

Investigations on Butterfly Fe/S Cluster S-Centered Anions $(\mu\text{-S}^-)_2\text{Fe}_2(\text{CO})_6$, $(\mu\text{-S}^-)(\mu\text{-RS})\text{Fe}_2(\text{CO})_6$, and Related Species

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Received February 24, 2003

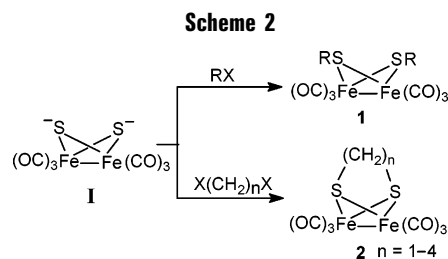
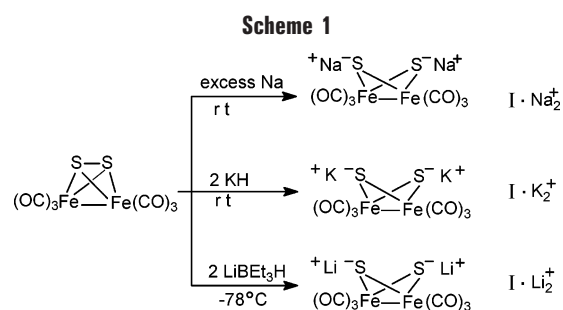
ABSTRACT

This Account describes the formation and chemical reactivities of the novel butterfly Fe/S cluster anions $(\mu\text{-S}^-)_2\text{Fe}_2(\text{CO})_6$ (**I**), $(\mu\text{-S}^-)(\mu\text{-RS})\text{Fe}_2(\text{CO})_6$ (**II**), $(\mu\text{-S}^-)(\mu\text{-RS})[\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})$ (**III**), $(\mu\text{-S}^-)(\mu\text{-RS})[\text{Fe}_2(\text{CO})_6]_3(\mu_4\text{-S})_2$ (**IV**), and $\{(\mu\text{-S}^-)(\mu_4\text{-S})[\text{Fe}_2(\text{CO})_6]_2\}_2(\mu\text{-SZS-}\mu)$ (**V**). It also gives a description of the novel structures, unique properties, and wide applications of the corresponding butterfly Fe/S cluster complexes produced from these anions. Anions **I–V** along with their products are important in the development of organometallic chemistry, cluster chemistry, catalysis, and material and life sciences.

Introduction

In recent years, Fe/S cluster complexes have drawn increased attention, mainly because of their unusual structures and novel chemical reactivities, as well as their close relationship with catalysis, material, and life sciences. For example, Fe/S clusters are known to occur at the active site of numerous proteins, and they can serve as an electron-transport function in various organisms.¹ Some of them are also known to be effective catalysts and even involved in some very important catalytic industrial processes, such as hydrodesulfurization (HDS).² Recently, the use of Fe/S clusters to make models for the nitrogenase and hydrogenase active sites has particularly shown the increasing significance in a variety of their important applications.³ Butterfly Fe/S cluster S-centered anions $(\mu\text{-S}^-)_2\text{Fe}_2(\text{CO})_6$ (**I**) and $(\mu\text{-S}^-)(\mu\text{-RS})\text{Fe}_2(\text{CO})_6$ (**II**) were discovered in 1979 by Seyferth's group.⁴ Since then, these two novel types of cluster anions along with other related species have been extensively studied. In this Account, we wish to summarize some of the interesting chemistry concerning the S-centered anions **I** and **II**, as well as the related species, $(\mu\text{-S}^-)(\mu\text{-RS})[\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})$ (**III**), $(\mu\text{-S}^-)(\mu\text{-RS})[\text{Fe}_2(\text{CO})_6]_3(\mu_4\text{-S})_2$ (**IV**), and $\{(\mu\text{-S}^-)(\mu_4\text{-S})[\text{Fe}_2(\text{CO})_6]_2\}_2$

Li-Cheng Song was born in China, in 1937, and graduated from Nankai University in 1962. He was a visiting scholar working in Professor D. Seyferth's group at MIT in 1979–1981 and a board member of Organometallics in 1992–1997. He has been a faculty member at Nankai University and is currently a professor. His research interests are the rational synthesis, reaction, structure, and properties of transition-metal clusters, fullerene-metal derivatives, and model compounds for the active site of Fe-only hydrogenases.



$(\mu\text{-SZS-}\mu)$ (**V**), which were developed from our laboratory and Seyferth's group, as well as the others during the last 2 decades.

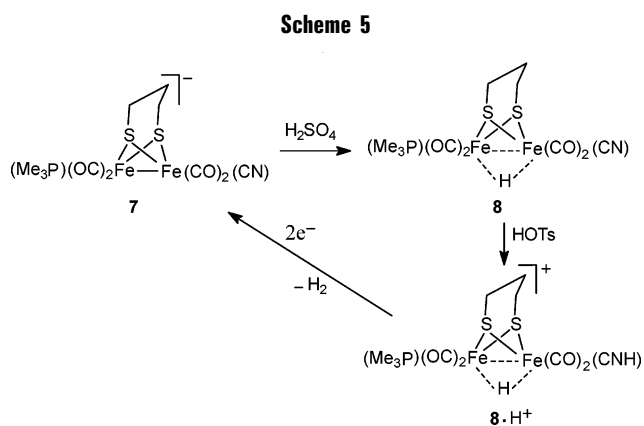
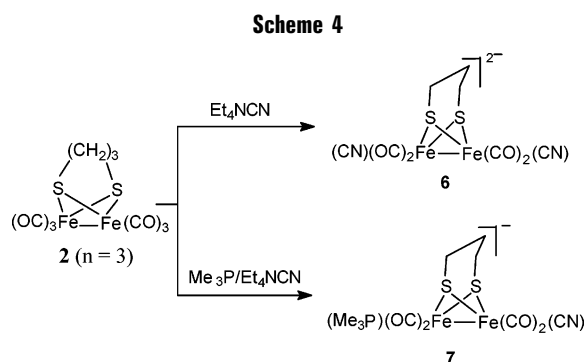
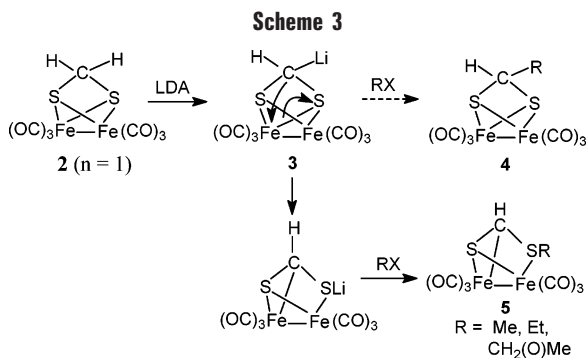
Single Butterfly S-Centered Dianion I

