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A Remarkable Ring Opening Observed in the Reaction of Cyclopropyl Ferrocenyl Thioketone with Triiron Dodecacarbonyl $Fe_3(CO)_{12}$

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Dedicated to Prof. Jozef Drabowicz on the occasion of his 75th birthday.

In continuation of the study focused on synthesis and structure of mimics of the active site of the [FeFe] hydrogenase enzyme, reaction of $Fe_3(CO)_{12}$ with cyclopropyl ferrocenyl thioketone **1** was carried out. Two different complexes with ring-opened cyclopropyl fragments were isolated and identified as η^4-1-thia-1,3-diene-type mononuclear tricarbonyl iron complex **2** and η^2-acyl-type hexacarbonyl diiron complex **3**, respectively. Structures of crystalline products were unambiguously confirmed by single crystal X-ray analysis. For the ring opening reaction of the cyclopropane moiety, leading to the formation of **2** and **3**, a multistep radical mechanism was postulated. Electrochemical investigations of **3**, being reminiscent of a [FeFe] hydrogenase mimic, were carried out at different scan rates.

Introduction

Recent decades witnessed rapid increase of importance of the cyclopropane and cyclopropene derivatives as relevant building blocks for syntheses of diverse compounds based on the methods of current organic chemistry. Importance of the cyclopropane ring as an useful pharmacophore has been demonstrated in a series of recent original and review publications.[1] Moreover, great attention is focused on applications of 'donor-acceptor' cyclopropanes as versatile building blocks for synthesis of *N*- and *S*-heterocycles with diverse ring size.[2] Finally, the cyclopropyl ring was found as an important structural motif for studying radical mechanisms in organic reactions within so called 'radical clock approach'.[3]

In our continuing studies with organosulfur compounds, diverse thiocarbonyls, especially thioketones, have been demonstrated to act as useful starting materials for preparation of five- and six-membered *S*-heterocycles via (3 + 2) cycloadditions[4] and hetero-Diels-Alder reactions.[5] In recognition of their unique reactivity, Huisgen and Sauer named thioketones as 'superdipolarophilic'[6] and 'superdienophilic'[7] reagents, respectively. In addition, thioketones were shown to act as versatile complexation reagents in organometallic chemistry. Importantly, replacement of aryl or heteroaryl rings by ferrocenyl moiety in aryl cyclopropyl thioketones results in remarkable increase of stability of thiocarbonyl compounds[8] and therefore enables performing of experiments with cyclopropyl ferrocenyl thioketone (**1**) under standard conditions. As reported in a series of publications over the past decades, reactions of thioketones with iron carbonyls, *e.g.* $Fe_3(CO)_{12}$, offer an attractive access to $[Fe_2(CO)_6]$ clusters[9] and [FeFe] hydrogenase mimics,[10] based on the active centre of the [FeFe] hydrogenase enzyme.[11] For example, in our earlier works reactions of thiobenzophenone **A** (Scheme 1) and its substituted analogues, leading to such complexes, were reported.[12] Notably, the reaction of ferrocenyl thienyl thioketone **B** with $Fe_3(CO)_{12}$ resulted in unprecedented dearomatization of the thienyl ring.[13] Similar reactions of diaryl thiochalcones (α,β-unsaturated thioketones), *e.g.* 1,3-diphenylprop-2-enthione **C**, with $Fe_3(CO)_{12}$ led unexpectedly to complexes containing a five-membered ring in a highly stereoselective reaction. Formation of these complexes was explained via a cascade of reactions involving a diradical mechanism that was well supported by quantum-chemical calculations.[14]

Motivated by these results, in the present work, we decided to study the reaction of cyclopropyl ferrocenyl thioketone **1** (Scheme 1) with $Fe_3(CO)_{12}$ in view of a possible radical-mediated ring opening reaction. This is worth of stressing that in contrast to unstable cyclopropyl phenyl analogue,[8a] **1** can be prepared and purified in a typical manner from corresponding ketone.

