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Reactions of Selected Aromatic Thioketones with Dodecarbonyltriiron

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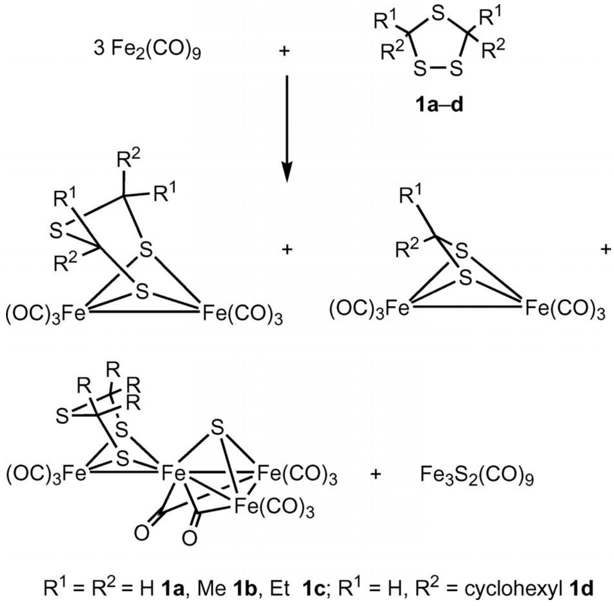
Dodecacarbonyltriiron reacts with 3,3,5,5-tetraphenyl-1,2,4-trithiolanes (**1e**) to give the *ortho*-metalated complex $Fe_2(CO)_6$-[κ,μ-*S*,η^2-($C_{13}H_{10}S$)] (**9a**), complexes of the type (Ph_2C)-$S_2Fe_2(CO)_6$ and the well known trinuclear complex $Fe_3S_2(CO)_9$ as by-products. Complex **9a** can also be obtained from the reaction of $Fe_3(CO)_{12}$ with thiobenzophenone (**2a**). In a similar way, 4,4′-bis(dimethylamino)thiobenzophenone (**2b**) reacts with $Fe_3(CO)_{12}$ to give $Fe_2(CO)_6$[κ,μ-*S*,η^2-($C_{17}H_{20}N_2S$)] (**9b**). The cyclic aromatic thioketones such as dibenzosuberenethione (**2c**) and xanthione (**2d**) react with $Fe_3(CO)_{12}$ to give the cyclometalated products $Fe_2(CO)_6$[κ,μ-*S*,η^2-($C_{15}H_{12}S$)] (**9c**) and $Fe_2(CO)_6$[κ,μ-*S*,η^2-($C_{13}H_8OS$)] (**9d**), respectively, and a small amount of $Fe_3S_2(CO)_9$. Complexes **9a**–**d** have been characterized by IR and NMR spectroscopies, elemental analyses, and X-ray single crystal structure analyses.

Introduction

In two recent papers we described the oxidative addition reactions of heterocyclic trisulfides, such as 1,2,4-trithiolanes, 1,2,5-trithiepanes, 1,2,5-trithiocanes, and 1,2,6-trithionanes to carbonyliron complexes to produce [FeFe]-hydrogenase model complexes with sulfur in the bridgehead position of the dithiolato ligand.[1,2] Within the last decade, numerous model compounds with suitability as the active site of the [FeFe]-hydrogenase were prepared.[3–27] Trisulfides with different ring sizes (five- to nine-membered rings) reacted with $Fe_2(CO)_9$ to give three major products containing dithiolatodiiron complexes.[1] The structures of these three products depend on the size of the trisulfide rings. Treatment of the di- or tetra-substituted five-membered 1,2,4-trithiolans **1a**–**d** with $Fe_2(CO)_9$ are reported to give the complexes shown in Scheme 1.[2]



Scheme 1. Reactions of 1,2,4-trithiolanes **1a**–**d** with $Fe_2(CO)_9$.

In continuation of our efforts in this field, the present work presents the reaction of 3,3,5,5-tetraphenyl-1,2,4-trithiolane (**1e**) as well as the selected aromatic thioketones **2a**–**d** with $Fe_3(CO)_{12}$. This interest stems from the study of the formation of similar thiobenzophenone–iron complexes **4a**,**b**, **5**, and **6** described by Alper et al. several decades ago (Scheme 2).[28–30] It is also known that 3,3,5,5-tetraphenyl-1,2,4-trithiolane (**1e**) undergoes [2+3]-cycloreversion at around 50 °C and forms an equilibrium mixture of thiobenzophenone *S*-sulfide (**7**), diphenyldithiirane (**8**), and thiobenzophenone (**2a**) (Scheme 3).[31–37] Reactions of aromatic thioketones **2a**,**b** with $Fe_2(CO)_9$ yielded the *ortho*-metalated complexes **4a**,**b** as the major products, together with small amounts of complexes of the type (Ar_2C)-$S_2Fe_2(CO)_6$ (**5** and **6**) and the well-known trinuclear complex $Fe_3S_2(CO)_9$ (Scheme 2).[29,30] The structures of the main products **4a**,**b** were suggested by Alper et al. based only on spectroscopic data and decomplexation reactions. In the present report, the structures of these complexes are presented, as determined by X-ray crystallography.

