



Reaction of three cyclic thioester ligands with triiron dodecacarbonyl and possible reaction mechanisms

ZHIYIN XIAO^{a,*}, YONGLI WANG^b, XUEYUAN CHEN^a, JIAO LONG^a and ZHENHONG WEI^b

^aCollege of Biological, Chemical Sciences and Engineering, Jiaying University, Jiaying 314001, China

^bDepartment of Chemistry, Nanchang University, Nanchang 330031, China

E-mail: zhiyin.xiao@mail.zjxu.edu.cn

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Abstract. Three cyclic thioesters of the formula “–SCH₂CH₂SCO(CH₂)_n–” (**L**₁, n = 0; **L**₂, n = 1, **L**₃, n = 2) and their reactions with Fe₃(CO)₁₂ are reported. All the reactions produced a known diiron complex, [Fe₂(μ-S₂C₂H₄)(CO)₆] (**1**), which suggested that in the reactions, cleavage of C-S bond to generate “SCH₂CH₂S” fragment is a common pathway for all the three ligands. In the case of ligand **L**₂, a new complex **2**, [Fe₂{μ-SC₂H₄(SCH₂)-κ}(CO)₆] was isolated and structurally characterized. In the reaction of ligand **L**₃, an unknown iron carbonyl product was isolated in addition to complex **1**. Although its precise structure was not established due to its instability and low yield, its infrared spectrum and decomposing into complex **1** implied that the product may be a cluster with higher nuclearity. The experimental observations suggested that with the increase of the ring size of the cyclic thioester ligands, further bond cleavages were involved in the reaction in addition to that leading to complex **1**.

Keywords. Iron-sulfur carbonyl complexes; cyclic thioesters; C-S bond cleavage; reaction mechanism.

1. Introduction

Diiron carbonyl complexes are a category of classic organo-iron compounds. Their preparation and further investigations in reactivity, for example, with nucleophiles, proton, and electron transfer gained fresh attention in the past decade because of their structural resemblance to the diiron subunit of [FeFe]-hydrogenase, a metalloenzyme with high efficiency and fast reaction rate in catalyzing both hydrogen evolution and oxidation.^{1–8} In the research, Fe₃(CO)₁₂ has been the main precursor to synthesize complexes possessing a core of “Fe₂(CO)_{6-x}” (x = 1, 2).⁹ This triiron precursor reacts with a variety of ligands of donor atoms S, N, P and C. Depending on the nature of a ligand employed, reaction products can be very diverse. In most cases, not all the products are isolable. Complexes of diiron core are probably the most common products^{10–13} and tetrairon or clusters with higher nuclearity are also not uncommon. Simple thiolates or bidentate dithiolate lead mostly to diiron complexes. But ligands with mixed donor atoms

could have much more complicated reactions. Breaking bonds of the ligands and thus forming new ones are often encountered.^{14–22} The latter type of reactions offers often novel iron-carbonyl complexes.

In this study, we report the synthesis of three cyclic thioester ligands, **L**_{1–3} and their reactions with Fe₃(CO)₁₂. All the reactions involved ring-opening to generate 1,2-ethanedithiolate which was present in the commonly isolated diiron hexacarbonyl complex, [Fe₂(μ-S₂C₂H₄)(CO)₆] (**1**).^{23,24} In addition to this known complex, other complexes could also be isolated depending on the ring-size of the ligands. NMR, infrared spectroscopies and X-ray single crystal diffraction analysis were used to identify some of the isolated products. Possible reaction mechanisms of the cyclic thioester ligands with triiron dodecacarbonyl are proposed.

2. Experimental

2.1 General procedures

All the reactions were carried out under an argon atmosphere using standard Schlenk techniques. All the solvents were

*For correspondence

appropriately dried prior to use. The precursor $\text{Fe}_3(\text{CO})_{12}$ was prepared using the literature procedure.²⁵ 1,3-dithiolane-2-thione,²⁶ 1,3-dithiolan-2-one (**L**₁),²⁷ 1,4-dithian-2-one (**L**₂)²⁸ and 1,4-dithiepan-5-one (**L**₃)²⁹ were synthesized following literature methods with slight modifications. 1,2-ethanedithiol was purchased from Alfa Aesar. All operations were manipulated in a fumehood because of the obnoxious odor of 1,2-ethanedithiol. Infrared spectra were recorded using a solution cell with a spacer of 0.1 mm for CH_2Cl_2 solution on Scimitar 2000 (Varian). NMR spectral data were collected on Bruker Advance 400/600 MHz or Varian MR-400 with tetramethylsilane as internal standard. Elemental analysis was performed by the Center of analysis and testing at Nanchang University (Vario EL III elemental analyzer).

