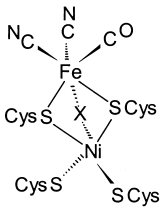
$[(C_6H_4S_2)Ni(\mu\text{-}'S_3')Fe(CO)(PMe_3)_2]$: A Dinuclear [NiFe] Complex Modeling the $[(RS)_2Ni(\mu\text{-}SR)_2Fe(CO)(L)_2]$ Core of [NiFe] Hydrogenase Centers**

Dieter Sellmann,* Franz Geipel, Frank Lauderbach, and Frank W. Heinemann

Dedicated to Professor Taube on the occasion of his 70th birthday

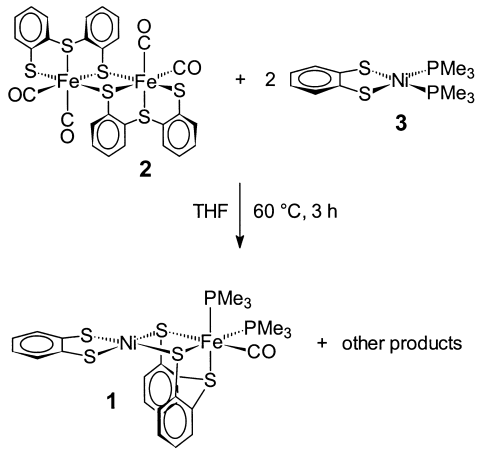
Hydrogenases are indispensable for the biological energy metabolism through catalysis of the reversible redox reaction $2H^+ + 2e^- \rightarrow H_2$.[1] Among the four types of [NiFe], [NiFeSe], Fe-only, and metal free hydrogenases, [NiFe] hydrogenases represent the majority.[2] Their active centers contain [Ni(S-cysteinate)$_4$] units bridged to [Fe(CN)$_2$(CO)] entities according to Scheme 1, which depicts the active center of hydrogenase from *D. gigas* in the oxidized form. "X" represents probably OH^- or O^{2-}.[3]



Scheme 1. Schematic structure of the active center from *D. Gigas* hydrogenase in the oxidized form ("X" = OH^- or O^{2-}).

In spite of the X-ray structure determination, the mechanism of [NiFe] hydrogenase reactions is still poorly understood, because major questions have remained unanswered. [NiFe] hydrogenases exist in numerous redox states designated by Ni–A, Ni–B, Ni–SU, Ni–SI, Ni–C, and Ni–R that can be labeled by their EPR spectra and individual ν(CO) frequencies.[2a, 4] However, it is not known how these redox states are related to the metal oxidation states, where the H_2 molecule is activated and turned over, or why two *different* metals are needed in [NiFe] hydrogenases. The relationship between ν(CO) frequencies and enzyme redox states is complicated in the sense that more reduced hydrogenase forms do not necessarily exhibit lower ν(CO) frequencies. Nickel oxidation states ranging from Ni^{III} to Ni^0, or, contrastingly, nickel thiyl species have been invoked to interprete the EPR spectra.[2c]

To solve these questions, there have been numerous attempts aimed at the synthesis of low molecular weight complexes that model the active site of [NiFe] hydrogenases. These attempts have yielded a large number of di- and oligonuclear NiFe complexes,[5] but never afforded a complex exhibiting a $[(RS)_2Ni(\mu\text{-}SR)_2Fe(CO)(CN)_2]$ core like [NiFe] hydrogenase centers. Not even analogous complexes with $[Fe(CO)(L)_2]$ entities (L = any other monodentate ligand) in place of the unique $[Fe(CO)(CN)_2]$ group could be achieved. Here we describe $[(C_6H_4S_2)Ni(\mu\text{-}'S_3')Fe(CO)(PMe_3)_2]$ (**1**), the first example of such a species ('S_3'$^{2-}$ = bis(2-mercaptophenyl)sulfide(2 –)). Complex **1** resulted from the reaction of $[Fe(CO)_2('S_3')]_2$ (**2**)[6] with labile $[Ni(PMe_3)_2('S_2')]$ (**3**),[7] according to [Eq. (1)].



Monitoring by IR spectroscopy showed that in addition to **1** several other CO-containing complexes formed. One of them, $[Fe(CO)(PMe_3)_2('S_3')]$ (**4**), which shows a ν(CO) band at 1938 cm^{-1} (in THF), could be synthesized independently from **2** and PMe_3,[8] and was completely characterized. The title complex **1** is sparingly soluble in THF and crystallized directly from the reaction solution in 20% yield.