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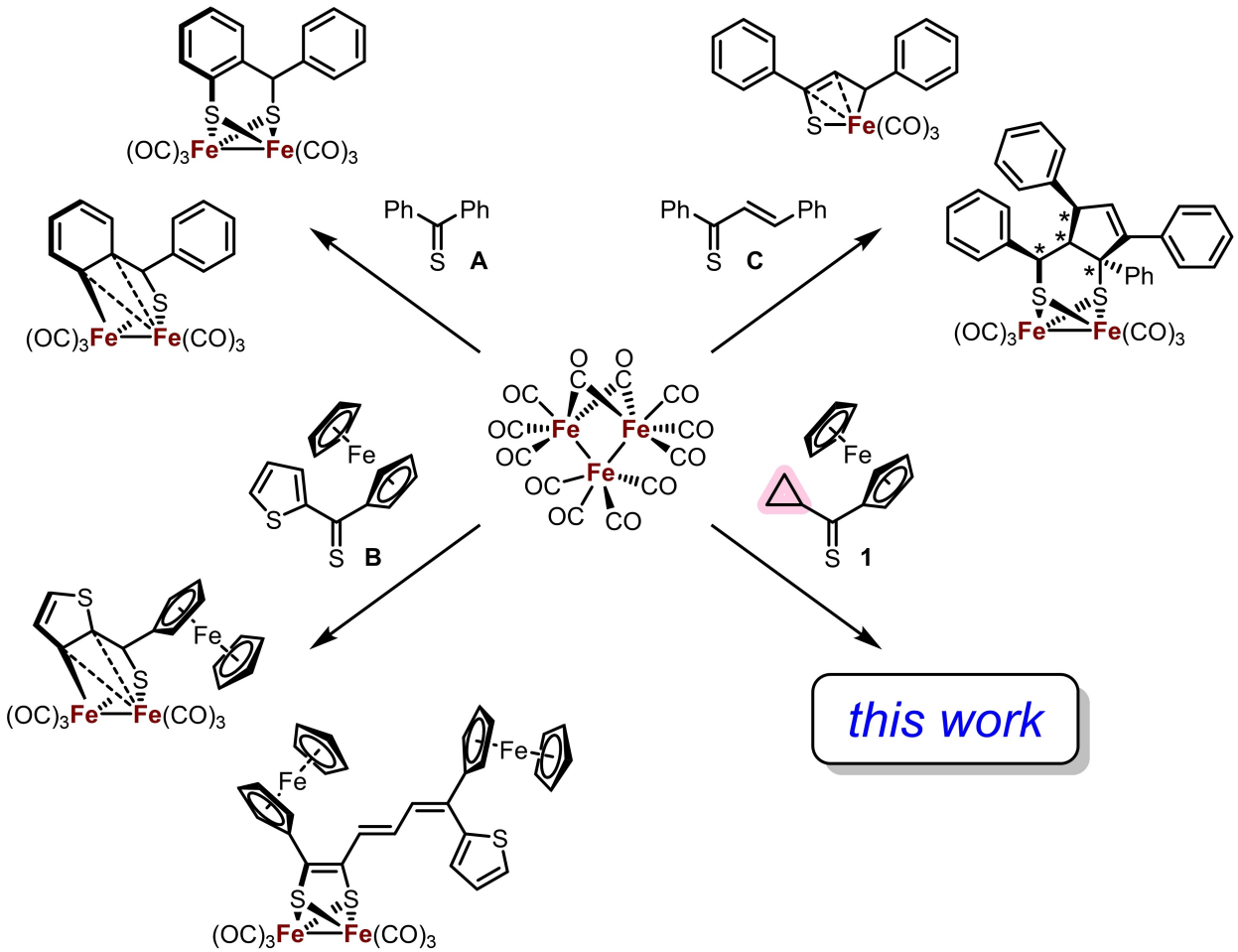


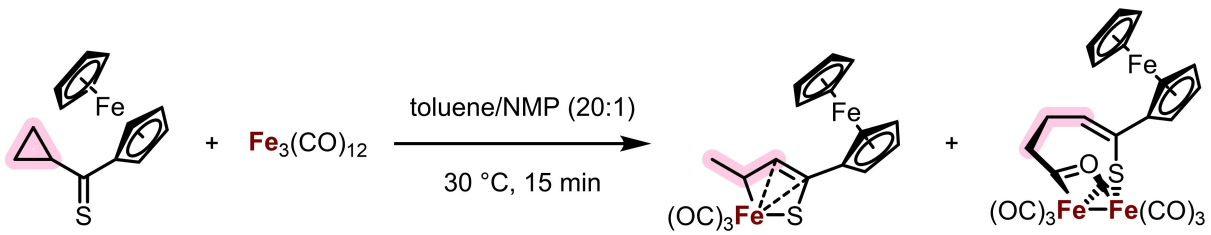
Scheme 1. Reactions of $Fe_3(CO)_{12}$ with thioketones like **A**[12a,c] and **B**[13–14] and thiochalcones like **C**,[14] leading to different types of $[Fe_2(CO)_6]$-based complexes.

