Trinuclear [NiFe] Clusters as Structural Models for [NiFe] Hydrogenase Active Sites[‡]

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[Fe($CH_3COCH=CHPh$)$(CO)_3$] reacts with [Ni(‘S_4’)]$_x$ (x = 1, 2) or [Ni(‘$S_4C_3Me_2$’)] [‘S_4’$^{2-}$ = 1,2-bis(2-mercaptophenylthio)ethane(2-),‘$S_4C_3Me_2$’$^{2-}$ = 1,3-bis(2-mercaptophenylthio)-2,2-dimethylpropane(2-)] to afford trinuclear [NiFe] clusters [Ni(‘S_4’){$Fe(CO)_3$}$_2$] (**1**) and [Ni(‘$S_4C_3Me_2$’){$Fe(CO)_3$}$_2$] (**2**) and the dinuclear $Fe^{II}Fe^0$ complex [Fe(CO)(‘$S_4C_3Me_2$’)$Fe(CO)_3$] (**3**). Clusters **1** and **2** have Ni–Fe bond lengths similar to those of active or reduced states of [NiFe] hydrogenases, a sulfur-dominated coordination sphere of Ni and iron-bound CO. Therefore, **1** and **2** may serve as structural model complexes for the [NiFe] hydrogenase active site. Combination of the ‘$S_4C_3Me_2$’ ligand with $FeCl_2·4H_2O$ yielded [Fe(‘$S_4C_3Me_2$’)]$_2$ (**4**), the dinuclearity of which suggests that the ‘$S_4C_3Me_2$’ ligand is less flexible than its ethylene-bridged derivative, which affords a tetrameric [Fe(‘S_4’)]$_4$ complex reported earlier. Compound **4** reacts with 2 equiv. of CO to give [Fe(CO)(‘$S_4C_3Me_2$’)]$_2$ (**5**), which like **4** is only sparingly soluble in all common organic solvents. Complex **5** easily loses CO even if stored in the solid state. [Fe($CH_3COCH=CHPh$)$(CO)_3$] reacts with **5** to afford **3** as the only product.

Introduction

Hydrogenases catalyze the reversible oxidation of molecular hydrogen according to $H_2 \rightleftarrows 2\,H^+ + 2\,e^-$ and, therefore, play a central role in hydrogen and energy metabolism in nature.[1] They are essential for many microorganisms, which acquire energy by the reduction of CO_2, carbonates, sulfates or nitrates.[2] These enzymes are of great biotechnological interest[3] as they can produce molecular hydrogen.[4] [NiFe] hydrogenases are the most predominant of the four major types of hydrogenases commonly known.[3,5] Figure 1 depicts the active centers of oxidized and reduced [NiFe] hydrogenases, consisting of Ni−S−Fe bridges.

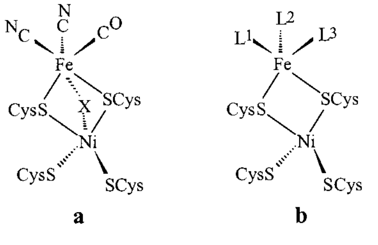

Figure 1. Schematic structure of the active center from (a) *D. gigas* in the oxidized form (X represents, probably, OH^- or O^{2-})[6a,6b] and (b) *D. vulgaris Miyazaki F* hydrogenase in the reduced form (L^1 = SO, CN or CO, L^2 = CN or CO, L^3 = CN or CO)[6c]

The mechanism of the reversible H_2 oxidation is still poorly understood. [NiFe] hydrogenases exist in various redox states that can be labeled by their EPR spectra and individual ν(CO) frequencies.[3,7] The relationship between these redox states and the metal oxidation states is still unclear. Furthermore, it is not known if only one or both metal atoms are involved in the activation process. To shed light on these questions, several di- and oligonuclear compounds have been synthesized.[8] Despite intensive research, the number of compounds containing sulfur−bridged Ni *and* Fe centers remains very limited.[9] Recently, we succeeded in synthesizing such complexes as [(‘S_2’)Ni−μ-(‘S_3’)Fe(CO)$(PMe_3)_2$] [‘S_2’$^{2-}$ = 1,2-benzenedithiolate(2−), ‘S_3’$^{2-}$ = bis(2-mercaptophenyl)sulfide(2−)][10] and [(‘S_2’){$Ni(PMe_3)$}$_2$Fe(CO)(‘S_2’)$_2$].[11] Moreover, the latter remarkably reduces protons to dihydrogen, affording the cationic species [(‘S_2’){$Ni(PMe_3)$}$_2$Fe(CO)(‘S_2’)$_2$]$^+$.[11] This exciting result encouraged us to further synthesize such complexes without any abiological phosphane ligands and to investigate their reactivity towards protons and hydrogen. Herein, we report the synthesis of the new trinuclear [NiFe] clusters [Ni(‘S_4’){$Fe(CO)_3$}$_2$] (**1**) and [Ni(‘$S_4C_3Me_2$’){$Fe(CO)_3$}$_2$] (**2**). The reaction of these complexes with H^+ and H_2 is also investigated.