2.2 Crystallographic data collection and structure determination

In the data collection for X-ray single crystal diffraction analysis of complex **2**, standard procedures were used for mounting the crystals on a Bruker Smart System CCD at 293(2) K. The crystals were routinely coated with paraffin oil before being mounted. Intensity data were collected using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K using φ - and ω -scan mode. The SAINT and SADABS programs in the APEX 2 software package were used for integration and absorption correction. The structure of complex **2** was solved by direct method using SHELXS-97 program and refined on F^2 with XSELL6.3.1, all non-hydrogen atoms being modelled anisotropically.

2.3 Synthesis

2.3a Preparation of 1,3-dithiolane-2-thione: A mixture of CS_2 (10 mL, 0.166 mol) and NaOH solution (5 g NaOH in 10 mL H_2O) were vigorously stirred at room temperature. A deep red oily liquid started to form at the interface when *n*-Bu₄NBr (0.2 g, 0.6 mmol) was added. After being stirred for 10 min, 1,2-dibromoethane (1 mL, 0.012 mol) was introduced in dropwise fashion. The color of the mixture turned slowly to yellow. A minimum amount of dichloromethane and H_2O were added after reaction for 24 h. The combined organic phase was extracted with dichloromethane ($3 \times 15 \text{ mL}$) and dried over anhydrous MgSO_4 . Removal of the solvents yielded a green-yellow oil product.

Yield: 70% (0.6 g). Microanalysis for $\text{C}_3\text{H}_4\text{S}_3$ (FW = 136.25), calc. (%): C, 26.45; H, 2.96; found (%): C, 27.03, H, 2.82. IR (DCM, cm^{-1}): $\nu_{\text{C}=\text{S}}$, 1074. ¹H NMR (δ , ppm in CDCl_3 , 298 K): 3.97 (s, 4H, 2CH_2). ¹³C NMR (δ , ppm in CDCl_3 , 298 K): 228.9 (C=S), 43.9 (CH_2).

2.3b 1,3-dithiolan-2-one (L**₁):** 1,3-dithiolane-2-thione (0.5 g, 3.68 mmol) and $\text{Hg}(\text{OAc})_2$ (3.17 g, 9.2 mmol) were mixed in $\text{CHCl}_3 / \text{AcOH}$ (3:1, 20 mL) under Ar. The mixture was stirred at room temperature over night. A white precipitate formed in the reaction was filtered off. The filtrate was extracted with NaHCO_3 solution ($3 \times 200 \text{ mL}$) and dried over

anhydrous MgSO_4 . A pale yellow oily liquid was obtained after the evaporation of the solvents.

Ligand **L₁:** Yield: 78% (0.39 g). IR (DCM, cm^{-1}): $\nu_{\text{C}=\text{O}}$, 1673. ¹H NMR (δ , ppm in CDCl_3 , 298 K): 3.67 (d, $J = 1.8 \text{ Hz}$, 4H, 2CH_2).

2.3c 1,4-dithian-2-one (L**₂) and 1,4-dithiepan-5-one (**L**₃):** A solution of 1,2-ethanedithiol (0.5 mL, 6 mmol) and triethylamine (1.68 mL, 12 mmol) in dichloromethane (80 mL) was cooled down to -78°C with an ice-acetone bath under Ar. To the pre-cooled mixture was dropwise added a solution of 3-chloroacetyl chloride (0.48 mL, 6 mmol) in dichloromethane (40 mL) over 1.5 h. After the addition, a white precipitate of triethylamine hydrochloride formed. The reaction mixture was left for stirring at room temperature for further 2 h. The precipitate was filtered off and the filtrate was washed with water ($3 \times 75 \text{ mL}$) and dried over MgSO_4 . Removal of the solvent under reduced pressure gave a clear liquid.

