$[Fe_2\{SeC_6H_2\text{-}2,4,6\text{-}Ph_3\}_2\{N(SiMe_3)_2\}_2]$ and $[Fe_2\{SeC_6H_2\text{-}2,4,6\text{-}Ph_3\}_4]$, the First Three-Coordinate Selenolatoiron Complexes

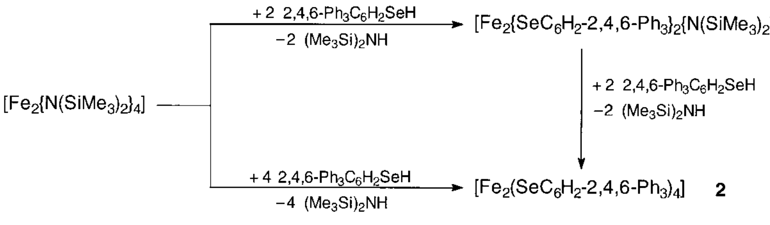
Ralf Hauptmann, Rainer Kliß, and Gerald Henkel*

Dedicated to Professor Bernt Krebs
on the occasion of his 60th birthday

Iron complexes with sterically nondemanding chalcogen ligands are characterized by a coordination number of 4 if the ligand donor functions are negatively charged. They comprise not only the mixed sulfidothiolato complexes of composition $[Fe_nS_n(SR)_4]^{2-/3-}$ but also the homoleptic thiolato complexes of general formula $[Fe(SR)_4]^{-/2-}$, which have attracted considerable interest as models for the active sites of 2Fe–2S ($n=2$) and 4Fe–4S ferredoxins ($n=4$) and of rubredoxins.[1, 2] Within the ferredoxin-like complexes, FeS_4 tetrahedra are connected through common S···S edges. Similar connectivity patterns also occur in the dinuclear homoleptic alkane thiolato complexes of general formula $[Fe_2(SR)_6]^{2-}$, if the sulfur atoms are bound to primary or secondary C atoms. This pattern may change, however, if *tert*-butane thiolato ligands are used instead, as illustrated by the unexpected formation of the dinuclear iron complex $[Fe_2(SC_4H_9)_5]^-$, in which the FeS_4 tetrahedra share a common face.[3] In the meantime, related cobalt and nickel complexes are also known.[4–6] In search of further parameters which may influence the coordination number and/or the degree of condensation within thiolatoiron complexes, sterically demanding thiolato ligands with bulky substituents have attracted increasing interest in the last few years. Following this concept, the first complexes of coordination number 2[7] and 3[8] were synthesized and structurally characterized.

Based on these considerations, we extended our approach to control the degree of condensation and/or the coordination number in transition metal chalcogenolate complexes by using selenolato ligands which combine high nucleophilicities with large spatial demands. Although we have obtained the first dinuclear cobalt complexes with face-sharing MSe_4 tetrahedra by using this concept,[9] comparable results for iron complexes have so far remained elusive. More successful, however, were our efforts to stabilize unusually low coordination numbers. In this paper we report on the first selenolatoiron complexes of coordination number 3.

During our investigations of the reactivity of 2,4,6-triphenylselenophenol towards iron(II) bis(trimethylsilyl)amide,[10] we isolated the novel molecular complexes **1** and **2** in crystalline form (Scheme 1). Whereas **1** was obtained from the reaction of iron(II) bis(trimethylsilyl)amide with 2,4,6-triphenylselenophenol in the molar ratio of 1:1 in a mixture of toluene and hexane, the reaction in the 1:2 molar ratio led to the formation of **2**. Complex **1** can also be converted to **2** by treatment with two further equivalents of 2,4,6-triphenylselenophenol. These results demonstrate that the partial (formation of **1**) or complete (formation of **2**) replacement of amide ligands in the complex iron(II) bis(trimethylsilyl)amide can be controlled by varying the reaction conditions.



Scheme 1. Synthesis of **1** and **2** from $[Fe_2\{N(SiMe_3)_2\}_4]$ and $2,4,6\text{-}Ph_3C_6H_2SeH$.

Complex **1** with a mixed selenolatoamido ligand sphere is the first member of a new class of complexes. Closely related to **1** is the complex **3**, in which iron is replaced by manganese and which contains additional thf ligands.[11] Interestingly, complexes with mixed thiolatoamido ligand spheres are also rare. The few examples known so far include the trinuclear complexes **4** (M = Zn[12] and Fe[8c]), the dinuclear complex **5**,[13] and the mononuclear complex **6**.[7] To date, complexes with mixed tellurolatoamido ligand spheres are completely unknown.