Results and Discussion

In order to obtain dinuclear [NiFe] complexes, [Fe($CH_3COCH=CHPh$)$(CO)_3$] and [Ni(L)]$_x$ (L = ‘S_4’, x = 1, 2;

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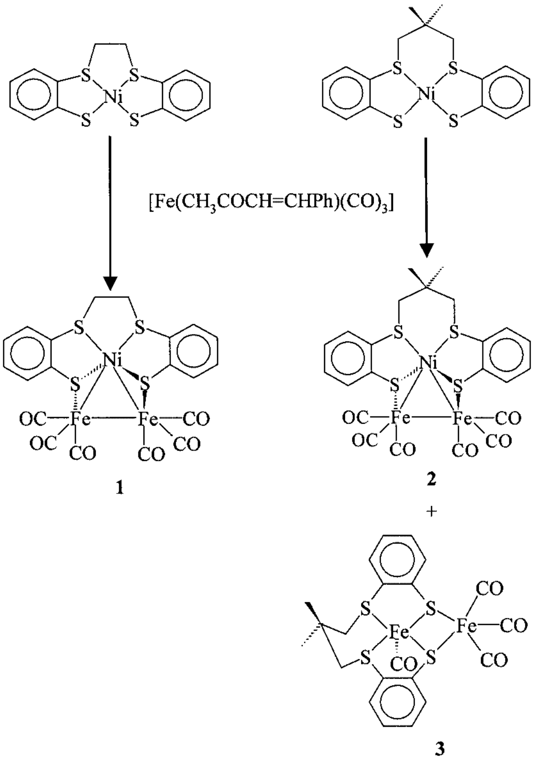
‘$S_4C_3Me_2$’, $x = 1$) were combined in equimolar ratio. Unexpectedly, this method did not yield dinuclear complexes but afforded instead the trinuclear clusters **1** and **2** (Scheme 1).



Scheme 1. Syntheses of [NiFe] clusters

During this reaction, the solution changed from bright red to dark red (L = ‘S_4’) or brown (L = ‘$S_4C_3Me_2$’). The complexes were isolated by column chromatography in 60% (**1**) and 29% (**2**) yield. During the preparation of **2**, an additional complex [Fe(CO)(‘$S_4C_3Me_2$’)Fe$(CO)_3$] (**3**) could be isolated (vide infra). Clusters **1** and **2** have good solubility in THF and CH_2Cl_2, but are insoluble in pentane. According to their NMR spectra, both **1** and **2** are diamagnetic and possess a twofold symmetry in solution. For **2**, which in contrast to **1** does not exhibit a crystallographically imposed C_2 symmetry, this may be explained by a rapid movement of the neopentylene bridge in solution. Figures 2 and 3 depict stereo views of the molecular structures of **1** and **2**. The coordination spheres of the metal atoms in both clusters exhibit no significant differences. Selected bond lengths and angles (Table 1) illustrate the similar structural properties of these complexes.

Both complexes consist of a trinuclear arrangement of two Fe and one Ni atom that are linked by additional metal–metal interactions. The Ni–Fe distances in **1** (248.6 pm) and **2** (ca. 250 pm) closely resemble that of the active sites of reduced [NiFe] hydrogenases (ca. 255 pm).[12] The average Ni–$S_{thiolate}$ bond length, 217.7 pm (**1**) and 218.5 pm (**2**), matches perfectly the reported Ni–S bond lengths.[13] One known complex, [Ni(‘$S_4C_3Me_2$’)], is the hypothetical residue when all [Fe$(CO)_3$] moieties of **2** are removed; it exhibits equal Ni–$S_{thioether}$ and Ni–$S_{thiolate}$ distances. The trinuclear clusters **1** and **2** show quite long Ni–$S_{thioether}$ bonds (227.8 pm in **1**, 227.4 pm in **2**) due to weaker back-bonding to the thioether ligands. This indicates a lower electron density at the Ni center, which may be caused by additional metal–metal interactions with the two iron atoms. Despite the resulting increased steric strain upon replacing an ethylene bridge in **1** with a neopentylene bridge in **2**, the structural parameters do not change significantly. Thus, only the S2–Ni–S3 angle in **2** (101.3°) is slightly larger than the corresponding S2–Ni–S2A angle in **1** (91.8°). This small variation does not decrease the $S_{thiolate}$–Ni–$S_{thiolate}$ angle in **2** as compared with **1**. Therefore, it is understandable that no dinuclear but only a trinuclear [NiFe] complex was observed. This argument agrees well with previous results on the influence of this angle on the selectivity of complex formation.[14] Very recently, two [Ni‘S_4’$Fe_2(CO)_6$] [‘S_4’ = $(RC_6H_3S_2)_2(CH_2)_3$; R = Me, H] complexes have been reported.[15] In these complexes, which are nearly a perfect match of the structural properties of **1** and **2**, again the corresponding $S_{thioether}$–Ni–$S_{thioether}$ angles [144.88(5)°, R = Me) and 143.22(3)°, R = H] are too big to lead to dinuclear [NiFe] compounds.