Results and discussion

Synthesis and characterization

In a typical experiment, the violet-blue thioketone **1** was reacted with $Fe_3(CO)_{12}$ in a mixture of toluene and *N*-methyl-pyrrolidone (NMP) (20:1) at 30 °C (Scheme 2). After 15 minutes, the iron carbonyl was completely consumed and TLC exposed the formation of two major products **2** and **3** which were separated by column chromatography. Both compounds were isolated as red coloured crystalline complexes, albeit in rather low yields, and characterized by NMR and IR spectroscopy, mass spectrometry and elemental analysis. Subsequently, single crystals suitable for X-ray structure analysis were obtained after crystallization from *n*-hexane solution.

The ^{1}H NMR spectrum of the less polar fraction shows two doublets at 1.60 (J = 6.43 Hz, 3H) and 5.96 ppm (J = 8.77 Hz, 1H) and a doublet of quartets at 2.41 ppm (J = 8.77, 6.43 Hz, 1H),



1 **2** (9 %) **3** (8 %)

Scheme 2. Reaction pathway to complexes **2** and **3** starting from cyclopropyl thioketone **1** and $Fe_3(CO)_{12}$.

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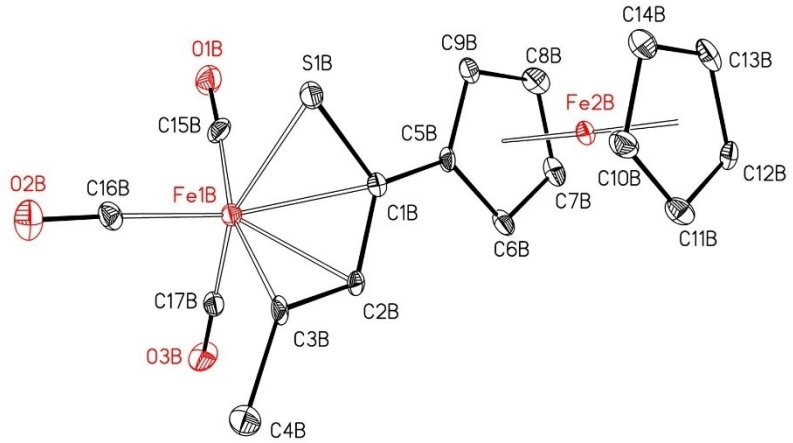

Figure 1. Molecular structure and atom labelling scheme of **2**.[18] The ellipsoids represent a probability of 50 %. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Fe1A–S1A 2.323(3), S1A–C1A 1.736(9), Fe1A–C1A 2.106(9), C1A–C2A 1.409(12), Fe1A–C2A 2.066(8), C2A–C3A 1.418(12), Fe1A–C3A 2.136(9), C3A–C4A 1.511(13); angles (°): C2A–Fe1A–C3A 39.4(3), C2A–Fe1A–C1A 39.5(3), C1A–Fe1A–S1A 45.8(2), C3A–Fe1A–S1A 81.8(3).

respectively. The ^{1}H-^{1}H COSY analysis allowed the assignment of these ^{1}H NMR resonances to two methine and three methyl protons, pointing to a ring opening of the cyclopropyl moiety. In addition, elemental analysis indicated the presence of a mononuclear iron complex with the molecular formula $C_{17}H_{13}Fe_2O_3S$. Finally, single X-ray structure analysis confirmed the formation of the η^4-1-thia-1,3-diene-type tricarbonyl iron complex **2** (Figure 1). Prior to this work, similar complexes have been found in reactions of 1,3-thiete with $Fe_2(CO)_9$[15] as well as some 1-thia-1,3-dienes with iron carbonyls, *i.e.* α,β-unsaturated thioamides and thioesters with $Fe_2(CO)_9$[16] and thiochalcones with $Fe_3(CO)_{12}$.[14] Very recently, a detailed theoretical study on both σ-type Fe–S and Fe–C bonds in complexes of the latter type was reported by our group.[17]

These calculations are in accordance with the ^{1}H NMR data of complex **2** that indicate the double bond character between C1 and C2 according to Scheme 2 and Figure 1. Notably, there is no CO signal in the ^{13}C{^{1}H} NMR spectrum but which was also not observed in previously described mononuclear complexes derived from thiochalcones.[14] In the abovementioned complexes with α,β-unsaturated thioamides and -esters the corresponding carbonyl ligands were registered as a broad signal.[16] Interestingly, cyclopropyl ethylene showed a similar behaviour upon treatment with iron carbonyl. In this case, however, the cyclopropyl ring underwent ring opening in favour of a 1,3-diene complex,[19] corroborating the stability of the [η^4-1,3-diene $Fe(CO)_3$] moiety. This type of complexes is well-known in η^4-1-oxa-, η^4-1-aza- or homodienic 1,3-diene $Fe(CO)_3$ derivatives.[20]