Ligand **L₂:** Yield: 60% (0.48 g). Microanalysis for $\text{C}_4\text{H}_6\text{OS}_2$ (FW = 134.21), calc. (%): C, 35.80; H, 4.51; found (%): C, 35.99, H, 4.32. IR (DCM, cm^{-1}): $\nu_{\text{C}=\text{O}}$, 1674. ¹H NMR (δ , ppm in CDCl_3 , 298 K): 3.45 (s, 2H, COCH_2), 3.41 (t, $J = 4 \text{ Hz}$, 2H, COSCH_2), 3.13 (t, $J = 4 \text{ Hz}$, 2H, CH_2). ¹³C NMR (δ , ppm in CDCl_3 , 298 K): 196.8 (C = O), 35.6 (CH_2), 31.4 (CH_2), 26.0 (CH_2).

Ligand **L₃** was analogously prepared by using 3-chloropropanoyl chloride (0.50 mL, 6 mmol) to replace 3-chloroacetyl chloride. The ligand was isolated as a white solid.

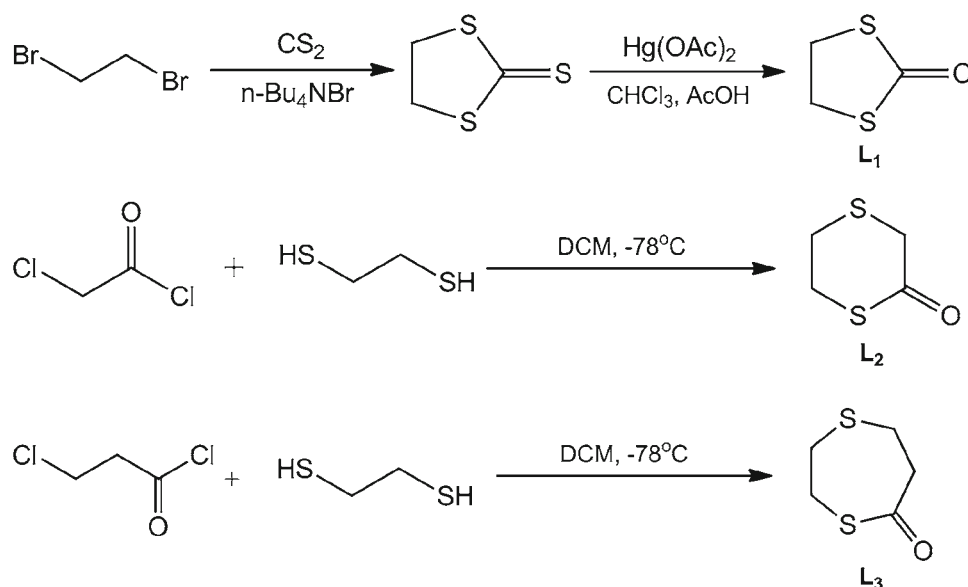
Ligand **L₃:** Yield: 34% (0.59 g). Microanalysis for $\text{C}_5\text{H}_8\text{OS}_2$ (FW = 148.24), calc. (%): C, 40.51; H, 5.44; found (%): C, 40.06, H, 5.31. IR (DCM, cm^{-1}): $\nu_{\text{C}=\text{O}}$, 1671. ¹H NMR (δ , ppm in CDCl_3 , 298 K): 3.58 (m, $J = 3.15 \text{ Hz}$, 2H, COCH_2), 3.08 (s, 2H, C^2H_2), 2.76 (q, $J = 4.8 \text{ Hz}$, 2H, COSCH_2), 2.13 (m, $J = 6.6 \text{ Hz}$, 2H, C^7H_2). ¹³C NMR (δ , ppm in CDCl_3 , 298 K): 197.5 (C=O), 43.8 (CH_2), 40.8 (CH_2), 28.7 (CH_2), 27.9 (CH_2).

2.3d Reaction of ligands **L**_{1–3} with $\text{Fe}_3(\text{CO})_{12}$

Ligand **L₁:** To a reaction flask containing THF (20 mL) were added **L**₁ (72 mg, 0.6 mmol) and $\text{Fe}_3(\text{CO})_{12}$ (303 mg, 0.6 mmol) under Ar. The reaction was heated to reflux for 2 h and the color of the reaction mixture turned from dark-green to brownish red. The reaction was cooled before being concentrated for purification using flash chromatography (eluent: ethyl acetate/petroleum ether = 1/8). The product (**complex 1**) was isolated as brownish red solid.