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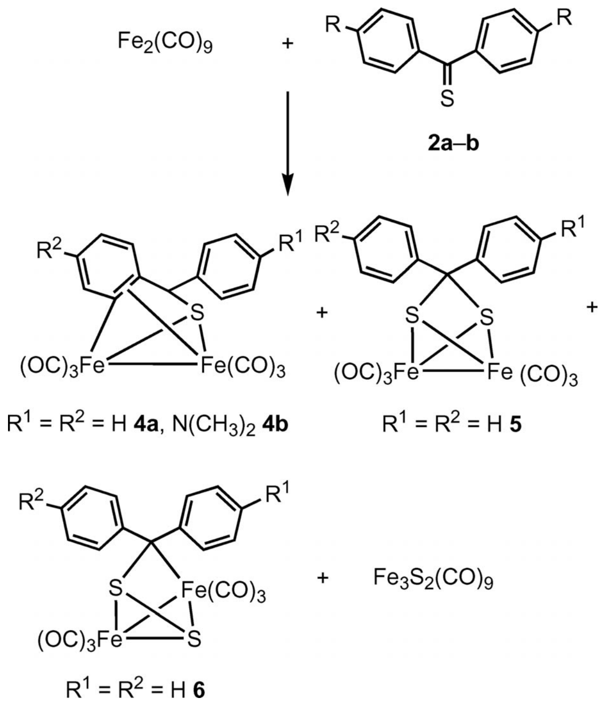
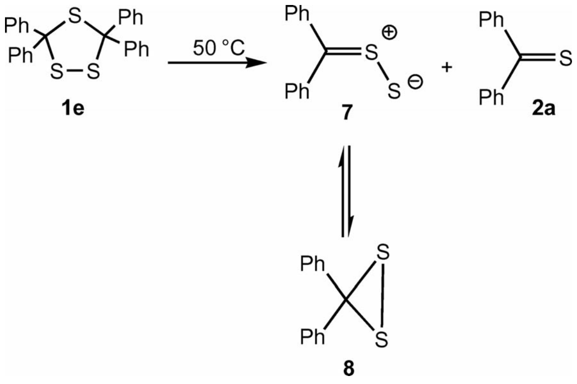


Scheme 2. Treatment of thiobenzophenone (**2a**) and 4,4′-bis(dimethylamino)thiobenzophenone (**2b**) with $Fe_2(CO)_9$ in anhydrous benzene at room temperature.

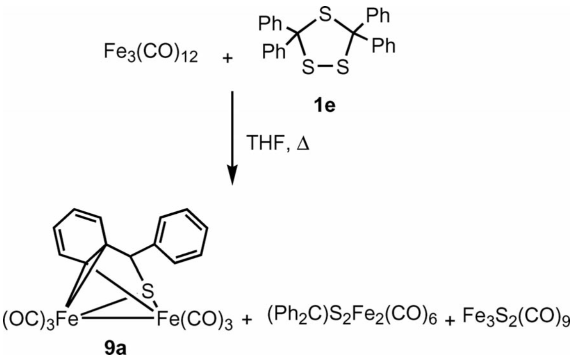


Scheme 3. Thermal cycloreversion of 3,3,5,5-tetraphenyl-1,2,4-trithiolane (**1e**).

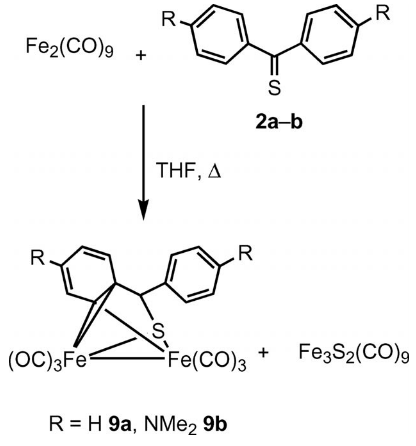
To date, reports of the reactions of aromatic thioketones with carbonyliron complexes are scarce.[28–30] Only very recently, a paper appeared in which the reactions of thiobenzophenone (**2a**) and 4,4′-bis(dimethylamino)thiobenzophenone (**2b**) with $Fe(CH_3)_2(PMe_3)_4$ were described.[38] In this case, *ortho*-metalation occurred to produce mononuclear (thiobenzophenone)iron complex with the elimination of methane. Treatment of Pt^0 complexes bearing bridged bisphosphane ligands with 3,3,5,5-tetraphenyl-1,2,4-trithiolane (**1e**) resulted in the formation of the dithiolato and η^2-thioketone complexes.[39] The latter complex was also prepared from the same Pt species and the corresponding thiobenzophenone.[39]

