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Synthesis and reactivity of *fac*-$[Fe(CO)_3(SR)_3]^-$ ($R = C_7H_4SN$, C_4H_3S, C_4H_2O-*o*-CH_3) and heterotrimetallic Fe(II)–Ni(II)–Fe(II)–thiolate complex

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Abstract

The reaction of 2 equiv. of diorganyl disulfides, (bis(2-benzothiazolyl) disulfide, di(2-thienyl) disulfide, and bis(2-methyl-3-furyl) disulfide), with 1 equiv. of $[HFe(CO)_4]^-$ affords the stable, tridentate *fac*-$[Fe(CO)_3(SR)_3]^-$ ($R = C_7H_4SN$ (**1**); C_4H_3S (**2**); C_4H_2O-*o*-CH_3 (**3**)) via the formation of intermediate $[RSFe(CO)_4]^-$, respectively. In contrast, oxidative addition of 2-aminophenyl disulfide to $[Fe(CO)_4(\text{–}SC_6H_4\text{-}o\text{-}NH_2)]^-$, obtained from reaction of $[HFe(CO)_4]^-$ and 2-aminophenyl disulfide, and concomitant displacement of $[SC_6H_4\text{-}o\text{-}NH_2]^-$ leads to the neutral monomeric compound *cis*-$[Fe(CO)_2(\text{–}SC_6H_4\text{-}o\text{-}NH_2)_2]$ (**6**). Obviously, the reactivity and stability of the iron–thiolate derivatives may be tailored by pendant ligand selection, and the reaction pathway is tailored according to the bond strength inherent in the organodisulfides and to the nucleophilicity of thiolate atoms in $[RSFe(CO)_4]^-$ complexes. In particular, compounds *fac*-$[Fe(CO)_3(SR)_3]^-$ serve as chelating metalloligand and intermetal thiolate ligand-transfer reagent to synthesize the linear heterotrinuclear $[(CO)_3Fe(\mu\text{-}SR)_3Ni(\mu\text{-}SR)_3Fe(CO)_3]$ (**4**) ($R = C_4H_2O$-*o*-CH_3) and the neutral $[Fe(CO)_2(SC_4H_3S)_2(bipy)]$ (**5**) (bipy = bipyridine). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Iron–thiolate; Iron–nickel–thiolate; Thiolate ligand-transfer; Metallochelating

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1. Introduction

The recent report of active-site structure of [Fe] and [NiFe] hydrogenases has highlighted the chemistry of dinuclear iron–thiolate cyanocarbonyl and heterobimetallic iron–nickel–thiolate cyanocarbonyl compounds individually [1–7]. The synthesis of iron(II)–terminal thiolate compounds and heterobimetallic nickel–iron–thiolate complexes presents challenges, particularly in the area of thiolate-bridged dinuclear systems where ideal precursors are apt to exist as stable polynuclear compounds [8,9]. Recent work in this laboratory has shown that the anionic iron-hydride carbonyl $[HFe(CO)_4]^-$ activates the E–E bond of diorganyl dichalcogenides (RE–ER, E = Te, Se) to yield *fac*-$[Fe(CO)_3(ER)_3]^-$ complexes which are useful in the syntheses of $[(CO)_3Fe(\mu\text{-}SePh)_3M(\mu\text{-}SePh)_3Fe(CO)_3]$ (M = Ni, Zn, Cd, Fe) with homoleptic hexaselenolatometal core [10], $[(CO)_3Mn(\mu\text{-}2\text{-}SC_4H_3S)_3Ni(\mu\text{-}SePh)_3Fe(CO)_3]^-$ with heteroleptic hexachalcogenolatonickel core NiS_3Se_3 [11], and distorted square planar $[Ni(CO)(SePh)_3]^-$, the biomimetic nickel-site structure of CO dehydrogenases and [NiFeSe] hydrogenases [12]. However, we have been unable to observe any indications of formation of *fac*-$[Fe(CO)_3(SPh)_3]^-$ complex in the reaction of $[HFe(CO)_4]^-$ and $(PhS)_2$ under the same reaction condition [10b]. The attempted synthesis of *fac*-$[Fe(CO)_3(SPh)_3]^-$ and the stable *fac*-$[Fe(CO)_3(SR)_3]^-$ in a manner analogous to *fac*-$[Fe(CO)_3(EPh)_3]^-$ (E = Te, Se) by reaction of 1 equiv. of $[HFe(CO)_4]^-$ and 2 equiv. of $(PhS)_2/(RS)_2$ affords only $[PhSFe(CO)_4]^-$ and the thermally extremely unstable *fac*-$[Fe(CO)_3(SR)_3]^-$ (SR = 4-nitrophenyl thiolate, 2,4,5-trichlorophenyl thiolate), respectively [10b].