Previous results had shown that **2** reacts with L = phosphane or CN^- to give stereoselectively $[Fe(CO)(L)_2('S_3')]$ complexes.[6] In line with this, the formation of **1** can be rationalized by a sequence of steps in the course of which PMe_3 dissociates from **3** and reacts with **2** to give **4**, which subsequently adds the $[Ni(C_6H_4S_2)]$ fragments resulting from **3**. Figure 1 depicts the molecular structure of **1** as determined

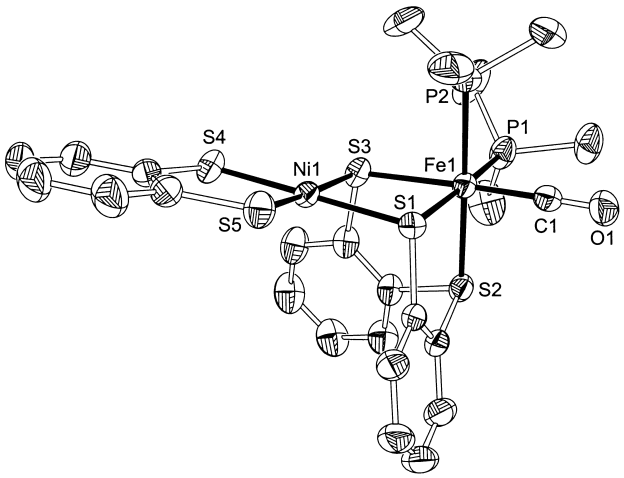


Figure 1. Molecular structure of **1** (50% probability ellipsoids; H atoms omitted). Selected distances [pm] and angles [°]: Ni1-S1 224.2(1), Ni1-S3 224.0(1), Ni1-S4 215.9(2), Ni1-S5 214.1(2), Fe1-S1 230.3(1), Fe1-S2 225.4(1), Fe1-S3 231.7(1), Fe1-C1 174.8(3), Fe1-P1 226.8(1), Fe1-P2 226.7(1), Ni1···Fe1 332.3(1), S1···S3 309.1(2); S1-Ni1-S3 87.19(4), S1-Ni1-S4 178.81(5), S1-Ni1-S5 89.43(5), S3-Ni1-S4 91.80(5), S3-Ni1-S5 173.83(5), S4-Ni1-S5 91.63(5), S1-Fe1-S2 88.44(4), S1-Fe1-S3 83.98(4), S2-Fe1-S3 88.57(4), S1-Fe1-P1 175.08(4), S1-Fe1-C1 93.0(1), S3-Fe1-P1 91.46(4), P1-Fe1-C1 91.5(1), S3-Fe1-C1 177.0(1), S2-Fe1-P2 176.62(4).

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by X-ray crystallography, together with selected distances and angles.[9]

The nickel center N1 is surrounded by four thiolate donors (S1, S3, S4, S5) in an essentially planar geometry, the iron center is pseudo-octahedrally coordinated. The CO ligand adopts a position *trans* to the bridging thiolate donor S3. The S1 and S3 thiolate donors of the $[Fe(CO)(PMe_3)_2(\text{'}S_3\text{'})]$ unit bridge the nickel and iron centers. The Ni–S distances lie in the range of 214–225 pm typical for diamagnetic four-coordinate Ni^{II} thiolate complexes.[5, 10] The bridging Ni–S distances (223.0(1) and 224.1(2) pm), however, are distinctly longer than the terminal Ni–S distances (215.9(1) and 214.1(2) pm), possibly indicating that a dissociation of the $[Ni(C_6H_4S_2)]$ unit is facilitated. The four-membered [NiS1S3Fe] ring exhibits a small dihedral angle of 11.40(6)° along the S1–S3 line. All distances and angles in the $[Fe(CO)(PMe_3)_2(\text{'}S_3\text{'})]$ unit are nearly identical to those found in mononuclear $[Fe(CO)(dppe)(\text{'}S_3\text{'})]$ (dppe = 1,2-(diphenylphosphanyl)ethane).[6] The Fe–S(thioether) distance is shorter than the Fe–S(thiolate) distances. Terminal and bridging Fe–S(thiolate) distances in mononuclear $[Fe(CO)(dppe)_2(\text{'}S_3\text{'})]$ and dinuclear **1** differ marginally by at best 1–2 pm. In this respect, the structure of **1** reflects the remarkable structural rigidity of $[Fe(\text{'}S_3\text{'})]$ fragments towards electronic effects exerted by coligands.[6] The Ni–Fe distance of **1** (332.3(1) pm) excludes a direct Ni–Fe bond, is similar to those found for other thiolate-bridged NiFe complexes (280–370 pm),[5] and is larger than the Ni–Fe distances found in the active sites of oxidized or reduced [NiFe] hydrogenases which range from 260 to 290 pm.[3, 11] The significance of these distances is matter of another controversial debate because theoretical calculations predict that [NiFe] hydrogenases may exhibit Ni–Fe distances of up to 345 pm when associating H_2.[12] As judged by its ^1H and ^{31}P NMR spectra, complex **1** is diamagnetic and contains, in accordance with the route of synthesis, low-spin Ni^{II} and Fe^{II} centers. The ν(CO) frequency of **1** appears at 1948 cm^{-1} (in KBr).