Although the molecular structures of **1** and **2** and the methods of their preparation are very similar, complex **3** is formed only in the reaction with the neopentylene-bridged nickel complex [Ni(‘$S_4C_3Me_2$’)]. IR monitoring of the synthesis carried out at 60 °C indicated an increased amount of **3** compared with **2**. Even then, we were unable to obtain exclusively one product. The two products could be separated by column chromatography and subsequent recrystallization. Dinuclear thiolate-bridged [Fe(CO)(‘$S_4C_3Me_2$’)-Fe$(CO)_3$] (**3**) consists of one 18 and one 16 valence electron fragment, containing Fe^0 and Fe^{II}. Complex **3** is diamagnetic and soluble in THF and CH_2Cl_2, but is insoluble in

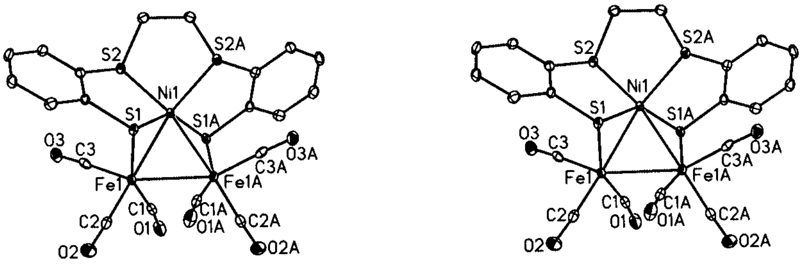


Figure 2. Stereo view of the molecular structure of **1** (50% probability ellipsoids, H atoms omitted)

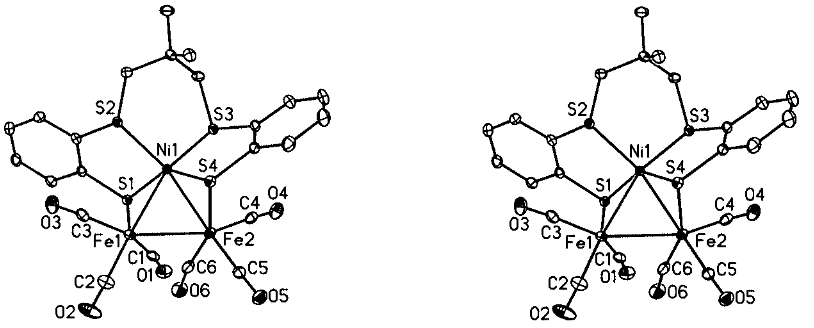


Figure 3. Stereo view of the molecular structure of **2** (50% probability ellipsoids, H atoms omitted)

Table 1. Selected bond lengths [pm] and angles [°] of clusters **1** and **2**

	1	**2**
Ni1−Fe1	248.59(6)	250.38(4)
Fe1−Fe1A[a]	260.50(7)	260.99(5)
Ni1−S1	217.67(6)	218.31(6)
Ni1−S2	227.79(7)	227.25(6)
Fe1−S1	227.32(7)	226.99(6)
Fe1−Ni1−Fe1A[a]	63.20(2)	62.94(2)
Ni1−Fe1−Fe1A[a]	58.40(1)	58.39(2)
S1−Ni1−S2	93.35(2)	93.37(2)
S2−Ni1−S2A[b]	91.76(4)	101.31(2)
S1−Ni1−S2A[b]	112.74(2)	112.10(2)
S1−Ni1−S1A[c]	142.72(4)	141.42(2)
Ni1−S1−Fe1	67.88(2)	68.39(2)
S1−Fe1−Fe1A[a]	84.29(2)	84.30(2)

[a] Fe1A in **1** = Fe2 in **2**. [b] S2A in **1** = S3 in **2**. [c] S1A in **1** = S4 in **2**.