Complex 1: Yield: 37% (0.080 g). IR (DCM, cm^{-1}): $\nu_{\text{C}=\text{O}}$, 2076, 2036, 2000, 1995. ¹H NMR (δ , ppm in CDCl_3 , 298 K): 2.37 (s, 4H, 2SCH_2). ¹³C NMR (δ , ppm in CDCl_3 , 298 K): 208.4 (CO), 36.4 (SCH_2).

Ligand **L₂:** A solution of **L**₂ (80 mg, 0.6 mmol) and $\text{Fe}_3(\text{CO})_{12}$ (303 mg, 0.6 mmol) was dissolved in tetrahydrofuran (THF, 20 mL) under Ar. The mixture was heated under stirring at 65°C for 2 h. When the color turned from dark green to red-brown, the solvent was evaporated to give crude product



Scheme 1. Syntheses of ligands L_{1-3} .

which was purified by column chromatography on silica gel with an eluent of a volume mixture of ethyl acetate/petroleum ether (1/8). Two products, $[\text{Fe}_2(\mu\text{-S}_2\text{C}_2\text{H}_4)(\text{CO})_6]$ (**1**) and $[\text{Fe}_2(\mu^2, \kappa\text{-S, C-SC}_2\text{H}_4\text{SCH}_2)(\text{CO})_6]$ (**2**) were successively isolated. Recrystallization of complex **2** from a mixed solvent of dichloromethane and hexanes (1/3) afforded yellow crystals suitable for X-ray single crystal diffraction analysis.

Complex 1: Yield: 16% (0.035 g). **Complex 2:** Yield: 38% (0.087 g). Microanalysis for $\text{Fe}_2\text{C}_9\text{H}_6\text{S}_2\text{O}_6$ (FW = 385.8), calc. (%): C, 28.01, H, 1.57; found (%): C, 28.01, H, 1.25. IR (DCM, cm^{-1}): $\nu_{\text{C=O}}$, 2066, 2022, 1994, 1981. $^1\text{H NMR}$ (δ , ppm in CDCl_3 , 298 K): 3.5–3.6 (m, 1H, $\text{C}^8\text{H}_a\text{H}_b$), 3.3–3.4 (m, 1H, $\text{C}^8\text{H}_a\text{H}_b$), 2.5–2.7 (m, 2H, $\text{SC}^7\text{H}_a\text{H}_b$), 1.63 (d-d, $J = 11.4$ Hz, 1H, $\text{C}^9\text{H}_a\text{H}_b$), 0.58 (d, $J = 11.4$ Hz, 1H, $\text{C}^9\text{H}_a\text{H}_b$) (refer to Figure 2 for the labelling of the carbon atom). $^{13}\text{C NMR}$ (δ , ppm in CDCl_3 , 298 K): 214.96 (CO), 211.09 (CO), 206.02 (CO), 47.48 (SCH_2), 26.60 (SCH_2), 2.69 (FeCH_2S).

Ligand L₃: The reaction of the ligand with the triiron was analogously performed with **L₃** (0.089 g, 0.6 mmol). The reaction produced first complex **1** and then second unknown product as a claret-colored solid (less than 5 mg). This complex is labile and only its IR spectrum was obtained.

Complex 1: Yield: 32% (0.071 g). **Unknown product:** Microanalysis (found %): C, 28.69; H, 3.79. IR (DCM, cm^{-1}): $\nu_{\text{C=O}}$, 2074, 2040, 2008, 1976, 1906.

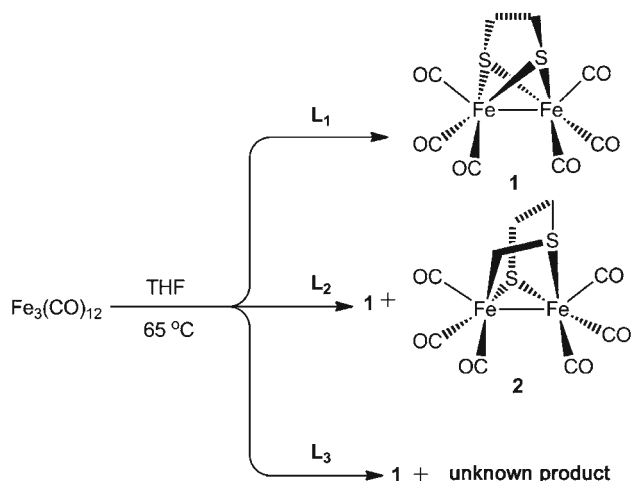
3. Results and Discussion

3.1 Synthesis

As shown in Scheme 1, cyclic thioester ligands L_{1-3} with the same fragment, “ $\text{SCH}_2\text{CH}_2\text{SCO}$ ”, were prepared by following the literature procedures *via* two-step (L_1) or one-step (L_{2-3}) reactions.^{27–29} Heating a solution of L_{1-3} and $\text{Fe}_3(\text{CO})_{12}$ (1/1) in tetrahydrofuran

