Transition metal complexes with sulfur ligands CIV.☆ Protonation and alkylation of thiolate donors of [Fe(CO)₂('S₄')] and [Fe(CO)('S₅')]: syntheses and properties of Fe(II) complexes with open-chain thioether ligands ('S₄'²⁻ = 1,2-bis(2-mercaptophenylthio)ethane(2−); 'S₅'²⁻ = 2,2'-bis(2-mercapto-phenylthio)diethylsulfide(2−))

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Abstract

[Fe(CO)₂('S₄')] and [Fe(CO)('S₅')] could be reversibly protonated in two steps by strong acids such as CF₃SO₃H yielding species whose ν(CO) bands are shifted to higher wavenumbers by ∼40 cm⁻¹ per equivalent of acid. The ν(CO) shifts are explained by protonation of the thiolate donors leading to a decrease of electron density at the metal centers and consecutive weakening of Fe–CO π backbonds. While the protonated species could be detected in solution only, analogous isoelectronic complexes which are alkylated at the thiolate donors were isolated and fully characterized spectroscopically and by X-ray structure analyses. Upon reaction with one or two equivalents of oxonium salts R₃OBF₄ (R = Me, Et), [Fe(CO)₂('S₄')] yielded [Fe(CO)₂(R-'S₄')]BF₄ (R = Me: [1a]BF₄, R = Et: [1b]BF₄) and [Fe(CO)₂(R₂-'S₄')](BF₄)₂ (R = Me: [3a](BF₄)₂, R = Et: [3b](BF₄)₂). In an analogous way, [Fe(CO)('S₅')] yielded [Fe(CO)(R-'S₅')]BF₄ (R = Me: [2a]BF₄, R = Et: [2b]BF₄) and [Fe(CO)(R₂-'S₅')](BF₄)₂ (R = Et: [5](BF₄)₂). The 'asymmetrically' alkylated [Fe(CO)₂(Me-'S₄'-Et)](BF₄)₂, [4](BF₄)₂, was obtained by reacting [Fe(CO)₂('S₄')] first with Me₃OBF₄ and subsequently with Et₃OBF₄. Further complexes obtained by alkylation were [Fe(CO)(Bz-'S₅')]PF₆ ([2c]PF₆), containing the benzylated 'S₅' ligand, [Fe(CO)(I)(Me₂-'S₄')]FeI₄ ([6]FeI₄) and [Fe(I)₂(Me₂-'S₄')] (7). Except 7, all Fe(II) complexes are diamagnetic containing low-spin Fe(II) centers. Per step of alkylation, the ν(CO) frequencies are raised by ∼40 cm⁻¹ in the case of [Fe(CO)₂('S₄')] and by ∼32 cm⁻¹ in case of [Fe(CO)('S₅')]. These ν(CO) shifts are explained in the same way as for the protonated species and corroborate the assumption that protonation takes place at the thiolate donors. X-ray structure determinations were carried out for [1b]BF₄, [3a](BF₄)₂, [3b](BF₄)₂, [5](BF₄)₂, [6]FeI₄ and 7. Although the ν(CO) shifts indicate large differences of the electron densities at the iron centers, in a remarkable way the average Fe–S distances of ∼228 pm remain practically invariant in all low-spin Fe(II) complexes regardless of the charge or the degree of alkylation. This is traced back to the transformation of Fe–S(thiolate) σ-donor bonds into Fe–S(thioether) σ-donor–π-acceptor bonds upon alkylation. This lowers the electron densities at the iron centers but leaves Fe–S distances unchanged because weakening of the σ bonds is compensated by the formation of additional π-acceptor bonds. The mono- and dialkylated complexes hydrolyze much more rapidly than the neutral parent complexes and allow the facile synthesis of the corresponding sulfur ligands in the free state. The complexes further prove that 3d metals can form stable complexes not only with crown thioethers but also with open chain thioethers. Correlation of states of protonation of iron sulfur ligand complexes with electron densities at the metal center and expected redox potentials allows the hypothesis to be made that reducing the N₂ molecule at either Fe–S or Mo–S sites of the cofactor in nitrogenases requires previous protonation of the S donors.

Keywords: Crystal structures; Protonation; Alkylation; Iron complexes; Thioether complexes; Carbonyl complexes

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1. Introduction

Activation and subsequent conversion of substrates by oxidoreductases with metal–sulfur centers usually require transfer of electrons *and* protons, e.g. the reduction of N_2 to NH_3 catalyzed by nitrogenases according to Eq. (1) [2]. The sulfur donors in the

$$N_2 + 8H^+ + 8e^- \longrightarrow 2NH_3 + H_2 \qquad (1)$$
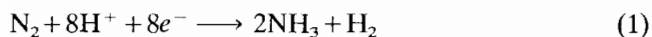
metal–sulfur centers belong to cysteine and methionine groups of the protein or are sulfide anions [3]. When coordinated, all these donors can still have remaining lone pairs of electrons. Two questions arise in this context. Can the sulfur donors function as Brönsted bases and become protonated in order to allow a sterically controlled transfer of protons, and equally important, how do such protonations influence the electronic situation at the metal centers?

Isolable complexes with RSH, H_2S or HS^- ligands are rare and could structurally be characterized only in a few cases [4]. We have tried to obtain such complexes having RSH ligands via protonation of $[Fe(CO)_2('S_4')]$ [5] and $[Fe(CO)('S_5')]$ [6].

$[Fe(CO)_2('S_4')]$ $[Fe(CO)('S_5')]$
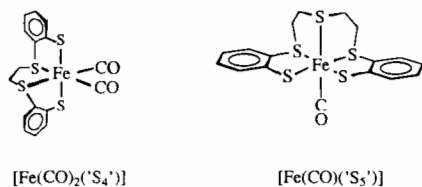
IR spectroscopically, reactions of these compounds with CF_3SO_3H or HBF_4 could be detected, but isolation of the protonated species failed. Analogous alkylations, however, gave isolable complexes.

2. Experimental

2.1. General

Unless otherwise noted, all operations were carried out in dried solvents under N_2 using Schlenk techniques at standard conditions. As far as possible, reactions were monitored by IR spectroscopy. Solution IR spectra were recorded in CaF_2 cuvettes with compensation of the solvent absorptions. The following spectrometers were used: Perkin Elmer infrared spectrophotometer 983, Perkin Elmer infrared spectrophotometer 1600 FT, Jeol JNM-GX 270 FT NMR spectrometer and Varian MAT 212 mass spectrometer. $[Fe(CO)_2('S_4')]$ [5] and $[Fe(CO)('S_5')]$ [6] were prepared as described in the literature.

2.2. Syntheses and reactions

2.2.1. Reactions of $[Fe(CO)_2('S_4')]$ and $[Fe(CO)('S_5')]$ with CF_3SO_3H or HBF_4; IR spectra

0.1 ml (1.1 mmol) of CF_3SO_3H was added to a strawberry red solution of 420 mg (1.0 mmol) of $[Fe(CO)_2('S_4')]$ in 25 ml of CH_2Cl_2 ($\nu(CO) = 2049$, 2004 cm^{-1}). The solution immediately changed color to reddish violet and the $\nu(CO)$ bands shifted to 2081 and 2044 cm^{-1}. Addition of a second equivalent of CF_3SO_3H yielded an orange solution exhibiting $\nu(CO)$ bands at 2118 and 2089 cm^{-1}, and oily drops of the product separated from the reaction solution to some degree. Subsequent addition of 1 ml of H_2O and stirring yielded again a strawberry red solution of $[Fe(CO)_2('S_4')]$ exhibiting $\nu(CO)$ bands at 2049 and 2004 cm^{-1}.

In the same way, a suspension of $[Fe(CO)('S_5')]$ in CH_2Cl_2 was protonated. The reaction took place in a fully analogous manner and showed a shift of the $\nu(CO)$ band of $[Fe(CO)('S_5')]$ from 1978 cm^{-1} via 2016 cm^{-1} ($+1CF_3SO_3H$) to 2059 cm^{-1} ($+2CF_3SO_3H$). Subsequent addition of water led to regeneration of the $\nu(CO)$ band of the starting material at 1978 cm^{-1}.

2.2.2. Reaction of $[Fe(CO)_2('S_4')]$ with HBF_4

0.14 ml (1.0 mmol) of HBF_4 (54% in Et_2O) was added to a solution of $[Fe(CO)_2('S_4')]$ (420 mg, 1.0 mmol). The color of the solution immediately deepened from strawberry red to reddish violet. After 20 min, the reaction mixture was evaporated to dryness yielding a viscous, deep red residue which was stirred with 50 ml of Et_2O for 1 h, separated and dried. The resulting red powder was identified as $[Fe(CO)_2('S_4')]$. Yield 410 mg (98%). *Anal.* Calc. for $C_{16}H_{12}FeO_2S_4$ (420.38): C, 45.72; H, 2.88. Found: C, 45.59; H, 2.55%. IR (cm^{-1}): 2040, 1988, vs, $\nu(CO)$. [^1]H NMR, CD_2Cl_2, δ (ppm): 2.45, 3.35 (m, C_2H_4, 4); 7.0–7.6 (m, C_6H_4, 8).

2.2.3. Alkylations
2.2.3.1. $[Fe(CO)_2(Me-'S_4')]BF_4$ ($[Ia]BF_4$)

5.23 g (35.30 mmol) of Me_3OBF_4 were added to a suspension of 14.82 g (35.25 mmol) of $[Fe(CO)_2('S_4')]$ in 85 ml of CH_2Cl_2. The mixture was stirred for 2 h in the course of which a nearly clear and deep red solution formed. The solution was filtered and evaporated to dryness yielding a reddish brown residue which was stirred with 150 ml of Et_2O for 10 h, separated, washed with 50 ml of Et_2O, and dried in vacuo. Yield 14.750 g (80%). *Anal.* Calc. for $C_{17}H_{15}BF_4FeO_2S_4$ (522.22): C, 39.10; H, 2.90; S, 24.56. Found: C, 39.52; H, 3.03; S, 24.84%. M^+: $m/e = 435$ (FD), $[Fe(CO)_2(Me-'S_4')]^+$. IR (cm^{-1}): 2075, 2024, vs, $\nu(CO)$; 1056, vs, br, $\nu(BF_4)$. [^1]H NMR, CD_2Cl_2, δ (ppm): 2.0–3.9 (m, C_2H_4, 4); 2.9 (s, CH_3, 3); 7.0–8.0 (m, C_6H_4, 8). $^{13}C\{^1H\}$ NMR, CD_2Cl_2, δ (ppm): 28.6 (CH_3); 43.1, 44.8 (C_2H_4); 125.8,

126.7, 130.3, 131.2, 131.8, 132.1, 132.2, 133.9, 133.2, 133.3, 138.6, 152.4 (C$_6$H$_4$); 204.1, 204.6 (CO).

2.2.3.2. [Fe(CO)$_2$(Et-'S$_4$')]BF$_4$ ([1b]BF$_4$)

950 mg (5.0 mmol) of Et$_3$OBF$_4$ were added to a stirred solution of 2100 mg (5.0 mmol) of [Fe(CO)$_2$('S$_4$')] in 50 ml of CH$_2$Cl$_2$. The color of the solution deepened from red to reddish violet, and microcrystals began precipitating after ~1 h. In order to complete precipitation, the solution was reduced to approx. one half in volume and layered with 25 ml of Et$_2$O. The precipitated crystals were separated after 1 day, washed with 5 ml of cold CH$_2$Cl$_2$, and dried in vacuo. Yield 2545 mg (93%). [Fe(CO)$_2$(Et-'S$_4$')]BF$_4$ crystallizes as [Fe(CO)$_2$(Et-'S$_4$')]BF$_4$·1.5CH$_2$Cl$_2$. The solvate CH$_2$Cl$_2$ could be removed by carefully pulverizing the crystals and drying the powder in vacuo for 24 h. *Anal.* Calc. for C$_{18}$H$_{17}$BF$_4$FeO$_2$S$_4$ (536.25): C, 40.32; H, 3.20; S, 23.92. Found: C, 40.05; H, 3.17; S, 23.92%. M^+: m/e = 449 (FD), [Fe(CO)$_2$(Et-'S$_4$')]$^+$. IR (cm^{-1}): 2074, 2024, vs, ν(CO); 1065, br, vs, ν(BF$_4$).