Table 2. Selected bond lengths [pm] and angles [°] of complex **3**

Fe1−Fe2	259.16(6)	Fe1−S1	220.59(9)
Fe1−S2	222.50(9)	Fe1−S3	223.03(10)
Fe1−S4	221.02(9)	Fe2−S1	229.97(9)
Fe2−S4	230.03(10)	S1−Fe1−S2	90.35(3)
S2−Fe1−S3	91.34(3)	S3−Fe1−S4	90.47(4)
Fe1−S1−Fe2	70.19(3)	Fe1−S4−Fe2	70.11(3)
S1−Fe1−S3	162.08(4)	S2−Fe1−S4	162.34(4)
C1−Fe1−S1	98.6(2)	C1−Fe1−S2	95.2(2)
C1−Fe1−S3	99.0(2)	C1−Fe1−S4	101.8(2)
C2−Fe2−C3	100.6(2)	C2−Fe2−C4	89.3(2)
C3−Fe2−C4	97.9(2)		

pentane. NMR results reveal that this complex is of twofold symmetry. Though in its crystal structure the molecules of **3** are not situated on a crystallographic mirror plane, the molecular structure exhibits a well approximated C_s symmetry. Figure 4 depicts a stereo view of the molecular structure of **3**, and Table 2 gives selected bond lengths and angles.

A rational synthesis of **3** was finally developed using fragments this complex consists of (Scheme 2). Treatment of the ligand with iron yielded the dinuclear compound **4**. The molecular structure of the diamagnetic dimeric complex **4** is shown in Figure 5. It exhibits a twofold symmetry and is sparingly soluble in common organic solvents. Two edge-linked square pyramids are formed by sulfur donors coordinating the Fe^{II} atoms. Table 3 shows selected bond lengths and angles. Regarding its dinuclearity, **4** clearly shows that the '$S_4C_3Me_2$' ligand is less flexible than its ethylene-bridged derivative 'S_4'. Reaction of the latter ligand with iron chloride affords the tetrameric [Fe('S_4')]$_4$ compound, as already reported.[16]

Complex **4** reacts with CO (2 equiv.) to give [Fe(CO)('$S_4C_3Me_2$')]$_2$ (**5**), which also shows low solubility in common organic solvents and slowly loses its CO ligand, even in the solid state at room temperature. Complex **5** can easily be identified by its IR ν(CO) frequency. As already reported, the [Fe(CO)('S_4')]$_2$ complex is a dimer.[17] It is anticipated that **5** also consists of a dimeric structure. If complex **5** is combined with [Fe($CH_3COCH{=}CHPh$)(CO)$_3$] (2 equiv.) and stirred at 60 °C for several hours, the solution's red color increases and the only IR detectable species in the reaction solution is **3**.

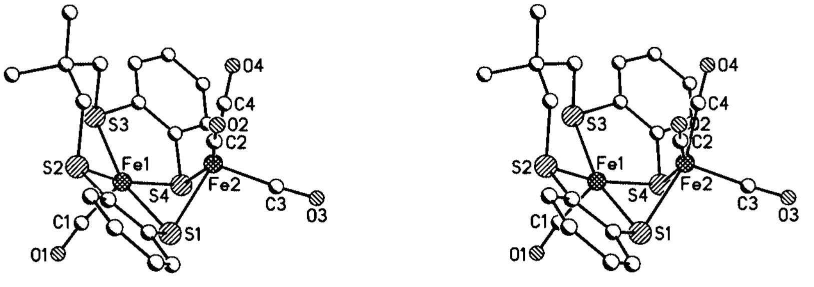
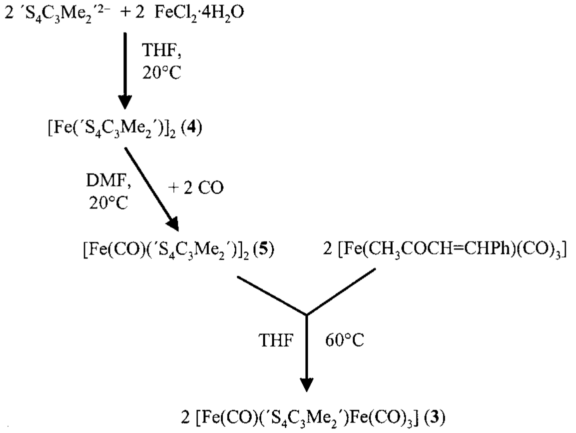


Figure 4. Stereo view of the molecular structure of **3** (H atoms omitted)