$[Mn_2(SeC_6H_2\text{-}2,4,6\text{-}i\text{Pr}_3)_2\{N(SiMe_3)_2\}_2(thf)_2]$ **3**

$[M_3(SC_6H_2\text{-}2,4,6\text{-}i\text{Pr}_3)_4\{N(SiMe_3)_2\}_4]$ **4**

$[Mo_2(St\text{Bu})_2(NMe_2)_4]$ **5**

$[Fe\{SC_6H_3\text{-}2,6\text{-}(C_6H_2\text{-}2,4,6\text{-}Me_3)_2\}\{N(SiMe_3)_2\}]$ **6**

During the formation of **1**, the selenolato ligand evidently prefers the bridging position probably because it is a softer base than the leaving amide group. From a chemical point of view, the mixed selenolatoamido complex is of special interest because it should be possible to introduce ligands other than those described here by a controlled replacement of the terminally bonded bis(trimethylsilyl)amide groups by suitable acid–base reactions. Therefore, **1** might serve as a starting material for the synthesis of complexes with mixed chalcogen ligand spheres (e.g. sulfur/selenium) or complexes of higher nuclearities.

Crystals of **1** (Figure 1) and **2** (Figure 2) consist of isolated electroneutral $[Fe_2\{SeC_6H_2\text{-}2,4,6\text{-}Ph_3\}_2\{N(SiMe_3)_2\}_2]$ and $[Fe_2\{SeC_6H_2\text{-}2,4,6\text{-}Ph_3\}_4]$ molecules, respectively.[14] In both cases, the iron atoms possess trigonal coordination geometries with pyramidally distorted $FeSe_2N$ (**1**) and $FeSe_3$ (**2**) coordination sites. The mean bond angles of the iron atoms are 115.8° in **1** and 116.3° in **2**, respectively. The iron atoms are brigded by two selenolato ligands. In **2**, each of the iron atoms binds a further selenolato ligand, whereas in the case of **1**, the

---

[*] Prof. Dr. G. Henkel, Dr. R. Hauptmann, Dipl.-Chem. R. Kliß
Institut für Synthesechemie der Universität
Lotharstrasse 1, D-47048 Duisburg (Germany)
Fax: (+49) 203-3792110
E-mail: biohenkel@uni-duisburg.de

[**] Financial support by the Deutsche Forschungsgemeinschaft (DFG), the Bundesminister für Bildung, Wissenschaft, Forschung und Technologie (BMBF) and the Fonds der Chemischen Industrie is gratefully acknowledged.

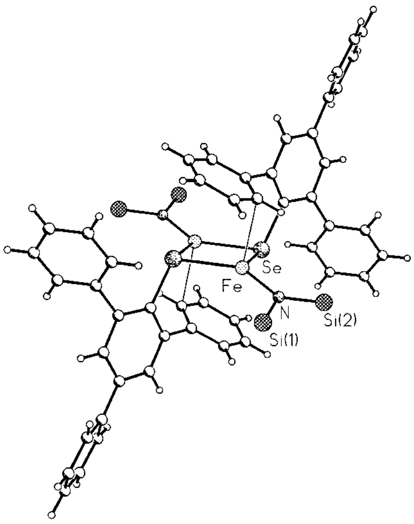


Figure 1. Structure of **1** in the crystal (methyl groups of the silyl substituents are omitted for clarity). Selected distances [Å] and angles [°]: Fe⋯Fe 3.170(1), Fe–Se 2.476(1) and 2.506(1), Fe–N 1.923(2), Fe⋯C 2.602(2); Se-Fe-N 116.6(1), Se-Fe-Se′ 101.0(1), N-Fe-Se′ 138.7(1), Se-Fe⋯C 88.3(1), Se′-Fe⋯C 95.6(1), N-Fe⋯C 101.7(1).