2.2.3.3. [Fe(CO)(Me-'S$_5$')]BF$_4$ ([2a]BF$_4$)

150 mg (1.0 mmol) of Me$_3$OBF$_4$ were added to a stirred suspension of 450 mg (1.0 mmol) of [Fe(CO)('S$_5$')] in 30 ml of CH$_2$Cl$_2$. The resulting deep red solution was filtered after 2 h and evaporated to dryness. The reddish brown residue was stirred with 100 ml of Et$_2$O for 4 h, separated, washed with ~100 ml of Et$_2$O, and dried in vacuo. Yield 515 mg (93%). *Anal.* Calc. for C$_{18}$H$_{19}$BF$_4$FeOS$_5$ (554.33): C, 39.00; H, 3.45; S, 28.92. Found: C, 39.34; H, 3.62; S, 28.45%. M^+: m/e = 467 (FD), [Fe(CO)(Me-'S$_5$')]$^+$. IR (cm^{-1}): 1989, vs, ν(CO); 1058, br, vs, ν(BF$_4$). ^{1}H NMR, CD$_2$Cl$_2$, δ (ppm): 2.1–3.7 (m, C$_2$H$_4$, 8); 2.9 (s, CH$_3$, 3); 7.0–8.0 (m, C$_6$H$_4$, 8). ^{13}C{^{1}H} NMR, CD$_2$Cl$_2$, δ (ppm): 26.6 (CH$_3$); 36.3, 37.0, 49.7, 50.6 (C$_2$H$_4$); 124.7, 130.3, 130.5, 131.3, 131.6, 131.7, 132.3, 132.6, 133.2, 133.7, 139.3, 152.8 (C$_6$H$_4$); 211.0 (CO).

2.2.3.4. [Fe(CO)(Et-'S$_5$')]BF$_4$ ([2b]BF$_4$)

380 mg (2.0 mmol) of Et$_3$OBF$_4$ were added to a stirred suspension of 900 mg (2.0 mmol) of [Fe(CO)('S$_5$')] in 50 ml of CH$_2$Cl$_2$. The mixture became a nearly clear and deep red solution which was filtered after 1 h and reduced in volume to 10 ml. 100 ml of cold Et$_2$O were added at −78 °C, the resulting brown precipitate of [Fe(CO)(Et-'S$_5$')]BF$_4$ was separated, rinsed twice with 100 ml of Et$_2$O, and dried in vacuo. Yield 1080 mg (95%). *Anal.* Calc. for C$_{19}$H$_{21}$BF$_4$FeOS$_5$ (568.36): C, 40.15; H, 3.72; S, 28.21. Found: C, 40.43; H, 3.62; S, 28.08%. IR (cm^{-1}): 1987, vs, ν(CO); 1060, br, vs, ν(BF$_4$).

2.2.3.5. [Fe(CO)(Bz-'S$_5$')]PF$_6$ ([2c]PF$_6$)

0.3 ml (2.5 mmol) of C$_6$H$_5$CH$_2$Br and 330 mg (2.0 mmol) of NH$_4$PF$_6$ were added to a suspension of 900 mg (2.0 mmol) of [Fe(CO)('S$_5$')] in 50 ml of CH$_2$Cl$_2$ and stirred for 12 h. Precipitating NH$_4$Br was filtered off, and the deep red filtrate was evaporated to dryness. The resulting reddish brown residue was dissolved in 10 ml of CH$_2$Cl$_2$, and 100 ml of cold Et$_2$O were added at −78 °C. The precipitate of light brown [Fe(CO)(Bz-'S$_5$')]PF$_6$ was separated, stirred with 100 ml of Et$_2$O for 10 h, washed with 150 ml of Et$_2$O, and dried in vacuo. Yield 1270 mg (92%). *Anal.* Calc. for C$_{24}$H$_{23}$F$_6$FeOPS$_5$ (688.59): C, 41.86; H, 3.37; S, 23.28. Found: C, 41.89; H, 3.40; S, 23.54%. IR (cm^{-1}): 1983, vs, ν(CO); 839, vs, ν(PF$_6$).

2.2.3.6. [Fe(CO)$_2$(Me$_2$-'S$_4$')](BF$_4$)$_2$ ([3a](BF$_4$)$_2$)

600 mg (4.0 mmol) of Me$_3$OBF$_4$ were added to a stirred solution of 840 mg (2.0 mmol) of [Fe(CO)$_2$('S$_4$')] in 50 ml of CH$_2$Cl$_2$. The yellow precipitate that formed was separated after 12 h, washed with 50 ml of CH$_2$Cl$_2$, and recrystallized from a saturated CH$_3$CN solution, which was layered with the same amount of Et$_2$O. Yield 1035 mg (83%). *Anal.* Calc. for C$_{18}$H$_{18}$B$_2$F$_8$FeO$_2$S$_4$ (624.06): C, 34.64; H, 2.91; S, 20.55. Found: C, 34.63; H, 2.92; S, 20.34%. IR (cm^{-1}): 2108, 2074, vs, ν(CO); 1054, br, vs, ν(BF$_4$). ^{1}H NMR, acetone-d$_6$, δ (ppm): 3.0, 4.3 (m, C$_2$H$_4$, 4); 3.45 (s, CH$_3$, 6); 7.75–8.5 (m, C$_6$H$_4$, 8).

2.2.3.7. [Fe(CO)$_2$(Et$_2$-'S$_4$')](BF$_4$)$_2$ ([3b](BF$_4$)$_2$)

760 mg (4.0 mmol) of Et$_3$OBF$_4$ were added to a stirred solution of 840 mg (2.0 mmol) of [Fe(CO)$_2$('S$_4$')] in 50 ml of CH$_2$Cl$_2$. The resulting yellow precipitate was separated after 10 h, washed with 30 ml of CH$_2$Cl$_2$, and recrystallized from a saturated CH$_3$CN solution which was layered with the same amount of Et$_2$O. Yield 1135 mg (87%). *Anal.* Calc. for C$_{20}$H$_{22}$B$_2$F$_8$FeO$_2$S$_4$ (652.11): C, 36.84; H, 3.40; S, 19.69. Found: C, 36.76; H, 3.38; S, 19.68%. IR (cm^{-1}): 2108, 2073, vs, ν(CO); 1057, br, vs, ν(BF$_4$). ^{1}H NMR, CD$_3$CN, δ (ppm): 1.6 (t, CH$_3$CH$_2$, 6); 2.5 (m, C$_2$H$_4$, 2); 3.5 (q, CH$_3$CH$_2$, 4); 3.8 (m, C$_2$H$_4$, 2); 7.8–8.2 (m, C$_6$H$_4$, 8). ^{13}C{^{1}H} NMR, CD$_3$CN, δ (ppm): 13.5 (CH$_3$CH$_2$); 41.3 (CH$_3$CH$_2$); 45.1 (C$_2$H$_4$); 129.6, 132.8, 133.9, 134.2, 134.6, 136.6 (C$_6$H$_4$); 200.8 (CO).

2.2.3.8. [Fe(CO)$_2$(Me-'S$_4$'-Et)](BF$_4$)$_2$ ([4](BF$_4$)$_2$)

300 mg (2.0 mmol) of Me$_3$OBF$_4$ were added to a stirred solution of 840 mg (2.0 mmol) of [Fe(CO)$_2$('S$_4$')] in 50 ml of CH$_2$Cl$_2$. After 1 h, 380 mg (2.0 mmol) of Et$_3$OBF$_4$ were added to the reddish violet solution, whereupon a yellow precipitate separated. It was filtered off after 10 h, washed with 30 ml of CH$_2$Cl$_2$, dried in vacuo, and recrystallized from a saturated CH$_3$CN solution which was layered with a tenfold amount of

Et_2O. Yield 930 mg (73%). Anal. Calc. for $C_{19}H_{20}B_2F_8FeO_2S_4$ (638.09): C, 35.76; H, 3.16; S, 20.10. Found: C, 35.75; H, 3.35; S, 19.76%. IR (cm^{-1}): 2108, 2073, vs, ν(CO); 1057, br, vs, ν(BF$_4$).

2.2.3.9. [Fe(CO)(Et$_2$-'S$_5$')](BF$_4$)$_2$ ([5](BF$_4$)$_2$)

760 mg (4.0 mmol) of Et_3OBF_4 were added to a stirred suspension of 900 mg (2.0 mmol) of [Fe(CO)('S$_5$')] in 50 ml of CH$_2$Cl$_2$, whereupon the color of the suspension changed from red to orange. 100 ml of Et$_2$O were added to the mixture, which was cooled to −78 °C, the solid material was separated, washed with 100 ml of Et$_2$O, and recrystallized from a saturated C$_2$H$_5$NO$_2$ solution which was layered with the same amount of Et$_2$O. Yield 1050 mg (77%). Anal. Calc. for $C_{21}H_{26}B_2F_8FeOS_5$ (684.22): C, 36.86; H, 3.83; S, 23.43. Found: C, 37.01; H, 3.90; S, 23.43%. IR (cm^{-1}): 2022, vs, ν(CO); 1062, br, vs, ν(BF$_4$).

2.2.3.10. [Fe(I)(CO)(Me$_2$-'S$_4$')]FeI$_4$ ([6]FeI$_4$)

5.0 ml (80 mmol) of CH$_3$I were added to a solution of 2100 mg (5.0 mmol) of [Fe(CO)$_2$('S$_4$')] in 100 ml of CH$_2$Cl$_2$. The mixture was stirred for 7 days, in the course of which the color changed from red to dark violet and some yellow precipitate formed. The mixture was filtered, and the dark violet filtrate was reduced in volume to ~5 ml. Precipitating black microcrystalline [Fe(I)(CO)(Me$_2$-'S$_4$')]FeI$_4$ was separated, washed with 75 ml of Et$_2$O, and dried in vacuo. Yield 1725 mg (62%). Anal. Calc. for $C_{17}H_{18}Fe_2I_5OS_4$ (1112.81): C, 18.35; H, 1.63. Found: C, 18.05; H, 1.38%. IR, CsI (cm^{-1}): 1996, vs, ν(CO); 235, s, ν(FeI$_4$).

2.2.3.11. [Fe(I)$_2$(Me$_2$-'S$_4$')] (7)

Small amounts of light brown single crystals of [Fe(I)$_2$(Me$_2$-'S$_4$')] (7) precipitated from the mother liquor of [6]FeI$_4$ after 10 days. They were separated and characterized by X-ray structure spectroscopy. Yield 50 mg (2%).

2.2.3.12. Me-'S$_4$'-H (8a)

A mixture of 3110 mg (6.0 mmol) of [1a]BF$_4$ and 3.0 ml (36 mmol) of 12 N HCl in 75 ml of CH$_2$Cl$_2$ was heated to reflux for 16 h, in the course of which the color changed from reddish violet to light yellow. The solution was filtered over Na$_2$SO$_4$, and the Na$_2$SO$_4$ was washed with 25 ml of CH$_2$Cl$_2$. The collected filtrates were evaporated to dryness leading to a light violet residue that was washed with 40 ml of CH$_3$OH and dried in vacuo to give 8a as a white powder. Yield 1090 mg (56%). Anal. Calc. for $C_{15}H_{16}S_4$ (324.56): C, 55.51; H, 4.97. Found: C, 55.80; H, 5.09%. M^+, m/e = 324 (FD). IR (cm^{-1}): 2550, vw, ν(SH). ^{1}H NMR, CD$_2$Cl$_2$, δ (ppm): 2.4 (s, CH$_3$, 3); 3.0 (s, C$_2$H$_4$, 4); 4.2 (s, SH, 1); 7.0–7.3 (m, C$_6$H$_4$, 8). ^{13}C{^{1}H} NMR, CD$_2$Cl$_2$, δ (ppm): 15.8 (CH$_3$); 33.3, 34.0 (C$_2$H$_4$); 125.3, 125.5,

126.2, 128.1, 128.4, 129.5, 131.8, 132.3, 132.5, 133.2, 136.9, 141.9 (C$_6$H$_4$).