Scheme 2. Rational synthesis for the dinuclear complex **3**

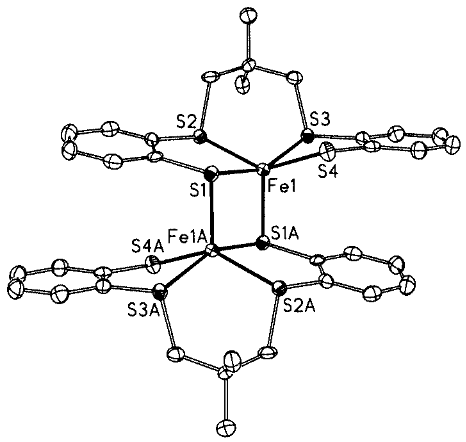


Figure 5. Molecular structure of **4** (80% probability ellipsoids, H atoms omitted)

Table 3. Selected bond lengths [pm] and angles [°] of compound **4**

Fe1−Fe1A	293.45(7)	Fe1−S1	240.72(7)
Fe1−S2	243.38(7)	Fe1−S3	250.27(8)
Fe1−S4	233.23(7)	S1−Fe1−S2	84.99(2)
S1−Fe1−S3	158.20(3)	S1−Fe1−S4	90.78(3)
S2−Fe1−S3	85.41(2)	S2−Fe1−S4	142.54(3)
S3−Fe1−S4	85.04(2)	S1−Fe1−S1A	104.28(2)
Fe1−S1−Fe1A	75.72(2)	S4−Fe1−S1A	115.22(3)
S3−Fe1−S1A	96.82(3)	S2−Fe1−S1A	101.85(2)

Reactivity of 2 and 3 towards Protons and H_2

IR monitoring indicated that compounds **2** and **3** decompose upon addition of one drop of HBF_4, with no hint of protonation or oxidation of the complexes after this treatment. The structural features of **1**−**3** encouraged us to investigate their reactivity towards hydrogen. Since **1** and **2** contain a sulfur-dominated distorted Ni coordination sphere, heterolytic splitting of the H_2 molecule might be possible, as was reported recently for related Ni−S complexes.[18] Complex **3** contains both a free coordination site and sulfur donors where hydrogen could bind and also be heterolyzed. However, even prolonged, high-pressure NMR experiments with **2** and **3** indicated no reaction between either complex and molecular hydrogen.

Summary

Although few di- and trinuclear [NiFe] complexes are known, we present here two examples of the small family of phosphane-free [NiFe] clusters that exhibit a sulfur-dominated coordination sphere of Ni, $Ni{-}S_{thiolate}{-}Fe$ bridges, Ni−Fe bond lengths as in the reduced active site of [NiFe] hydrogenases, and iron-bound carbon monoxide. The clusters are stable for weeks, both in solution and in the solid state. When changing the bridging alkyl chain from an ethylene bridge in **1** to a neopentylene bridge in **2**, the structural parameters did not change. Unlike the synthesis of **1**, with **2** an additional dinuclear Fe complex (**3**) was formed. Higher yields of **3** were obtained for the synthesis at 60 °C. Even when the steric strain of the ligand in **1** was increased in **2**, their structural properties did not differ significantly. These new complexes demonstrate that *cis*-thiolate ligands can connect Ni and Fe, resulting in trinuclear [NiFe] clusters with a sulfur-dominated coordination sphere.

Experimental Section

General Remarks: All manipulations were carried out in absolute solvents under exclusion of air. ‘$S_4C_3Me_2$’−H_2,[13b] ‘S_4’−H_2[19] ligands and the complexes [Ni(‘S_4’)]$_x$ [20] (x = 1 or 2) and [Ni(‘$S_4C_3Me_2$’)][13b] were prepared as described in the literature. IR: Perkin−Elmer 983, 1620 FT IR and 16PC FT-IR; NMR: Jeol FT-JNM-GX 270 and EX 270; mass spectrometry: Jeol MSTATION 700; elemental analysis: Carlo−Erba EA 1106 or 1108.