under reflux resulted in the formation of complex **1**, $[\text{Fe}_2(\mu\text{-S}_2\text{C}_2\text{H}_4)(\text{CO})_6]$, a widely reported diiron complex^{23,24} (Scheme 2). For ligand L_1 , this complex was the solely isolable product. But for the other ligands, additional complexes were isolated, Scheme 2. In the case of ligand L_2 , a diiron complex (**2**) was isolated in good yield (38%). In this complex, the bridging moiety is associated with a thioether thiol, 2-(methylthio)ethanethiol. The thiolate bridged to the two iron atoms in μ -manner, as found in many other diiron complexes, whereas the thioether S and the carbene carbon equivalent to deprotonated form (SCH_2) of the methylthio group (SCH_3) acted as another bridge in κ -mode between the two iron atoms. This complex was readily crystallized as yellow crystal blocks from a mixed solution of dichloromethane and hexanes (1/3) under Ar atmosphere. The yields for complexes **1** and **2** were approximately at a ratio of 1/2. The decent yield allowed full characterization of complex **2** by using FTIR, $^1\text{H NMR}$, $^{13}\text{C NMR}$, elemental analysis and X-ray single crystal structure analysis. For ligand L_3 , although an additional claret product was isolated in extremely small quantity, its instability did not allow us to complete further characterization except infrared spectroscopic and elemental analysis.

The infrared spectra of all the isolated complexes are shown in Figure 1. For comparison, the spectrum of the known complex **1** in dichloromethane was also presented (2076, 2036, 2000, and 1995 cm^{-1}). Compared to the spectrum of complex **1**, complex **2** shows a similar spectral profile with absorption bands at 2066, 2022, 1994 and 1981 cm^{-1} . All the absorption bands undergo “red-shift” by about 10 cm^{-1} . This shift



Scheme 2. Reaction of cyclic thioester ligands L_1 – L_3 with $\text{Fe}_3(\text{CO})_{12}$ and structures of isolated iron carbonyl products.

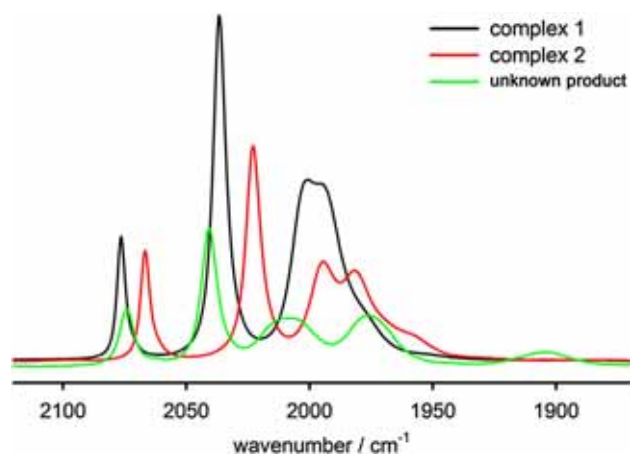


Figure 1. Infrared spectra of the isolated iron carbonyl complexes in dichloromethane.

is certainly attributed to the strong electron-donating ability of the carbene group presented in the complex. For the unknown product, as shown in Figure 1, which does comprise of the spectral characteristic absorption bands analogous to diiron complexes such as complex **1** but additional absorption bands indicate that it possesses more complicated iron-carbonyl unit in addition to a “ $\text{Fe}_2(\text{CO})_6$ ” unit. This is confirmed by its slow decomposition which produced a species with identical infrared spectrum to that of complex **1**. Previously, we reported clusters of tri-diiron-carbonyl units.¹³ The clusters showed also multiplicity in their infrared spectra. Therefore, it is likely that the unknown product is a cluster containing more than one diiron-carbonyl units.

3.2 Crystallographic analysis of complex **2**

Diffusion of hexanes into a dichloromethane solution of complex **2** afforded yellow crystals suitable for X-ray single crystal diffraction analysis by storing the mixture

Table 1. Crystallographic data and processing parameters for complex **2**.