2.2.3.13. Et-'S$_4$'-H (8b)

A mixture of 2675 mg (5.0 mmol) of [1b]BF$_4$ and 5.0 ml (60 mmol) of 12 N HCl in 150 ml of CH$_3$OH was heated to reflux for 30 min. The resulting nearly colorless solution was evaporated to dryness, the residue was extracted with 100 ml of CCl$_4$, and the CCl$_4$ extract was filtered over Na$_2$SO$_4$. Solvent removal in vacuo yielded 8b as a pale pink oil. Yield 1285 mg (76%). Anal. Calc. for $C_{16}H_{18}S_4$ (338.58): C, 56.76; H, 5.39. Found: C, 56.85; H, 5.44%. M^+, m/e = 338 (FD). IR, NaCl (cm^{-1}): 2512, m, ν(SH). ^{1}H NMR, CD$_2$Cl$_2$, δ(ppm): 1.4 (t, CH$_3$CH$_2$, 3); 3.0 (q, CH$_3$CH$_2$, 2); 3.1 (s, C$_2$H$_4$, 4); 4.4 (s, SH, 1); 7.1–7.5 (m, C$_6$H$_4$, 8). ^{13}C{^{1}H} NMR, CD$_2$Cl$_2$, δ (ppm): 14.1 (CH$_3$CH$_2$); 27.2 (CH$_3$CH$_2$); 33.0, 34.0 (C$_2$H$_4$); 126.1, 126.2, 127.4, 128.2, 128.4, 129.2, 130.5, 132.2, 133.4, 134.7, 137.1, 139.1 (C$_6$H$_4$).

2.2.3.14. Et-'S$_5$'-H (9)

A mixture of 5680 mg (10.0 mmol) [2b]BF$_4$ and 5.0 ml (60 mmol) of 12 N HCl in 75 ml of CH$_3$OH was heated to reflux for 45 min to give a yellow solution. Solvent removal in vacuo led to a viscous brown oil, which was dried in vacuo at 50 °C and subsequently extracted with 125 ml of CH$_2$Cl$_2$. The CH$_2$Cl$_2$ extract was dried with MgSO$_4$ for 30 min, and filtered over SiO$_2$ (60 mesh). The SiO$_2$ was washed with additional 30 ml of CH$_2$Cl$_2$. The collected filtrates were evaporated in vacuo yielding a colorless oil, which was dried in vacuo for an additional 48 h. Yield 2710 mg (68%). Anal. Calc. for $C_{18}H_{22}S_5$ (398.70): C, 54.23; H, 5.56; S, 40.21. Found: C, 54.43; H, 5.52; S, 40.37%. M^+, m/e = 398 (FD). IR, NaCl (cm^{-1}): 2509, m, ν(SH). ^{1}H NMR, CD$_2$Cl$_2$, δ (ppm): 1.4 (t, CH$_3$CH$_2$, 3); 2.8 (m, C$_2$H$_4$, 4); 3.0 (q, CH$_3$CH$_2$, 2); 3.1 (m, C$_2$H$_4$, 4); 4.4 (s, SH, 1); 7.1–7.5 (m, C$_6$H$_4$, 8). ^{13}C{^{1}H} NMR, CD$_2$Cl$_2$, δ (ppm): 14.1 (CH$_3$CH$_2$); 27.2 (CH$_3$CH$_2$); 31.6, 31.7, 33.8, 34.9 (C$_2$H$_4$); 126.1, 126.3, 127.4, 128.2, 128.5, 129.5, 130.8, 132.4, 133.4, 134.9, 137.1, 139.3 (C$_6$H$_4$).

2.2.3.15. Me-'S$_4$'-Et (10)

A mixture of 640 mg (1.0 mmol) of [4](BF$_4$)$_2$ and 1.0 ml (12.0 mmol) of 12 N HCl in 10 ml of CH$_3$OH was stirred for 30 min. The resulting white precipitate was separated, washed with 15 ml of CH$_3$OH, and dried in vacuo. Yield 235 mg (67%). Anal. Calc. for $C_{17}H_{20}S_4$ (352.61): C, 57.91; H, 5.72; S, 36.38. Found: C, 58.12; H, 5.79; S, 36.50%. M^+, m/e = 352 (FD). ^{1}H NMR, CD$_2$Cl$_2$, δ (ppm): 1.35 (t, CH$_3$CH$_2$, 3); 2.47 (s, CH$_3$, 3H); 2.95 (q, CH$_3$CH$_2$, 2H); 3.12 (s, C$_2$H$_4$, 4); 7.05–7.35 (m, C$_6$H$_4$, 8). ^{13}C{^{1}H} NMR, CD$_2$Cl$_2$, δ (ppm): 14.0 (CH$_3$CH$_2$); 15.8 (CH$_3$); 27.2 (CH$_3$CH$_2$); 32.9, 33.3 (C$_2$H$_4$); 125.3, 125.5, 126.1, 127.3, 128.1, 128.2, 130.5, 132.1, 132.5, 134.8, 139.1, 142.0 (C$_6$H$_4$).

2.3. X-Ray structure analyses of [Fe(CO)$_2$(Et-'S$_4$')]BF$_4$·1.5CH$_2$Cl$_2$ ([1b]BF$_4$·1.5CH$_2$Cl$_2$), [Fe(CO)$_2$-(Me$_2$-'S$_4$')](BF$_4$)$_2$ ([3a](BF$_4$)$_2$), [Fe(CO)$_2$(Et$_2$-'S$_4$')](BF$_4$)$_2$ ([3b](BF$_4$)$_2$), [Fe(CO)(Et$_2$-'S$_5$')](BF$_4$)$_2$ ([5](BF$_4$)$_2$), [Fe(I)(CO)(Me$_2$-'S$_4$')]FeI$_4$·CH$_2$Cl$_2$ ([6]FeI$_4$·CH$_2$Cl$_2$) and [Fe(I)$_2$(Me$_2$-'S$_4$')] (7)

Light brown single crystals of [1b]BF$_4$·1.5CH$_2$Cl$_2$ formed when a saturated CH$_2$Cl$_2$ solution slowly evaporated (~12 h) in an open Erlenmeyer flask. Single crystals of yellow [3a](BF$_4$)$_2$ and [3b](BF$_4$)$_2$ and orange [5](BF$_4$)$_2$ were grown from saturated CH$_3$CN solutions which were layered with a tenfold amount of Et$_2$O. In the course of 14 days, single crystals of black [6]FeI$_4$ and brown 7 formed when CH$_2$Cl$_2$ solutions were kept in Schlenk tubes sealed with rubber stoppers through which CH$_2$Cl$_2$ slowly evaporated.

Suitable single crystals were selected, sealed in glass capillaries, and mounted on the diffractometer. One of the BF$_4^-$ anions of [5](BF$_4$)$_2$ is disordered, exhibits very high temperature coefficients, and was only refined isotropically. An additional semiempiric absorption correction was carried out for [6]FeI$_4$·CH$_2$Cl$_2$. It contains two independent ion pairs in the unit cell and high temperature coefficients as well as non-plausible bond distances of one of the CH$_2$Cl$_2$ molecules. The final difference Fourier analysis pointed to disorder in the respective CH$_2$Cl$_2$ region. Structures were solved by direct methods (SHELXTL-PLUS); non-hydrogen atoms were refined with anisotropic thermal parameters, hydrogen atoms with a common isotropic thermal parameter. Aromatic hydrogen atoms were placed at calculated positions and refined as rigid groups; methyl and methylene hydrogen atoms were placed at ideal tetrahedral positions and allowed to rotate around their central carbon atom during refinement.

Tables 1 and 2 contain selected crystallographic data, fractional atomic coordinates and equivalent thermal parameters of [1b]BF$_4$·1.5CH$_2$Cl$_2$, [3a](BF$_4$)$_2$, [3b](BF$_4$)$_2$, [5](BF$_4$)$_2$, [6]FeI$_4$·CH$_2$Cl$_2$ and 7. See also Supplementary material.

3. Results and discussion

3.1. Protonation of [Fe(CO)$_2$('S$_4$')] and [Fe(CO)('S$_5$')]

Addition of equivalent amounts of acids such as CF$_3$SO$_3$H in CH$_2$Cl$_2$ or HBF$_4$ in Et$_2$O to CH$_2$Cl$_2$ solutions of [Fe(CO)$_2$('S$_4$')] or [Fe(CO)('S$_5$')] immediately led to a color change from strawberry red to reddish violet according to Eq. (2). Monitoring the

$$[Fe(CO)_2('S_4')] + CF_3SO_3H \xrightarrow[20\ °C]{CH_2Cl_2}$$

$$'[Fe(CO)_2(H-'S_4')]CF_3SO_3' \quad (2)$$
reddish violet solution
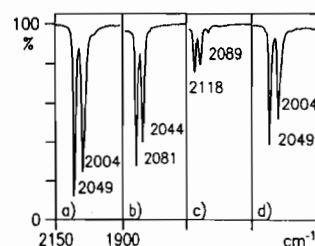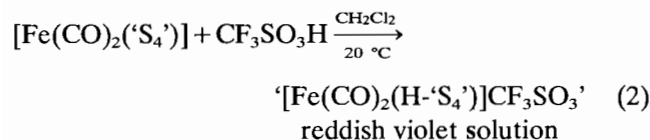
Fig. 1. ν(CO) regions (2150–1900 cm^{-1}) for the IR spectra of (a) [Fe(CO)$_2$('S$_4$')] in CH$_2$Cl$_2$, (b) after addition of 1 CF$_3$SO$_3$H, (c) after addition of 2 CF$_3$SO$_3$H and (d) subsequent addition of 1 ml of H$_2$O. (The decrease of ν(CO) intensities in (c) is due to partial precipitation of the product as oily drops.)

reaction by IR spectroscopy (Fig. 1) showed that the ν(CO) bands of [Fe(CO)$_2$('S$_4$')] at 2049 and 2004 cm^{-1} had disappeared and two new bands at 2081 and 2044 cm^{-1} had emerged. Addition of a second equivalent of acid led to a color change to orange, a further ν(CO) shift of about 40 cm^{-1}, and the appearance of two bands at 2118 and 2089 cm^{-1}.

In an analogous way, color changes of the solution and simultaneous shifts of the ν(CO) band from 1978 via 2016 cm^{-1} (1 equiv. of acid) to 2059 cm^{-1} (2 equiv. of acid) occurred in the case of [Fe(CO)('S$_5$')].

The increase of the ν(CO) frequencies can plausibly be explained by a consecutive protonation of both the thiolate functions in [Fe(CO)$_2$('S$_4$')] or [Fe(CO)('S$_5$')], e.g. according to Eq. (3). As consequence of the proto-

$$(3)$$
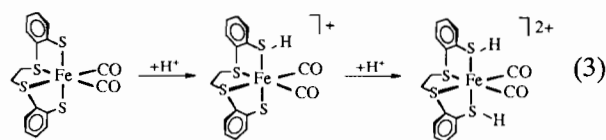
nation, the electron density at the iron center is lowered leading to a weakening of the Fe–CO π backbonds and strengthening of the CO triple bonds.

In the ^{1}H NMR spectra of the reaction mixtures, no signals could be assigned unambiguously to SH functions, and all attempts to isolate the supposed protonated complexes also failed. They could neither be crystallized nor precipitated in solid form. Addition of Et$_2$O or H$_2$O to the CH$_2$Cl$_2$ solutions led to regeneration of [Fe(CO)$_2$('S$_4$')] or [Fe(CO)('S$_5$')]. This indicates that the protonations are reversible and do not lead to cleavage of the [Fe('S$_4$')] or [Fe('S$_5$')] cores.