Results and Discussion

The reaction of **1e** with $Fe_3(CO)_{12}$ in boiling THF furnished complex **9a** as the major product, and complexes of the type $(Ph_2C)S_2Fe_2(CO)_6$ and $Fe_3S_2(CO)_9$ as by-products (Scheme 4). Complex $Fe_3(CO)_{12}$ is used for the reaction instead of $Fe_2(CO)_9$ because of its higher solubility and selectivity. Complex **9a** can also be obtained from the reaction of $Fe_3(CO)_{12}$ with **2a** as shown in Scheme 5. A conceivable explanation for this result is that in the case of **1e** the thermal dissociation of the trithiolane results in the formation of the equilibrium mixture containing some amount of thiobenzophenone (**2a**) (Scheme 3). The subsequent step may correspond to a formal [4+2] cycloaddition in which **2a** plays the role of a heterodiene; the initially formed [4+2]-cycloadduct undergoes spontaneous rearomatization through a 1,3-H shift to give the final complex **9a**.



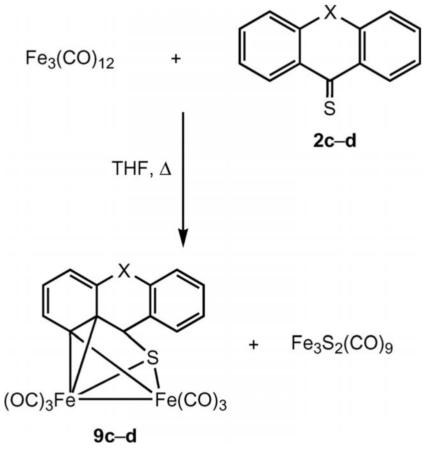
Scheme 4. Reaction of 3,3,5,5-tetraphenyl-1,2,4-trithiolane (**1e**) with $Fe_3(CO)_{12}$.



Scheme 5. Reactions of thiobenzophenone (**2a**) and 4,4′-bis(dimethylamino)thiobenzophenone (**2b**) with $Fe_3(CO)_{12}$ to give the *ortho*-metalated complexes **9a** and **9b**, respectively.

The reaction of 4,4′-bis(dimethylamino)thiobenzophenone (**2b**) with $Fe_3(CO)_{12}$ produces the *ortho*-metalated complex **9b**, in an analogous manner to complex **9a** (Scheme 5). Similar results were obtained by Alper et al. in the early 1970's[28–30] and based on the spectroscopic data complexes **9a** and **9b** seem to be identical to those reported by Alper et al.[29]

Refluxing a THF solution of dibenzosuberenethione (**2c**) or xanthione (**2d**) with $Fe_3(CO)_{12}$ yields, in both cases, the major product **9c** and **9d**, respectively, and the iron sulfur cluster as shown in Scheme 6. These complexes are stable for a longer time in the solid state and for several hours in solution. In addition, they are soluble in most common organic solvents, including hydrocarbons. In all reactions of the aromatic thioketones **2a–d** with $Fe_3(CO)_{12}$, trace amounts of a red-colored fraction (with an R_f value lower than that of the products) were obtained, however, to date we have not been able to characterize these. The IR spectra of **9c** and **9d** exhibit three strong vibration bands located in regions of 2069–2072, 2033–2037, and 1995–2001 cm^{-1}, which correspond to the terminal carbonyl groups bonded to the iron atoms. These ranges are comparable to those observed for **9a** and **9b** reported by Alper.[29] The C–S bond stretching frequency for compounds **9a–d** is found in the range 572–581 cm^{-1} indicating high single-bond character. The mass spectra of complexes **9a–d** show, in addition to the molecular ion peaks, the fragmentation of the six CO groups.



Scheme 6. Treatment of dibenzosuberenethione [**2c**, X = $(CH_2)_2$] and xanthione (**2d**, X = O) with $Fe_3(CO)_{12}$ to give the *ortho*-metallated complexes **9c** and **9d**, respectively.