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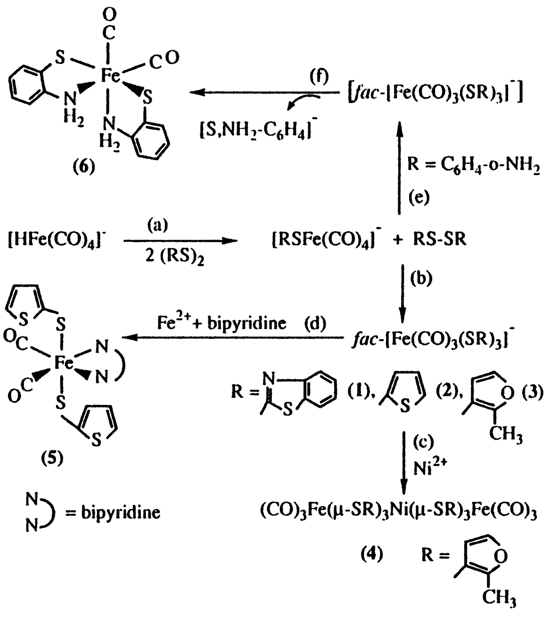
In our continued work on the synthesis of homodinuclear iron–thiolate and heterodinuclear iron–nickel–thiolate complexes [7,8], the potential biomimetic active-site structural models of [Fe] and [NiFe] hydrogenases individually, we have concentrated our attention on the development of the stable *fac*-$[Fe(CO)_3(SR)_3]^-$ and a synthetic route to iron–nickel–thiolate compounds employing *fac*-$[Fe(CO)_3(SR)_3]^-$ as a chelating ligand and intermetal ligand-transfer reagent. Obviously, the reactivity and stability of iron thiolate derivatives may be tailored by pendant ligand selection. One aspect of the reactivity of $[RSFe(CO)_4]^-$ toward organodisulfides can be mentioned: the reaction pathway is tailored according to the bond strength inherent in the organodisulfides and to the nucleophilicity of thiolate atoms in $[RSFe(CO)_4]^-$ complexes.

2. Results and discussion

The chemistry reported herein is summarized in Scheme 1. Reaction of 2 equiv. of diorganyl disulfides $(RS)_2$ ($R = C_7H_4SN$, C_4H_3S, C_4H_2O-*o*-CH_3) and 1 equiv. of coordinatively unsaturated, low-valent, anionic $[PPN][HFe(CO)_4]$ (or $[Et_4N][HFe(CO)_4]$) proceeds readily with evolution of gaseous CO in THF at room temperature. IR measurements of ν_{CO} (C_{3v}) showed the formation of *fac*-$[Fe(CO)_3(SR)_3]^-$ ($R = C_7H_4SN$ (**1**); C_4H_3S (**2**); C_4H_2O-*o*-CH_3 (**3**)) via the formation of intermediate $[RSFe(CO)_4]^-$ (Scheme 1a and b) [10a]. The iron(II)–thiolate derivatives **1**–**3** appear to be stable to air, and are soluble in most polar organic solvents, such as THF and CH_2Cl_2. Surprisingly, complex **1** is stable either as a solid or in organic solution under N_2 atmosphere at 50 °C. However, upon being stirred for extended periods in THF at 30 °C, the solution of complexes **2** and **3** converted into an insoluble solid.



Scheme 1.

Subsequent reaction of complex **3** with $Ni(ClO_4)_2$ produced the neutral heterotrimetallic $(CO)_3Fe(\mu\text{-}SR)_3Ni(\mu\text{-}SR)_3Fe(CO)_3$ (**4**) complex ($R = C_4H_2O$-*o*-CH_3), as a thermally stable, dark brown solid (Scheme 1c). Complex **4** is soluble in THF and CH_2Cl_2, sparingly soluble in common organic solvents like acetonitrile and hexane. The IR carbonyl stretching and ^1H NMR spectra are consistent with the presence of the hexacoordination of d^8 Ni(II) and the octahedral, low-spin d^6 Fe(II) with facial tricarbonyls. It is notable that *fac*-$[Fe(CO)_3(SR)_3]^-$ can serve as an effective metallo chelating ligand for stabilizing the hexacoordinate d^8 nickel(II) core [10c].