3.2. Alkylation of [Fe(CO)$_2$('S$_4$')] and [Fe(CO)('S$_5$')]

In order to obtain isoelectronic complexes which are isolable we investigated alkylations. The oxonium salts Me$_3$OBF$_4$ and Et$_3$OBF$_4$ proved to be the best suited alkylation reagents.

Table 1

Selected crystallographic data of [Fe(CO)$_2$(Et-'S$_4$')]BF$_4$·1.5CH$_2$Cl$_2$ ([1b]BF$_4$·1.5CH$_2$Cl$_2$), [Fe(CO)$_2$(Me$_2$-'S$_4$')](BF$_4$)$_2$ ([3a](BF$_4$)$_2$), [Fe(CO)$_2$(Et$_2$-'S$_4$')](BF$_4$)$_2$ ([3b](BF$_4$)$_2$), [Fe(CO)(Et$_2$-'S$_5$')](BF$_4$)$_2$ ([5](BF$_4$)$_2$ ([5](BF$_4$)$_2$, [6]FeI$_4$·CH$_2$Cl$_2$ ([6]FeI$_4$·CH$_2$Cl$_2$) and [Fe(I)$_2$(Me$_2$-'S$_4$')] (7)

Compound	[1b]BF$_4$·1.5CH$_2$Cl$_2$	[3a](BF$_4$)$_2$	[3b](BF$_4$)$_2$	[5](BF$_4$)$_2$	[6]FeI$_4$·CH$_2$Cl$_2$	7
Formula	C$_{18}$H$_{17}$BF$_4$FeO$_2$S$_4$·1.5CH$_2$Cl$_2$	C$_{18}$H$_{18}$B$_2$F$_8$FeO$_2$S$_4$	C$_{20}$H$_{22}$B$_2$FeO$_2$S$_4$	C$_{21}$H$_{26}$B$_2$F$_8$FeOS$_5$	C$_{17}$H$_{18}$Fe$_2$I$_5$OS$_4$·CH$_2$Cl$_2$	C$_{16}$H$_{18}$FeI$_2$S$_4$
M$_r$ (g/mol)	663.6	624.0	652.1	684.2	1197.7	648.2
Crystal dimensions (mm)	0.70×0.40×0.40	0.30×0.20×0.20	0.90×0.50×0.40	0.60×0.40×0.40	0.50×0.20×0.20	0.40×0.30×0.20
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	triclinic	monoclinic
Space group	P2$_1$/n	P2$_1$/c	P2$_1$/c	P1̄	P1̄	C2/c
a (pm)	1143.0(5)	1303.2(9)	1417.1(5)	1047.5(4)	856.2(2)	1657.4(5)
b (pm)	2110.6(8)	1123.1(15)	1129.1(8)	1125.8(4)	1766.0(5)	882.3(2)
c (pm)	1208.2(5)	1651.0(10)	1617.9(5)	1308.6(5)	2203.0(7)	1487.0(3)
α (°)	90.00	90.00	90.00	71.98(3)	93.19(2)	90.00
β (°)	117.42(4)	97.98(6)	95.42(3)	66.48(4)	94.46(2)	98.82(2)
γ (°)	90.00	90.00	90.00	88.13(3)	93.62(2)	90.00
Cell volume (pm³)	2587(2)×10⁶	2393(3)×10⁶	2576(2)×10⁶	13384(10)×10⁶	3307(2)×10⁶	2148(1)×10⁶
Z	4	4	4	2	4	4
D$_c$ (g/cm³)	1.69	1.73	1.68	1.70	2.41	2.00
μ (cm⁻¹)	12.6	10.7	9.9	10.3	59.6	39.6
Temperature (K)	200	200	200	293	293	293
Diffractometer	Siemens P4	Siemens P4	Siemens P4	Siemens P4	Siemens P4	Siemens P4
Radiation (pm)	Mo Kα (71.073)	Mo Kα (71.073)	Mo Kα (71.073)	Mo Kα (71.073)	Mo Kα (71.073)	Mo Kα (71.073)
Scan technique	ω-scan	ω-scan	ω-scan	ω-scan	ω-scan	ω-scan
2θ Range (°)	3.0–54.0	3.0–54.0	3.0–54.0	3.0–54.0	3.0–54.0	3.0–54.0
Scan speed (°/min)	3.00–30.00	1.50–29.30	3.00–29.30	3.00–29.30	3.00–29.30	3.00–30.00
Measured reflexions	6244	2854	6611	6418	15976	4507
Independent reflexions	5657	2638	5680	5884	14533	2352
Observed reflexions	3532	918	4179	3155	5961	1260
Absorption correction	none	none	none	none	semi-empirical	none
Program	SHELXTL-PLUS	SHELXTL-PLUS	SHELXTL-PLUS	SHELXTL-PLUS	SHELXTL-PLUS	SHELXTL-PLUS
Weighting scheme	1/σ²	1/σ²	1/σ²	1/σ²	1/σ²	1/σ²
σ Criterion	F>4.0σ(F)	F>4.0σ(F)	F>4.0σ(F)	F>4.0σ(F)	F>4.0σ(F)	F>4.0σ(F)
Refined parameters	316	166	334	318	548	105
R; R$_w$ (%)	5.7; 5.2	9.0; 7.0	4.3; 4.0	7.9; 7.0	4.9; 4.4	4.6; 4.5

Table 2
Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($pm^2 \times 10^{-1}$)

Table 2 (continued)

	x	y	z	U_{eq}[a]
[Fe(CO)₂(Et-'S₄')]BF₄ · 1.5CH₂Cl₂ ([1b]BF₄ · 1.5CH₂Cl₂)				
Fe(1)	1833(1)	2544(1)	1784(1)	24(1)
C(1)	1220(6)	2282(3)	199(6)	29(3)
O(1)	803(4)	2115(2)	−812(4)	39(2)
C(2)	2877(6)	3142(3)	1634(5)	29(3)
O(2)	3534(5)	3538(2)	1597(4)	45(2)
S(1)	3458(1)	1801(1)	2572(1)	25(1)
S(2)	451(2)	1859(1)	2079(2)	29(1)
S(3)	2498(2)	2920(1)	3768(1)	27(1)
S(4)	180(2)	3285(1)	1044(1)	31(1)
C(15)	1448(6)	1175(3)	2794(5)	26(3)
C(14)	926(7)	682(3)	3175(6)	38(3)
C(13)	1692(7)	150(3)	3695(6)	40(3)
C(12)	2965(7)	107(3)	3834(6)	35(3)
C(11)	3495(6)	611(3)	3469(5)	29(3)
C(10)	2721(6)	1141(3)	2936(5)	25(2)
C(25)	1518(6)	3611(3)	3534(5)	26(3)
C(24)	1748(6)	3981(3)	4568(6)	34(3)
C(23)	994(7)	4514(3)	4415(7)	42(3)
C(22)	39(7)	4684(3)	3249(7)	37(3)
C(21)	−194(6)	4314(3)	2207(6)	31(3)
C(20)	536(6)	3763(3)	2343(6)	27(3)
C(16)	360(7)	2195(3)	3426(6)	36(3)
C(26)	1705(6)	2389(3)	4409(5)	32(3)
C(3)	3804(7)	1456(3)	1356(6)	36(3)
C(4)	4433(7)	1930(3)	872(6)	43(3)
[Fe(CO)₂(Me₂-'S₄')](BF₄)₂ ([3a](BF₄)₂)				
Fe(1)	1836(4)	266(4)	3228(2)	29(2)
C(1)	1546(19)	1816(23)	3092(14)	21(7)
O(1)	1410(15)	2780(20)	3002(12)	54(6)
C(2)	574(27)	−63(25)	3538(16)	37(8)
O(2)	−246(18)	−311(20)	3587(11)	61(7)
S(1)	2704(6)	525(7)	4507(4)	33(3)
S(2)	2164(7)	−1735(7)	3329(4)	36(3)
S(3)	1151(6)	−66(6)	1909(4)	29(3)
S(4)	3411(6)	535(7)	2777(4)	37(3)
C(15)	2982(21)	−1888(22)	4294(14)	21(7)
C(14)	3309(19)	−3030(23)	4488(15)	24(7)
C(13)	3937(21)	−3151(26)	5272(16)	36(8)
C(12)	4219(22)	−2171(26)	5765(17)	43(8)
C(11)	3884(20)	−1103(24)	5542(15)	33(8)
C(10)	3212(21)	−858(27)	4783(17)	38(8)
C(25)	3052(25)	795(23)	1734(16)	29(7)
C(24)	3800(23)	1258(23)	1265(16)	35(8)
C(23)	3551(23)	1491(25)	430(17)	45(9)
C(22)	2506(22)	1253(21)	91(15)	28(7)
C(21)	1751(23)	829(24)	521(16)	39(8)
C(20)	2057(22)	592(23)	1336(15)	23(7)
C(16)	3067(19)	−1912(24)	2613(15)	30(8)
C(26)	3888(21)	−976(22)	2743(18)	37(8)
C(17)	1835(19)	726(24)	5238(14)	32(7)
C(27)	−9(20)	841(25)	628(15)	41(8)
[Fe(CO)₂(Et₂-'S₄')](BF₄)₂ ([3b](BF₄)₂)				
Fe(1)	1924(1)	307(1)	8248(1)	24(1)
C(1)	756(3)	97(3)	8591(2)	30(1)
O(1)	15(2)	−82(3)	8774(2)	49(1)
C(2)	1751(3)	1897(3)	8138(2)	30(1)
O(2)	1638(2)	2868(2)	8037(2)	47(1)
S(1)	2668(1)	531(1)	9548(1)	27(1)
S(2)	2153(1)	−1696(1)	8354(1)	28(1)
S(3)	3385(1)	483(1)	7774(1)	27(1)
S(4)	1323(1)	33(1)	6907(1)	30(1)

(continued)