Synthesis, spectroscopic properties and structure of **1** permit a series of conclusions. The synthesis of **1** demonstrates that complexes containing $[(RS)_2Ni(\mu\text{-}SR)_2Fe(CO)(L)_2]$ cores can form in "self-assembly" type reactions. The spectroscopic properties of **1** enable one to assess the influence of binding a $[Ni(SR)_2]$ to a $[Fe(CO)(CN)_2(SR)_2]$ unit upon the ν(CO) frequency, whether the ν(CO) frequency is red- or blue-shifted, and to comment upon the controversial assignment of metal oxidation states for the various redox forms of [NiFe] hydrogenases. The three complexes **1**, **4**, and **5** synthesized previously[6] exhibit ν(CO) frequencies in KBr at 1948 cm^{-1} (**1**), 1932 cm^{-1} (**4**), and 1924 cm^{-1} (**5**). Comparison of **4** and **5** demonstrates that replacing CN^- by PMe_3 blue-shifts the ν(CO) frequency by 8 cm^{-1}. This is rationalized by the fact that PMe_3 is a poorer donor and better acceptor than CN^-. Binding $[Ni(C_6H_4S_2)]$ to **4** further blue-shifts the ν(CO) frequency by 16 cm^{-1}. This shows that the $[Ni(SR)_2]$ unit withdraws electron density from the iron center of the $[Fe(CO)(L)_2(SR)_2]$ core. Combining the ν(CO) data of **1**, **4**, and **5** results in a ν(CO) frequency of about 1940 cm^{-1} for the as-yet hypothetical $[(C_6H_4S_2)Ni(\mu\text{-}\text{'}S_3\text{'})Fe(CO)(CN)_2]^{2-}$ ion. This anion nearly duplicates the donor atom set of [NiFe] hydrogenase centers, hence its expected frequency of 1940 cm^{-1} would be indicative for a Ni^{II}/Fe^{II} oxidation state of the active site. The ν(CO) frequency of 1940 cm^{-1} corresponds to the Ni–R state of hydrogenases, which is the most reduced ("fully reduced") state of hydrogenase, EPR silent (as is **1**), and directly involved in the turnover of H_2.[4]

$[(C_6H_4S_2)Ni(\mu\text{-}\text{'}S_3\text{'})Fe(CO)(PMe_3)_2]$ **1** 1948 cm^{-1}

$[Fe(CO)(PMe_3)_2(\text{'}S_3\text{'})]$ **4** 1932 cm^{-1}

$(NEt_4)_2[Fe(CO)(CN)_2(\text{'}S_3\text{'})]$ [6] **5** 1924 cm^{-1}

The molecular parameters of **1** suggest the reason for the unique arrangement of two cyano and one carbonyl ligand at the iron center in [NiFe] hydrogenase. One purpose of the CN^- and CO ligands is assumed to keep the Fe^{II} center in the low-spin state throughout all hydrogenase reactions.[1b] The other one could be to warrant a tight binding of the $[Ni(SR)_2]$ unit. The structure of **1** exhibits bridging Ni–S(thiolate) distances that are almost 10 pm longer than the terminal ones. Replacing PMe_3 in **1** by the more electron-donating CN^- ligands can be expected to enhance the nucleophilicity of the 'S$_3$' thiolate donors and in turn the bonding to the nickel. An identical mechanism might hold true for the hydrogenase centers, and our efforts to synthesize the dicyano derivative of **1** will be continued.

