(Carbonyl)Iron-Selenolates: New Synthetic Methods and Reactions with Electrophiles. Crystal Structures of $[(CO)_6Fe_2(\mu-SeR)_2]$; R = Me₃SiCH₂ and p-O₂NC₆H₄CH₂, $\{(CO)_6Fe_2[\mu-\eta^2-Se,Se'-o-(SeCH_2C_6H_4CH_2Se)]\}$, and $[(CO)_6Fe_2(\mu-SeFe(CO)_2cp)_2]$

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Dedicated to Professor Armand Blaschette on the Occasion of his 65th Birthday

Abstract. The reactions of $Fe(CO)_5$ or $Fe_3(CO)_{12}$ with NaBEt₃H or KB[CH(CH₃)C₂H₅]₃H, respectively and treatment of the resulting carbonylates $M_2Fe(CO)_4$, M = Na, K with elemental selenium in appropriate ratios lead to the formation of $M_2[Fe_2(CO)_6(\mu-Se)_2]$. Subsequent reactions with organo halides or the complex fragment $cpFe(CO)_2^+$, $cp = \eta^5 - C_5 H_5$ afforded the selenolato complexes $[Fe_2(CO)_6(\mu-SeR)_2], R = CH_2SiMe_3$ (1), CH₂Ph (2), p- $CH_2C_6H_4NO_2$ (3), *o*- $CH_2C_6H_4CH_2$ (4) and $cpFe(CO)_2^+$ (5) in moderate to good yields. A similar reaction employing $Ru_3(CO)_{12}$, Se and $p-O_2NC_6H_4CH_2Br$ leads to the formation of the corresponding organic diselenide. The X-ray structures of 1, 3, 4 and 5 were determined and revealed butterfly structures of the Fe_2Se_2 cores. The substituents in 1, 3 and 5 adopt different conformations depending on their steric demand. In 4, the conformation is fixed because of the chelate effect of the ligand. The Fe–Se bond lengths lie in the range 235 to 240 pm, with corresponding Fe–Fe bond lengths of 254 to 256 pm. The ⁷⁷Se NMR data of the new complexes are discussed and compared with the corresponding data of related complexes.

Keywords: Iron; ruthenium; selenolato complexes; crystal structure; ⁷⁷Se NMR

(Carbonyl)Eisen-Selenolate: Neue Synthesen und Reaktionen mit Elektrophilen. Kristallstrukturen von [(CO)₆Fe₂(μ -SeR)₂]; R = Me₃SiCH₂ and p-O₂NC₆H₄CH₂, {(CO)₆Fe₂[μ - η ²-Se,Se'-o-(SeCH₂C₆H₄CH₂Se)]} und [(CO)₆Fe₂(μ -SeFe(CO)₂cp)₂]

Inhaltsübersicht. Die Reaktionen von Fe(CO)₅ und Fe₃(CO)₁₂ mit NaBEt₃H oder KB[CH(CH₃)C₂H₅]₃H liefern die Carbonylate M₂Fe(CO)₄, M = Na, K, die ihrerseits mit elementarem Selen in geeigneten Verhältnissen zu den Selenolaten M₂[Fe₂(CO)₆(μ -Se)₂] reagieren. Umsetzungen mit organischen Halogeniden oder dem Komplexfragment cpFe(CO)₂⁺, cp = η^5 -C₅H₅ liefern die Selenolato-Komplexe [Fe₂(CO)₆(μ -SeR)₂], R = CH₂SiMe₃ (1), CH₂Ph (2), *p*-CH₂C₆H₄NO₂ (3), *o*-CH₂C₆H₄CH₂ (4) and cpFe(CO)₂⁺ (5) in moderaten bis guten Ausbeuten. Eine ähnliche Reaktion, ausgehend von Ru₃(CO)₁₂, Se und *p*-O₂NC₆H₄CH₂Br führt zur Bildung des entsprechenden organischen Diselenids. Die Kristallstrukturen von 1, 3, 4 und 5 wurden bestimmt. Sie zeigen alle eine Butterfly-Struktur am zentralen Fe_2Se_2 Ring. Die Substituenten in 1, 3 und 5 nehmen in Abhängigkeit ihres sterischen Anspruches unterschiedliche Konformationen ein. Aufgrund des Chelat-Effekts des Liganden ist die Konformation in 4 fixiert. Die Fe–Se Bindungslängen liegen im Bereich von 235 bis 240 pm mit entsprechenden Fe–Fe Bindungslängen von 254 bis 256 pm. Die ⁷⁷Se NMR Spektren der neuen Komplexe werden diskutiert und mit den entsprechenden Daten verwandter Komplexe verglichen.