The ^{1}H NMR spectra of **9a–d** show singlet resonances at δ = 5.55, 5.28, 6.12, and 4.60 ppm, respectively, corresponding to the methine protons. The ^{1}H NMR resonances of the methylene protons in complex **9c** appear as three sets of multiplets at δ = 2.96, 3.40, and 3.66 ppm. The ^{1}H NMR spectrum of **9b** consists of singlets at δ = 2.86 and 3.02 ppm assigned to the 12 protons of the two NMe_2 groups. The hydrogen atoms on the coordinated aromatic rings in compounds **9a–d** are generally deshielded, possibly by the tricarbonyliron group, with the protons next to the Fe–C sigma bond being the most deshielded. Their resonances appear as doublets at δ = 8.36 (**9a**; ^3J = 8.2 Hz), 7.49 ppm (**9b**; ^3J = 9.0 Hz), and 7.95 ppm (**9d**; ^3J = 8.0 Hz) and a multiplet at δ = 7.97 ppm (**9c**). The C–S sigma bonds in **9a–d** are evidence by the characteristic chemical shifts in the $^{13}C\{^1H\}$ NMR (δ = 63.3, 63.3, 60.2, and 52.5 ppm for **9a–d**, respectively). In addition, the ^{13}C NMR spectra for **9a–d** illustrate the resonances of the carbonyl C atoms in the range of 208–211 ppm.

Crystals suitable for the X-ray structure determinations of **9a–d** (Figures 1–4) were obtained from hexane solution at –25 °C. The aromatic thioketone ligand is bonded to the two iron centers through the sulfur atom, with the Fe–S

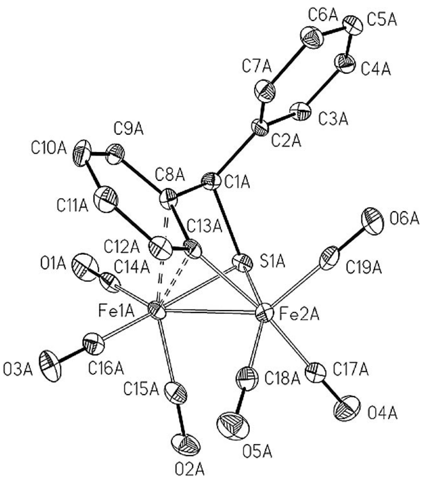


Figure 1. ORTEP drawing of $Fe_2(CO)_6[\kappa,\mu\text{-}S,\eta^2\text{-}(Ph_2CHS)]$ (**9a**) with thermal ellipsoids set at the 50% probability level (hydrogen atoms have been omitted for clarity). Selected distances [Å] and angles [°]: Fe1–Fe2 2.4986(8), Fe1–S1 2.2629(12), Fe2–S1 2.2369(13), S1–C1 1.838(4), Fe2–C13 1.996(4), Fe1–C13 2.189(4), Fe1–C8 2.290(4), F2–C13–Fe1 73.15(14), Fe1–Fe2–S1 56.77(3), Fe1–S1–Fe2 67.46(4), Fe2–Fe1–S1 55.78(3).

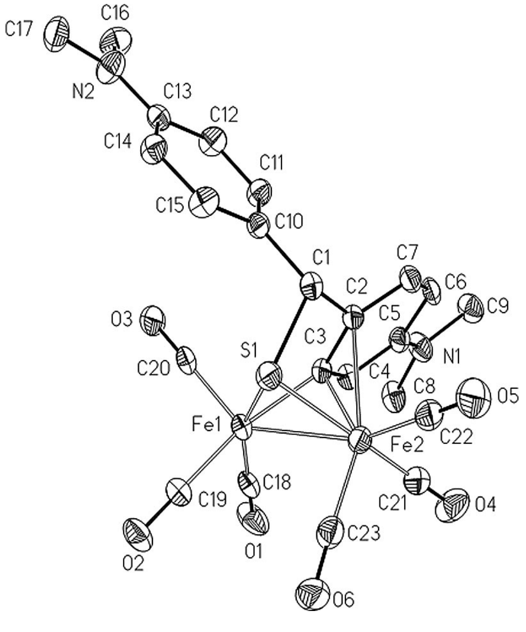


Figure 2. ORTEP drawing of $Fe_2(CO)_6[\kappa,\mu\text{-}S,\eta^2\text{-}(C_{17}H_{20}N_2S)]$ (**9b**) with thermal ellipsoids set at the 50% probability level (hydrogen atoms have been omitted for clarity). Selected distances [Å] and angles [°]: Fe1–Fe2 2.5216(10), Fe1–S1 2.2471(14), Fe2–S1 2.2467(14), S1–C1 1.840(5), Fe1–C3 1.996(4), Fe2–C3 2.211(5), Fe2–C2 2.315(5), F2–C3–Fe1 73.45(16), Fe1–Fe2–S1 55.87(4), Fe1–S1–Fe2 68.27(4), Fe2–Fe1–S1 55.86(4).