[Ni(‘S_4’){Fe(CO)$_3$}$_2$] (1): A solution of [Fe($CH_3COCH{=}CHPh$)(CO)$_3$] (460 mg, 1.609 mmol) in THF (20 mL) was added to 1/x equiv. of [Ni(‘S_4’)]$_x$ (500 mg, 1.609 mmol). The reaction suspension was then stirred for 24 h and the obtained solid material was removed and the solution concentrated to dryness. The resultant residue was dissolved in toluene and separated by column chromatography (silica gel, 60 cm, eluent: toluene). After the first two starting material containing fractions were eluted, a large red product fraction was washed with MeOH from the silica gel and the solvents evaporated to dryness. The residue was redissolved in THF (20 mL) and pentane (120 mL) was added. The resulting brown microcrystalline material was washed with pentane (60 mL) and dried in vacuo. Yield 310 mg (60%). ^1H NMR (269.6 MHz, CD_2Cl_2): δ = 8.06 (m, 2 H, C_6H_4), 7.70 (m, 2 H, C_6H_4), 7.32 (m, 4 H, C_6H_4), 3.60 (m, 2 H, CH_2), 2.38 (m, 2 H, CH_2). $^{13}C\{^1H\}$ NMR (67.7 MHz, CD_2Cl_2): δ = 213.3 (CO), 157.3, 133.0, 132.4, 130.0, 128.2, (C_6H_4), 42.4 (CH_2). IR (KBr): $\tilde{\nu}$ = 2028, 1993, 1942 (CO) cm^{-1}. MS (FD, THF): m/z = 646 [Ni(‘S_4’){Fe(CO)$_3$}$_2$]$^+$. $C_{20}H_{12}Fe_2NiO_6S_4$ (645.76): calcd. C 37.13, H 1.87, S 19.82; found C 38.91, H 2.08, S 19.36.

[Ni(‘$S_4C_3Me_2$’){Fe(CO)$_3$}$_2$] (2): A solution of [Fe($CH_3COCH{=}CHPh$)(CO)$_3$] (736 mg, 2.573 mmol) in THF (40 mL) was added to [Ni(‘$S_4C_3Me_2$’)] (1050 mg, 2.566 mmol). The reaction suspension was then stirred for 24 h and the resultant solid material was removed and the solution concentrated to dryness. The residue was then dissolved in a toluene/hexane (3:1) mixture, and a column for chromatography was prepared (silica gel, 60 cm, toluene/hexane, 3:1). Red and brown fractions were collected and the solvents were evaporated to dryness. The brown fraction was redissolved in THF (6 mL) and filtered; pentane (100 mL) was then added and the mixture was stored at −20 °C for 5 d, after which the solvent was decanted carefully and the resulting crystalline material was dried in vacuo. Yield 260 mg (29%). ^{1}H NMR (269.6 MHz, CD_2Cl_2): δ = 8.13 (m, 2 H, C_6H_4), 7.61 (m, 2 H, C_6H_4), 7.30 (m, 4 H, C_6H_4), 3.18 (d, 2 H, CH_2, $^2J_{H,H}$ = 13.2 Hz), 2.64 (d, 2 H, CH_2, $^2J_{H,H}$ = 13.2 Hz), 0.84 (s, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (67.7 MHz, CD_2Cl_2): δ = 212.5 (*C*O), 157.2, 137.0, 131.8, 131.4, 129.0, 127.9, (C_6H_4), 49.1 (CH_2), 36.3 (C_q), 28.1 (CH_3). IR (KBr): ṽ = 2033, 1992, 1957 (CO) cm^{-1}. MS (FD, THF): *m*/*z* = 688 [Ni(‘$S_4C_3Me_2$’){$Fe(CO)_3$}$_2$]$^+$. $C_{23}H_{18}Fe_2NiO_6S_4$ (687.80): calcd. C 40.09, H 2.63, S 18.61; found C 39.85, H 2.50, S 18.21.

[Fe(CO)(‘$S_4C_3Me_2$’)Fe(CO)$_3$] (3). (a) The red fraction obtained from column chromatography during the synthesis of **2** (see above) was concentrated to dryness and redissolved in THF (6 mL). The solution was then treated with pentane (100 mL) and kept at −20 °C for 5 d, after which the solvent was decanted carefully and the resulting crystalline material was dried in vacuo. Yield 210 mg (14%). ^{1}H NMR (269.6 MHz, CD_2Cl_2): δ = 7.82 (m, 4 H, C_6H_4), 7.33 (m, 4 H, C_6H_4), 3.55 (d, 2 H, CH_2, $^2J_{H,H}$ = 9.7 Hz); 2.23 (d, 2 H, CH_2, $^2J_{H,H}$ = 10.0 Hz), 1.50 (s, 3 H, CH_3), 1.19 (s, 3 H, CH_3). $^{13}C\{^1H\}$ NMR (67.7 MHz, CD_2Cl_2): δ = 216.9, 213.9 (*C*O), 148.9, 141.2, 131.5, 131.5, 128.6, 127.4, (C_6H_4), 54.1 (CH_2), 36.8 (C_q), 32.6, 24.1 (CH_3). IR (KBr): ṽ = 2009, 1944, 1921 (CO) cm^{-1}. MS (FD, THF): *m*/*z* = 574 [Fe(CO)(‘$S_4C_3Me_2$’)Fe(CO)$_3$}]$^+$. $C_{21}H_{18}Fe_2O_4S_4$ (573.88): calcd. C 43.92, H 3.16, S 22.33; found C 43.90, H 3.25, S 22.26. **(b)** A solution of [Fe(CH_3COCH=CHPh)(CO)$_3$] (66 mg, 0.23 mmol) in THF (10 mL) was added to a suspension of **5** (100 mg, 0.12 mmol) in THF (20 mL) and the resultant reaction mixture was stirred at 60 °C for 24 h. After filtration, the solution was then dried in vacuo, redissolved in THF (2 mL), and pentane (50 mL) was added. This mixture was then kept at −30 °C for 6 d to afford microcrystalline material that was isolated, washed with pentane (15 mL) and dried in vacuo. Yield 50 mg (38%).