Introduction

The current interest in selenium- and tellurium-containing complexes arises from their potential activity in catalytic processes and their potential use as precursors for solid state materials [1]. Common syn-

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theses of chalcogenolato complexes are metatheses, amine elimination processes and oxidative additions of organic dichalcogenides to unsaturated metal fragments, whereas chalcogenido complexes are accessible via reactions of soluble Zintl ions (e.g. $\mathrm{Se_n^{2-}}$, $\mathrm{Te_4^{2-}}$) with metal halides and carbonyls or by reacting silylated chalcogenide reagents with appropriate metal fragments.

(Carbonyl)iron chalkogenides of the type $Fe_2(CO)_6(E_2)$ and $Fe_3(CO)_9(E)_2$, E = S, Se, Te were first synthesized

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by *Hieber* and *Gruber* in 1958 via redox reactions of iron carbonylates with S_5^{2-} or EO_3^{2-} , respectively [2]. Starting from the dinuclear complexes $Fe_2(CO)_6(E_2)$, iron-selenolato complexes can be prepared by addition of alkynes or by reductive E–E bond cleavage and subsequent reactions with electrophiles [3, 4].

Recently we have found that selenolato complexes can be prepared alternatively via selenium insertion into alkali-metal transition-metal bonds of carbonylates and subsequent reactions with organic electrophiles [5]. This led to complexes of the type [cpM(CO)₃SeR], M = Mo, W and [Mn(CO)₄SeR]₂. In the case of tungsten, the organometallic selenolate intermediates [cpW(CO)₃Se_n]⁻, n = 2, 3, 4 can be easily oxidized to produce the corresponding selenido complexes [6].

Here we report on the synthesis of dinuclear ironselenolato complexes of the type $[Fe_2(CO)_6(\mu-SeR)_2]$ via insertion of selenium into the alkali metal-iron bonds of the carbonylates M₂Fe(CO)₄, M = Na, K and subsequent reactions with selected electrophiles. Additionally, a corresponding reaction of the Ru(CO)₄²⁻ anion with selenium followed by treatment with *p*-O₂NC₆H₄CH₂Br is described.

Results and Discussion

The highly nucleophilic tetracarbonylferrate dianion $[Fe(CO)_4]^{2-}$ readily reacts with elemental grey selenium in a 1:2 ratio to produce the selenium-centred dianion $[(CO)_6 Fe_2(\mu - Se)_2]^{2-}$ in good yield. Treatment of the reaction solutions with the organic electrophiles C₆H₅CH₂Cl, Me₃SiCH₂Cl, p-O₂NC₆H₄CH₂Cl and o- $C_6H_4(CH_2Cl)_2$ leads to the corresponding organoselenolato-iron(I) complexes, whereas cpFe(CO)₂Cl produces the tetranuclear iron complex $[Fe_2(CO)_6(\mu SeFe(CO)_2 cp)_2$]. The transformations can be performed as one-pot syntheses starting from $Fe(CO)_5$ or $Fe_3(CO)_{12}$ (Scheme 1). From the stoichiometry of the selenium addition, the formation of the alkali-metal selenides M_2Se_2 , M = Na, K seems probable. However, the addition of the organic electrophiles does not produce the corresponding organic diselenides, probably because of the higher nucleophilicity of $[(CO)_6Fe_2(\mu-Se)_2]^{2-}$ compared with the Se₂²⁻ anion. $[(CO)_6Fe_2(\mu-Se)_2]^{2-}$ was first synthesised by Seyferth via reductive Se–Se bond cleavage of $[(CO)_6 Fe_2(\mu, \eta^1 -$ Se₂)] with LiBEt₃H solutions in THF [4 a]. This transformation proceeds in nearly quantitative yield, but the synthesis of the starting complex requires more complicated steps, namely the reaction of $[Fe(CO)_4]^{2-1}$ with Se_5^{2-} under acidic conditions or the oxidation of $[Fe(CO)_4]^{2-}$ with SeO_3^{2-} under acidic conditions; $[(CO)_9Fe_3(\mu_3-Se)_2]$ is formed first and must be transformed into the binuclear iron complex by reaction with NaOMe [2].