	x	y	z	U_{eq}[a]
C(15)	2899(3)	−1864(3)	9301(2)	28(1)
C(14)	3255(3)	−2982(3)	9509(3)	35(1)
C(13)	3889(3)	−3099(3)	10214(3)	40(1)
C(12)	4161(3)	−2134(4)	10699(3)	42(1)
C(11)	3796(3)	−1023(3)	10494(3)	37(1)
C(10)	3157(3)	−887(3)	9797(2)	29(1)
C(25)	3117(3)	816(3)	6703(2)	27(1)
C(24)	3837(3)	1242(3)	6259(3)	36(1)
C(23)	3654(3)	1446(4)	5420(3)	44(2)
C(22)	2756(3)	1228(4)	5030(3)	44(2)
C(21)	2031(3)	831(4)	5466(2)	39(1)
C(20)	2208(3)	627(3)	6317(2)	30(1)
C(16)	3012(3)	−1931(3)	7600(2)	32(1)
C(26)	3811(3)	−1043(3)	7706(2)	34(1)
C(17)	1768(3)	667(4)	10280(2)	34(1)
C(18)	2185(3)	860(4)	11161(3)	44(1)
C(27)	304(3)	1025(4)	6593(3)	48(2)
C(28)	−588(4)	501(5)	6770(4)	78(2)
[Fe(CO)(Et₂-'S₅')](BF₄)₂ ([5](BF₄)₂)				
Fe(1)	2778(2)	4711(1)	8225(1)	41(1)
C(1)	2566(9)	5280(8)	9402(8)	44(5)
O(1)	2371(8)	5564(6)	10198(6)	63(4)
S(1)	4657(3)	6052(2)	6871(2)	46(1)
S(2)	1384(3)	6077(3)	7713(2)	55(1)
S(3)	2892(3)	3911(3)	6803(2)	68(2)
S(4)	951(3)	3287(2)	9486(2)	46(1)
S(5)	4213(3)	3396(2)	8802(2)	51(1)
C(15)	2525(11)	7268(9)	6477(8)	45(5)
C(14)	1960(11)	8242(10)	5891(9)	58(6)
C(13)	2846(14)	9121(10)	4910(10)	70(7)
C(12)	4260(14)	9081(10)	4504(9)	71(7)
C(11)	4833(11)	8157(10)	5074(9)	57(6)
C(10)	3949(10)	7238(9)	6086(8)	45(5)
C(25)	1649(11)	2163(9)	10331(9)	47(5)
C(24)	733(12)	1301(10)	11342(9)	61(6)
C(23)	1283(14)	428(11)	12007(10)	70(7)
C(22)	2704(16)	423(12)	11659(12)	82(9)
C(21)	3593(12)	1305(10)	10682(11)	63(6)
C(20)	3058(11)	2180(9)	10005(9)	50(5)
C(16)	624(13)	5362(11)	7018(11)	81(8)
C(17)	1762(15)	4808(11)	6167(10)	88(8)
C(26)	639(11)	2386(9)	8646(9)	57(6)
C(27)	1923(12)	2391(10)	7631(9)	64(6)
C(18)	5397(11)	6978(9)	7473(9)	56(5)
C(19)	6134(11)	6180(10)	8150(9)	68(6)
C(28)	5287(11)	2569(12)	7801(12)	90(8)
C(29)	6664(15)	3134(13)	7216(13)	133(10)
[Fe(I)(CO)(Me₂-'S₄')]FeI₄ · CH₂Cl₂ ([6]FeI₄ · CH₂Cl₂)				
Fe(1)	9519(2)	1289(1)	3748(1)	38(1)
Fe(2)	4445(2)	3850(1)	1294(1)	39(1)
C(1)	8452(17)	1987(9)	3368(8)	45(6)
C(2)	3342(18)	3191(9)	1692(8)	46(7)
O(1)	7761(12)	2407(6)	3108(6)	60(5)
O(2)	2625(13)	2776(6)	1952(6)	65(5)
I(1)	7039(1)	978(1)	4349(1)	70(1)
I(2)	1848(1)	4178(1)	668(1)	62(1)
S(1)	8476(5)	406(2)	3013(2)	49(2)
S(2)	10677(4)	339(2)	4247(2)	45(2)
S(3)	11726(4)	1532(2)	3288(2)	39(1)
S(4)	10485(5)	2093(2)	4541(2)	49(2)
S(5)	3947(5)	4776(2)	1995(2)	47(2)
S(6)	5714(4)	4755(2)	775(2)	44(2)
S(7)	6750(4)	3584(2)	1758(2)	39(1)
S(8)	4804(5)	3003(2)	524(2)	49(2)

(continued)

Table 2 *(continued)*

	x	y	z	U_{eq}[a]
C(15)	10126(18)	−496(9)	3754(8)	50(7)
C(14)	10706(19)	−1188(10)	3934(9)	63(8)
C(13)	10316(24)	−1830(10)	3554(11)	93(11)
C(12)	9373(24)	−1800(11)	3002(12)	104(12)
C(11)	8804(20)	−1113(10)	2853(9)	72(8)
C(10)	9221(18)	−463(9)	3224(8)	53(7)
C(25)	12802(16)	2277(8)	3743(7)	40(6)
C(24)	14166(17)	2593(8)	3543(7)	45(6)
C(23)	14946(20)	3213(10)	3886(9)	67(8)
C(22)	14373(22)	3500(10)	4427(10)	75(9)
C(21)	13025(20)	3182(9)	4630(8)	63(8)
C(20)	12195(17)	2545(8)	4285(8)	47(6)
C(16)	12748(15)	515(9)	4093(7)	48(6)
C(26)	12912(16)	757(8)	3443(7)	45(6)
C(17)	9274(19)	513(9)	2297(7)	70(8)
C(27)	9330(18)	2888(9)	4669(8)	72(8)
C(35)	5613(18)	5616(9)	1236(8)	51(7)
C(34)	6258(20)	6290(10)	1051(9)	72(9)
C(33)	6142(24)	6956(11)	1392(12)	94(11)
C(32)	5388(23)	6951(11)	1911(11)	81(10)
C(31)	4757(22)	6288(10)	2091(9)	77(9)
C(30)	4855(18)	5613(10)	1759(8)	56(7)
C(45)	7406(16)	2825(8)	1297(7)	37(6)
C(44)	8789(16)	2518(8)	1481(8)	45(6)
C(43)	9255(19)	1904(9)	1134(9)	58(8)
C(42)	8360(19)	1593(9)	639(9)	64(8)
C(41)	7035(20)	1901(9)	440(8)	62(7)
C(40)	6519(16)	2529(8)	781(8)	46(6)
C(36)	7793(16)	4564(8)	942(7)	50(7)
C(46)	8110(15)	4375(8)	1593(7)	41(6)
C(37)	5086(18)	4699(8)	2744(7)	62(7)
C(47)	3405(17)	2219(8)	451(8)	87(9)
[Fe(I)$_2$(Me$_2$-'S$_4$')] (7)				
Fe(1)	0	−1261(1)	3654(2)	2500	49(1)
I(1)	−1261(1)	5608(1)	2539(1)	62(1)
S(1)	327(2)	3436(3)	4186(2)	55(1)
S(2)	1024(2)	1448(3)	2583(2)	59(1)
C(15)	1345(6)	1122(11)	3759(7)	47(3)
C(14)	1954(8)	59(14)	4015(8)	66(5)
C(13)	2273(8)	−191(15)	4918(8)	71(5)
C(12)	1981(8)	667(16)	5567(8)	73(5)
C(11)	1389(8)	1734(14)	5353(7)	61(4)
C(10)	1087(7)	1989(13)	4441(7)	54(4)
C(16)	385(9)	−175(11)	2286(7)	73(5)
C(17)	−465(8)	2726(15)	4741(7)	69(5)

[a]Equivalent isotropic U as one third of the trace of the orthogonalized U_{ij} tensor.

3.2.1. Monoalkylation

Upon reaction with 1 equiv. of Me$_3$OBF$_4$ or Et$_3$OBF$_4$ [Fe(CO)$_2$('S$_4$')] gave the monoalkylated products [Fe(CO)$_2$(Me-'S$_4$')]BF$_4$ ([1a]BF$_4$) and [Fe(CO)$_2$(Et-'S$_4$')]BF$_4$, ([1b]BF$_4$) according to Eq. (4).

R = CH$_3$, [1a]BF$_4$; C$_2$H$_5$, [1b]BF$_4$
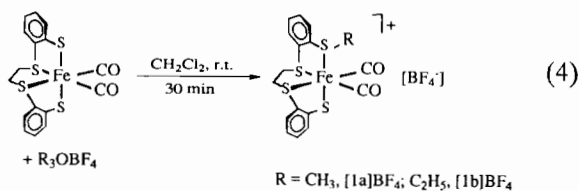
Analogously, the monoalkylation of [Fe(CO)('S$_5$')] yielded [Fe(CO)(Me-'S$_5$')]BF$_4$ ([2a]BF$_4$) and [Fe(CO)-(Et-'S$_5$')]BF$_4$ ([2b]BF$_4$) according to Eq. (5).

R = CH$_3$, [2a]BF$_4$; C$_2$H$_5$, [2b]BF$_4$ (5)
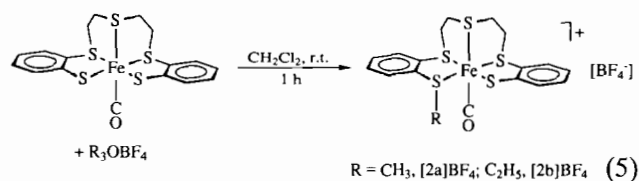
[Fe(CO)('S$_5$')] could also be alkylated with benzyl bromide. In order to obtain a characterizable product, NH$_4$PF$_6$ had to be added in this case. Then [Fe(CO)(Bz-'S$_5$')]PF$_6$ ([2c]PF$_6$) formed according to Eq. (6).

$$[Fe(CO)('S_5')] + C_6H_5CH_2Br \xrightarrow[-NH_4Br]{CH_2Cl_2, \ r.t., \ 12 \ h} + NH_4PF_6$$

$$[Fe(CO)(Bz-'S_5')]PF_6 \quad (6)$$
$$[2c]PF_6$$
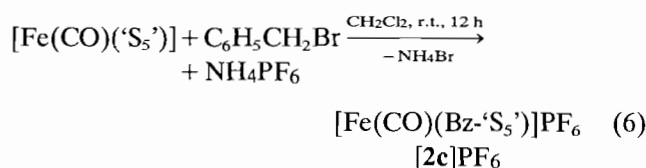
The syntheses gave good to high yields. The complexes were isolated as reddish brown microcrystals ([1b]BF$_4$) or powders, and they are soluble in CH$_2$Cl$_2$, THF, acetone and also MeOH, in which, however, they slowly decomposed. In the mass spectra, only the cations of the respective salts could be observed.

3.2.2. Dialkylations

The reaction of [Fe(CO)$_2$('S$_4$')] with 2 equiv. of Me$_3$OBF$_4$ or Et$_3$OBF$_4$ yielded the corresponding dialkylated complexes [Fe(CO)$_2$(Me$_2$-'S$_4$')](BF$_4$)$_2$ ([3a]-(BF$_4$)$_2$) and [Fe(CO)$_2$(Et$_2$-'S$_4$')](BF$_4$)$_2$ ([3b](BF$_4$)$_2$), according to Eq. (7).

R = CH$_3$, [3a](BF$_4$)$_2$; C$_2$H$_5$, [3b](BF$_4$)$_2$
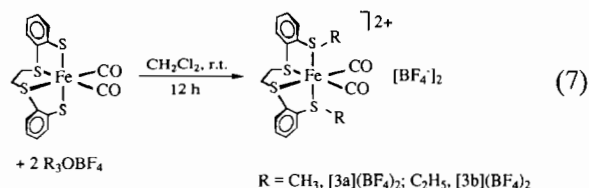
By the 'asymmetrical' dialkylation of [Fe(CO)$_2$('S$_4$')] with Me$_3$OBF$_4$ and Et$_3$OBF$_4$, [Fe(CO)$_2$(Me-'S$_4$'-Et)](BF$_4$)$_2$ ([4](BF$_4$)$_2$) could be obtained proving the alkylation steps to take place step by step. In this case, at first Me$_3$OBF$_4$ was added to a solution of [Fe(CO)$_2$('S$_4$')], and, approximately 1 h later, Et$_3$OBF$_4$ in a single-pot reaction according to Eq. (8).

[4](BF$_4$)$_2$

[Fe(CO)('S₅')] and Et₃OBF₄ yielded [Fe(CO)(Et₂-'S₅')](BF₄)₂ ([5](BF₄)₂), according to Eq. (9).

$$+ 2 (C_2H_5)_3OBF_4 \qquad\qquad [5](BF_4)_2 \qquad (9)$$

In order to drive the reactions to completion, all dialkylations required longer times of ~12 h in comparison to the monoalkylations which only needed ~1 h. This plausibly corresponds to the fact that the first alkylation step leads to mono-cations in which the nucleophilicity of the remaining thiolate donors is already distinctly lowered.

[3](BF₄)₂, [4](BF₄)₂ and [5](BF₄)₂ precipitated from the reaction solutions as yellow or orange powders and could be obtained in crystalline form by recrystallization from MeCN/Et₂O or EtNO₂/Et₂O mixtures. They are soluble in MeOH, MeCN, EtNO₂ and acetone, but are insoluble in THF, CH₂Cl₂, Et₂O and n-hexane.