[Fe(‘$S_4C_3Me_2$’)]$_2$ (4): The ligand ‘$S_4C_3Me_2$’−H_2 (120 mg, 0.34 mmol) in MeOH (7 mL) was treated with LiOMe (2 equiv., 26 mg, 0.68 mmol) and added to a solution of $FeCl_2 \cdot 4H_2O$ (68 mg, 0.34 mmol) in MeOH (5 mL). The resultant brown microcrystalline precipitate was filtered off, washed with MeOH (20 mL) and dried in vacuo. Yield 125 mg (90%). ^{1}H NMR (269.6 MHz, [D$_7$]DMF): δ = 7.60 (m, 2 H, C_6H_4), 7.45 (m, 2 H, C_6H_4), 7.25 (m, 4 H, C_6H_4), 3.20 (s, 4 H, CH_2), 1.15 (s, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (67.7 MHz, [D7]DMF): δ = 139.7, 134.6, 134.4, 129.1, 127.6, 125.9, (C_6H_4), 48.4 (CH_2), 38.2 (C_q), 26.2 (CH_3). MS (FD, DMF): *m*/*z*: = 406 [Fe(‘$S_4C_3Me_2$’)]$^+$. $C_{34}H_{36}Fe_2S_8 \cdot CH_3OH$ (843.95): calcd. C 49.76, H 4.77, S 30.36; found C 49.24, H 4.84, S 30.61.

[Fe(CO)(‘$S_4C_3Me_2$’)]$_2$ (5): CO (2 equiv., 22.4 mL, 1 mmol) was added through a septum to a suspension of **4** (405 mg, 0.50 mmol) in DMF (20 mL). This mixture was then stirred for 12 h, and the resultant solid material was filtered off, washed with DMF (10 mL) and THF (20 mL), and dried in vacuo. Yield 315 mg (73%). ^{1}H NMR (269.6 MHz, [D$_7$]DMF): δ = 7.94−6.82 (m, 8 H, C_6H_4), 3.93 (d, 1 H, CH_2, $^2J_{H,H}$ = 11.3 Hz), 3.63 (d, 1 H, CH_2, $^2J_{H,H}$ = 11.6 Hz), 2.49 (d, 1 H, CH_2, $^2J_{H,H}$ = 11.6 Hz); 2.22 (d, 1 H, CH_2, $^2J_{H,H}$ = 11.3 Hz), 1.17 (s, 3 H, CH_3), 0.68 (s, 3 H, CH_3); $^{13}C\{^1H\}$ NMR (67.7 MHz, [D7]DMF): δ = 217.3 (*C*O), 157.1, 145.6, 145.1, 135.2, 133.7, 130.7, 129.8, 128.9, 128.7, 128.1, 126.5, 121.6 (C_6H_4), 50.7, 49.7 (CH_2), 36.1 (C_q), 31.9, 23.1 (CH_3). IR (KBr): ṽ = 1938 (CO) cm^{-1}. MS (FD, DMF): *m*/*z*: = 406 [Fe(‘$S_4C_3Me_2$’)]$^+$. $C_{18}H_{18}FeOS_4$ (867.92): calcd. C 49.77, H 4.18, S 29.52; found C 49.77, H 4.18, S 28.60.