The NMR spectroscopic investigations of the more polar fraction revealed a different complexation mode. Here, in the ^{1}H NMR spectrum, four multiplets with in total five protons are present between 2.15–2.33 (2H), 3.01–3.16 (1H), 3.30–3.41 (1H) and 6.65–6.78 ppm (1H), hinting again at an opened cyclopropyl ring after the reaction. Subsequently, this was confirmed by ^{1}H-^{1}H COSY and ^{1}H-^{13}C{^{1}H} HSQC techniques. Furthermore, the elemental analysis indicated a higher iron content than that in **2**, suggesting the presence of a dinuclear iron complex with the molecular formula $C_{21}H_{14}Fe_3O_7S$. Finally, single X-ray structure analysis revealed the unusual architecture of complex **3** (Figure 2) that is reminiscent of a [FeFe] hydrogenase mimic.

The Fe1–Fe2 distance of 2.5355(4) Å is in a typical range for such model compounds. The common butterfly structure of the $[S_2Fe_2(CO)_6]$ moiety in [FeFe] hydrogenase mimics is compensated by a 'pseudo-butterfly' coordination with S1 coordinating

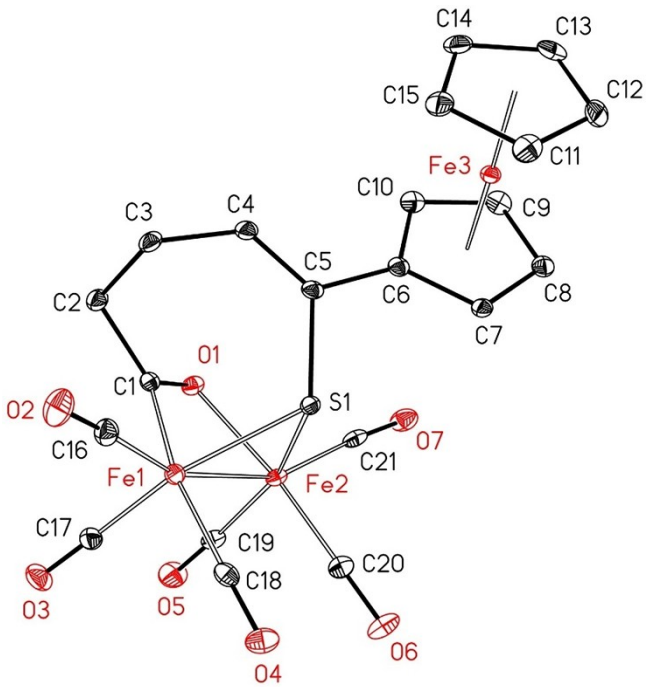

Figure 2. Molecular structure and atom labelling scheme of **3**.[18] The ellipsoids represent a probability of 50 %. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Fe1–C1 1.943(2), Fe1–S1 2.2459(5), Fe1–Fe2 2.5355(4), Fe2–O1 1.9993(14), Fe2–S1 2.2828(5), O1–C1 1.250(2), O2–C16 1.136(3), C1–C2 1.501(3), C2–C3 1.556(3), C3–C4 1.498(3), C4–C5 1.342(3); angles (°): S1–Fe2–Fe1 55.265(15), O1–Fe2–Fe1 72.83(4), O1–Fe2–S1 85.57(4), C1–Fe1–Fe2 68.76(6).

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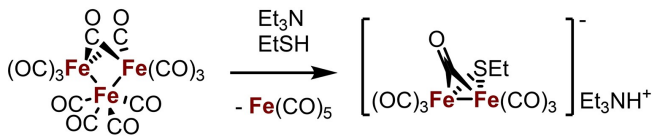
Fe1 and Fe2, C1 coordinating Fe1 and O1 coordinating Fe2. The ligation type of the O1–C1 bond can be considered as η^2-acyl character. The $[S(\eta^2(RC{=}O))Fe_2(CO)_6]$ moiety found in **3** is well-known in iron carbonyl chemistry and shows a typical η^2-acyl bond length of 1.250(2) Å.[21] Such complexes were initially described by Seyferth *et al.* in 1985, who reacted ethylthiol, triethylamine and $Fe_3(CO)_{12}$ with benzoyl chloride to afford isomeric η^2-acyl complexes.[22] They proposed an anionic intermediate with a bridging CO ligand (Scheme 3), shifting into a terminal position after C-bonded acyl ligation of the benzoyl unit, followed by CO loss and η^2-acyl ligation.[22–23] Generally, the η^2-acyl unit displays characteristic spectroscopic features. Based on reported data for similar complexes,[21,23] the $^{13}C\{^1H\}$ NMR spectrum of **3** displays C1 as very low-field signal at 304.6 ppm. Moreover, the IR spectrum shows ν(CO) at 1503 cm^{-1}. Similar insertion reactions resulting from treatment of some cyclopropane derivatives with iron carbonyls leading to C-bonded acyl complexes were reported in earlier publications.[24]