Dianion **I** was first prepared as its disodium and dipotassium salts by reaction of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ with sodium sand or potassium hydride in THF in moderate yield (Scheme 1).⁴ Later on, it was found to be prepared as its dilithium salt from $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ and lithium triethylborohydride, so-called “Super Hydride”, in THF in an essentially quantitative yield (Scheme 1).⁵

In view of its ready availability, particularly by using the latter LiEt_3BH method and its high chemical reactivity, dianion **I** has now become a general reagent for preparation of a great diversity of Fe/S cluster complexes. For example, dianion **I** can react with various alkyl mono- and dihalides to give a series of “open” and “closed” Fe/S cluster complexes **1** and **2** in satisfactory yields (Scheme 2).^{4–6} While the “open” type of complex **1** can be converted under different conditions into organosulfur compounds RSH, RSR, RSSR, or RSO_3H in a nearly quantitative yield,⁷ one of the “open” types of complex **1** ($\text{R} = \text{Me}$) and its phosphine-substituted derivatives have been found to be effective catalysts for the CO substitution reactions on some transition-metal carbonyl complexes.⁸

Interestingly, the “closed” type of complex **2** ($n = 1$) is found to be easily reacted with lithium diisopropylamide (LDA) to give an organolithium reagent **3** (Scheme 3). However, it was surprising that when electrophiles such as MeI , EtBr , and $\text{BrCH}_2\text{C}(\text{O})\text{Me}$ were added to the solution of **3**, the expected product **4** was not formed, but instead, the corresponding $\text{Fe}_2(\text{CO})_6$ complex of dithioformic acid esters **5** had been produced. The formation of such an unexpected product **5** is possibly by intramolecular nu-

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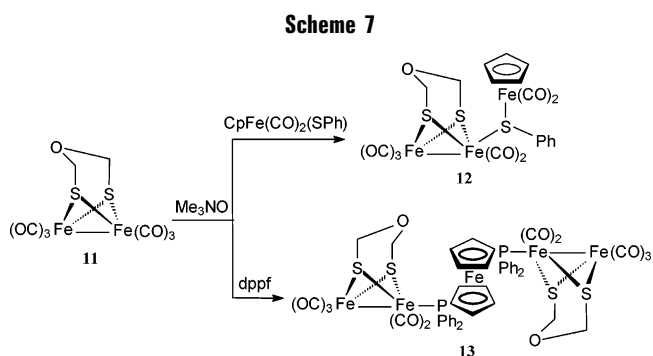
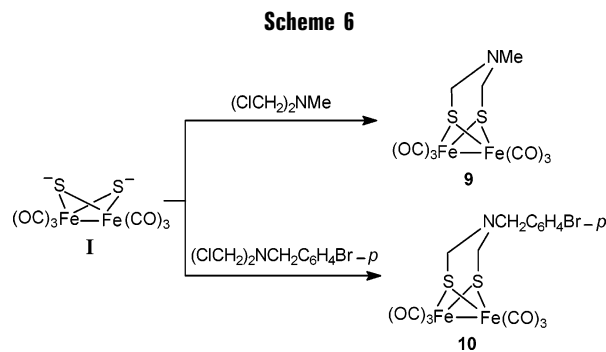


cleophilic attack by the organolithium center at the iron with displacement of mercaptide from iron followed by alkylation at the coordinated sulfide ion (Scheme 3).⁹

Recently, the “closed” type of complex **2** ($n = 3$) and some of its derivatives have attracted much attention, because these diiron 1,3-propanedithiolate (PDT) complexes can act as models for the active site of Fe-only hydrogenases. Among these complexes, for example, model compound **6** can be prepared by the CO substitution reaction of complex **2** ($n = 3$) with Et₄NCN, whereas **7** can be prepared similarly by CO substitution with Me₃P followed by treatment with Et₄NCN (Scheme 4).¹⁰

Among such PDT model compounds, **7** has been found to be an active catalyst for proton reduction. Scheme 5 shows its catalytic cycle, in which the intermediates **8** and **8·H⁺** are formed respectively by the reaction of **7** with aqueous H₂SO₄ and by the reaction of **8** with toluene-sulfonic acid (HOTs).¹¹

Another series of model compounds for the active site of Fe-only hydrogenases are diiron azadithiolate (ADT) derivatives. Among such ADT model compounds, com-