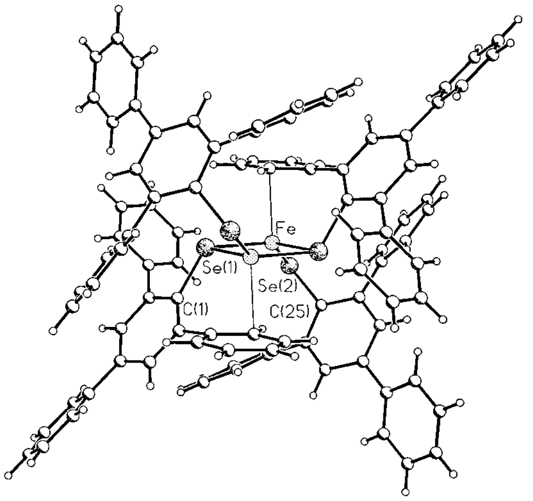


Figure 2. Structure of **2** in the crystal. Selected distances [Å] and angles [°]: Fe⋯Fe 3.207(1), Fe–Se(1) 2.491(1), Fe–Se(2) 2.383(1), Fe–Se(1)′ 2.449(1), Fe⋯C 2.530(2); Se(1)-Fe-Se(2) 129.2(1), Se(1)-Fe-Se(1′) 99.0(1), Se(2)-Fe-Se(1′) 120.7(1), Se(1)-Fe⋯C 87.2(3), Se(2)-Fe⋯C 119.9(3), Se(1)′-Fe⋯C 90.5(3).

coordination is completed by a terminal bis(trimethylsilyl)amide group.

In both complexes, the iron atoms deviate from the plane defined by the coordinating atoms by distances of 0.24 Å (**1**) and 0.46 Å (**2**), respectively. This is probably due to a specific orientation of the ligands which allows for a weak Fe⋯C interaction. One of the phenyl rings of each bridging selenolato ligand is oriented approximately parallel to the central Fe_2Se_2 unit, thus supporting this iron–carbon contact, which is roughly normal to the plane defined by the Se_2N or Se_3 donor set, respectively. As a consequence, the Fe atom is shifted from this plane in the direction of the phenyl ring. The corresponding Fe⋯C distances are 2.602(2) (**1**) and 2.530(3) Å (**2**), respectively. A similar weak Fe⋯C interaction has been discussed in the complex $[Fe(SC_6H_3\text{-}2,6\text{-}Mes_2)_2]$ with formally two-coordinate iron centers (Fe⋯C 2.470 Å).[7] In all these cases, however, the additional interactions have to be considered rather weak because Fe–C distances observed in other iron complexes containing η^2-η^6-coordinated carbon ligands range from 1.90 to 2.25 Å.[15]

The similar geometries of the central Fe_2Se_2 units are reflected in the comparable Fe⋯Fe distances in **1** (3.170(1) Å) and **2** (3.207(1) Å). The corresponding (μ_2-Se)-Fe-(μ_2-Se) angles are as small as 101.0(1) and 99.0(1)°, and the Fe-(μ_2-Se)-Fe angles are 79.0(1) and 81.0(1)°, respectively. The mean Fe–(μ_2-Se) bond lengths in **1** (2.491 Å) and **2** (2.470 Å) differ only slightly. As expected, the terminal Fe–Se bonds in **2** are significantly shorter (2.383(1) Å). The Fe–N distance in **1** (1.923(2) Å) is in the same range as in the iron(II) bis(trimethylsilyl)amide used as starting material.[16]

The results presented here clearly demonstrate that synthetically versatile and sterically demanding selenolato ligands can be used to prepare novel coordinatively unsaturated complexes that are stabilized by a weak binding interaction between the metal center and a carbon atom of a neighboring ligand. This type of interaction could be of interest to explain the stabilization and activation of the FeMo cofactor of nitrogenases (binding of small exogenic molecules such as H_2O or N_2), which contains coordinatively unsaturated trigonal FeE_3 units (E = S).[17] Investigations of the reactivity of related sulfur complexes have already shown that small neutral molecules with suitable donor functions such as acetonitrile can be added very easily under expansion of the coordination sphere of the iron atom.[18]

Experimental Section

All operations were performed in glove boxes under a pure dinitrogen atmosphere.

1: A solution of 2,4,6-triphenylselenophenol (1.93 g, 5 mmol) in toluene (20 mL) was added dropwise to a solution of iron(II) bis(trimethylsilyl)amide (1.88 g, 5 mmol) in toluene/hexane (1:1; 20 mL). The red-brown reaction mixture was stirred for 24 h at ambient temperature and then filtered. Within a period of three days at 2 °C, pale brown crystals were obtained. Yield: 0.63 g (21 %).