The new iron complexes are dark red air-stable crystalline materials. The molecular structures of the disubstituted complexes $[Fe_2(CO)_6(\mu$ -SeCH₂SiMe₃)₂] (1), $[Fe_2(CO)_6(\mu$ -SeCH₂Ph)₂] (2) and $[Fe_2(CO)_6(\mu$ -p-SeCH₂C₆H₄NO₂)₂] (3) in solution correspond to the three possible geometrical isomers (Scheme 2).

From the ¹H and ⁷⁷Se NMR data it can be seen that in **1** the CH_2SiMe_3 groups are equivalent. This is attributable to the geometrical isomers *aa* or *ee*. Because of the bulky substituent, isomer *ee* is sterically favoured and it is found also in the solid state



Scheme 1 The one-pot syntheses of $[Fe_2(CO)_6(\mu-SeR)_2]$ starting from $Fe(CO)_5$ and $Fe_3(CO)_{12}$



Scheme 2 The three geometrical isomers of $[Fe_2(CO)_6(\mu-SeR)_2]$

(vide infra). In 2 all three possible isomers can be detected. The corresponding ⁷⁷Se NMR spectrum shows three singlets with comparable intensities indicating three conformational energy minima with low transition barriers. The *p*-nitrobenzyl substituted derivative **3** adopts two configurations in solution, whereas in the bridged complex [Fe₂(CO)₆(μ - η ²-Se,Se'-o-SeCH₂C₆H₄CH₂Se)] (**4**) the only possible isomer is *aa*. The tetranuclear complex **5** displays three singlets for the cp-rings in the ¹H and ¹³C NMR spectra indicating the presence of all three possible geometrical isomers in solution. However, in the solid state only the isomer *ae* is observed (vide infra).

The observed ⁷⁷Se NMR chemical shifts of the new complexes lie in the range +29 to +310 ppm. These values are comparable with those in other $[Fe_2(CO)_6(\mu$ - SeR_{2} complexes and strongly depend on the electronic influences of the organic groups at the selenium atoms and their orientations. In 1 the CH₂SiMe₃ possesses a strong +I-effect and therefore the ⁷⁷Se signal $(\delta = +90.4)$ is shifted to high field in comparison with the other complexes. In the benzyl complexes 2 and 3the signals appear in the range +220 to +310 ppm. The chemical shift of the o-xylylselenolato complex 4 at $\delta = +221.3$ suggests that the comparable value in 2 $(\delta = +222.6)$ corresponds to the *aa* isomer, since the electronic influences of benzyl and xylyl groups do not differ greatly. Following this argument, the observed values for the nitrobenzyl-substituted complex 3 should correspond to the isomers ae and ee. However, in the case of 2 and 3 the observed isomers only occur in solution and their low transition barriers do not permit separation via column chromatographic methods. Similar to the benzyl complex 2, the tetranuclear iron complex 5 displays three singlets in the ⁷⁷Se NMR spectrum with a range from +29 ppm to +306 ppm, probably due to completely different electronic influences of the $cpFe(CO)_2$ group compared to the above mentioned organic substituents. Several reports concerning ⁷⁷Se NMR shifts in organic substituted $[Fe_2(CO)_6(\mu-Se)_2]$ complexes have appeared in the literature; typical values are +40 to +70 ppm for alkyl derivatives (e. g. $\delta = +45.5$ in $[Fe_2(CO)_6(\mu -$ SeMe)₂] [4b], +67.6 in $[Fe_2(CO)_6(\mu$ -SeCH₂Se)] [3i]) and +350 to +460 ppm for the corresponding alkyne complexes (e.g. $\delta = +369.3$ and +458.8 $[Fe_2(CO)_6Se_2]_2(\mu$ -s-trans-C₄H₂) [3 f]).