When [Fe(CO)₂('S₄')] or [Fe(CO)('S₅')] were alkylated with Me₃OBF₄ or Et₃OBF₄, no loss of CO ligands was observed. This took place when CH₃I was used. A large excess of CH₃I was necessary in order to observe a reaction; the reaction was slow and yielded products in which one or both CO ligands of the starting complex had been substituted by iodo ligands according to Eq. (10). The major product was the iodo complex

[Fe(I)(CO)(Me₂-'S₄')]FeI₄, ([6]FeI₄), while the fully decarbonylated complex [Fe(I)₂(Me₂-'S₄')] (7) formed only as a by-product in very small yields.
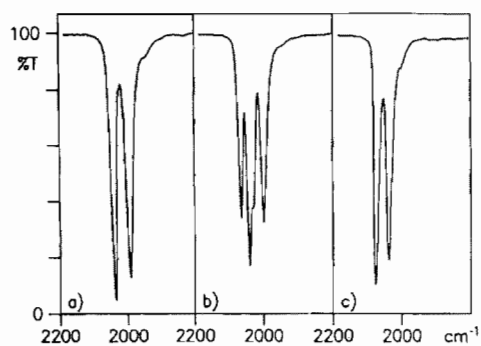
Black [6]FeI₄ dissolves in CH₂Cl₂, acetone, MeOH or THF, but slowly decomposes in these solvents. When concentrated H₂SO₄ is added to solid [6]FeI₄, elemental iodine is released. The formation of [6]FeI₄ and 7 can plausibly be explained by assuming that primary alkylation products such as [Fe(CO)₂(Me₂-'S₄')]I₂ react with nucleophilic iodide anions. Substitution of the CO ligands yields [6]⁺ and 7, and the partial decomposition of these products subsequently leads also to the [FeI₄]⁻ anion.

3.3. Hydrolyses of the complexes

Hydrolyses with concentrated aqueous HCl, for example according to Eq. (11), have proved a convenient method for dissociating polydentate thioether–thiol ligands from parent complexes which had been synthesized before by template reactions [7]. In boiling

$$[Fe(CO)_2('S_4')] \xrightarrow[\sim 65\ °C,\ THF]{+\ exc.\ HCl/H_2O}$$

$$'S_4'\text{-}H_2 + 2CO + FeCl_2 \qquad (11)$$

THF, these hydrolyses required several hours in the cases of [Fe(CO)₂('S₄')] and [Fe(CO)('S₅')]. Under similar conditions, the monoalkylated complexes decomposed considerably faster, and the dialkylated complexes dissociated even at room temperature. This method rendered accessible the free ligands whose conventional syntheses via alkylations of the corresponding thiols are very difficult or even impossible.

[Fe(CO)₂(R-'S₄')]BF₄ (R = Me, Et) yielded the tetradentate thioether–thiol ligands R-'S₄'-H (R = Me (8a), Et (8b)) according to Eq. (12).

$$R = CH_3, 8a; C_2H_5, 8b$$

$$(12)$$

In an analogous way, Et-'S₅'-H (9) and the asymmetrical thioether Me-'S₄'-Et (10) were obtained by hydrolysis of [Fe(CO)(Et-'S₅')]BF₄ and [Fe(CO)₂(Me-'S₄'-Et)](BF₄)₂.

8a and Me-'S₄'-Et (10) were isolated as white powders, 8b and 9 as viscous oils. 8, 9 and 10 are soluble in THF, acetone, CH₂Cl₂, MeOH and n-hexane. All new ligands were characterized spectroscopically and by elemental analyses.

3.4. IR spectra

The alkylations of [Fe(CO)₂('S₄')] and [Fe(CO)('S₅')] could also be conveniently monitored by IR spectroscopy using the ν(CO) bands as probe. Fig. 2 shows the alkylation of [Fe(CO)₂('S₄')] by Et₃OBF₄ as an example. After addition of the oxonium salt, the emergence of new ν(CO) bands can be seen the intensities of which increase by the same measure as the ν(CO) bands of the starting complexes disappear. Their wavenumbers and their shifts per step of alkylation are listed in Table 3.

Fig. 2. ν(CO) region of the IR spectra of (a) [Fe(CO)$_2$('S$_4$')] in CH$_2$Cl$_2$, (b) 10 min after addition of Et$_3$OBF$_4$, and (c) after 1 h and complete reaction to [Fe(CO)$_2$(Et-'S$_4$')]BF$_4$.

Table 3 shows that the average ν(CO) frequencies of the [Fe('S$_4$')] and [Fe('S$_5$')] complexes increase by about 40 and 32 cm^{-1} per step of alkylation. Thus, alkylation of the thiolate donors evidently lowers the electron density at the iron centers and consecutively weakens the Fe–CO π backbonds in quite an analogous way as protonations do. Because the alkylated complexes can be isolated, they further confirm the assumption that protonation takes place at the thiolate donors of [Fe(CO)$_2$('S$_4$')] and [Fe(CO)('S$_5$')]. It is to be noted that protonation and alkylation of [Fe(CO)$_2$('S$_4$')] cause nearly the same ν(CO) shifts (77 versus 81 cm^{-1}), whereas protonation of [Fe(CO)('S$_5$')] effects a distinctly larger ν(CO) shift than alkylation (81 versus 64 cm^{-1}).

A special case in Table 3 is [Fe(I)(CO)(Me$_2$-'S$_4$')]FeI$_4$. It contains the doubly alkylated Me$_2$-'S$_4$' ligand, however, its ν(CO) frequency (1996 cm^{-1}) is almost 100 cm^{-1} lower than the average ν(CO) frequency of the related [Fe(CO)$_2$(Et$_2$-'S$_4$')](BF$_4$)$_2$. This demonstrates that substitution of a σ–π ligand such as CO by σ ligands like iodide, which possibly acts also as a π donor, has a considerably stronger impact on the electron density at the iron center than alkylation of the thiolate donors.

3.5. X-ray structure analyses and bonding

The shift of the ν(CO) frequencies clearly proves that alkylation of thiolate donors influences the electron density at the iron centers. Thus, it was of interest to elucidate by X-ray structure determinations if and in what way these electronic changes alter structural characteristics, for example the Fe–S bond lengths. In addition, due to the chirality of [Fe('S$_4$')] complexes, alkylation causes the prostereogenic thiolate donors to become stereogenic thioether donors [8], and consequently, diastereomers of the alkylated complexes can theoretically result [9]. X-ray structural analyses could be expected to answer also the questions as to which one of these diastereomers forms preferentially.

For these reasons we determined the molecular structure of [Fe(CO)$_2$(Et-'S$_4$')]BF$_4$·1.5CH$_2$Cl$_2$ ([1b]BF$_4$·1.5CH$_2$Cl$_2$), [Fe(CO)$_2$(Me$_2$-'S$_4$')](BF$_4$)$_2$ ([3a](BF$_4$)$_2$), [Fe(CO)$_2$(Et$_2$-'S$_4$')](BF$_4$)$_2$ ([3b](BF$_4$)$_2$), [Fe(CO)(Et$_2$-'S$_5$')](BF$_4$)$_2$ ([5](BF$_4$)$_2$), [Fe(I)(CO)(Me$_2$-'S$_4$')]FeI$_4$·CH$_2$Cl$_2$ ([6]FeI$_4$·CH$_2$Cl$_2$) and [Fe(I)$_2$(Me$_2$-'S$_4$')] (7) by X-ray structure analyses. Fig. 3 shows the molecular structures of [1b]$^+$, [3]$^{2+}$, [5]$^{2+}$, [6]$^+$ and 7; Table 4 contains selected distances and angles.

All salts consist of discrete cations and anions. Except in the tetrahedral [FeI$_4$]$^-$ anion of [6]FeI$_4$, the iron centers are always coordinated pseudooctahedrally by six donor atoms, and the CO or iodo ligands occupy cis positions. The Fe–S(thiolate) distance of [1b]$^+$ (229.4(2) pm) and the average Fe–S(thioether) distances of [1b]$^+$, [3]$^{2+}$, [5]$^{2+}$ and [6]$^+$ (224.6(4)–228.7(2) pm) lie in the range which is typical for diamagnetic thioether–thiolate complexes of iron(II). The average Fe–C and average C–O distances of the neutral and monocationic or dicationic complexes show no significant differences. The high-spin complex 7 exhibits a strongly distorted coordination polyhedron due to the bulky iodo ligands and the large Fe–S(thioether) distances (248.9(2) and 257.3(4) pm). As a consequence, the S1–Fe1–S1A angle is not 180°, but only 171.1(1)°. Although the Fe–I distance of 271.6(2) pm still lies in the range of covalent Fe–I bonds [10], it is distinctly larger than the Fe–I distance of the diamagnetic [Fe(I)(CO)(Me$_2$-'S$_4$')]$^+$ cation. The large Fe–I and Fe–S distances of 7 are typical of high-spin Fe(II) complexes and can be traced back to two electrons occupying antibonding metal–ligand σ orbitals [11].

Table 3
ν(CO) IR bands (KBr, cm^{-1}) of the synthesized complexes

Complex	ν(CO)	$\bar{\nu}$(CO)[a]	$\Delta\bar{\nu}$(CO)[b]	Complex	ν(CO)	$\Delta\nu$(CO)[b]
[Fe(CO)$_2$('S$_4$')]	2035, 1985	2010		[Fe(CO)('S$_5$')]	1958	
			39			31
[Fe(CO)$_2$(Et-'S$_4$')]$^+$	2074, 2024	2049		[Fe(CO)(Et-'S$_5$')]$^+$	1989	
			42			33
[Fe(CO)$_2$(Et$_2$-'S$_4$')]$^{2+}$	2108, 2073	2091		[Fe(CO)(Et$_2$-'S$_5$')]$^{2+}$	2022	
[Fe(I)(CO)(Me$_2$-'S$_4$')]$^+$		1996[c]				

[a]Average ν(CO).
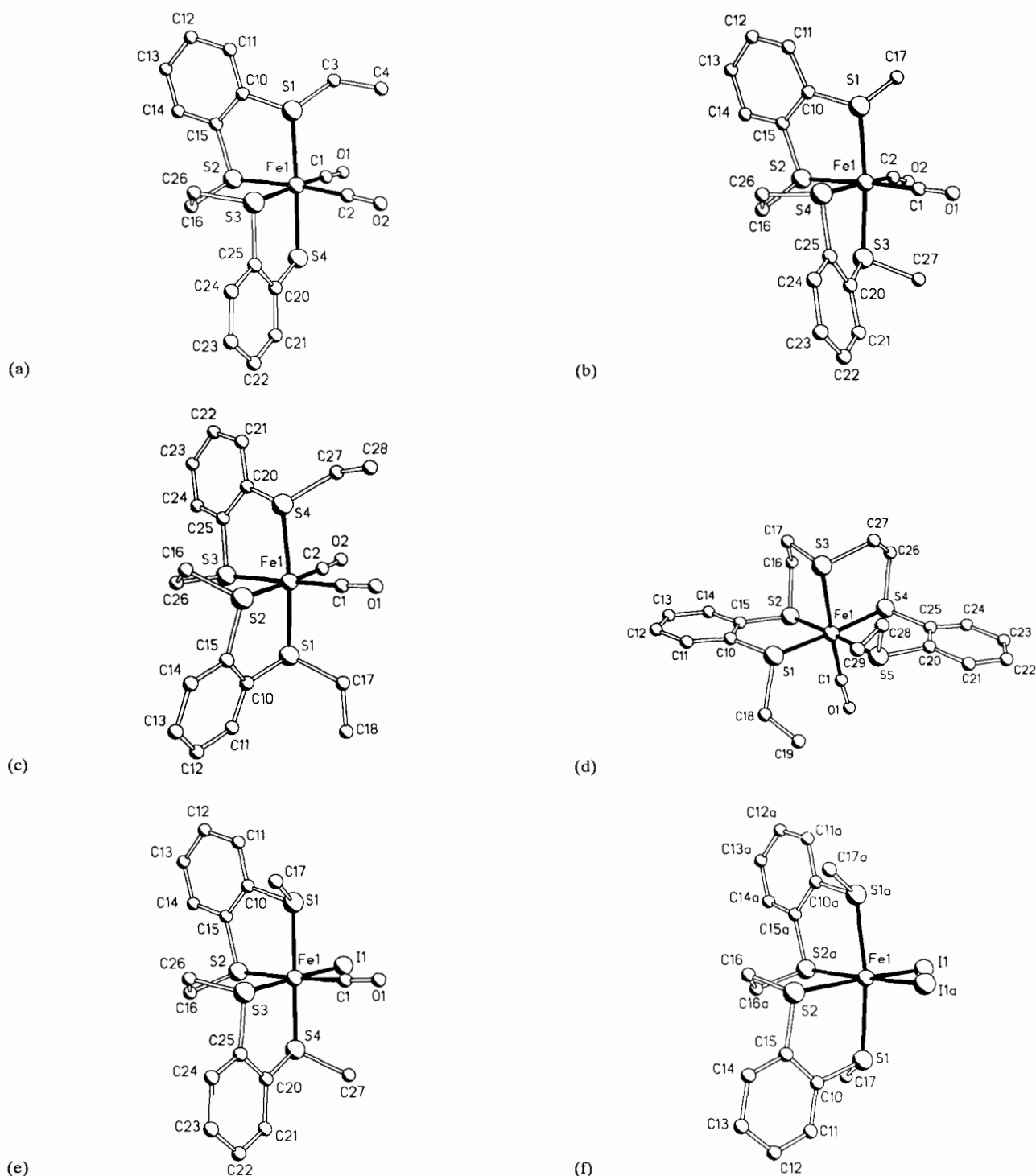[b]Average ν(CO) shift per step of alkylation.
[c]In CsI.