2: A solution of 2,4,6-triphenylselenophenol (1.31 g, 3.4 mmol) in toluene (20 mL) was added slowly to a solution of iron(II) bis(trimethylsilyl)amide (0.64 g, 1.7 mmol) in toluene (10 mL). After stirring for 48 h at ambient temperature, the red-brown reaction mixture was evaporated to dryness. The residue was recrystallized from hexane/toluene (1:2; 15 mL). Within two days at ambient temperature, red crystals were obtained. Yield: 0.84 g (30 %).

Received: May 4, 1998
Revised version: September 30, 1998 [Z11809IE]
German version: *Angew. Chem.* **1999**, *111*, 389–391

Keywords: iron · nitrogen · nitrogenase · selenium

---

[1] S. J. Lippard, J. M. Berg, *Bioanorganische Chemie*, Spektrum, Heidelberg, **1995**.

[2] a) G. Henkel, B. Krebs, *Angew. Chem.* **1991**, *103*, 785; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 769; b) R. H. Holm, K. S. Hagen, *Inorg. Chem.* **1984**, *23*, 418.

[3] C. Chen, G. Henkel, *Inorg. Chem.* **1993**, *32*, 1064.

[4] S. Weißgräber, G. Henkel, *Angew. Chem.* **1992**, *104*, 1382; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1368.

[5] K. Ruhlandt-Senge, P. P. Power, *J. Chem. Soc. Dalton Trans.* **1993**, 649.

[6] A. Silver, M. Millar, *J. Chem. Soc. Chem. Commun.* **1992**, 948.

[7] J. J. Ellison, K. Ruhlandt-Senge, P. P. Power, *Angew. Chem.* **1994**, *106*, 1248; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1178.

[8] a) P. P. Power, S. C. Shoner, *Angew. Chem.* **1991**, *103*, 308; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 330; b) K. Ruhlandt-Senge, P. P. Power, *Bull. Soc. Chim. Fr.* **1992**, *129*, 594; c) F. M. MacDonnell, K. Ruhlandt-Senge, J. J. Ellison, R. H. Holm, P. P. Power, *Inorg. Chem.* **1995**, *34*, 1815.

[9] G. Henkel, S. Weißgräber, unpublished results.

[10] R. A. Andersen, K. Faegri, J. C. Green, A. Haaland, W.-P. Leung, K. Rypdal, *Inorg. Chem.* **1988**, *27*, 1782.

[11] N. Bochmann, A. K. Powell, X. Song, *Inorg. Chem.* **1994**, *33*, 400.

[12] H. Grützmacher, K. Steiner, H. Pritzkow, L. Zsolnai, G. Huttner, A. Sebald, *Chem. Ber.* **1992**, *125*, 2199.

[13] M. H. Chisholm, J. F. Corning, J. C. Huffman, *Inorg. Chem.* **1983**, *22*, 38.

[14] Crystal data: Siemens P4RA four circle diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), graphite monochromator, rotating-anode generator, scintillation counter, 150 K, empirical absorption corrections, SHELXTL-PLUS programs, direct methods, least-squares refinements, one scaling factor, one isotropic extinction parameter. **1**: $C_{60}H_{70}N_2Si_4Fe_2Se_2$, formula weight 1201.16, monoclinic, space group $P2_1/n$, $a = 10.822(1)$, $b = 17.705(3)$, $c = 15.720(2)$ Å, $\beta = 106.34(1)^\circ$, $V = 2890.35$ Å^3, $Z = 2$, $\rho_{calcd} = 1.380\,g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 1.88\,mm^{-1}$, transmission range 0.818–0.754, crystal dimensions ca. $0.77 \times 0.32 \times 0.28$ mm, ω scan, $2\theta_{max} = 48^\circ$, 4729 unique reflections, $R(R_w) = 0.0266$ (0.0285) for 3833 observed reflections ($I > 2\sigma(I)$), 323 variables, non-hydrogen atoms anisotropic, H atoms at idealized positions. **2**: $C_{96}H_{68}Fe_2Se_4$, formula weight 1649.04, monoclinic, space group $P2_1/n$, $a = 12.073(4)$, $b = 18.531(7)$, $c = 16.563(6)$ Å, $\beta = 98.39(3)^\circ$, $V = 3665.90$ Å^3, $Z = 2$, $\rho_{calcd} = 1.494\,g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 2.43\,mm^{-1}$, transmission range 0.654–0.471, crystal dimensions ca. $0.62 \times 0.25 \times 0.19$ mm, ω scan, $2\theta_{max} = 54^\circ$, 7953 unique reflections, $R(R_w) = 0.0461$ (0.0376) for 4749 observed reflections ($I > 2\sigma(I)$), 462 variables, non-hydrogen atoms anisotropic, H atoms at idealized positions. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101550 (**1**) and CCDC-101551 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[15] A. J. Deeming in *Comprehensive Organometallic Chemistry* (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon, Oxford, **1984**.