As shown in Scheme 1d, addition of 2 equiv. of complex **2** to a mixture of $Fe(ClO_4)_2 \cdot 6H_2O$ and 3 equiv. of bipyridine in a mixed solvent CH_3CN–THF under nitrogen atmosphere at ambient temperature, finally led to the dark red–brown *cis*-$Fe(CO)_2(SC_4H_3S)_2(bipy)$ (**5**) complex (bipy = bipyridine). Complex **5** is a stable, diamagnetic species soluble in organic solvents. Its IR spectrum shows two strong CO stretching bands, supporting a *cis* position of two CO ligands [13]. The ^1H and ^{13}C NMR spectra show the expected signals for the $[S–C_4H_3S]^-$ ligands in a diamagnetic d^6 Fe(II) species. The formation of complex **5** indicates the thiolate and CO ligand-transfer from one iron(II) center to another. This redistribution reaction suggests that complexes **1**–**3** may be employed as an intermetal thiolate-transfer reagent.

In contrast, reaction of 1 equiv. of $[HFe(CO)_4]^-$ and 2 equiv. of 2-aminophenyl disulfide in THF finally led to the formation of the known neutral *cis*-$Fe(CO)_2(–SC_6H_4$-*o*-$NH_2)_2$ (**6**) identified by IR, and X-ray diffraction, and the insoluble $[PPN][SC_6H_4$-*o*-$NH_2]$ (Scheme 1e and f) [14]. The anionic $[SC_6H_4$-*o*-$NH_2]^-$ ligands in complex **6** bind to the Fe(II) atom in a bidentate manner, forming two five-membered chelate rings. As illustrated in Scheme 1e and f, the proposed mechanism involves cleavage of sulfur–sulfur bond to yield the monodentate (S-bonded) $[Fe^0(CO)_4(–SC_6H_4$-*o*-$NH_2)]^-$ with the liberation of $H–SC_6H_4$-*o*-NH_2, and the subsequent oxidative addition of 2-aminophenyl disulfide to the anionic $[Fe(CO)_4(–SC_6H_4$-*o*-$NH_2)]^-$ yielding the intermediate *fac*-$[Fe(CO)_3(–SC_6H_4$-*o*-$NH_2)_3]^-$ (Scheme 1e). Subsequent elimination of $[SC_6H_4$-*o*-$NH_2]^-$, concomitant dissociation of CO and coordination of nitrogen atom of the bidentate $[–SC_6H_4$-*o*-$NH_2–]^-$ ligands to the Fe(II) result in the formation of the neutral complex **6** (Scheme 1f). Complex **6** is soluble and stable in THF–hexane solution. The IR spectrum of complex **6** showing two strong CO stretching bands supports a *cis* orientation of two CO ligands.

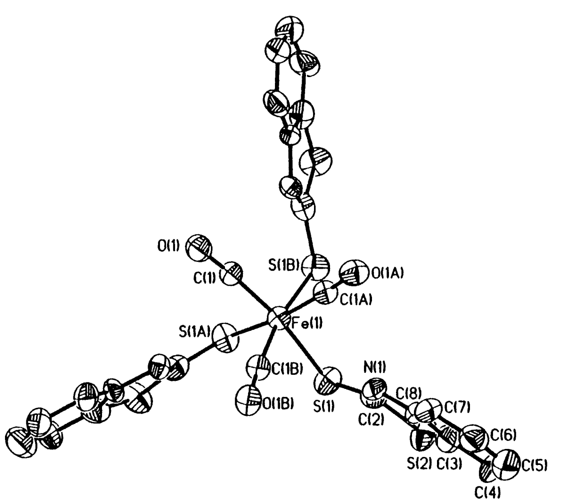


Fig. 1. ORTEP drawing and labeling scheme of *fac*-$[Fe(CO)_3(SC_7H_4SN)_3]^-$ with thermal ellipsoids drawn at the 50% probability level.

Table 1
Selected bond distances (Å) and bond angles (°) for complexes **1** and **2**

Complex 1			
Bond distances			
Fe(1)–S(1)	2.337(3)	Fe(1)–S(1A)	2.337(3)
Fe(1)–S(1B)	2.337(6)	Fe(1)–C(1)	1.825(8)
Fe(1)–C(1A)	1.825(8)	Fe(1)–C(1B)	1.825(8)
Bond angles			
C(1A)–Fe(1)–C(1)	93.2(4)	C(1)–Fe(1)–C(1B)	93.2(4)
C(1)–Fe(1)–S(1B)	96.9(3)	C(1A)–Fe(1)–S(1A)	169.8(3)
C(1B)–Fe(1)–S(1)	85.0(3)	S(1A)–Fe(1)–S(1)	85.29(11)
S(1B)–Fe(1)–S(1A)	85.29(11)	S(1B)–Fe(1)–S(1)	85.28(11)
Complex 2			
Bond distances			
Fe–C(1)	1.784(6)	Fe–C(2)	1.778(6)
Fe–C(3)	1.791(5)	Fe–S(1)	2.348(1)
Fe–S(3)	2.338(1)	Fe–S(5)	2.365(2)
Bond angles			
C(1)–Fe–C(2)	94.7(2)	C(1)–Fe–C(3)	95.0(2)
C(1)–Fe–S(3)	87.1(2)	C(2)–Fe–S(1)	171.3(2)
C(3)–Fe–S(1)	85.1(2)	C(2)–Fe–S(5)	85.7(2)
C(3)–Fe–S(5)	92.3(2)	S(1)–Fe–S(5)	85.65(5)
S(1)–Fe–S(3)	83.82(5)	S(3)–Fe–S(5)	85.48(6)