Fig. 3. Molecular structures of (a) [1b]$^+$, (b) [3a]$^{2+}$, (c) [3b]$^{2+}$, (d) [5]$^{2+}$, (e) [6]$^+$ and (f) 7 (H atoms omitted).

A comparison of distances in the [Fe('S$_4$')] and [Fe('S$_5$')] cores of the neutral, monocationic and dicationic complexes, which are listed in Table 5, shows that corresponding Fe–S distances exhibit minor differences only. Taking into account the standard deviations, these differences are so small that no elongation or shortening of Fe–S bonds can be detected when thiolate donors are alkylated. This even holds for

the pair of complexes [Fe(CO)$_2$(Et$_2$-'S$_4$')]$^{2+}$ and [Fe(I)(CO)(Me$_2$-'S$_4$')]$^+$.

In summary it can be stated: (i) as noted previously [9d,12], Fe–S(thiolate) and Fe–S(thioether) distances of the neutral complexes are nearly identical; (ii) alkylation of the thiolate donors does not significantly change the Fe–S distances. This becomes clearer when the averaged Fe–S distances are compared. In all dia-

Table 4
Selected distances (pm) and angles (°)

[Fe(CO)₂(Et-'S₄')]BF₄·1.5CH₂Cl₂ ([1b]BF₄·1.5CH₂Cl₂)

Fe(1)–S(1)	227.7(2)	Fe(1)–C(2)–O(2)	175.9(6)
Fe(1)–S(2)	228.7(2)	C(1)–Fe(1)–C(2)	93.4(3)
Fe(1)–S(3)	229.7(2)	C(2)–Fe(1)–S(2)	174.3(2)
Fe(1)–S(4)	229.4(2)	S(1)–Fe(1)–S(3)	89.3(1)
Fe(1)–C(1)	179.7(7)	Fe(1)–S(1)–C(3)	111.9(2)
Fe(1)–C(2)	180.2(7)		
C(1)–O(1)	114.3(8)		
C(2)–O(2)	113.9(9)		

[Fe(CO)₂(Me₂-'S₄')](BF₄)₂ ([3a](BF₄)₂)

Fe(1)–S(1)	227.3(8)	Fe(1)–C(1)–O(1)	177.0(23)
Fe(1)–S(2)	227.3(9)	C(1)–Fe(1)–C(2)	92.8(12)
Fe(1)–S(3)	226.8(8)	C(1)–Fe(1)–S(2)	176.8(8)
Fe(1)–S(4)	228.4(10)	S(1)–Fe(1)–S(4)	86.2(3)
Fe(1)–C(1)	177.6(26)	Fe(1)–S(1)–C(17)	111.6(8)
Fe(1)–C(2)	181.7(35)		
C(1)–O(1)	109.6(34)		
C(2)–O(2)	111.1(42)		

[Fe(CO)₂(Et₂-'S₄')](BF₄)₂ ([3b](BF₄)₂)

Fe(1)–S(1)	227.7(2)	Fe(1)–C(1)–O(1)	176.3(3)
Fe(1)–S(2)	228.9(2)	C(1)–Fe(1)–C(2)	92.4(2)
Fe(1)–S(3)	228.4(2)	C(1)–Fe(1)–S(3)	177.0(1)
Fe(1)–S(4)	227.5(2)	S(2)–Fe(1)–S(4)	88.6(1)
Fe(1)–C(1)	181.0(4)	Fe(1)–S(4)–C(27)	113.0(2)
Fe(1)–C(2)	181.8(4)		
C(1)–O(1)	113.6(5)		
C(2)–O(2)	111.9(5)		

[Fe(CO)(Et₂-'S₅')](BF₄)₂ ([5](BF₄)₂)

Fe(1)–S(1)	224.6(3)	Fe(1)–C(1)–O(1)	175.1(7)
Fe(1)–S(2)	222.3(3)	C(1)–Fe(1)–S(3)	175.9(3)
Fe(1)–S(3)	226.8(4)	C(1)–Fe(1)–S(2)	90.0(3)
Fe(1)–S(4)	223.6(3)	S(1)–Fe(1)–S(3)	87.7(1)
Fe(1)–S(5)	225.6(3)	S(1)–Fe(1)–S(5)	89.3(1)
Fe(1)–C(1)	177.7(12)	Fe(1)–S(1)–C(18)	114.0(3)
C(1)–O(1)	112.3(15)		

[Fe(I)(CO)(Me₂-'S₄')]FeI₄·CH₂Cl₂ ([6]FeI₄·CH₂Cl₂)

Fe(I)–S(1)	227.5(5)	Fe(I)–C(1)–O(1)	177.1(13)
Fe(I)–S(2)	229.2(5)	C(1)–Fe(1)–S(2)	174.9(5)
Fe(I)–S(3)	224.4(4)	I(1)–Fe(1)–S(3)	176.3(1)
Fe(I)–S(4)	226.1(5)	C(1)–Fe(1)–I(1)	88.5(5)
Fe(I)–C(1)	178.7(16)	C(1)–Fe(1)–S(1)	88.7(5)
C(1)–O(1)	113.1(20)	I(1)–Fe(1)–S(1)	87.5(1)
Fe(1)–I(1)	263.7(3)		

[Fe(I)₂(Me₂-'S₄')] (7)

Fe(1)–S(1)	248.9(3)	I(1)–Fe(1)–I(1A)	101.2(1)
Fe(1)–S(2)	257.3(4)	S(2)–Fe(1)–S(2A)	81.7(2)
Fe(1)–I(1)	271.6(2)	S(1)–Fe(1)–S(1A)	171.1(1)

magnetic complexes, they stretch over a very narrow range around 228 pm and are independent of the charges. Only the couple [Fe(CO)('S₅')]/[Fe(CO)(Et₂-'S₅')]²⁺ could possibly indicate shortening of Fe–S bonds upon alkylation. (The special case of paramagnetic [Fe(I)₂(Me₂-'S₄')] was discussed above.)

In contrast to the Fe–S distances of the complexes, the ν(CO) frequencies show large differences. Thus, it has to be concluded that either the electronic effects are so small to be detectable only by (the more sensitive) IR spectroscopy, or that the electronic effects are

intense, but do not cause any changes of the Fe–S distances because metal–sulfur bonds possess particular properties. We assume the second possibility to hold. As has been discussed previously and is generally accepted [13], metal–sulfur bonds may exhibit σ-bond properties and additional π-donor or π-acceptor properties. When it is further taken into account that the xy, xz and yz d orbitals of Fe(II) in pseudooctahedral low-spin complexes are fully occupied and able to form π backbonds, then it is plausible to assume that the Fe–S(thioether) bonds of neutral complexes such as [Fe(CO)₂('S₄')] will have σ-donor–π-acceptor character, whereas the Fe–S(thiolate) bonds will have mainly σ donor character. Alkylating these thiolate donors will weaken the Fe–S σ bonds, because a strong thiolate σ donor becomes a weaker thioether σ donor, the thioether donor, however, simultaneously acquires π-acceptor ability such that Fe–S backbonding becomes possible. The net effect will be that the electron density at the iron centers decreases, however, the Fe–S distances do not change because the antagonistic effects of weakening σ bonds and strengthening π bonds compensate each other. In the case of molecules like CO which are bound as σ-donor–π-acceptor ligands such a decrease of the electron density at the metal center causes simultaneous weakening of σ-donor bonds and π backbonds leading to an increase of ν(CO) frequencies. X-ray structural substantiation of the Fe–CO bond weakening, however, was not possible, because standard deviations of the respective distances were too large.

With respect to the possible diastereomerism of the alkylated complexes, in the X-ray structure analyses only one diastereomer (as a pair of enantiomers) was observed for all cases. ¹H and ¹³C{¹H} NMR spectra of the recrystallized complexes also showed signals of only one diastereomer, however, NMR spectra of the pure but not yet recrystallized products exhibited additional signals of small intensity indicating formation of other diastereomers in yields of less than 5%. Accordingly the alkylations take place with a high degree of stereoselectivity of up to 95%.

4. Discussion and conclusions

The results show that thioether–thiolate complexes like [Fe(CO)₂('S₄')] and [Fe(CO)('S₅')] can reversibly be protonated to give thioether–thiol complexes. While the thioether–thiol complexes could be detected in solution only, isoelectronic mono- and dialkylated complexes, e.g. [Fe(CO)₂(Et-'S₄')]BF₄, [Fe(CO)₂(Et₂-S₄')]-(BF₄)₂, [Fe(CO)(Et-'S₅')]BF₄ and [Fe(CO)(Et₂-'S₅')]-(BF₄)₂, were successfully isolated and completely characterized. These complexes prove that the thiolate

Table 5
Comparison of corresponding Fe–S distances (pm) in the [Fe('S₄')] and [Fe('S₅')] cores of the complexes
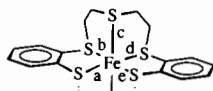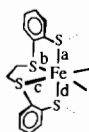
Complex	d(Fe–S)					$\bar{d}$(Fe–S)
	a	b	c	d	e	
[Fe(CO)₂('S₄')]	228.9(3)	227.1(3)	228.5(3)	229.2(3)		228.4(3)
[Fe(CO)₂(Et-'S₄')]⁺	227.7(2)	228.7(2)	229.7(2)	229.4(2)		228.9(2)
[Fe(CO)₂(Et₂-'S₄')]²⁺	227.5(2)	228.4(2)	228.9(2)	227.7(2)		228.1(2)
[Fe(I)(CO)(Me₂-'S₄')]⁺	227.5(5)	229.2(5)	224.4(4)	226.1(5)		226.8(5)
[Fe(I)₂(Me₂-'S₄')]	248.9(3)	257.3(4)	257.3(4)	248.9(3)		253.1(4)
[Fe(CO)('S₅')]	229.9(1)	225.0(1)	231.1(1)	225.1(1)	229.9(1)	228.2(1)
[Fe(CO)(Et₂-'S₅')]²⁺	224.6(3)	222.3(3)	226.8(4)	223.6(3)	225.6(3)	224.6(4)

··· : Bonds to alkyl groups in the alkylated complexes.

donors of [Fe(CO)₂('S₄')] and [Fe(CO)('S₅')] can act as Brönsted and Lewis bases. Protonations and alkylations take place stepwise and cause a decrease of the electron density at the metal centers. This follows from the ν(CO) frequencies which increase per step of protonation or alkylation such that the ν(CO) frequencies of the neutral and dicationic complexes differ by 80 cm^{-1}. This ν(CO) shift is nearly as large as in the series of the isoelectronic carbonyl complexes [Mn(CO)₆]⁺ (2090 cm^{-1}), [Cr(CO)₆] (200 cm^{-1}) and [V(CO)₆]⁻ (1860 cm^{-1}) [14] in which the metal oxidation states change by full units.