[16] M. M. Olmstead, P. P. Power, S. C. Shoner, *Inorg. Chem.* **1991**, *30*, 2547.

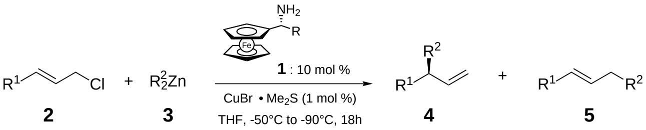
[17] a) J. Kim, D. C. Rees, *Nature* **1992**, *360*, 553; b) J. Kim, D. C. Rees, *Science* **1992**, *257*, 1667; c) M. K. Chan, J. Kim, D. C. Rees, *Science* **1993**, *260*, 792; d) J. T. Bolin, A. E. Ronco, T. V. Morgan, L. E. Mortenson, *Proc. Natl. Acad. Sci. USA* **1993**, *90*, 1078; e) H. Schindelin, C. Kisker, J. L. Schlessman, J. B. Howard, D. C. Rees, *Nature* **1997**, *387*, 370.

[18] R. Hauptmann, R. Kliß, J. Schneider, G. Henkel, *Z. Anorg. Allg. Chem.* **1998**, *624*, 1927.

Copper(I)-Catalyzed Enantioselective Substitution of Allyl Chlorides with Diorganozinc Compounds**

Frank Dübner and Paul Knochel*

Catalytic asymmetric allylic substitutions are potentially useful methods for the preparation of a wide range of chiral molecules. Several highly enantioselective palladium(0)-catalyzed allylic substitutions have been described in recent years;[1] however, these reactions are generally limited to symmetrical substrates. Only recently, several regioselective palladium(0)-catalyzed asymmetric allylation reactions have been reported.[2] Alternatively, copper(I)-catalyzed asymmetric allylations can be performed. These reactions proceed with high S_N2' regioselectivity and therefore accommodate unsymmetrical allylic substrates as starting materials. A further advantage is that a broad range of organometallic compounds (organolithium, Grignard, and organozinc reagents) can be used in these allylic substitutions.[3] Unfortunately, only moderate enantioselectivities are usually obtained in these copper(I)-catalyzed allylations.[4] To develop such an asymmetric reaction, we have screened a broad range of ligands (amines, diamines, phosphanes, phosphites, sulfur derivatives) and have observed that primary amines show the highest catalytic activity. Further fine-tuning of chiral primary amines indicated that chiral ferrocenyl amines of type **1** are highly effective ligands. Thus, the substitution of various unsymmetrical allyl chlorides of type **2** with diorganozinc reagents **3** in the presence of CuBr · Me_2S (1 mol %) and **1** (10 mol %) as catalyst leads to the desired allylated products **4**. The reaction is highly regioselective (ratio **4**:**5** > 90:10) and affords products **4** with up to 87 % *ee* (Scheme 1 and Table 1).



Scheme 1. Copper(I)-catalyzed enantioselective allylation. The groups R^1 and R^2 are given in Table 1, and the group R is defined in Scheme 2.

The ligands **1** are readily prepared from the ferrocenyl ketones **6** by Corey–Bakshi–Shibata (CBS) reduction, leading to the ferrocenyl alcohols **8** with high enantioselectivity (>99 % *ee*).[5] Acylation of alcohols **8a–d** with acetic anhydride furnishes in quantitative yield the intermediate ferrocenyl acetates **9a–d**. Treatment with an aqueous NH_3 solution in CH_3CN provides the desired ferrocenyl amines **1a–d** in 44–66 % yield (Scheme 2).

---

[*] Prof. Dr. P. Knochel, Dipl.-Chem. F. Dübner
Fachbereich Chemie der Universität
Hans-Meerwein-Strasse, D-35032 Marburg (Germany)
Fax: (+49) 6421-28-21-89
E-mail: knochel@ps1515.chemie.uni-marburg.de

[**] F.D. thanks Zeneca Ltd. for a fellowship and the Fonds der Chemischen Industrie for generous support. We thank the BASF AG, Degussa AG, Bayer AG, and Chemetall GmbH for generous gift of chemicals.