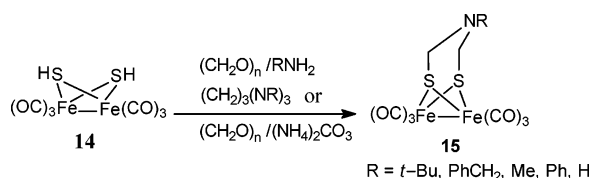
plexes (μ -SCH₂NRCH₂S- μ)Fe₂(CO)₆ (**9**, R = Me; **10**, R = *p*-BrC₆H₄CH₂) have been synthesized by reaction of the Li⁺ salt of dianion **I** with (ClCH₂)₂NMe or with (ClCH₂)₂NCH₂C₆H₄Br-*p* in ca. 50% yield (Scheme 6).^{12,13} Model compound **10** has been also found to be an active catalyst for proton reduction. However, the suggested catalytic cycle for model **10** is different from that for model **7**, which involves protonation of its nitrogen heteroatom in the first step of the suggested catalytic cycle.¹³

Very recently, we prepared a series of diiron oxadithiolate (ODT) model compounds. In this series, the simplest one, compound **11**, is prepared by the nucleophilic substitution reaction of the Li⁺ salt of dianion **I** with (ClCH₂)₂O, while **11** reacts further with Me₃NO followed by treatment with CpFe(CO)₂(SPh) or dppf to produce compounds **12** and **13**, respectively (Scheme 7).¹⁴ In fact, the oxadithiolatodiiron [3Fe₂S] assembly **12** is so far the first model to mimic not only the Fe₂S₂ subsite but also the cysteine-S-[Fe₄S₄] subsite in the active site of Fe-only hydrogenases.¹⁴

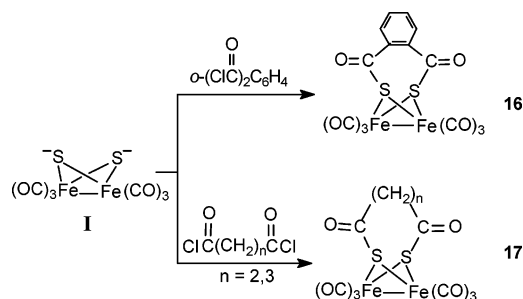
Dianion **I** as its lithium salt can be protonated by CF₃-CO₂H to give the bridging dithiol complex in an essentially quantitative yield.⁵ This dithiol complex was reported to be used to prepare model compounds for the active site of Fe-only hydrogenases. For instance, reaction of **14** with a premixed THF solution of paraformaldehyde and *tert*-butylamine (benzylamine), with the trimeric imines 1,3,5-(CH₂)₃(NR)₃ (R = Me, Ph) or with a premixed solution of paraformaldehyde and (NH₄)₂CO₃ produces **15** (Scheme 8).¹⁵

Diacid chlorides such as *o*-phthaloyl chloride, succinyl chloride, and glutaroyl chloride react with Li⁺ salt of dianion **I**, through intermolecular acylation and then intramolecular acylation, to give dithiocarboxylato ligand-containing complexes **16** and **17** (Scheme 9).¹⁶

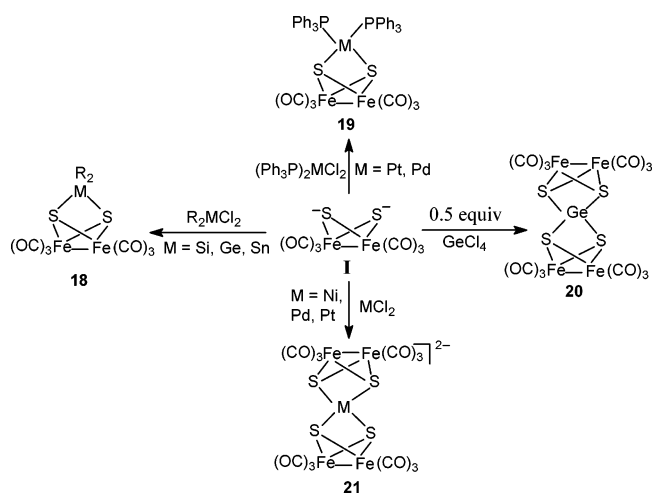
Scheme 8



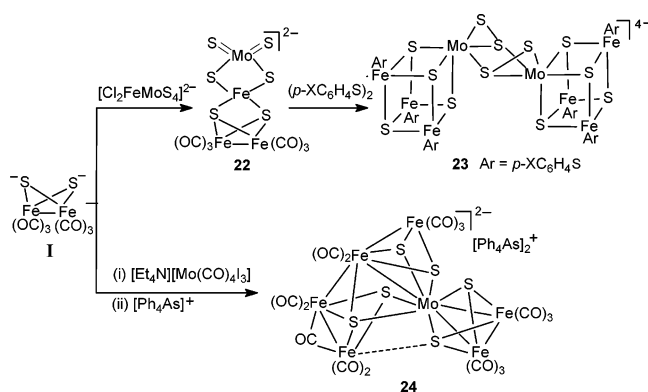
Scheme 9



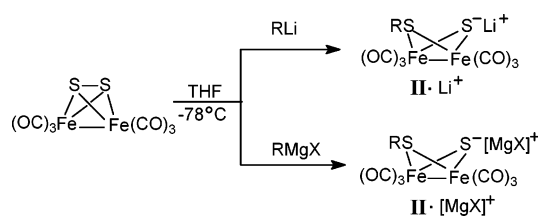
Scheme 10



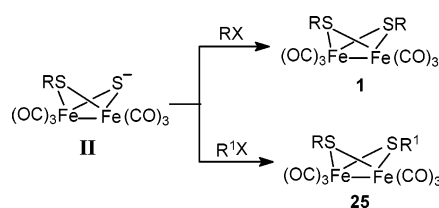
Scheme 11



Scheme 12



Scheme 13



The Li⁺ salt of dianion **I** reacts with diverse main-group and transition-element di- and tetrahalides to give products such as **18–21** in which there are various bridges between sulfur atoms of the (μ-S₂)Fe₂(CO)₆ structural unit (Scheme 10).⁶