The reaction of $Ru_3(CO)_{12}$ with $KB[CH(CH_3)C_2H_5]_3H$ in THF according to the method of *Gladysz* affords a fawn-coloured suspension of $K_2Ru(CO)_4$ which reacts readily with elemental selenium to form a red-brown solution that presumably contains $K_2[Ru_2(CO)_6(\mu-$ Se₂)] [7]. Treatment of this solution with p- $O_2NC_6H_4CH_2Br$ resulted in the formation of the organic diselenide [p- $O_2NC_6H_4CH_2Se]_2$ in good yield accompanied by $Ru_3(CO)_{12}$. A reductive elimination process from a Ru_2Se_2 core seems likely, since in most complexes with Ru_2Se_2 cores additional stabilizing ligands (e.g. phosphines, Cp) are present. Carbonylates and the corresponding selenocarbonylates are strong reducing agents and a more facile synthesis of selenolato ruthenium carbonyl complexes is the oxidative addition of organic diselenides to $Ru_3(CO)_{12}$ (e.g. $[Ru_2(CO)_6(\mu$ -SePh)_2] from Ph₂Se₂ and $Ru_3(CO)_{12}$) [8]. In the case of tellurium, a reduction of the Ru–Ru bond in [Cp*RuCl₂]₂ on reaction with Me₃SiTeR was observed, which led to the formation of a RTeTeR unit on the two ruthenium centers [9].

Crystal Structures of $[Fe_2(CO)_6(\mu-SeCH_2SiMe_3)_2]$ (1), $[Fe_2(CO)_6(\mu-p-SeCH_2C_6H_4NO_2)_2]$ (3), $[Fe_2(CO)_6(\mu-\eta^2-Se,Se'-o-SeCH_2C_6H_4CH_2Se)]$ (4) and $[Fe_2(CO)_6(\mu-SeFe(CO)_2cp)_2]$ (5)

The molecular structure of **1** is presented in Fig. 1. The central Fe₂Se₂ moietiy displays a butterfly geometry with a corresponding hinge angle of $95.19(3)^{\circ}$. Both Me₃SiCH₂ groups are attached at the selenium atoms in the equatorial position so that the overall structure corresponds to the geometric isomer ee. The same isomer was found in the crystal structure of $[Fe_2(CO)_6(\mu$ -SeMe)_2] [4b]. The Fe–Se bond lengths (238.25(8) to 238.81(8) pm) are comparable with those observed in $[Fe_2(CO)_6(\mu-SeMe)_2]$ (236.5(10) 239.8(9) pm), $[Fe_2(CO)_6 \{\mu - SeC(Ph) = C(H)Se\}]$ to (237.92(9) to 239.01(9) pm) and other related complexes [3] and in the non-substituted complex $[Fe_2(CO)_6(\mu-Se_2)]$ (235.4(2) to 237.8(2) pm) [10]. The Fe-Fe bond length of 255.56(9) pm is attributable to a single bond and falls into the observed range of 251 to 258 pm in related complexes [3, 4b]. According to the butterfly geometry, the selenium atoms are in relatively close non-bonding contact (297.4(1) pm vs.



Fig. 1 Molecular structure of $[Fe_2(CO)_6(\mu$ -SeCH₂SiMe₃)₂] (1) (50% probability ellipsoids, H atoms omitted for clarity)^[a]

^[a] Selected bond lengths [pm] and angles [°]: Fe1–Fe2 255.56(9), Fe1–Se1 238.25(8), Fe1–Se2 238.59(8), Fe2–Se1 238.81(8), Fe2–Se2 238.44(8), Se1...Se2 297.4(1), Se1–C7 196.8(4), Se2–C11 197.0(4); Se1–Fe1–Se2 77.18(3), Fe1–Se1–Fe2 64.78(2), Se1–Fe2–Se2 77.11(3), Fe1–Se2–Fe2 64.79(3), Fe1–Se1–C7 111.01(13), Fe2–Se1–C7 111.80(12), Fe1–Se2–C11 110.30(12), Fe2–Se2–C11 113.82(12).

229.3(2) pm in $[Fe_2(CO)_6(\mu-Se_2)]$). Common features of the Fe₂Se₂ cores in Se-substituted complexes are small endocyclic bond angles at the selenium atoms (ranging from 63 to 66°) with corresponding angles at iron atoms ranging from 74 to 83°, depending on the substituent at the selenium atom and the chelate effect of bidental "bis-selenolate"-ligands. In 1, the endocyclic angles at the selenium atoms are 64.78(3)° (Fe1-Se1-Fe2) and 64.79(3)° (Fe1-Se2-Fe2). The corresponding bond angles at the iron atoms, 77.11(3)° (Se1-Fe2-Se2) and 77.18(3)° (Se1-Fe1-Se2), lie near the middle of the above mentioned range. Almost the same values were found in $[Fe_2(CO)_6(\mu-SeMe)_2]$. In complexes with a bridging C₂ unit the endocyclic angles at the iron atoms become larger (e.g. $82.26(3)^{\circ}$ in $[Fe_2(CO)_6(\mu$ -SeCH₂CH₂Se)]), whereas a bridging CH₂ group causes smaller angles at iron (e.g. 74.27(2)°, 74.43(3)° in $[Fe_2(CO)_6(\mu$ -SeCH₂Se)] without affecting the angles at the selenium atoms [3i]. All other bond distances and angles are unexceptional.