The structure of the *fac*-$[Fe(CO)_3(S–SNC_7H_4)_3]^-$ unit in Et_4N^+ salt is shown in Fig. 1. Selected bond distances and angles are collected in Table 1. The X-ray crystal structure of complex **1** consists of two crystallographically independent molecules. As expected, the geometry around Fe is a distorted octahedral with bond angles 85.29(11)° for S(1B)–Fe(1)–S(1A), 93.2(4)° for C(1A)–Fe(1)–C(1), and 85.0(3)° for C(1)–Fe(1)–S(1A) confirming the spectral assignment of a *fac*-configuration. The mean Fe(II)–S bond of length 2.337(3) Å (average) in complex **1** is slightly shorter than the terminal Fe(II)–S distances in complex **2** (2.350(2) Å average). The anionic complex **2** is isostructural with the anionic complex **1**. Fig. 2 displays a thermal ellipsoid plot of the anionic complex **2** and selected distances and angles are given in Table 1. The S···S contact distances in **1** and **2** are in the range 2.991–3.172 and 2.929–3.038 Å, respectively, indicative of the absence of direct S–S bonding.

The X-ray structural analysis of complex **4**, shown in Fig. 3, reveals a linear chain of one nickel(II) and two iron(II) atoms. The centrosymmetric trinuclear iron–nickel–iron thiolate complex **4** appears to have no precedent in iron–nickel–thiolate chemistry [15]. The central Ni(II) is in a distorted octahedral arrangement with the sulfur atoms of thiolates in two parallel faces of the octahedron capped by tricarbonyl iron(II) frag-

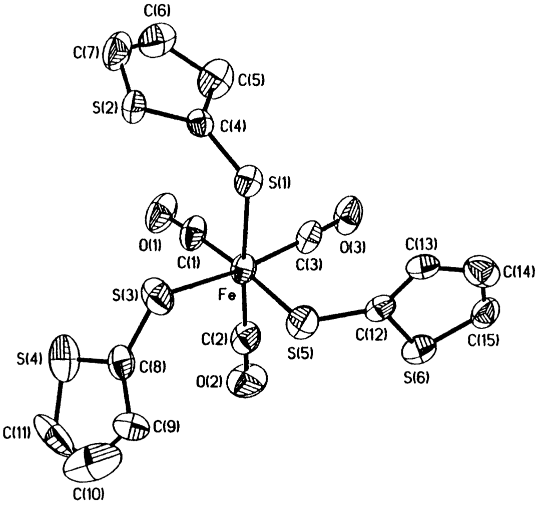


Fig. 2. ORTEP drawing and labeling scheme of *fac*-$[Fe(CO)_3(SC_4H_3S)_3]^-$ with thermal ellipsoids drawn at the 30% probability level.

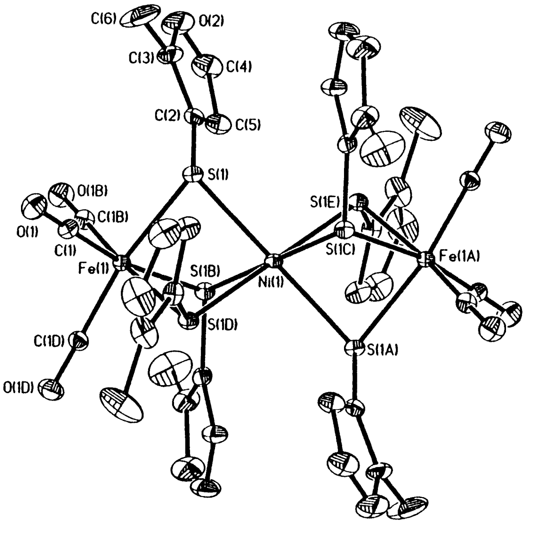


Fig. 3. ORTEP drawing and labeling scheme of $(CO)_3Fe(SC_4H_2O\text{-}o\text{-}CH_3)_3Ni(SC_4H_2O\text{-}o\text{-}CH_3)_3Fe(CO)_3$ with thermal ellipsoids drawn at the 30% probability level.