It is well-known that dianion **I** has been utilized to prepare a series of models for the FeMo cofactor (FeMo-co) of nitrogenases. For example, the Li⁺ salt of dianion **I** reacts with the [Et₄N]⁺ salt of cluster [Cl₂FeMoS₄]²⁻ followed by oxidative decarbonylation of the intermediate cluster **22** with (p-XC₆H₄S)₂ (X = Cl, Br) to give the novel double cubane type of anionic model compound [Mo₂-Fe₆S₁₂(SC₆H₄X-p)₆]⁴⁻ (**23**), whose two subclusters are joined by two μ₂-η³ persulfide bridges (Scheme 11).¹⁷ In addition, dianion **I** reacts with [Et₄N][Mo(CO)₄]₃ and subsequent treatment with quaternary cations such as [Ph₄As]⁺ to afford model compound [Ph₄As]₂[MoFe₆S₆(CO)₁₆] (**24**), which was reported to be the first synthetic Mo-Fe-S cluster to approximate not only the core stoichiometry but also the Mo-Fe distance distribution of the FeMo-co.¹⁸

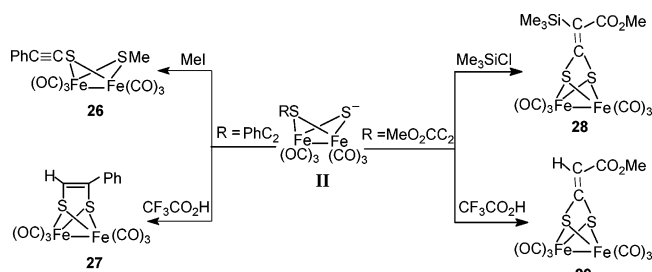
Single Butterfly S-Centered Monoanions II

The monoanions **II** as their Li⁺ and [MgX]⁺ salts can be prepared by reductive cleavage of the S-S bond of (μ-S₂)Fe₂(CO)₆ with organolithium and Grignard reagents in THF at -78 °C in high yield (Scheme 12).^{4,19}

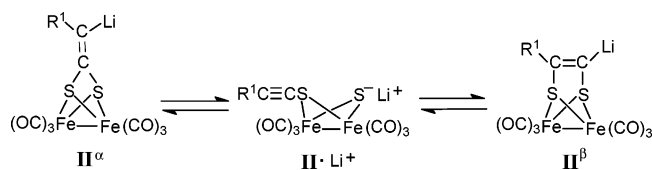
Like dianion **I**, monoanions **II** have been also widely used to synthesize a great variety of novel Fe/S cluster compounds. For example, the Li⁺ and [MgX]⁺ salts of monoanions **II** can be alkylated by organic halides RX or R¹X to give symmetrical and unsymmetrical Fe/S cluster complexes **1** and **25** in high yields (Scheme 13).^{4,19} Apparently, this type of reaction is of unique utility in its application to the preparation of unsymmetrical complexes **25**, although symmetrical complexes **1** are more readily prepared by the alkylation of dianion **I** as described in Scheme 2. The kinetics for the isomerization reaction regarding one of the unsymmetrical complex **25** (R = PhCH₂, R¹ = *t*-Bu) was studied by means of dynamic ¹H NMR spectroscopy.²⁰

Interestingly, reactions of monoanions **II** containing acetylenic substituents with electrophiles have been found, mainly dependent upon the nature of substituents and the electrophilic substrates, to give not only the expected “open” type of products but also the unexpected “closed” type of products. For instance,²¹ (i) the Li⁺ salt of monoanion **II** (R = PhC≡C) reacts with MeI to give “open” product **26**, whereas its protonation with CF₃CO₂H does

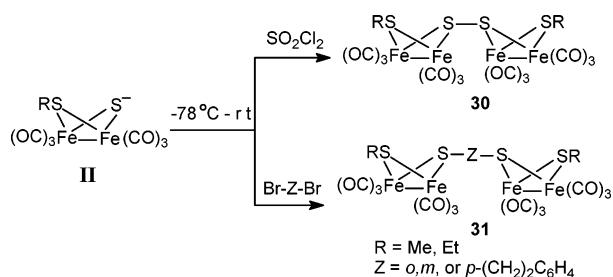
Scheme 14



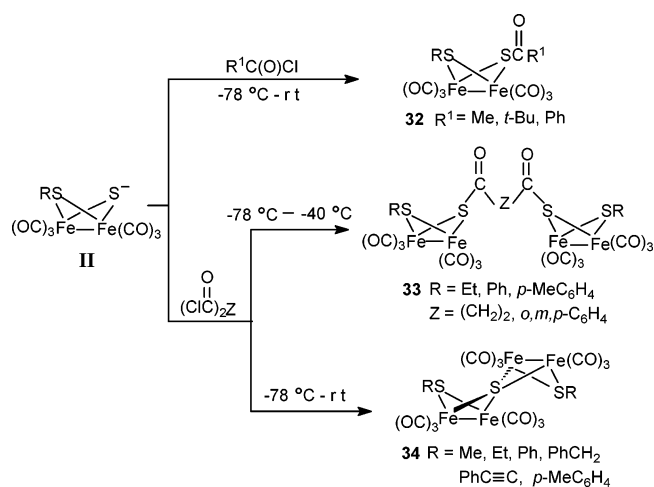
Scheme 15



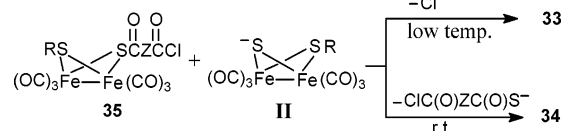
Scheme 16



Scheme 17



Scheme 18



not give $(\mu\text{-HS})(\mu\text{-PhC}\equiv\text{CS})\text{Fe}_2(\text{CO})_6$, rather the product is a dithiolenic complex **27** with the “closed” type of structure, and (ii) reactions of the Li⁺ salt of **II** (R = MeO₂-CC≡C) with Me₃SiCl and CF₃CO₂H produce the “closed” products **28** and **29**, all with a one-carbon bridge between the sulfur atoms (Scheme 14).