bond length in the range of 2.23–2.27 Å. It is also σ bonded to one Fe atom through the ortho carbon of one phenyl ring (1.99–2.01 Å) and is π-bonded to the other Fe atom through one C–C π-bond [*ortho*-C (2.18–2.21 Å) and the carbon atom next to C–S group (2.29–2.48 Å)]. The Fe–Fe distances in these complexes are found to be in the range of 2.495–2.521 Å, which are slightly shorter than the corresponding bond in the hydrogenase model complexes.[1–15] The Fe–S bond lengths are found to be within the same range observed for the hydrogenase model complexes.[10–18,24–26] The C–S average bond length (1.83 Å) is within the same range for a C–S single bond (1.80–1.85 Å) [40] and is significantly longer than the corresponding bond of $Fe(PMe_3)_3(Me)(\kappa,S,C\text{–}Ph_2C{=}S)$ [1.675(4) Å][38], which contains a C=S bond. The bite angles of the butterfly shape are within the same ranges observed for the hydrogenase model complexes indicating a distorted octahedral geometry around each iron center.[1–20]

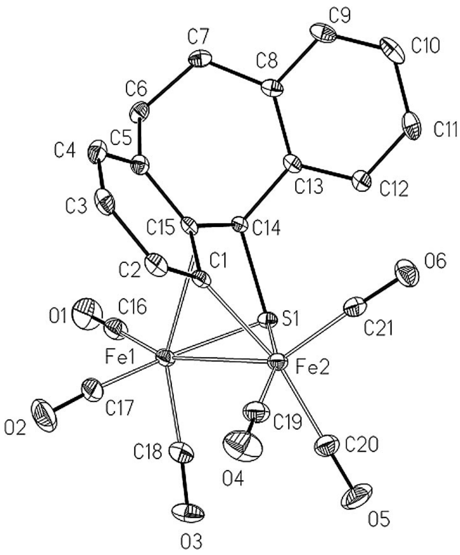


Figure 3. ORTEP drawing of $Fe_2(CO)_6[\kappa,\mu\text{-}S,\eta^2\text{-}(C_{15}H_{12}S)]$ (**9c**) with thermal ellipsoids set at the 50% probability level (hydrogen atoms have been omitted for clarity). Selected distances [Å] and angles [°]: Fe1–Fe2 2.4950(5), Fe1–S1 2.2717(7), Fe2–S1 2.2444(7), S1–C14 1.825(2), Fe2–C1 2.011(2), Fe1–C1 2.180(2), Fe1–C15 2.405(2), F2–C1–Fe1 72.95(8), Fe1–Fe2–S1 56.99(2), Fe1–S1–Fe2 67.07(2), Fe2–Fe1–S1 55.94(2).

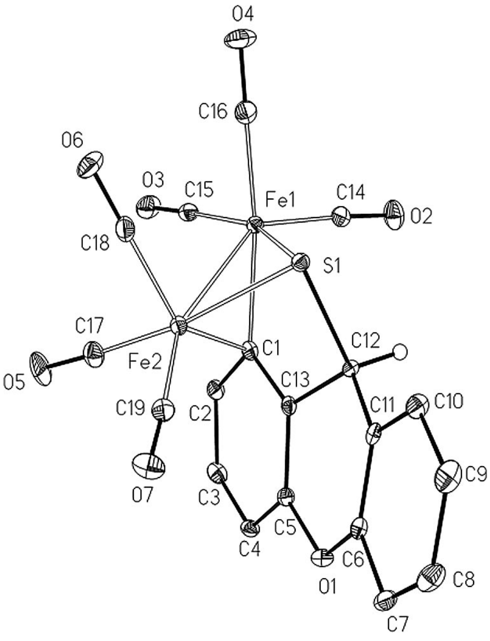


Figure 4. ORTEP drawing of $Fe_2(CO)_6[\kappa,\mu\text{-}S,\eta^2\text{-}(C_{15}H_{12}S)]$ (**9d**) with thermal ellipsoids set at the 50% probability level (hydrogen atoms have been omitted for clarity). Selected distances [Å] and angles [°]: Fe1–Fe2 2.4993(6), Fe1–S1 2.2425(9), Fe2–S1 2.2543(8), S1–C12 1.837(3), Fe1–C1 2.011(3), Fe2–C1 2.203(3), Fe2–C13 2.372(3), F1–C1–Fe2 72.60(9), Fe1–Fe2–S1 56.01(2), Fe1–S1–Fe2 67.53(2), Fe2–Fe1–S1 56.46(2).