Proposed mechanistic pathway for the formation of complexes 2 and 3

The Fe(0)-mediated cyclopropane ring opening in **1** suggests a multistep reaction mechanism leading to complexes **2** and **3**. The first step in the cascade of reactions is the formation of an unstable adduct of $Fe_3(CO)_{12}$ with thioketone **1**, that undergoes a post-transition state bifurcation leading to isolated products **2** and **3**. In the case of **2**, adduct formation is followed by oxidation of a Fe(0) centre to Fe(I) accompanied by reduction of the thiocarbonyl carbon atom to generate a carbon-centred radical intermediate which is well-known as reactive species in spin-trapping thiocarbonyl compounds.[25] In the course of this redox step, resulting in thiolate formation, a $Fe_2(CO)_9$ moiety could formally be released, but its formation has not been proofed. Since cyclopropane rings located next to carbon-centred radicals are known to undergo ring opening easily,[3,26] the next step in the described cascade is an opening process accompanied by radical rearrangement. Structural characterization of **2** exposed the presence of a terminal methyl group in the complex. Thus, 1,2-*H* shift is resulting in a resonance-stabilized intermediate radical. Finally, the Fe(I) centre is oxidized to Fe(II) delivering an electron to create the σ-type Fe–C bond and the five-membered ring in **2**.

In a similar radical mechanism, the dinuclear complex **3** could be formed via an alternative pathway. As postulated for the generation of **2**, initial adduct formation between $Fe_3(CO)_{12}$ and **1** could be followed by a redox step resulting in a Fe(I) site and a carbon-centred radical. Release of the residual iron carbonyl fragment, *i.e.* $Fe(CO)_5$, could afford an intermediate with a bridging carbonyl ligand, based on a resembling anionic species postulated analogously in the reaction between $Fe_3(CO)_{12}$, EtSH and NEt_3 (Scheme 3).[22–23] Again, cyclopropane ring opening could lead to a terminal radical, which attacks the bridging carbonyl ligand resulting in the formation of an oxygen-centred radical. This type of radical-mediated insertion reactions in metal-coordinated CO ligands is rather scarcely reported.[27] Finally, oxidation of the second Fe(0) centre to Fe(I) leads to η^2-acyl coordination in **3** (Scheme 4).



Scheme 3. Proposed intermediate in the reaction of $Fe_3(CO)_{12}$ with ethylthiol leading to $[Fe_2(CO)_6]$-type complexes with organic bridging ligands.[22–23]

Electrochemical investigation of 3

We examined the electrochemical properties of complex **3** by cyclic voltammetry. Here, at a scan rate of 0.2 Vs^{-1} (Figure 3), the quasi-reversible Fe^{II}/Fe^{III} redox couple ($E_{1/2} = 0.06$ V) of the adjacent ferrocene moiety is evident. Following a scan to negative potentials, three reduction events at $E_{pc} = -1.56$, −1.74 and −2.14 V, respectively, were observed and all of them turned out to be irreversible, obvious from separate scans stopped after the corresponding reduction (Figure S1). Such redox profile indicates decomposition of **3** upon first reduction, followed by another two redox steps putatively involving residual complex fragments. In detail, according to an analysis of cyclic voltammetry performed at various scan rates ($0.1\ Vs^{-1} \le \nu \le 10\ Vs^{-1}$) by the current function (Figure S2), the irreversible reduction processes can be assigned to single electron transfers. However, at scan rates higher than 1 Vs^{-1}, the current of the second and third reduction gradually decreases indicating faster electrochemical scan than chemical decomposition dynamics. Likewise, the first and second reduc-