Table 2
Selected bond distances (Å) and bond angles (°) for complexes **4** and **5**

*Complex **4***			
Bond distances			
Ni(1)–S(1)	2.413(1)	Ni(1)–S(1A)	2.413(1)
Fe(1)–S(1)	2.342(1)	Fe(1)–S(1B)	2.342(1)
Bond angles			
S(1)–Ni(1)–S(1A)	180.0	S(1A)–Ni(1)–S(1C)	80.11(4)
S(1B)–Ni(1)–S(1)	99.89(4)	C(1)–Fe(1)–C(1B)	96.3(2)
C(1B)–Fe(1)–S(1)	93.73(14)	C(1)–Fe(1)–S(1B)	169.3(2)
*Complex **5***			
Bond distances			
Fe–S(1)	2.343(2)	Fe–S(3)	2.327(2)
Fe–N(1)	1.973(4)	Fe–N(2)	1.974(5)
Fe–C(1)	1.763(5)	Fe–C(2)	1.789(8)
Bond angles			
S(1)–Fe–S(3)	170.78(6)	S(1)–Fe–N(1)	87.45(13)
S(1)–Fe–N(2)	91.31(14)	S(1)–Fe–C(1)	91.6(2)
S(1)–Fe–C(2)	88.4(3)	S(3)–Fe–N(1)	84.05(13)
S(3)–Fe–N(2)	90.99(14)	S(3)–Fe–C(1)	97.03(19)
N(1)–Fe–N(2)	81.7(3)	N(1)–Fe–C(1)	177.1(4)

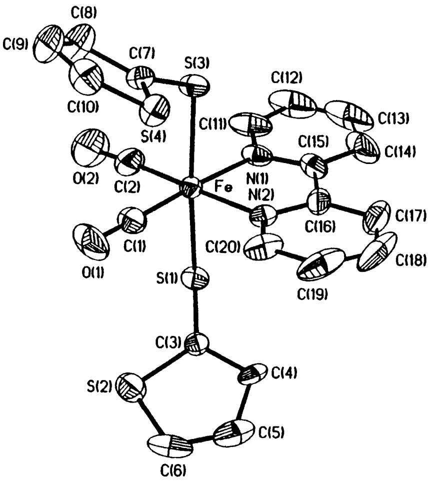


Fig. 4. ORTEP drawing and labeling scheme of *cis*-Fe$(CO)_2(SC_4H_3S)_2$(bipy) (bipy = bipyridine) with thermal ellipsoids drawn at the 30% probability level.

ments. The arrangement of the thiolate substituents is symmetrical so that the Fe–Ni–Fe vector lies on a threefold rotation axis, and the staggered conformation of two parallel triangular thiolate faces promises the best minimization of interactions between the thiolates. The average Fe(II)–S distance of 2.342(1) Å is close to the value of 2.337(3) and 2.350(2) Å in complexes **1** and **2** individually. The average Ni(II)–S bond length of 2.413(1) Å in complex **4** is significantly longer than the terminal Ni(II)–S distances in distorted tetrahedral $[Ni(SPh)_4]^{2-}$ (average 2.281(1) Å) (Table 2) [16]. Also, the Fe···Ni distances, average 3.121 Å, exclude any direct metal–metal interaction. Obviously, the structure is best described as two tridentate *fac*-$[Fe(CO)_3(SC_4H_2O\text{-}o\text{-}CH_3)_3]^-$ ligands coordinated to Ni(II).

Fig. 4 displays a thermal ellipsoid plot of the neutral complex **5** and selected distances and angles are collected in Table 2. The constraints of the bipyridine ligand generates an angle of 81.21(24)° N(1)–Fe–N(2), enforcing a distortion from an octahedra at the six-coordinate iron site. The Fe(II)–S distances (2.334(2) Å average) are comparable with the terminal Fe(II)–S distances of 2.337(3) and 2.350(2) Å in complexes **1** and **2** individually.

In summary, the stable *fac*-$[Fe(CO)_3(SR)_3]^-$ complexes have been prepared by reaction of $[HFe(CO)_4]^-$ and diorganyl disulfide (bis(2-benzothiazolyl) disulfide, di(2-thienyl) disulfide, and bis(2-methyl-3-furyl) disulfide) under mild conditions. It is notable that *fac*-$[Fe(CO)_3(SR)_3]^-$ can serve as an effective tridentate metallo ligand for stabilizing the hexacoordinate d^8 Ni(II) core of the heterotrimetallic iron(II)–nickel(II)–iron(II) thiolate complex **4**, and can also be employed as an intermetal thiolate ligand-transfer reagent to synthesize complex **5**. Also, the reaction of 2-aminophenyl disulfide with $[HFe(CO)_4]^-$ affords the neutral monomeric compound **6**, *cis*-$Fe(CO)_2(\text{–}SC_6H_4\text{-}o\text{-}NH_2\text{–})_2$, the result is consistent with the S, NH_2-chelating $[\text{–}SC_6H_4\text{-}o\text{-}NH_2\text{–}]$ ligand enhancing the stability of iron in the higher oxidation state (Fe(II) state). The reactivity and stability of iron thiolate derivatives may be tailored by pendant ligand selection, and the reaction pathway is tailored according to the bond strength inherent in the organodisulfides and to the nucleophilicity of thiolate atoms in $[RSFe(CO)_4]^-$ complexes.