Conclusion

The reactivity of 3,3,5,5-tetraphenyl-1,2,4-trithiolane (**1e**) is different form that of the corresponding tetraalkyl-substituted analogues **1a**–**d**. The latter reacts with $Fe_3(CO)_{12}$ leading to the product of oxidative addition along the S–S bond. The former, however, dissociates according to the pathway presented in Scheme 3. The fragments (e.g., $Ph_2C{=}S$) react with carbonyliron compounds to yield thioketone complexes as major products. This result prompted us directly to investigate the reaction of carbonyliron compounds with thioketones. Accordingly, four *ortho*-metalated complexes $Fe_2(CO)_6[\kappa,\mu\text{-}S,\eta^2\text{-}(C_{13}H_{10}S)]$ (**9a**), $Fe_2(CO)_6[\kappa,\mu\text{-}S,\eta^2\text{-}(C_{17}H_{20}N_2S)]$ (**9b**), $Fe_2(CO)_6[\kappa,\mu\text{-}S,\eta^2\text{-}(C_{15}H_{12}S)]$ (**9c**), and $Fe_2(CO)_6[\kappa,\mu\text{-}S,\eta^2\text{-}(C_{13}H_8OS)]$ (**9d**) were prepared and characterized. The formation mechanism for these complexes can be explained by a formal [4+2] cycloaddition in which the aromatic thioketones act as heterodienes with $Fe_3(CO)_{12}$. The subsequent step may correspond to 1,3-H shift giving the final complex. Only one major product was obtained with high yield from the reactions of the cyclic aromatic thioketones **2c** and **2d** with $Fe_3(CO)_{12}$. In contrast, the reactions of **2a** and **2b** with $Fe_3(CO)_{12}$ yielded the *ortho*-metalated complexes **9a** and **9b** as major products, together with complexes of the type $(Ar_2C)S_2Fe_2(CO)_6$. as by-products. The ^1H NMR spectra of **9a**–**d** indicate that the protons at the coordinated aromatic ring are generally deshielded. Furthermore, the protons next to the Fe–C sigma bond are the most deshielded.

Experimental Section

General Comments: All reactions were carried out under inert atmosphere by using standard Schlenk techniques. The ^1H and $^{13}C\{^1H\}$ NMR and 2D NMR spectra were recorded with a Bruker AVANCE 200 or 400 MHz spectrometers at r.t. using the solvent as a standard. Mass spectra were obtained by using a FINNIGAN MAT SSQ 710 instrument. Infrared spectra were measured on a Perkin–Elmer System 2000 FT-IR spectrometer. Thiobenzophenone,[41] 4,4′-bis(dimethylamino)thiobenzophenone,[41] 3,3,5,5-tetraphenyl-1,2,4-trithiolanes,[42] dibenzosuberenethione,[43] and xanthione[43] were prepared according to literature procedures. Solvents and $Fe_3(CO)_{12}$ were purchased from Sigma–Aldrich; all solvents were dried and distilled prior to use according to standard methods. Silica gel 60 (0.015–0.040 mm) was used for column chromatography. TLC was done using Merck TLC aluminum sheets Silica gel 60 F254. Elemental analyses were performed with a Vario EL III CHNS (Elementaranalyse GmbH Hanau) as single determinations.

$Fe_2(CO)_6$(κ,μ-S,η^2-Ph_2CHS) (9a): Thiobenzophenone (**2a**) (50 mg, 0.25 mmol) or **1e** (107 mg, 0.25 mmol) was added to a solution of $Fe_3(CO)_{12}$ (127 mg, 0.25 mmol) in THF (30 mL). The reaction mixture was heated to 65 °C with stirring for 30 min under argon. The resulting solution was cooled to r.t. and the solvent was removed under reduced pressure. The crude product was purified by column chromatography by using hexane as eluent. The dark red fraction was collected and the solvent was removed. Crystals suitable for X-ray diffraction analysis were obtained from a solution of hexane at –25 °C; yield 30 mg, 0.063 mmol (25%). $C_{19}H_{10}Fe_2O_6S$ (478): calcd. C 47.74, H 2.11, S 6.71; found C 47.33, H 2.29, S 6.39. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 5.55 (s, 1 H, 1A-H), 6.43 (m, 1 H, 4A-H), 7.05–7.21 (m, 4 H, Ar-H), 7.27 (t, ^3J = 7.6 Hz, 1 H, 10A-H), 7.32 (t, ^3J = 7.7 Hz, 1 H, 11A-H), 7.54 (d, ^3J = 7.6 Hz, 1 H, 9A-H) 8.36 (d, 1 H, ^3J = 8.2 Hz, 12A-H) ppm. $^{13}C\{^1H\}$ NMR (400 MHz, $CDCl_3$): δ = 63.3 (C-1A), 125.5, 126.5, 128.2, 128.5, 129.7, 129.7, 129.9, 131.6, 143.0, 149.6, 150.0, 155.2, (2Ph), 209.4, 209.6 (CO) ppm. FTIR (C_5H_{12}): $\tilde{\nu}_{C\equiv O}$ = 2071 (vs), 2035 (vs), 2001 (vs), 1981 (s, sh) ν_{C-S} 574 cm^{-1}. DEI-MS: m/z = 478 [M^+], 450 [M^+ – CO], 422 [M^+ – 2CO], 394 [M^+ – 3CO], 366 [M^+ – 4CO], 338 [M^+ – 5CO], 310 [M^+ – 6CO].