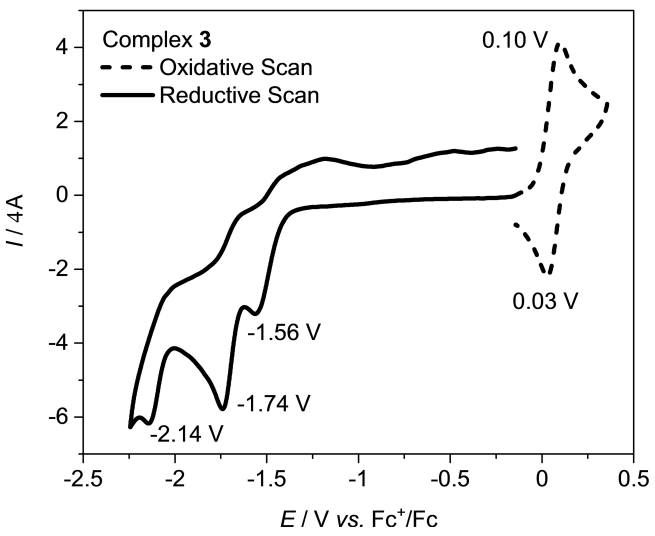


Figure 3. Cyclic voltammetry of 0.5 mM **3** in 0.1 M $[NBu_4][BF_4]$-CH_2Cl_2 solution at a scan rate of 0.2 Vs^{-1}. The scan direction in the oxidative scan was from 0 to 0.5 V and back and in the negative scan from 0 to −2.1 V and back. All potentials are referenced against the Fc^+/Fc couple.

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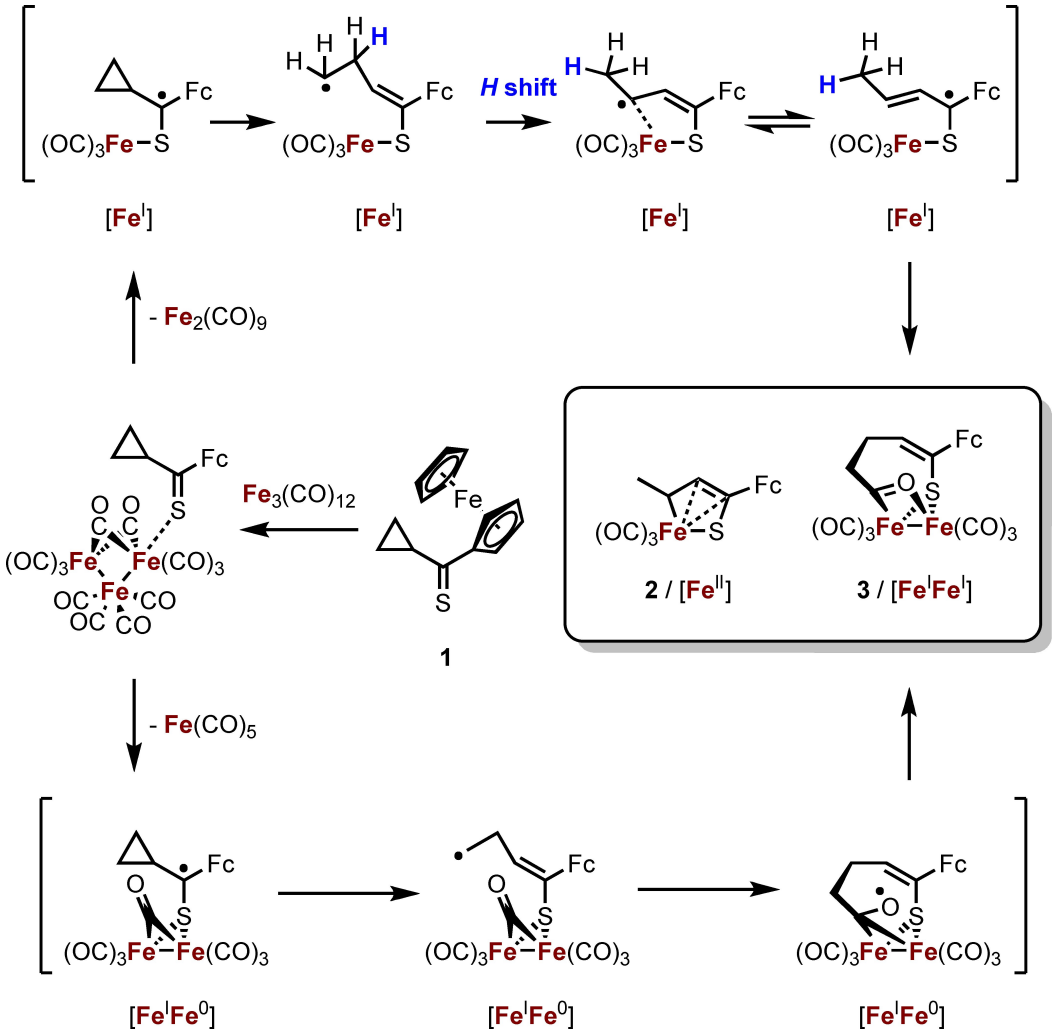

Scheme 4. Proposed radical mechanisms leading to complexes **2** and **3** starting with thioketone **1** and $Fe_3(CO)_{12}$; (Fc = ferrocenyl).

tion gradually collapse. Obviously, the unusual organometallic centre in **3** complicates its electrochemistry compared to [FeFe] hydrogenase mimics with a typical $[S_2Fe_2(CO)_6]$ unit clearly showing the quasi-reversible $[Fe^IFe^I]/[Fe^0Fe^I]$ or $[Fe^IFe^I]/[Fe^0Fe^0]$ redox couple.[28] At the current state of research, we assume that an electrocatalytic investigation of **3** would not be reasonable due to an unclear fate of the complex during electrochemical scan.