Experimental Section

All manipulations were carried out in absolute solvents under exclusion of air. $[Fe(CO)_2(\text{'}S_3\text{'})]_2$[6] and $[Ni(PMe_3)_2(\text{'}S_2\text{'})]$[7] were prepared as described in the literature.

1: A THF suspension (25 mL) of $[\{Fe(CO)_2(\text{'}S_3\text{'})\}_2]$ (326 mg, 0.45 mmol) and $[Ni(PMe_3)_2(\text{'}S_2\text{'})]$ (318 mg, 0.90 mmol) was heated to 60 °C for 3 h. MeOH (60 mL) was added to the resulting dark red to black solution, and the mixture was reduced in volume by about one fourth. Black material which precipitated was removed by filtration, and the filtrate was stored at room temperature. Dark red to black crystals which crystallized from the solution were separated after two weeks, washed with Et_2O, and dried in vacuo. Yield: 114 mg (19%). IR (KBr): $\tilde{\nu} = 1948\ cm^{-1}$ (CO); IR (Nujol): $\tilde{\nu} = 1952\ cm^{-1}$ (CO); elemental analysis calcd (%) for $C_{25}H_{30}FeNiOP_2S_5$ (683.29): C 43.95, H 4.43, S 23.46; found: C 44.04, H 4.57, S 23.33. Complex **1** is sparingly soluble in all common solvents and slowly decomposes in CH_2Cl_2 or THF solution. NMR spectra could be recorded in CD_2Cl_2. ^1H NMR (399.7 MHz, CD_2Cl_2): $\delta = 8.01$ (m, 1H; 'S$_3$'), 7.89 (m, 1H; 'S$_3$'), 7.87 (m, 1H; 'S$_3$'), 7.76 (m, 1H; 'S$_3$'), 7.38–7.23 (m, 4H; 'S$_3$'), 7.03 (m, 2H; $C_6H_4S_2$), 6.61 (m, 2H; $C_6H_4S_2$), 2.34 (d, 9H, $^2J_{P,H} = 9.8$ Hz; PMe_3), 1.21 (d, 9H, $^2J_{P,H} = 8.8$ Hz; PMe_3); $^{31}P\{^1H\}$ NMR (161.7 MHz, CD_2Cl_2): $\delta = 18.69$ (d, $^2J_{P,P} = 47.2$ Hz), 11.67 (d, $^2J_{P,P} = 47.4$ Hz) (PMe_3).

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[8] $[Fe(CO)(PMe_3)_2(`S_3')]$ (**4**): A THF suspension (30 mL) of $[\{Fe(CO)_2(`S_3')\}_2]$ (240 mg, 0.33 mmol) and PMe_3 (0.25 mL, 2.4 mmol) was stirred for one day. Undissolved material was removed by filtration and the red filtrate was evaporated to dryness. Purification of the residue by dissolution in MeOH (20 mL), filtration, evaporation to dryness, re-dissolution of the remaining residue in toluene (3 mL), and precipitation by adding *n*-pentane (15 mL) yielded pure **4** as red-brown powder. Yield 200 mg (62 %) .Elemental analysis calcd (%) for $C_{19}H_{26}FeOP_2S_3$ (483.39): C 47.11, H 5.41, S 19.86; found: C 47.19, H 5.59, S 20.06; IR (KBr): $\tilde{\nu} = 1932\ cm^{-1}$ (CO); MS (FD, CH_3CN); *m*/*z*: 484 $[Fe(CO)(PMe_3)_2(`S_3')]^+$; ^1H NMR (399.7 MHz, CD_2Cl_2): $\delta = 7.68$ (m, 1H; C_6H_4), 7.54 (m, 1H; C_6H_4), 7.42 (m, 2H; C_6H_4), 6.97 (m, 2H; C_6H_4), 6.83 (m, 2H; C_6H_4), 1.61 (d, 9H, $^2J_{P,H} = 9.4$ Hz; PC_3H_9), 1.36 (d, 9H, $^2J_{P,H} = 8.9$ Hz; PC_3H_9); $^{13}C\{^1H\}$ NMR (100.4 MHz, CD_2Cl_2): $\delta =$ 214.9 (dd, $^2J_{P,C} = 20.1$ Hz, $^2J_{P,C} = 21.1$ Hz, CO), 156.9 (d, $J_{P,C} = 9.1$ Hz), 154.7 (d, $J_{P,C} = 12.9$ Hz), 139.5 (d, $J_{P,C} = 17.4$ Hz), 138.5, 130.9, 130.5, 130.1, 129.0, 128.9, 128.1, 121.7, 121.3, (C_6H_4), 18.6 (d, $^1J_{P,C} = 29.2$ Hz), 18.0 (d, $^1J_{P,C} = 26.6$ Hz) (PCH_3); $^{31}P\{^1H\}$ NMR (161.7 MHz, CD_2Cl_2): $\delta = 21.05$, 14.23 (d, $^2J_{P,P} = 50.4$ Hz PC_3H_9).