3. Experimental

Manipulations, reactions, and transfers of samples were conducted under nitrogen according to standard Schlenk techniques or in a glove-box (argon gas). Solvents were distilled under nitrogen from appropriate drying agents (diethyl ether from CaH_2; acetonitrile from CaH_2–P_2O_5; methylene chloride from P_2O_5; hexane and tetrahydrofuran (THF) from sodium–benzophenone) and stored in dried, N_2-filled flasks over 4 Å molecular sieves. A nitrogen purge was used on these solvents before use and transfers to reaction vessels were via stainless-steel cannula under N_2 at a positive pressure. The reagents 2-aminophenyl disulfide, bis(2-benzothiazolyl) disulfide, di(2-thienyl) disulfide, and bis(2-methyl-3-furyl) disulfide, bis(triphenylphosphoranylidene)ammonium chloride (Lancaster/Aldrich) were used as received. IR spectra were recorded in a spectrometer (Bio-Rad FTS-185) with sealed solution cells (0.1 mm) and KBr windows. NMR spectra in a Bruker AC 200 spectrometer, ^1H and ^{13}C chemical shifts being relative to tetramethylsilane and UV–Vis spectra in a GBC 918 spectrophotometer. Analyses of carbon, hydrogen and nitrogen were obtained with a CHN analyzer (Heraeus).

3.1. Preparation of *fac*-$[Et_4N][Fe(CO)_3(SC_7H_4SN)_3]$ (**1**) (*fac*-$[PPN][Fe(CO)_3(SC_4H_3S)_3]$ (**2**), *fac*-$[PPN][Fe(CO)_3(SC_4H_2O\text{-}o\text{-}CH_3)_3]$ (**3**))

The compound $[PPN][HFe(CO)_4]$ (0.2 mmol, 0.142 g) or $[Et_4N][HFe(CO)_4]$ (0.2 mmol, 0.06 g) [17] was loaded into a 50-ml Schlenk flask with 0.133 g (0.4 mmol) of bis(2-benzothiazolyl) disulfide (0.092 g (0.4 mmol) of di(2-thienyl) disulfide; 76 μl (0.4 mmol) of bis(2-methyl-3-furyl) disulfide), and 5 ml of THF was added. The reaction mixture was stirred at ambient temperature for 20 min, after which 10 ml of hexane was added. The reaction mixture was filtered, and the orange solid was dried under vacuum to afford the pure product in quantitative yield (0.070 g, 46% for **1**; 0.111 g, 53% for **2**). X-ray quality crystals were obtained by diffusion of hexane into a THF solution of complexes **1** and **2** individually at −15 °C for 4 weeks. Complex **1**: IR (THF, cm^{-1}): ν(CO) 2083 (vs) 2035 (s, br). ^1H NMR (C_4D_8O, δ ppm): 6.97 (t), 7.12 (t) (C_7H_4SN). Absorption spectrum: λ_{max} (nm) (ε, $M^{-1}\,cm^{-1}$) (THF): 393 (2352), 383 (2392). *Anal.* Found: C, 61.77; H, 4.24; N, 4.40. Calc. for $C_{32}H_{32}O_3N_4S_6Fe$: C, 61.21; H, 4.08; N, 4.76%. Complex **2**: IR (THF, cm^{-1}): ν(CO) 2053 (vs), 1994 (s, br). ^1H NMR (C_4D_8O, δ ppm): 7.04 (d), 6.83 (d), 6.65 (t) ($S–C_4H_3S$). ^{13}C NMR (C_4D_8O, δ ppm): 209.47 (CO). Absorption spectrum: λ_{max} (nm) (ε, $M^{-1}\,cm^{-1}$) (THF): 467 (1250), 340 (9378). *Anal.* Found: C, 59.74; H, 3.94; N, 1.30. Calc. for $C_{51}H_{39}O_3P_2S_6NFe$: C, 59.82; H, 3.84; N, 1.37%. Complex **3** (isolated as the dark brown oily product): IR (CH_3CN, cm^{-1}): ν(CO) 2049 (vs), 1987 (s, br). ^1H NMR (C_4D_8O, δ ppm): 2.31 (s), 6.34 (br), 6.97 (br) (SC_4H_2O-*o*-CH_3).

Caution: Perchlorate salts of metal complexes with organic ligands are potentially explosive; only small amounts of material should be prepared and handled with great caution.