The formation of the two types of “closed” products can be rationalized based on the intramolecular nucleophilic reactivity of the “open” S-centered monoanions **II** containing the acetylenic R¹C≡C substituents. Thus, the Li⁺ salts of such “open” monoanions **II** must be in equilibrium with both or one of the “closed” organolithium reagents **II**^α and **II**^β derived from intramolecular S⁻ nucleophilic addition to the α and/or β carbon atom of the acetylene groups (Scheme 15). The “closed” products **27**–**29** described above are apparently produced through reactions of the corresponding electrophiles with **II**^α and/or **II**^β, while **II**^α is observed when R¹ can effectively stabilize an adjacent carbanionic center.²¹

Monoanions **II** as their Li⁺ and [MgX]⁺ salts have been found to undergo oxidative coupling reactions in the presence of SO₂Cl₂ to produce double Fe/S cluster complex **30** in high yield,²² whereas the xylene-bridged double cluster complex **31** can be satisfactorily prepared by the nucleophilic substitution reaction of the [MgX]⁺ salts of monoanions **II** with xylene dibromides (Scheme 16).²³

The X-ray diffraction analysis for **30** (R = Ph) indicated that its two subcluster cores are connected through an *e* (equatorial) type of S–S bond and the two Ph groups are bonded to S atoms by an *a* (axial) type of bond, respec-

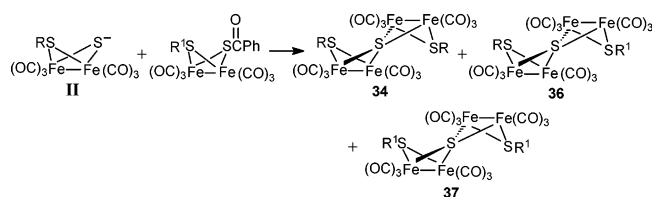
tively.²² In addition, the X-ray diffraction analysis for **31** (R = Me, Z = *m*-(CH₂)₂C₆H₄) revealed that the Me and CH₂C₆H₄CH₂ groups are attached to S atoms by *e* and *a* types of bonds, respectively.²³

While monoanions **II** can be acylated readily by monoacid chlorides and in high yield to give acylthio-bridged complex **32**,¹⁶ they react with diacid chlorides to afford two types of bridged double Fe/S cluster complexes **33** and **34** (Scheme 17).²⁴ In fact, the reactions that were carried out from -78 to about -40 °C afford the first type of complexes **33** in which the diacyl group derived from the corresponding diacid chlorides bridges the two monoanion structural units, whereas those reactions carried out from -78 °C to room temperature produce the second type of complexes **34** in which a tetrahedral μ₄-S atom bridges four iron atoms. It is noteworthy that only the methyl member of complex **34** (R = Me) had been prepared in only 1% yield,²⁵ before we found this convenient and general procedure for the synthesis of type of complexes **34** in high yield (61–91%).²⁴

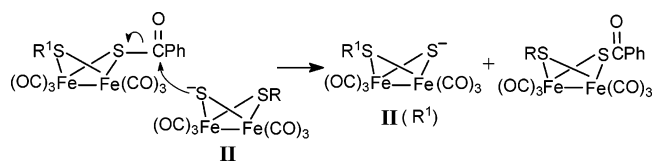
To account for the formation of double clusters **33** and **34**, a possible type of intermediate complex **35** has been proposed, which is believed to be generated by nucleophilic substitution of **II** for one chlorine atom of diacid chlorides. Because **35** still contains one reactive chlorine atom, it can be replaced at low temperatures by nucleophilic substitution of another molecule of **II** to give **33**. However, at higher temperatures, the Fe atom of **35** can be preferentially attacked by the negatively charged S atom of **II**, followed by coordination of the S atom to another Fe atom of **35** and subsequent loss of the SC(O)-ZC(O)Cl group to give symmetrical μ₄-S cluster **34** (Scheme 18).²⁶

Furthermore, monoanions **II** have been proven to react with an equimolar quantity of $(\mu\text{-R}^1\text{S})[\mu\text{-PhC}(\text{O})\text{S}]\text{Fe}_2(\text{CO})_6$

Scheme 19



Scheme 20



to afford both symmetrical and unsymmetrical $\mu_4\text{-S}$ clusters **34**, **36**, and **37** (Scheme 19).^{26,27}