[9] X-ray structure analysis of **1**: Dark red to black blocks of **1** were obtained directly from a saturated THF/MeOH reaction solution. Suitable single crystals were embedded in protecting perfluoropolyether oil. Data were collected on a Siemens P4 diffractometer using $Mo_{K\alpha}$ radiation ($\lambda = 71.073$ pm), a graphite monochromator, and ω-scan technique. Absorption correction was applied on the basis of ψ scans ($T_{min} = 0.123$, $T_{max} = 0.149$). $C_{25}H_{30}FeNiOP_2S_5$, crystal size $0.09 \times 0.56 \times 0.52$ mm, monoclinic, space group $P2_1/n$, $a = 1032.4(2)$, $b = 1702.2(2)$, $c = 1712.6(3)$ pm, $\beta = 104.72(1)$, $V = 2.9109(7)$ nm^3, $Z = 4$, $\rho_{calcd} = 1.559$ g cm^{-3}, $T = 220(2)$ K, $\mu = 1.632$ mm^{-1}, 8715 measured reflections ($4.2 < 2\theta < 56^\circ$), 7035 unique reflections, 5476 observed reflections, 438 parameters, $wR2 = 0.0832$, $R1 = 0.0379$ ($I > 2\sigma(I)$). The structure was solved by direct methods and refined by full-matrix least-squares calculations on F^2. The structure of **1** contains both enantiomers of **1**. A disorder is observed in which the two enantiomers share a single site. The site occupation factors have been refined giving 93.4(2) % for the major and 6.6(2) % for the minor component. The non-hydrogen atoms of the major component have been refined with anisotropic displacement parameters while the corresponding atoms of the minor component have been refined isotropically with group-wise refined isotropic diplacement parameters for the carbon atoms. The hydrogen atoms of the major component of **1** were taken from a difference Fourier map and were kept fixed with a common isotropic displacement parameter. No hydrogen atoms were taken into account for the minor component. CCDC 172509 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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Highly Enantioselective Preparation of Multifunctionalized Propargylic Building Blocks**

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Optically active propargylic alcohols are versatile building blocks in the synthesis of a broad variety of natural compounds and drugs.[1] Therefore, numerous synthetic approaches have been developed to obtain propargylic alcohols with high enantiomeric excesses. Chemical methods offer straightforward access to these compounds, for example, enantioselective reductions[2] or asymmetric zinc-mediated additions to aldehydes,[3] as well as enzymatic methods with oxidoreductases[4] or lipases[5]. Nevertheless, most published procedures do not give enantiomerically pure α,β-alkynyl-substituted methanols. Moreover, there has been only one report of a chiral α,β-alkynyl α-chloro- or α-bromohydrin. Corey and co-workers obtained (*R*)-4-triisopropylsilyl-1-chloro-3-butyn-2-ol by oxazaborolidine reduction of the corresponding ketone. However, the authors indicated that the bulky triisopropylsilyl group was essential for an *ee* of 95 %.[2c] In general, reduction methods applied to α-chloro- or α-bromo ketones need to be mild as a result of possible side reactions at the activated α position. Furthermore, zinc-mediated additions to aldehydes cannot be used for the preparation of α,β-alkynyl α-chloro- or α-bromohydrins.[6] Nevertheless, propargylic α-chlorohydrins could be easily transformed, for example, into epoxides, thus offering novel comprehensive applications in organic syntheses.

In preceding studies, we synthesized a broad variety of enantiopure propargylic alcohols by the enzymatic reduction of alkynones.[7] Thus, both enantiomers of α,β-alkynyl-substituted methanols are accessible. Our interest in a general approach to obtain optically pure building blocks as intermediates in organic syntheses encouraged us to continue our

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