Conclusions

In summary, the present study showed that the reaction of cyclopropyl ferrocenyl thioketone **1** with $Fe_3(CO)_{12}$ leads to formation of two, hitherto unknown iron-sulfur complexes. Using spectroscopic methods and single crystal X-ray analysis, their structures were identified as mononuclear η^4-1-thia-1,3-diene-type iron tricarbonyl complex **2** and dinuclear η^2-acyl diiron hexacarbonyl complex **3**, respectively. Formation of both compounds was accompanied by opening of the cyclopropane ring. Due to the radical 'cascade mechanism' of formation of **2** and **3**, remarkable amounts of non-identified decomposition products were formed, and therefore, the yields of isolated complexes were rather low. Both products **2** and **3** display a well-known coordination site, although the proposed radical mechanism leading to their formation is a novel pathway. Likewise, the η^2-acyl ligand formation via a radical insertion reaction into a carbonyl ligand has not yet been described. Electrochemical investigations of **3** revealed an irreversible redox profile upon reduction presumably leading to unidentified decomposition products. Thus, at the current state of research, an electrocatalytic investigation of **3** would not be reasonable.

Experimental Section

Cyclopropyl ferrocenyl ketone

Cyclopropyl carboxylic acid (430 mg, 5 mmol) was dissolved in CH_2Cl_2 (6 mL) and trifluoroacetic anhydride (TFAA) (0.7 mL, 5 mmol) was added dropwise at room temperature. After two minutes of stirring a portion of trifluoromethylsulfonic acid (0.44 mL, 5 mmol) and ferrocene (930 mg, 5 mmol) were added. Stirring was continued for ten minutes at room temperature and the violet coloured solution was diluted with water (ca. 15 mL). The reaction mixture was transferred to a separatory funnel, whereupon the organic layer was separated and dried over magnesium sulfate. Pure product was obtained as red coloured crystals after silica gel column chromatography using CH_2Cl_2/MeOH mixture (99:1) as eluent. Yield 920 mg (77 %).

^{1}H NMR (600 MHz, $CDCl_3$): δ ppm 4.83 (s, 2H, Fc), 4.49 (s, 2H, Fc), 4.21 (s, 5H, Fc), 2.27–2.22 (m, 1H, *c*Pr), 1.19–1.16 (m, 2H, *c*Pr), 0.96–0.93 (m, 2H, *c*Pr); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ ppm 203.9 (*C*=O), 80.0 (Fc), 72.2 (Fc), 70.0 (Fc), 69.3 (Fc), 18.1 (*C*H, *c*Pr), 10.5 (CH_2, *c*Pr); m. p. 65–67 °C (literature: 65–66 °C[29]).

Cyclopropyl ferrocenyl thioketone 1

Cyclopropyl ferrocenyl ketone (4.47 g, 17.6 mmol) in dry tetrahydrofuran (20 mL) was treated with Lawesson's reagent (485 mg, 1.2 mmol) and the reaction mixture was heated up to 65 °C for five minutes. After that, the solvent was evaporated in vacuo and the crude product was purified on silica gel column using CH_2Cl_2 as eluent. Pure product was obtained as viscous oil, which was recrystallized from petroleum ether to afford violet prisms. Yield 4.30 g (90 %).

^{1}H NMR (600 MHz, $CDCl_3$): δ ppm 5.06–5.11 (m, 2H, Fc), 4.69–4.73 (m, 2H, Fc), 4.20 (s, 5H, Fc), 2.86–2.98 (m, 1H, *c*Pr), 1.49–1.52 (m, 2H, *c*Pr), 1.16–1.20 (m, 2H, *c*Pr); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ ppm 246.0 (*C*=S), 90.2 (Fc), 74.0 (Fc), 71.2 (Fc), 70.0 (Fc), 29.1 (CH, *c*Pr), 17.3 (CH_2, *c*Pr); HRMS (Direct infusion ESI+): *m/z* calcd for $C_{14}H_{14}FeS$ ($[M]^+$): 271.0166, found: 271.0229, fragmentation: 186.0120 ($[C_{10}H_9Fe+H]^+$); Elemental analysis calcd (%) for $C_{14}H_{14}Fe_S$: C 62.24, H 5.22, S 11.87, found: C 62.29, H 5.42, S 11.88; m. p. 85–87 °C.