3.2. Preparation of $[(CO)_3Fe(SC_4H_2O\text{-}o\text{-}CH_3)_3Ni\text{-}(SC_4H_2O\text{-}o\text{-}CH_3)_3Fe(CO)_3]$ (**4**)

A solution containing $[PPN][HFe(CO)_4]$ (1 mmol, 0.71 g), bis(2-methyl-3-furyl) disulfide (2 mmol, 0.378 ml), and $Ni(ClO_4)_2{\cdot}6H_2O$ (0.5 mmol, 0.146 g) in acetonitrile (10 ml) was stirred under nitrogen atmosphere at ambient temperature for 1 h. A brown solution accompanied by a dark brown solid was formed. The mother-liquor was removed under a positive pressure of N_2 and the dark brown solid was washed twice with CH_3CN. Tetrahydrofuran was added to extract the product, and then hexane was slowly added to precipitate a dark brown solid (yield 0.330 g, 64%). The crystals, suitable for X-ray crystallography, were recrystallized by vapor diffusion of hexane into a concentrated THF solution at −15 °C. IR (THF, cm^{-1}): ν(CO) 2076 (vs), 2023 (vs). ^1H NMR (CD_2Cl_2, δ ppm): 33.19 (br), 4.11 (br), 0.34 (br) (SC_4H_2O-*o*-CH_3). Absorption spectrum: λ_{max} (nm) (ε, $M^{-1}\,cm^{-1}$) (THF): 390 (23 376), 477 (234 751). *Anal.* Found: C, 42.89; H, 2.88. Calc. for $C_{36}H_{30}O_{12}Fe_2S_6Ni$: C, 42.50; H, 2.97%.

3.3. Preparation of *cis*-$[Fe(CO)_2(SC_4H_3S)_2(bipy)]$ (bipy = bipyridine) (**5**)

A solution containing *fac*-$[PPN][Fe(CO)_3(SC_4H_3S)_3]$ (0.410 g, 0.4 mmol) in CH_3CN (5 ml) was added to a mixture of bipyridine (0.094 g, 0.6 mmol) and $Fe(NO_3)_2{\cdot}6H_2O$ (0.073 g, 0.2 mmol) (or $Fe(ClO_4)_2{\cdot}6H_2O$) in THF (5 ml). After stirring overnight at room temperature (r.t.) the solvent was removed under reduced pressure. The residue was dissolved in THF (10 ml) under N_2, and the dark red–brown solution filtered to remove $[PPN][ClO_4]$. The filtrate (THF) was concentrated under vacuum and then hexane was slowly added to precipitate a dark brown solid (yield 78%). The crystals, suitable for X-ray crystallography, were recrystallized by vapor diffusion of hexane into a concentrated THF solution of complex **5** at −15 °C. IR (THF, cm^{-1}): ν(CO) 2024 (s), 1979 (s). ^1H NMR (C_4D_8O, δ ppm): 9.15 (d), 8.18 (d), 7.97 (t), 7.52 (t), 6.78 (d), 6.41 (t), 6.05 (d) (SC_4H_3S). ^{13}C NMR (C_4D_8O, δ ppm): 153.82, 138.32, 133.69, 127.38, 127.24, 126.56, 123.41 (SC_4H_3S, phen). Absorption spectrum: λ_{max} (nm) (ε, $M^{-1}\,cm^{-1}$) (THF): 322 (22 711). *Anal.* Found: C, 48.19; H, 2.83; N, 5.62. Calc. for $C_{20}H_{14}O_2N_2S_4Fe$: C, 48.13; H, 3.00; N, 5.48%.

3.4. Preparation of *cis*-$[Fe(CO)_2(–SC_6H_4\text{-}o\text{-}NH_2–)_2]$ (**6**)

$[PPN][HFe(CO)_4]$ (0.2 mmol, 0.142 g) [17] was added to 2-aminophenyl disulfide (0.4 mmol, 0.100 g) in THF (8 ml) at ambient temperature. After 12 h of stirring at r.t., hexane (8 ml) was added into the solution. The red–brown solution was then filtered to remove $[PPN][SC_6H_4$-*o*-$NH_2]$. The filtrate was stored at −15 °C for 4 weeks to induce precipitation of dark red brown crystals of the known *cis*-$[Fe(CO)_2(–SC_6H_4$-*o*-$NH_2–)_2]$, identified by IR, and X-ray crystallography [14]. IR (THF, cm^{-1}): ν(CO) 2027 (s), 1971 (s). *Anal.* Found: C, 47.10; H, 2.31; N, 7.99. Calc. for $C_{14}H_{12}O_2N_2S_2Fe$: C, 47.21; H, 2.26; N, 7.86%.