Table 4. Selected crystallographic data for [Ni(‘S_4’){$Fe(CO)_3$}$_2$] (**1**), [Ni(‘$S_4C_3Me_2$’){$Fe(CO)_3$}$_2$]·THF (**2**·THF), [Fe(CO)(‘$S_4C_3Me_2$’)-Fe(CO)$_3$] (**3**), and [Fe(‘$S_4C_3Me_2$’)]$_2$ (**4**)

	1	**2·THF**	**3**	**4**
Empirical formula	$C_{20}H_{12}Fe_2NiO_6S_4$	$C_{27}H_{26}Fe_2NiO_7S_4$	$C_{21}H_{18}Fe_2O_4S_4$	$C_{34}H_{36}Fe_2S_8$
M_r [g·mol^{-1}]	646.95	761.13	574.29	812.81
Crystal system	monoclinic	triclinic	monoclinic	orthorhombic
Space group	*P*2/*c*	$P\bar{1}$	*P*2$_1$/*n*	*Pbca*
a [pm]	1997.6(2)	1141.61(2)	1001.62(7)	1384.9(1)
b [pm]	997.58(8)	1226.32(2)	1649.20(7)	1160.2(1)
c [pm]	1176.92(7)	1296.79(2)	1411.8(2)	2152.1(2)
α [°]	90	67.808(1)	90	90
β [°]	103.772(5)	77.265(1)	91.399(6)	90
γ [°]	90	64.779(1)	90	90
V [nm^3]	2.2779(3)	1.51691(4)	2.3315(3)	3.4579(5)
Z	4	2	4	4
$\rho_{calcd.}$ [g·cm^{-3}]	1.886	1.666	1.636	1.561
μ [mm^{-1}]	2.478	1.876	1.628	1.348
Crystal size [mm]	0.21 × 0.14 × 0.03	0.38 × 0.28 × 0.12	0.25 × 0.24 × 0.17	0.13 × 0.10 × 0.05
T_{min}/T_{max}	0.648/0.926	0.662/0.874	0.741/1.000	0.898/1.000
Measured reflections	39372	40271	16767	34714
Independent reflections	5429	10461	5773	3797
Observed reflections[a]	4192	6696	3419	2716
Refined parameters	335	448	333	253
Max./min. residual density [e·nm^{-3}]	511/−651	630/−745	432/−451	383/−360
*R*1,[a] *wR*2[b] [%]	3.21, 6.59	3.88, 8.64	4.38, 8.88	3.46, 7.08

[a] $[I > 2\sigma(I)]$. [b] All data.

Reaction of 2 and 3 with Protons: $HBF_4{\cdot}Et_2O$ (one drop) was added to a solution of **2** (5 mg, 0.007 mmol) or **3** (5 mg, 0.009 mmol) in CH_2Cl_2 (5 mL). IR monitoring showed a decrease in CO band intensity and many new small CO bands.

Reaction of 2 and 3 with Hydrogen: A solution of **2** (10 mg, 0.015 mmol) or **3** (10 mg, 0.017 mmol) in $[D_8]$THF (0.4 mL) in a high-pressure NMR tube (524-PV-1, Wilmad, USA) was treated with D_2O (one drop) and 15 bar of H_2. ^1H NMR spectra were then collected over the following 70 d. Between measurements, the high-pressure NMR tubes were rotated continuously.

X-ray Structure Determination of $[Ni('S_4')\{Fe(CO)_3\}_2]$ (1), $[Ni('S_4C_3Me_2')\{Fe(CO)_3\}_2]{\cdot}THF$ (2·THF), $[Fe(CO)('S_4C_3Me_2')\text{-}Fe(CO)_3]$ (3), and $[Fe('S_4C_3Me_2')]_2$ (4): Slow diffusion of pentane into a saturated THF solution of **1** at 10 °C yielded, after 4 weeks, black plates of **1**. Black blocks of **2·THF** were obtained by maintaining a layered saturated THF solution of **2** with pentane at −30 °C for 1 week. Slow diffusion of pentane into a saturated THF solution of **3** yielded dark brown crystals of **3**. A saturated DMF solution of **4** prepared at 120 °C was cooled to room temperature, filtered, and kept at −30 °C to give, after 8 weeks, black plates of **4**. Suitable single crystals were embedded in protective perfluoro polyether oil. Data were collected at 100 K with a Nonius KappaCCD diffractometer using Mo-K_α radiation (λ = 71.073 pm), and a graphite monochromator. For **1** and **2** a numerical absorption correction was applied.[21] For **3** and **4**, a semiempirical absorption correction on the basis of multiple scans was performed.[22] Structures were solved by direct methods; full-matrix least-squares refinement was carried out on F^2 using SHELXTL NT 6.12[23] (**1**, **3**, **4**) or SHELXTL NT 5.1 (**2**).[24] All non-hydrogen atoms were refined anisotropically. All H atom positions were derived from a difference Fourier synthesis and refined with a fixed common isotropic displacement parameter. Selected crystallographic data are summarized in Table 4.[25]

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[25] CCDC-243920 (**1**), -243921 (**2**), -243922 (**3**) and -243923 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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