe3.[92]

Similarly, the Mössbauer signals of the following Fe_6S_6 clusters were assigned (Chart 12).[92]

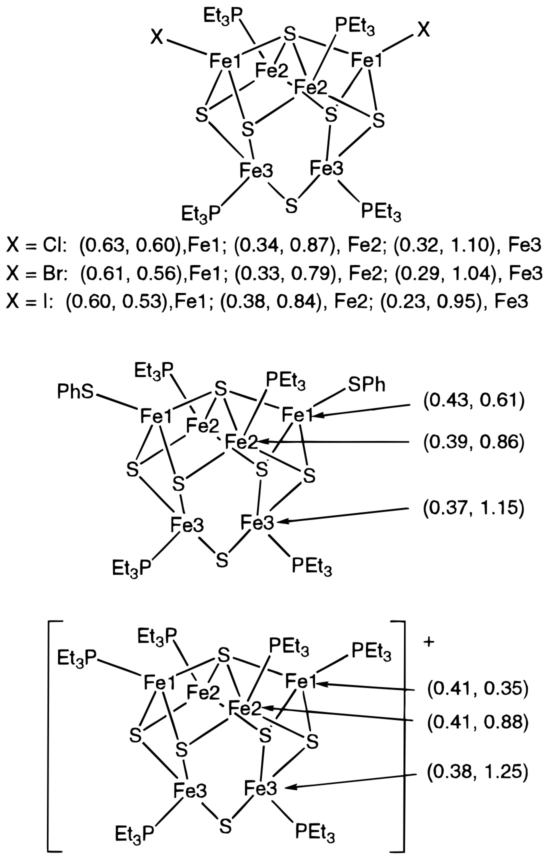
For an Fe_6S_6 cluster with carbonyl ligands $(BzEt_3N)_2[(OC)_{12}Fe_6S_6]$, the isomer shifts and quadrupole splittings (δ, ΔE_Q) are (0.30, 0.91) and (0.07, 0.80) and the intensity ratio is 1:2. These data are consistent with the assignment shown in Chart 13.[66]

Chart 11



The values of isomer shift and quadrupole splitting (δ, ΔE_Q)

Chart 12



X = Cl: (0.63, 0.60),Fe1; (0.34, 0.87), Fe2; (0.32, 1.10), Fe3
X = Br: (0.61, 0.56),Fe1; (0.33, 0.79), Fe2; (0.29, 1.04), Fe3
X = I: (0.60, 0.53),Fe1; (0.38, 0.84), Fe2; (0.23, 0.95), Fe3

Chart 13

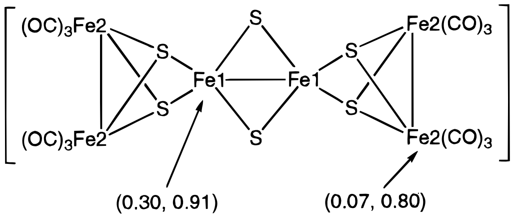
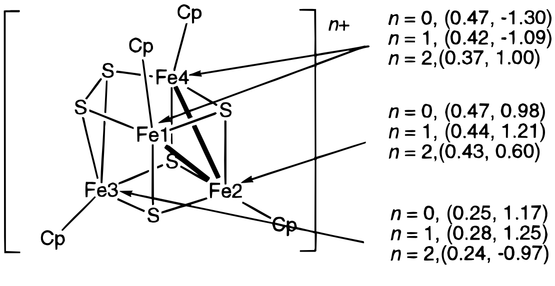


Chart 14



In some clusters, despite the existence of iron atoms in more than one environment, the Mössbauer spectra show only one quadrupole doublet. For example, $(ON)_4Fe_4S_2(\mu_3\text{-}NCMe_3)_2$ has two kinds of iron atoms in different environments, but shows only one doublet in the Mössbauer spectrum. This means that the four iron sites in the cluster possess equivalent environments in a Mössbauer time scale.[16,52]

In $[Cp_4Fe_4S_5]$ with three μ_3-S and one μ_3-S_2 ligands, the average isomer shift value of the three tetracoordinated iron sites, Fe1, Fe2, and Fe4, decreases upon oxidation, whereas the five-coordinated Fe3 remains essentially unaffected by the same process (Chart 14). This implies that the redox process is localized predominantly of Fe1, Fe2, and Fe4. This assumption was also supported by the crystal structure analysis of these clusters which revealed significant structural changes at the Fe1, Fe2, and Fe4 sites but not at the five-coordinated Fe3 site.[77]

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