4. Crystallography

Crystallographic data of complexes **1**, **2**, **4** and **5** are summarized in Tables 3 and 4, and as supporting information (see Section 5). The crystals of **1**, **2**, **4** and **5** are chunky. The crystals of **1**, **2**, **4**, **5** chosen for X-ray diffraction studies measured 0.36 × 0.24 × 0.20 mm, 0.30 × 0.25 × 0.05 mm, 0.15 × 0.15 × 0.10 mm, and

Table 3
Crystallographic data and structure refinements parameters for complexes **1** and **2**

	1	**2**
Empirical formula	$C_{32}H_{32}O_3N_4S_6Fe$	$C_{51}H_{39}NO_3P_2S_6Fe$
Formula weight	768.83	1023.98
Crystal system	trigonal	monoclinic
Temperature (K)	150(1)	295(2)
Space group	$P31c$	$P2_1$
λ (Å) (Mo Kα)	0.7107	0.7107
Unit cell dimensions		
a (Å)	12.9022(1)	9.7591(2)
b (Å)	12.9022(1)	26.0605(4)
c (Å)	24.9774(5)	9.8472(2)
α (°)	90	90
β (°)	90	97.187(1)
γ (°)	120	90
V (Å^3)	3600.85(8)	2484.73(8)
Z	4	2
D_{calc} (g cm^{-3})	1.418	1.369
μ (cm^{-1})	8.05	6.62
R [a]	0.0994	0.0451
R_{WF^2} [b]	0.2760	0.0881
Goodness-of-fit on F^2	1.053	0.948

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.
[b] $R_{WF^2} = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table 4
Crystallographic data and structure refinements parameters for complexes **4** and **5**

	4	**5**
Empirical formula	$C_{36}H_{30}O_{12}NiS_6Fe_2$	$C_{20}H_{14}O_2N_2S_4Fe$
Formula weight	1017.37	498.43
Crystal system	rhombohedral	monoclinic
Temperature (K)	150(1)	295(2)
Space group	$R3$	$P2_1$
λ (Å) (Mo Kα)	0.7107	0.7107
Unit cell dimensions		
a (Å)	18.0122(4)	10.747(3)
b (Å)	18.0122(4)	10.573(3)
c (Å)	11.3103(4)	10.837(3)
α (°)	90	90
β (°)	90	119.21(2)
γ (°)	120	90
V (Å^3)	3177.9(2)	1074.8(5)
Z	3	2
D_{calc} (g cm^{-3})	1.595	1.540
μ (cm^{-1})	14.69	11.09
R [a]	0.0577	0.0447
R_{WF^2} [b]	0.1538	0.1194
Goodness-of-fit on F^2	1.038	1.076

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.
[b] $R_{WF^2} = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

0.60 × 0.60 × 0.40 mm, respectively. Each crystal was mounted on a glass fiber. Unit-cell parameters for complex **5** were obtained by the least-square refinement from 25 reflections with 2θ between 17.26 and 28.00°. Least-squares refinement of the positional and anisotropic thermal parameters for all non-hydrogen atoms and fixed hydrogen atoms contribution was based on F^2. Diffraction measurements were carried out in a Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation [18]. A φ scan absorption correction was made. The SHELXTL package of programs was employed for structure solution and refinement [19]. In complex **5** (Fig. 4), the positions of S(4) and C(8) atoms are disordered (50%). Diffraction measurements for complexes **1**, **2** and **4** were carried out in a Siemens SMART CCD diffractometer with graphite-monochromated Mo Kα radiation (λ 0.7107 Å) and θ between 1.63 and 26.37° for complex **1**, between 1.56 and 26.37° for complex **2**, and between 2.22 and 27.50° for complex **4**. Least-squares refinement of the positional and anisotropic thermal parameters for all non-hydrogen atoms and fixed hydrogen atoms contribution was based on F^2. A SADABS [20] absorption correction was made. The SHELXTL [19] structure refinement program was employed. In complex **2** (Fig. 2), the positions of S(2) and C(5) atoms are disordered (50%).

5. Supplementary material

Tables of crystal data and experimental conditions for the X-ray studies, atomic coordinates and B_{eq} values, complete listings of bond lengths and bond angles, and anisotropic temperature factors for *fac*-$[Et_4N][Fe(CO)_3(S{-}C_7H_4SN)_3]$, *fac*-$[PPN][Fe(CO)_3(S{-}C_4H_3S)_3]$, $(CO)_3Fe(SC_4H_2O$-*o*-$CH_3)_3Ni(SC_4H_2O$-*o*-$CH_3)_3Fe(CO)_3$, and *cis*-$[Fe(CO)_2(SC_4H_3S)_2(bipy)]$. This material is available free of charge at the CSD.

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