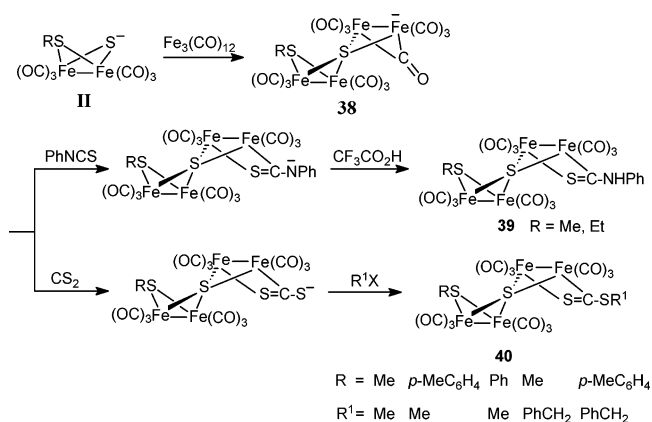
A possible pathway has been suggested to account for the formation of clusters **34**, **36**, and **37**.²⁶ First, the negatively charged S atom of nucleophile **II** attacks the carbonyl carbon of group PhC(O)S in electrophile $(\mu\text{-R}^1\text{S})[\mu\text{-PhC(O)S}]\text{Fe}_2(\text{CO})_6$ to give another nucleophile **II**(R¹) and another electrophile $(\mu\text{-RS})[\mu\text{-PhC(O)S}]\text{Fe}_2(\text{CO})_6$ (Scheme 20). Then, further nucleophilic attack of the negatively charged S atom of **II** or **II**(R¹) at one of the Fe atoms in electrophiles $(\mu\text{-RS})[\mu\text{-PhC(O)S}]\text{Fe}_2(\text{CO})_6$ and $(\mu\text{-R}^1\text{S})[\mu\text{-PhC(O)S}]\text{Fe}_2(\text{CO})_6$ followed by coordination of the S atom to another Fe atom and subsequent loss of the PhC(O)S group yields both symmetrical and unsymmetrical $\mu_4\text{-S}$ clusters **34**, **36**, and **37**. The crystal structures of **34** (R = Me,²⁵ Et²⁴) and **36** (R = *n*-Bu, R¹ = Ph;²⁶ R = Et, R¹ = Ph²⁷) have been established by X-ray crystallography.

The $[\text{Et}_3\text{NH}]^+$ salts of monoanions **II** can be prepared by the in situ reaction of the $[\text{Et}_3\text{NH}]^+$ salts of Fe-centered anions $[(\mu\text{-RS})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]^-$ (formed from $\text{Fe}_3(\text{CO})_{12}$, RSH, and Et_3N) with elemental sulfur in THF.^{28,29} These salts have been found to react with toluene-4-sulfonyl chloride to give the expected *p*-MeC₆H₄SO₂S-bridged complexes $(\mu\text{-RS})(\mu\text{-}p\text{-MeC}_6\text{H}_4\text{SO}_2\text{S})\text{Fe}_2(\text{CO})_6$ along with some unexpected $\mu_4\text{-S}$ clusters **34**.²⁹ The unexpected complex **34** has been proven to be formed via nucleophilic attack of the negatively charged S atom of monoanions **II** at one of the iron atoms of the *p*-MeC₆H₄SO₂S-bridged complexes, followed by coordination of the sulfur atom to another iron atom and concomitant loss of the *p*-MeC₆H₄SO₂S group.³⁰

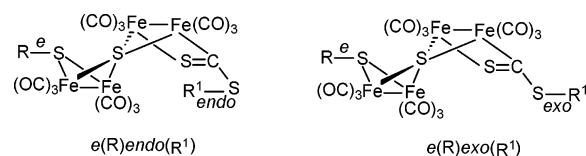
Interestingly, reaction of the $[\text{MgX}]^+$ salts of monoanions **II** with $\text{Fe}_3(\text{CO})_{12}$ gives rise to the corresponding salts of double butterfly Fe/S cluster Fe-centered anion **38**, which reacts in situ with electrophiles such as PhNCS/ $\text{CF}_3\text{CO}_2\text{H}$ or $\text{CS}_2/\text{R}^1\text{X}$ to give double butterfly Fe/S cluster complexes **39** and **40**, respectively (Scheme 21).³¹

In principle, product **40** may exist as two isomers, namely, *e*(R)*endo*(R¹) and *e*(R)*exo*(R¹) (Scheme 22). Fortunately, for one of the products the isomer *e*(R)*exo*(R¹) (R = R¹ = Me) has been confirmed by X-ray diffraction techniques.³¹

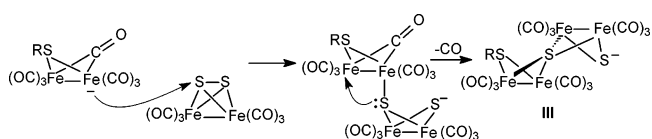
Scheme 21



Scheme 22



Scheme 23



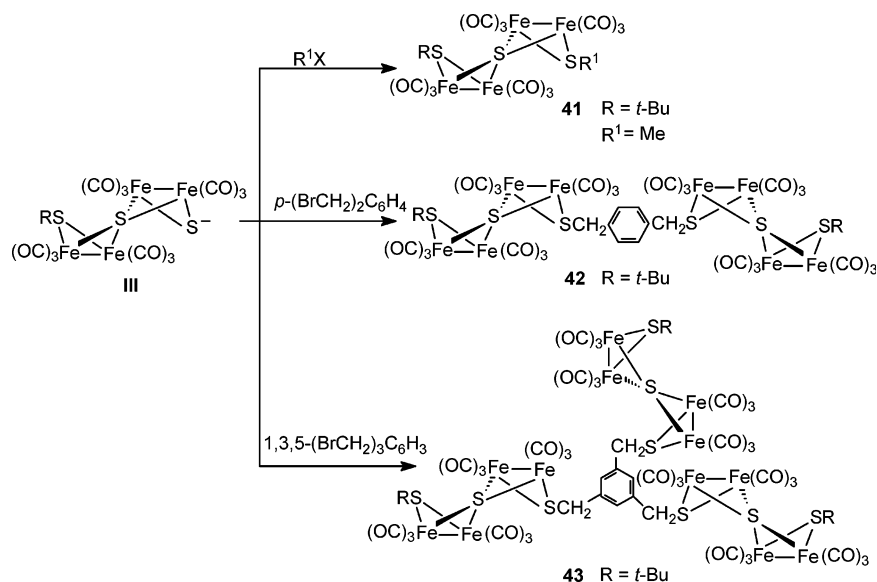
Double Butterfly S-Centered Monoanions III