Formula	$\text{C}_9\text{H}_6\text{Fe}_2\text{O}_6\text{S}_2$
Formula weight (g/mol)	385.98
Temperature (K)	296(2)
Crystal System	Monoclinic
Space group	P 21/n
a (Å)	9.203(2)
b (Å)	13.912(3)
c (Å)	11.055(3)
α (deg)	90
β (deg)	101.907(2)
γ (deg)	90
V (Å ³)	1384.9(5)
Z	4
Crystal size (mm)	0.34 × 0.32 × 0.30
D _{calc} (g/cm ³)	1.851
Absorption coefficient (mm ⁻¹)	2.411
F(0 0 0)	768.0
θ (°)	2.39 to 28.46
Limiting indices	−12 ≤ h ≤ 12, −18 ≤ k ≤ 17, −14 ≤ l ≤ 14
Reflections collected	12481
Reflections unique	3464 [R_{int}] = 0.0264
Completeness to θ_{max}	99.1%
Max. and min. transmission	0.485 and 0.58
GOF on F^2	1.068
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0535$, $wR_2 = 0.1578$
Final R indices [all data]	$R_1 = 0.0820$, $wR_2 = 0.1847$
Largest diff. peak and hole (e/Å ³)	1.931 and −0.422

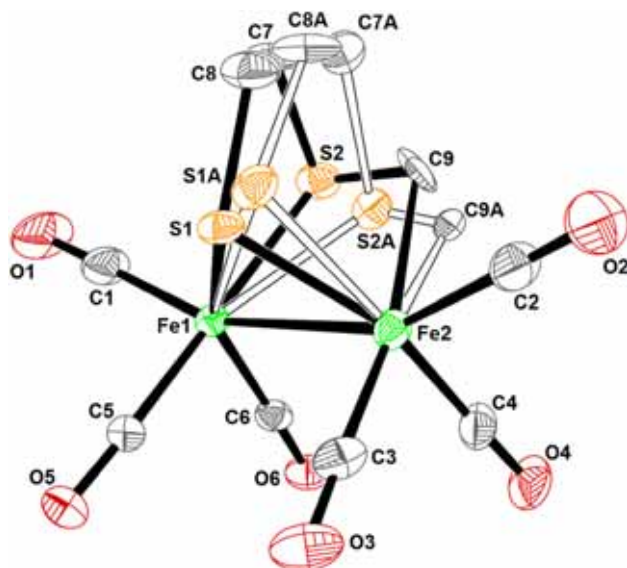
$$R_1 = \frac{\sum \|F_o\| - |F_c|}{\sum |F_o|} \text{ and } wR_2 = \frac{[\sum (|F_o^2 - F_c^2|)^2]}{\sum (wF_o^2)^2}^{1/2}$$

at -20°C for several days. Its crystallographic details and selected bond lengths and angles are tabulated in Tables 1 and 2, respectively. As shown in Figure 2, the wobbling of the bridging head led to severe disorder in its crystal structure. Due to the disorder, the bridging group in complex **2** exhibited disorder over two positions, S(1)-C(7)-C(8)-C(9)-S(2) and S(1A)-C(7A)-C(8A)-C(9A)-S(2A). The occupancy between the two is 0.64/0.36. Nevertheless, in complex **2**, in addition to the μ -thiolato bridging mode, the two iron atoms are also bridged by “ SCH_2 ” in κ -mode which lowered the symmetry of the molecule. The entire bridging moiety is “ $\text{SCH}_2\text{CH}_2\text{SCH}_2$ ”.

Structurally, the complex is analogous to those with bridging moieties of “ SCH_2S (or CH_2) CH_2SCH_2 ”¹⁴ and “ $\text{SeCH}_2\text{SCH}_2\text{SeCH}_2$ ”.¹⁶ It is this bridging mode that allows the entire moiety more flexibility compared to those diiron complexes with two μ -thiolato bridges and

Table 2. Selected bond lengths (Å) and angles (°) for complex **2**.