$Fe_2(CO)_6$(κ,μ-*S*,η^2-$C_{17}H_{20}N_2S$) (9b): 4,4′-Bis(dimethylamino)thiobenzophenone (**2b**) (50 mg, 0.18 mmol) was added to a solution of $Fe_3(CO)_{12}$ (90 mg, 0.18 mmol) in THF (30 mL) under argon. The reaction mixture was heated to 65 °C with stirring for 30 min. The solvent was removed under vacuum. The crude product was purified by column chromatography using hexane as eluent. From the major dark red fraction, **9b** was obtained and recrystallized from a solution of hexane at –25 °C; yield 32 mg, 0.057 mmol (31%). $C_{23}H_{20}Fe_2N_2O_6S$ (564.2): calcd. C 48.97, H 3.57, S 5.68; found calcd. C 49.38, H 3.61, S 5.26. ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 2.86, 3.02 (2 s, 12 H, NMe_2), 5.28 (s, 1 H, 1-H), 6.23 (d, ^3J = 8.8 Hz, 1 H, CH), 6.45 (d, ^3J = 8.8 Hz, 1 H, CH), 6.60 (d, ^3J = 8.8 Hz, 1 H, CH), 6.81 (d, ^3J = 9.0 Hz, 1 H, CH), 7.05 (d, ^3J = 9.0 Hz, 1 H, 6-H), 7.27 (d, ^4J = 2.6 Hz, 1 H, 4-H), 7.49 (d, ^3J = 9.0 Hz, 1 H, 7-H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 40.1, 40.5 (NMe_2), 63.3 (C-1), 111.8, 112.0, 117.9, 118.9, 124.0, 125.6, 127.2, 127.6, 131.1, 135.9, 146.6, 151.2 (Ph), 210.3, 210.9 (CO) ppm. FTIR (C_5H_{12}): $\tilde{\nu}_{C\equiv O}$ = 2062 (vs), 2026 (vs), 1986 (s), 1972 (sh) ν_{C-S} 580 cm^{-1}. DEI-MS: m/z = 565 [M^+], 536 [M^+ – CO], 508 [M^+ – 2CO], 480 [M^+ – 3CO], 452 [M^+ – 4CO], 424 [M^+ – 5CO], 396 [M^+ – 6CO].

$Fe_2(CO)_6$(κ,μ-*S*,η^2-($C_{15}H_{12}S$) (9c): $Fe_3(CO)_{12}$ (150 mg, 0.30 mmol) was dissolved in THF (40 mL) and dibenzosuberenethione (**2c**) (67 mg, 0.30 mmol) was added. The mixture was stirred at 65 °C for 30 min under argon. The volatile components were removed in vacuo. The crude product was purified by column chromatography using hexane as eluent. The dark red fraction was collected and the solvent removed. Complex **9c** was recrystallized from a solution of hexane at –25 °C; yield 135 mg, 0.27 mmol (88%). $C_{21}H_{12}Fe_2O_6S$ (504.1): calcd. for $C_{21}H_{12}Fe_2O_6S{\cdot}1.0C_6H_{14}$ C 51.15, H 2.86 S 6.15; found C 51.21, H 2.58, S 5.85. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.96 (m, 2 H, C7H_AH_B), 3.40 (m, 1 H, C6H_CH_D), 3.66 (m, 1 H, C6H_CH_D), 6.12 (s, 1 H, 14-H), 6.94 (m, 1 H, 3-H), 7.25 (m, 1 H, 4-H), 7.97 (m, 1 H, 2-H), 7.0–7.20. (m, 4 H, 9–12-H) ppm. $^{13}C\{^1H\}$ NMR (200 MHz, $CDCl_3$): δ = 33.3 (C-7), 33.7 (C-6), 60.2 (C-14), 125.5, 126.1, 127.4, 127.8, 130.6, 131.1, 134.7, 138.5, 141.3, 145.7, 155.2 (Ph), 209.4, 209.8 (CO) ppm. FTIR (C_5H_{12}): $\tilde{\nu}_{C\equiv O}$ = 2069 (vs), 2033 (vs), 1994 (vs), 1981 (sh) ν_{C-S} 583 cm^{-1}. DEI-MS: m/z = 504 [M^+], 476 [M^+ – CO], 448 [M^+ – 2CO], 420 [M^+ – 3CO], 392 [M^+ – 4CO], 364 [M^+ – 5CO], 336 [M^+ – 6CO].