Such large ν(CO) shifts indicate significant electronic changes at the metal centers leading to a distinctly different reactivity of neutral, mono- and dicationic complexes. This expectation was confirmed by the finding that mono- and dialkylated complexes hydrolyzed much faster than the parent compounds, or that [Fe(I)(CO)Me₂-'S₄')]⁺ forms from [Fe(CO)₂(Me₂-'S₄')]²⁺ and iodide at room temperature via substitution of one CO ligand while the CO ligands of [Fe(CO)₂('S₄')] are inert.

We had previously observed similar influences upon reactivity with the [Ru(PPh₃)('S₄')] fragment. If it is protonated, it coordinates even hard ligands such as chloride anions to yield [Ru(HCl)(PPh₃)('S₄')] [15], but in its deprotonated neutral form it preferentially binds σ–π ligands such as CO, PPh₃ [16] or N₂H₂ [12a], while derivatives with hard σ ligands such as N₂H₄ or NH₃ [16] are extremely labile or not known at all. Due to the lack of a suitable probe, however, this fragment did not allow the spectroscopic monitoring of electronic modifications at the metal center that are caused by protonations or alkylations.

Although the ν(CO) shifts indicate large differences of the electron densities at the iron centers upon alkylation of thiolate donors, the Fe–S distances of the investigated complexes, in contrast to initial expectations, stay practically invariant. In all diamagnetic complexes with low-spin Fe(II) centers, Fe–S(thioether) and likewise Fe–S(thiolate) distances lie in the narrow range of 226 to 228 pm.

This invariability of Fe–S distances can plausibly be explained by the characteristic features of metal–sulfur bonds. In the low-spin 18 valence electron complexes, which were investigated here, σ-donor–π-acceptor character can be assumed for the Fe–S(thioether) bonds and mainly σ-donor character for the Fe–S(thiolate) bonds. Alkylation of the S(thiolate) donors then causes a weakening of the Fe–S σ bond, but simultaneously a Fe–S π backbond forms such that in the end the Fe–S distances stay unchanged although, according to the ν(CO) frequencies, the electron density at the metal undoubtedly has changed.

In comparison to phosphines, thioethers are 'poor' ligands [17]. Stable complexes of 3d metals could only be obtained with cyclic thioethers like [9]aneS₃, [16]aneS₄, [18]aneS₆ or Bzo₂[18]aneS₆, and the stability of these complexes preferentially results from the macrocyclic effect or, for example, the conformation of free 9[ane]S₃ [18]. To our knowledge, the complexes described here are the first Fe(II) complexes with open-chain thioether ligands which could be characterized also by X-ray structure analysis [19]. The Fe–S distances of these complexes indicate that the previous attempts of synthesizing Fe(II) complexes with open-chain thioether ligands may have been unsuccessful due to kinetic but not thermodynamic reasons.

The results are also of interest with regard to the question of how the reduction of molecular dinitrogen is achieved by nitrogenases. As shown and discussed above, protonation of the thiolate donors decreases the

electron density at the iron centers. This might influence the reducibility of the iron centers and whole [FeS] cores whose reduction can be expected to require a less negative potential in the protonated state than in the deprotonated state. In other words, take-up of electrons is anticipated to be easier when the [FeS] cores are protonated. This assumption is supported by the oxidation potentials of $[Fe(CO)_2('S_4')]$ which increase when $[M(CO)_5)]$ fragments (M = Cr, Mo, W) are coordinated to the thiolate donors [20]. Exactly the same might hold when N_2 is coordinated to the metal–sulfur centers of the cofactors in nitrogenases. This means that reduction of the [metal–sulfur–N_2] unit in the active centers of nitrogenases could become possible only if the S donors have been protonated before. Furthermore, a close vicinity of the resulting SH functions and the N_2 ligand can be expected. It should favor the sterically controlled H^+ transfer from the S donors to the N_2 unit, the making of N–H bonds, and finally the formation of diazene as the first key-intermediate of N_2 fixation.

In conclusion, the thiolate donors of $[Fe(CO)_2('S_4')]$ and $[Fe(CO)('S_5')]$ can be protonated and alkylated. This lowers the electron density at the iron centers to an unexpectedly large extent as evidenced by $\nu(CO)$ frequencies. Due to the characteristic feature of metal–sulfur bonds, however, the iron–sulfur cores remain invariant. Correlation of states of protonation with electron densities at the metal centers and expected redox potentials allows the hypothesis to be made that reducing the N_2 molecule at either Fe–S or Mo–S sites of the cofactors in nitrogenases requires previous protonation of the sulfur donors.

5. Supplementary material

Further details of the X-ray crystal structure analyses of $[Fe(CO)_2(Et-'S_4')]BF_4 \cdot 1.5CH_2Cl_2$, $[Fe(CO)_2(Me_2-'S_4')](BF_4)_2$, $[Fe(CO)_2(Et_2-'S_4')](BF_4)_2$, $[Fe(CO)(Et_2-'S_5')](BF_4)_2$, $[Fe(I)(CO)(Me_2-'S_4')]FeI_4 \cdot CH_2Cl_2$ and $[Fe(I)_2(Me_2-'S_4')]$ have been deposited with the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-76344 Eggenstein-Leopoldshafen 2, and can be obtained by quoting Deposition No. CSD 400589 for $[Fe(CO)_2(Et-'S_4')]BF_4 \cdot 1.5CH_2Cl_2$, CSD-400591 for $[Fe(CO)_2(Me_2-'S_4')](BF_4)_2$, CSD-400582 for $[Fe(CO)_2(Et_2-'S_4')](BF_4)_2$, CSD-400590 for $[Fe(CO)(Et_2-'S_5')]$-$(BF_4)_2$, CSD-400592 for $[Fe(I)(CO)(Me_2-'S_4')]FeI_4 \cdot CH_2Cl_2$ and CSD-400588 for $[Fe(I)_2(Me_2-'S_4')]$, the authors' names, and the reference.

Acknowledgements

References

[1] D. Sellmann, G. Mahr and F. Knoch, Inorg. Chim. Acta, 224 (1994) 35.

[2] P.M. Harrison (ed.), Metalloproteins, Vol. 1, Metal Proteins with Redox Roles, Verlag Chemie, Weinheim, Germany, 1985.

[3] (a) R. Cammack (ed.), Advances in Inorganic Chemistry, Vol. 38, Iron–Sulfur Proteins, Academic Press, San Diego, CA, 1992; (b) C.R. Kissinger, E.T. Adman, L.C. Sieker and L.H. Jensen, J. Am. Chem. Soc., 110 (1988) 8721.

[4] (a). P.M. Treichel and L.D. Rosenhein, Inorg. Chem., 20 (1981) 942; (b) M.Y. Darensbourg, W.-F. Liaw and C.G. Riordan, J. Am. Chem. Soc., 111 (1989) 8051; (c) P.M. Treichel, M.S. Schmidt and R.A. Crane, Inorg. Chem., 30 (1991) 379; (d) M.P. Byrn, B.A. Katz, N.L. Keder, K.R. Levan, C.J. Magurany, K.M. Miller, J.W. Pritt and C.E. Strouse, J. Am. Chem. Soc., 105 (1983) 4916; (e) D.M.L. Goodgame, A.M.Z. Slawin, D.J. Williams and P.W. Zard, Inorg. Chim. Acta, 116 (1986) L7; (f) J. Amarasekera and T.B. Rauchfuss, Inorg. Chem., 28 (1989) 3875; (g) D.W. Stephan, Inorg. Chem., 23 (1984) 2207; (h) S. Jeannin, Y. Jeannin and G. Lavigne, Inorg. Chem., 18 (1979) 3528; (i) D. Sellmann, P. Lechner, F. Knoch and M. Moll, Angew. Chem., 103 (1991) 599; Angew. Chem., Int. Ed. Engl., 30 (1991) 552; (j) P.G. Jessop and R.M. Morris, Inorg. Chem., 32 (1993) 2236.

[5] D. Sellmann, H.E. Jonk, H.R. Pfeil, G. Huttner and J.V. Seyerl, Organomet. Chem., 191 (1980) 171.

[6] (a) D. Sellmann and U. Kleine-Kleffmann, J. Organomet. Chem., 247 (1983) 307; (b) 258 (1983) 315; (c) D. Sellmann, G. Binker, M. Moll and E. Herdtweck, J. Organomet. Chem., 327 (1987) 403.

[7] D. Sellmann and W. Reisser, J. Organomet. Chem., 294 (1985) 333.

[8] K. Mislow and J. Siegel, J. Am. Chem. Soc., 106 (1984) 3319.

[9] (a) D. Sellmann, F. Grasser, F. Knoch and M. Moll, Z. Naturforsch., Teil B, 46 (1991) 1343; (b) D. Sellmann, P. Lechner and M. Moll. Z. Naturforsch., Teil B, 46 (1991) 1459; (c) D. Sellmann, P. Lechner, F. Knoch and M. Moll, Z. Naturforsch., Teil B, 46 (1991) 1585; (d) D. Sellmann, R. Weiss, F. Knoch, G. Ritter and J. Dengler, Inorg. Chem., 29 (1990) 4107.

[10] A. Hills, D.L. Hughes, M. Jimenez-Tenorio, G.J. Leigh, A. Houlton and J. Silver, J. Chem. Soc., Chem. Commun., 22 (1989) 1774.

[11] D. Sellmann, W. Soglowek, F. Knoch, G. Ritter and J. Dengler, Inorg. Chem., 31 (1992) 3711.

[12] (a) D. Sellmann, E. Böhlen, M. Waeber, G. Huttner and L. Zsolnai, Angew. Chem., 97 (1985) 984; Angew. Chem., Int. Ed. Engl., 24 (1985) 981; (b) D. Sellmann, P. Lechner, F. Knoch and M. Moll, J. Am. Chem. Soc., 114 (1992) 922.

[13] D. Sellmann, M. Geck, F. Knoch, G. Ritter and J. Dengler, J. Am. Chem. Soc., 113 (1991) 3819.

[14] F.A. Cotton and G. Wilkinson, Anorganische Chemie, Verlag Chemie, Weinheim, Germany, 4th edn., 1982, p. 87.

[15] D. Sellmann, I. Barth and M. Moll, Inorg. Chem., 29 (1990) 176.

[16] D. Sellmann and E. Böhlen, Z. Naturforsch., Teil B, 37 (1982) 1026.

[17] S.G. Murray and F.R. Hartley, *Chem. Rev., 81* (1981) 365.

[18] (a) A.J. Blake and M. Schröder, *Adv. Inorg. Chem., 35* (1990) 1; (b) S.R. Cooper, *Acc. Chem. Res., 21* (1988) 141; (c) K. Wieghardt, H.J. Küppers and J. Weiss, *Inorg. Chem., 24* (1985) 3067; (d) D. Sellmann and L. Zapf, *Angew. Chem., 96* (1984) 799; *Angew. Chem., Int. Ed. Engl., 23* (1984) 807;

(e) D. Sellmann, H.P. Neuner and F. Knoch, *Inorg. Chim. Acta, 190* (1991) 61.

[19] W. Levason, C.A. McAuliffe, S.G. Murray and S.M. Nelson, *Inorg. Chim. Acta, 19* (1976) L15.

[20] D. Sellmann, R. Weiss, F. Knoch and M. Moll, *J. Organomet. Chem., 391* (1990) 327.