Fe(1)-Fe(2)	2.5996(10)	\angle Fe(2)-S(1)-Fe(1)	71.11(9)
Fe(1)-S(1)	2.238(4)	\angle S(2)-C(9)-Fe(2)	102.9(5)
Fe(1)-S(2)	2.261(2)	\angle C(9)-S(2)-Fe(1)	104.1(5)
Fe(2)-S(1)	2.232(3)	\angle C(9)-Fe(2)-Fe(1)	75.7(4)
Fe(2)-C(9)	2.307(17)	\angle S(1)-Fe(2)-Fe(1)	54.55(12)
S(2)-C(9)	1.522(18)	\angle S(1)-Fe(1)-Fe(2)	54.34(10)
Fe(1)-C(1)	1.798(7)	\angle S(2)-Fe(1)-Fe(2)	76.88(15)
Fe(2)-C(2)	1.801(7)		

**Figure 2.** Crystal structure of complex **2** with disorder (ellipsoids were drawn at a thermal probability of 50% and hydrogen atoms were omitted for clarity reasons).

thus exhibited the observed disorder. NMR spectra of the complex echo in accordance with the structure. As seen in Figure S10 (Supplementary Information), ^{13}C NMR showed cleanly three signals belonging to the organic bridging linkage (“ $\text{SC}^8\text{H}_2\text{C}^7\text{H}_2\text{SC}^9\text{H}_2$ ”) in high field besides three peaks in low field which could be assigned to the bound CO. However, its ^1H NMR spectrum (Figure S11 in SI) is more complicated. Due to cyclic effect, the two protons on carbon C(9) were split to a pair of doublet, 1.63 and 0.58 ppm, respectively. While one of the protons shows a doublet at 0.58 ppm with the coupling constant of 11.4 Hz, the other proton exhibits a pseudo-quartet signal at 1.63 ppm. The fine structure of the signals at 1.63 ppm can be attributed to remote coupling with the protons on C(7) with a small coupling constant (1.2 Hz). As being found in other asymmetric analogues we reported recently,³⁰ its asymmetry leads to more complicated infrared spectrum compared to complex **1**. But, noticeably, the variation does not alter its

overall structure compared to other analogous diiron carbonyl complexes reported in the literatures.^{13,30–37}

3.3 Possible reaction mechanisms

The common product for the three reactions is complex **1** possessing 1,2-dithiolate as bridging linkage. Since all the three ligands have the motif, “ $\text{SCH}_2\text{CH}_2\text{S}$ ”, and one of the sulfur atoms adjacent to the carbonyl group (Scheme 1), this suggests strongly that in the three reactions, the ring opening *via* two C-S bond cleavages generated complex **1**. According to our recent calculations, such cleavages occur successively upon the coordination of S atom to one of the iron atoms of the precursor.³⁰ For ligand **L**₁, the two successive C-S bond cleavages released one CO. Thus, it is consistent with the observation that complex **1** was the solely isolable product in the reaction. In the reaction of ligand **L**₂ with $\text{Fe}_3(\text{CO})_{12}$, in addition to the cleavages related to the formation of complex **1**, alternative bond cleavage occurred. In the second bond cleavage, it occurred, likely, after the second iron atom had been assembled. The CH_2 group in the fragment – SCH_2CO – involved in bridging (binding) together with the S atom to the other iron atom in κ -mode and this binding initiated the decarboxylation to form complex **2**. There is, undoubtedly, additional bond(s) cleavages similar to that occurred in the reaction of ligand **L**₂ with the triiron precursor. But failure to determine the fine structure of the unknown product generated from the reaction of ligand **L**₃ with $\text{Fe}_3(\text{CO})_{12}$ did not allow more detailed elucidation of its reaction mechanism.

4. Conclusions

In summary, the synthesis and characterization of three cyclic thioester ligands possessing common “ $\text{SCH}_2\text{CH}_2\text{S}$ ” unit and their reactions with $\text{Fe}_3(\text{CO})_{12}$ are reported. The isolation of the same product in all the reactions, complex **1**, asserts how the bond cleavages occurred upon the reaction with the precursor in the three reactions. The isolation of complex **2** in the reaction of ligand **L**₂ with $\text{Fe}_3(\text{CO})_{12}$ indicated other pathway(s) of bond cleavage in addition to the S-C bond cleavage when the ring size of the ligand increases.

Supplementary Information (SI)

Crystallographic data for the structural analysis of complex **2** which has been deposited with the Cambridge Crystallographic Data Center, with the number of 895034,

can be obtained free of charge at <http://www.ccdc.cam.ac.uk>. NMR spectra of the ligands and the new complex **2** are presented in Supplementary Information, available at <http://www.ias.ac.in/chemsci>.

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