$Fe_2(CO)_6$(κ,μ-*S*,η^2-($C_{13}H_8OS$) (9d): A mixture of $Fe_3(CO)_{12}$ (134 mg, 0.27 mmol) and xanthione (**2d**) (57 mg, 0.27 mmol) in THF (40 mL) was stirred at 45 °C for 10 min. The mixture was

Table 1. Crystal data and refinement details for the X-ray structure determinations of the compounds **9a**, **9b**, **9c**, and **9d**.

	9a	**9b**	**9c**	**9d**
Formula	$C_{19}H_{10}Fe_2O_6S$	$C_{23}H_{20}Fe_2N_2O_6S$	$C_{21}H_{12}Fe_2O_6S$	$C_{19}H_8Fe_2O_7S$
Mw [$g\,mol^{-1}$]	478.03	564.17	504.07	492.01
T [°C]	–90(2)	–90(2)	–90(2)	–140(2)
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a [Å]	15.3041(5)	9.1297(6)	9.5488(4)	8.0761(4)
b [Å]	27.7392(9)	7.9376(5)	10.0657(4)	10.3929(6)
c [Å]	8.9523(2)	33.3551(16)	11.6416(4)	11.4083(6)
α [°]	90	90	104.994(3)	87.972(3)
β [°]	96.861(2)	92.624(3)	95.791(3)	85.257(3)
γ [°]	90	90	109.866(2)	76.707(3)
V [$Å^3$]	3773.25(19)	2414.6(2)	994.32(7)	928.57(9)
Z	8	4	2	2
ρ [$g\,cm^{-3}$]	1.683	1.552	1.684	1.760
μ [cm^{-1}]	16.82	13.29	16	17.15
Measured data	23332	11403	6851	6525
Data with $I > 2\sigma(I)$	4517	3199	3452	3156
Unique data/R_{int}	8544/0.1009	5319/0.1058	4478/0.0281	4237/0.0333
wR_2 (all data, on F^2)[a]	0.1180	0.1802	0.0843	0.0823
R_1 [$I > 2\sigma(I)$][a]	0.0524	0.0714	0.0358	0.0414
s[b]	0.959	1.042	1.008	0.999
Residual el. density [$e\,Å^{-3}$]	0.512/–0.523	0.639/–0.479	0.339/–0.377	0.395/–0.412
Absorption correction	none	none	none	none

[a] Definition of the R indices: $R_1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$; $P = [2F_c^2 + \max(F_o^2]/3$. [b] $s = \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

cooled to r.t. and the solvent was removed under reduced pressure. The crude product was purified by column chromatography using hexane as eluent. From the major dark red fraction, **9d** was obtained and recrystallized from a solution of hexane of at –25 °C; yield 118 mg, 0.24 mmol (84%). $C_{19}H_8Fe_2O_7S$ (491.8): calcd. C 46.38, H 1.64, S 6.52; found C 46.01, H 1.84, S 6.06. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.63 (s, 1 H, 12-H)), 6.81 (d, ^3J = 7.6 Hz, 1 H, 7-H), 7.00 (dd, ^3J = 7.8 Hz, 1 H, 9-H), 7.2 (d, ^3J = 8.2 Hz, 1 H, 10-H), 7.27 (dd, ^3J = 7.7 Hz, 1 H, 8-H), 7.38 (dd, ^3J = 7.7 Hz, 1 H, 3-H), 7.53 (d, ^3J = 7.6 Hz, 1 H, 4-H), 7.95 (d, ^3J = 8.0 Hz, 1 H, 2-H) ppm. $^{13}C\{^1H\}$ NMR (400 MHz, $CDCl_3$): δ = 52.5 (C-12), 112.3, 104.5, 116.4, 123.9, 124.7, 126.7, 128.6, 129.7, 147.6, 150.5, 152.2, 156.9, 208.7 (CO) ppm. FTIR (C_5H_{12}): $\tilde{\nu}_{C\equiv O}$ = 2072 (vs), 2037 (vs), 2001 (vs), 1985 (s, sh) $\nu_{C–S}$ 583 cm^{-1}. DEI-MS: *m*/*z* = 492 [M^+], 464 [M^+ – CO], 436 [M^+ – 2CO], 408 [M^+ – 3CO], 380 [M^+ – 4CO], 352 [M^+ – 5CO], 324 [M^+ – 6CO].

Crystal Structure Determination: The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects but not for absorption effects.[44,45] Crystallographic data as well as structure solution and refinement details are summarized in Table 1. The structures were solved by direct methods (SHELXS)[46] and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97).[47] The hydrogen at C12 for complex **9d** was located by difference Fourier synthesis and refined isotropically. All other hydrogen atom positions were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.[47] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

CCDC-768287 (for **9a**), CCDC-768288 (for **9b**), CCDC-768289 (for **9c**) and CCDC-768290 (for **9d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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