Complexes 2 and 3

Cyclopropyl ferrocenyl thioketone **1** (137 mg, 0.51 mmol) was dissolved in toluene/NMP (20:1) (21 mL) and the solution was heated up to 40 °C. Subsequently, $Fe_3(CO)_{12}$ (255 mg, 0.51 mmol) was added, whereupon the solution turned green. Within five minutes the colour changed to red, indicating the finished complexation reaction. After 15 minutes the solution was allowed to cool to room temperature, before it was transferred into a separating funnel. After washing three times with water, the organic phase was dried over sodium sulfate. Dry silica was added and the solvent was removed in vacuo. Column chromatography over SiO_2 with *n*-hexane/CH_2Cl_2 as eluent afforded **2** and **3** as red solids. No further products could be isolated from the reaction mixture.

Complex **2**: Yield 12 mg (9 %); ^{1}H NMR (400 MHz, CD_2Cl_2) δ ppm 1.60 (d, *J*=6.43 Hz, 3H, H4), 2.41 (dq, *J*=8.77, 6.43 Hz, 1H, H3), 4.17 (s, 5H, Fc), 4.35–4.49 (m, 2H, Fc), 4.79–4.91 (m, 2H, Fc), 5.96 (d, *J*=8.77 Hz, 1H, H2); ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ ppm 117.8 (*C*1), 91.8 (*C*2), 85.9 (Fc), 70.8 (Fc), 70.7 (Fc), 70.6 (Fc), 69.4 (Fc), 67.8 (*C*3), 66.2 (Fc), 18.8 (*C*4); HRMS (Direct infusion ESI+): *m/z* calcd for $C_{17}H_{13}Fe_2O_3S$ ($[M+H]^+$): 409.9362, found: 409.9354; MS (EI, 70 eV): *m/z* (%)=410 (25) ($[M+H]^+$), 354 (30) ($[M\text{-}2\ CO+H]^+$), 326 (100) ($[M\text{-}3\ CO+H]^+$); IR: $\tilde{\nu}$=2922 (w), 2853 (w), 2064 (s), 2056 (s), 2017 (m), 2002 (vs), 1974 (vs), 1026 (m), 815 (vs) cm^{-1}; Elemental analysis calcd (%) for $C_{17}H_{13}Fe_2O_3S \cdot 1/8\ C_6H_{14}$: C 50.78, H 3.54, S 7.64, found C 50.91, H 3.93, S 7.41.

Complex **3**: Yield 14 mg (8 %); ^{1}H NMR (500 MHz, CD_2Cl_2) δ ppm 2.15–2.33 (m, 2H, H2, H3), 3.01–3.16 (m, 1H, H3), 3.30–3.41 (m, 1H, H2), 4.16 (s, 5H, Fc), 4.23–4.36 (m, 2H, Fc), 4.46–4.55 (m, 1H, Fc), 4.87–4.93 (m, 1H, Fc), 6.65–6.78 (m, 1H, H4); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ ppm 23.2 (*C*3), 64.9 (*C*4), 67.8 (Fc), 69.0 (Fc), 69.2 (Fc), 69.6 (Fc), 70.5 (Fc), 90.1 (Fc), 128.7 (*C*4), 135.6 (*C*5), 202.2, 208.4, 209.1, 211.0, 213.4, 214.8 (all *C*O), 304.6 (*C*1); HRMS (Direct infusion ESI+): *m/z* calcd for $C_{21}H_{14}Fe_3O_7S$ ($[M]^+$): 577.8508, found: 577.8509, fragmentation: 493.8661 ($[M\text{-}3\ CO]^+$); MS (EI, 70 eV): *m/z* (%)=577.4 (10) ($[M]^+$), 521.6 (5) ($[M\text{-}2\ CO]^+$), 493.7 (20) ($[M\text{-}3\ CO]^+$), 465.7 (10) ($[M\text{-}4\ CO]^+$), 437.7 (20) ($[M\text{-}5\ CO]^+$), 409.7 (20) ($[M\text{-}6\ CO]^+$), 381.7 (100) ($[C_{14}H_{14}Fe_3S]^+$); IR: $\tilde{\nu}$=2071 (s), 2026 (s), 2004 (vs), 1986 (vs), 1972 (vs), 1957 (vs) (terminal *C*O), 1503 (s) (acyl), 818 (vs) cm^{-1}; Elemental analysis calcd (%) for $C_{21}H_{14}Fe_3O_7S$: C 43.64, H 2.44, S 5.55, found C 44.11, H 2.67, S 5.56.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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