When a THF solution of the $[\text{Et}_3\text{NH}]^+$ salts of Fe-centered anions $[(\mu\text{-RS})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]^-$ is treated with an equimolar quantity of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$, the novel type of $\mu_4\text{-S}$ -bridged double butterfly S-centered monoanions **III** are formed. Anions **III** are believed to be produced by nucleophilic attack of the negatively charged Fe atom of $[(\mu\text{-RS})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]^-$ at the S atom of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ followed by a loss of their $\mu\text{-CO}$ ligands and concurrent coordination of the $\mu_3\text{-S}$ atom to another Fe atom (Scheme 23).³²

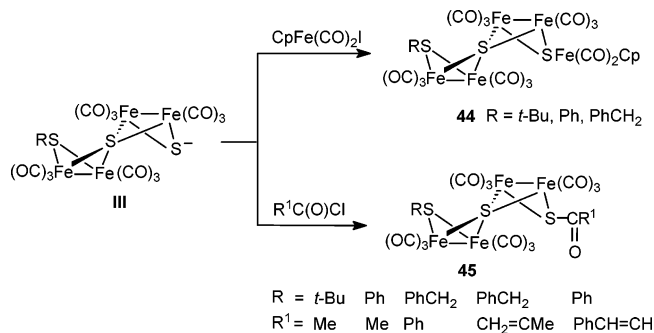
The $[\text{Et}_3\text{NH}]^+$ salts of this type of S-centered anions react in situ with alkyl mono-, di-, or trihalides in THF to give a series of double and multiple butterfly Fe/S cluster complexes **41**–**43** (Scheme 24),^{32,33} whereas they react with electrophiles $\text{CpFe}(\text{CO})_2\text{I}$ or monoacid chlorides in THF from -78°C to room temperature to afford double Fe/S cluster complexes **44** and **45** (Scheme 25).^{34,35}

More interestingly, the $[\text{Et}_3\text{NH}]^+$ salts of S-centered monoanions **III** prepared from 0.5 mmol of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ and ca. 1 mmol of the $[\text{Et}_3\text{NH}]^+$ salts of Fe-centered anion $[(\mu\text{-RS})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]^-$ react with 0.5 mmol of SO_2Cl_2 from -78°C to room temperature, through intermediate complex **46**, to give triple butterfly Fe/S cluster complex **47** (Scheme 26).³² The formation of product **47** is unexpected because the single butterfly S-centered anions **II** undergo an oxidative coupling reaction under the action of SO_2Cl_2 .²² It is believed that intermediate **46** is generated in situ from the nucleophilic substitution reaction of anions **III** with SO_2Cl_2 , which react further with an excess

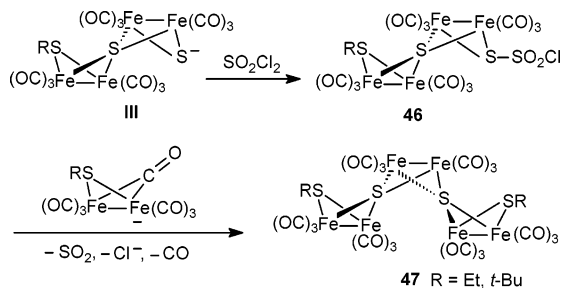
Scheme 24



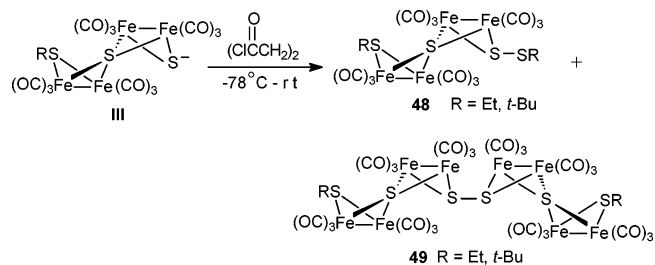
Scheme 25



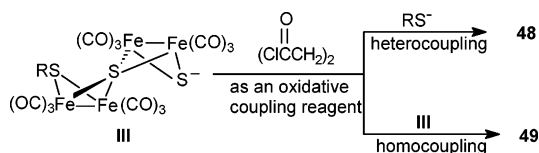
Scheme 26



Scheme 27



Scheme 28



of $[(\mu\text{-RS})(\mu\text{-CO})[\text{Fe}_2(\text{CO})_6]^-]$ via nucleophilic attack of the negatively charged Fe atom of $[(\mu\text{-RS})(\mu\text{-CO})[\text{Fe}_2(\text{CO})_6]^-]$ at the bridged S atom attached to the SO_2Cl group, followed by loss of the SO_2Cl group and $\mu\text{-CO}$ ligand to give **47**.³²

The $[\text{Et}_3\text{NH}]^+$ salts of monoanions **III** have been also found to react in situ with 0.5 equiv of succinyl chloride in THF from -78°C to room temperature to give double and quadruple butterfly complexes **48** and **49** (Scheme 27).³⁶

The X-ray diffraction analysis revealed that **49** ($R = t\text{-Bu}$) is probably the longest (ca. 1 nm) multibutterfly Fe/S cluster complex characterized crystallographically, and such nanometer-scale multibutterfly clusters might be expected to have unique optical and electronic properties.

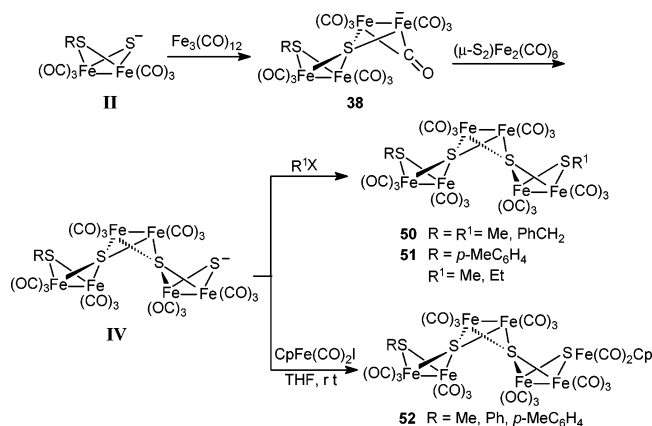
At present, although the mechanism for the novel reaction that yields double and quadruple clusters **48** and **49** is not clear, the products may be regarded as generated through oxidative coupling under the action of succinyl chloride between 2 molecules of anions **III** and between 1 molecule of anions **III** and 1 molecule of mercaptide anions RS^- derived from all possible RS-containing intermediates (Scheme 28).³⁶

Triple and Quadruple Butterfly S-Centered Monoanions IV and V

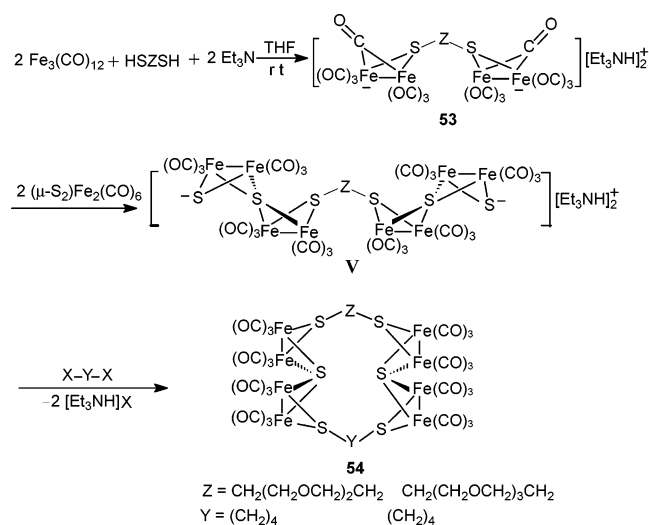
The $[\text{MgX}]^+$ salts of triple butterfly S-centered monoanions **IV** have been found to be formed by a sequential reaction that involves the reaction of the $[\text{MgX}]^+$ salts of monoanions **II** with $\text{Fe}_3(\text{CO})_{12}$ and subsequent treatment of the intermediate salt **38** with $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$. Interestingly, further reaction of the $[\text{MgX}]^+$ salts of monoanions **IV** in situ with alkyl halides and $\text{CpFe(CO)}_2\text{I}$ affords not only symmetrical triple butterfly cluster complex **50** but also unsymmetrical complexes **51** and **52** (Scheme 29).^{31,37}

The crystallographic studies on products **50** ($R = R^1 = \text{PhCH}_2$)³¹ and **52** ($R = p\text{-MeC}_6\text{H}_4$)³⁷ indicated that both

Scheme 29



Scheme 30



molecules consist of three butterfly Fe_2S_2 cluster cores joined together by two $\mu_4\text{-S}$ atoms and that the two substituents ($\text{R} = \text{R}' = \text{PhCH}_2$ for **50**; $\text{R} = p\text{-MeC}_6\text{H}_4$ and $\text{Cp}(\text{CO})_2\text{Fe}$ for **52**) are attached to the bridged S atoms by an equatorial type of bond, respectively.

The quadruple butterfly S-centered dianions **V** were recently synthesized by reaction of $\text{Fe}_3(\text{CO})_{12}$ with dithiols HSZSH in the presence of Et_3N followed by treatment of the intermediate Fe-centered dianion **53** with two molecules of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$. This novel type of dianion has been successfully applied to synthesize a great variety of novel linear and macrocyclic quadruple butterfly complexes, such as the macrocyclic complex **54** (Scheme 30).^{38,39}

Product **54** ($\text{Y} = (\text{CH}_2)_4$, $\text{Z} = \text{CH}_2(\text{CH}_2\text{OCH}_2)_3\text{CH}_2$) is a 25-membered macrocyclic compound, in which both the ether chain and the butylene group are attached to the subclusters by an equatorial type of bond, which has been confirmed by X-ray diffraction analysis. Such macrocycles can be regarded as an unique type of organometallic crown ether, and thus, they might have some applications in various fields, such as ion transport and molecular recognition.⁴⁰

Summary

The formation and chemical reactivities of the butterfly Fe/S cluster S-centered anions **I**, **II**, and related species **III–V** are described. These anions can be produced readily by reductive cleavage of the S–S bond of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ by the corresponding reagents such as LiBEt_3H , organolithium reagents, and Grignard reagents, as well as the complex salts of Fe-centered anions of $[(\mu\text{-RS})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]^-$, $\{(\mu\text{-RS})(\mu\text{-CO})[\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})\}^-$, and $\{[(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]_2(\mu\text{-SZS}\mu)\}^{2-}$. The S-centered anions **I–V** are rich in chemical reactivity, which have been found to react with organic, inorganic, and organometallic substrates to give a wide range of single, double, and multiple butterfly Fe/S cluster complexes with unique structures and novel properties. For instance, a series of model compounds for the active site of Fe-only hydrogenases and various macrocyclic crown ethers containing butterfly Fe/S cluster cores have been synthesized by reactions of anions **I** and **V**, respectively. Some of the former model compounds have been proven to be active catalysts for proton reduction, whereas some of the latter compounds might be regarded as an unique type of crown ethers potentially useful in ion transport and molecular recognition. In addition, on the basis of the studies regarding anions **I–V**, a series of new reactions and new synthetic methods have been developed. Therefore, the S-centered mono- and dianions **I–V** are of both theoretical and practical interest, which have played and will continue to play an important role in the development of organometallic chemistry, cluster chemistry, catalysis, as well as material and life sciences.

The author thanks the National Natural Science Foundation of China for financial support and all co-workers for their skillful and diligent research work.

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AR030004J