The molecular structure of **3** is presented in Fig. 2. The molecule corresponds to the geometric isomer *ae*. Because of the different steric demand of the *p*- $O_2NC_6H_4CH_2$ group, the hinge angle in **3** is somewhat larger (101.56(3)°) than in **1**. This is in accordance with the observed values for the endocyclic angles at iron (Se1–Fe1–Se2: 81.27(3)° and Se1–Fe2–Se2: 81.59(3)°) and therefore a significantly longer nonbonding Se–Se distance of 309.3(1) pm. Again the endocyclic angles at selenium are not affected, with values in the usually observed range (Fe1–Se1–Fe2: $65.03(3)^\circ$, Fe1–Se2–Fe2: $65.57(3)^\circ$). The Fe–Fe and Fe–Se bond lengths are closely similar to those determined in **1**. All other bond metricals are as expected.

The molecular structure of the xylyl-bridged derivative **4** is shown in Fig. 3. Because of the chelating ligand, it corresponds to the geometrical isomer *aa*. Because of the less pronounced bite of a C₄ unit, the butterfly angle becomes larger (111.83(5)°). As a direct consequence, the non-bonding Se–Se contact is again longer (332.6(1) pm) and the endocyclic bond angles at iron are strongly affected (Se1–Fe1–Se2: 88.89(5)°, Se1–Fe2–Se2: 88.61(4)°). All other bond metricals are similar to those observed in **1** and **3**.

The molecular structure of the tetranuclear complex **5** is presented in Fig. 4. Crystal structures with Se-bonded metal atoms at Fe₂Se₂ cores are rare and apart from one example with a bridging PtPPh₃ moiety [11] and one with a μ_4 -Ru(CO)₃ unit [12] only complexes with additional Fe-containing moieties were examined.

The hinge angle of the central Fe_2Se_2 butterfly is 99.00(3)°. The overall structure corresponds to the geometrical isomer *ae* with the endocyclic angles at the selenium atoms 65.53(3)° (Fe2–Se1–Fe1) and 64.44(3)° (Fe1–Se2–Fe2). The corresponding angles at



Fig. 2 Molecular structure of

 $[Fe_2(CO)_6(\mu$ -*p*-SeCH₂C₆H₄NO₂)₂] · CH₂Cl₂ (**3**) in the crystal (50% probability ellipsoids, H atoms and CH₂Cl₂ omitted for clarity)^[a]

^[a] Selected bond lengths [pm] and angles [°]: Fe1–Fe2 255.84(9), Fe1–Se1 238.34(8), Fe1–Se2 236.64(8), Fe2–Se1 237.60(9), Fe2–Se2 235.84(8), Se1...Se2 309.3(1), Se1–C7 200.0(3), Se2–C14 199.0(4); Se1–Fe1–Se2 81.27(3), Fe1–Se1–Fe2 65.03(3), Se1–Fe2–Se2 81.59(3), Fe1–Se2–Fe2 65.57(3), Fe1–Se1–C7 111.97(11), Fe2–Se1–C7 109.53(11), Fe1–Se2–C14 113.11(11), Fe2–Se2–C14 112.86(11).



Fig. 3 Molecular structure of $[Fe_2(CO)_6(\mu-\eta^2-Se,Se'-o-SeCH_2C_6H_4CH_2Se)]$ (4) in the crystal (50% probability ellipsoids, H atoms omitted for clarity)^[a]

 $^{[a]}$ Selected bond lengths [pm] and angles [°]: Fe1–Fe2 254.8(2), Fe1–Se1 237.69(13), Fe1–Se2 237.34(14), Fe2–Se1 237.13(13), Fe2–Se2 239.11(14), Se1 \cdots Se2 332.6(1), Se1–C7 199.1(7), Se2–C14 200.9(6); Se1–Fe1–Se2 88.89(5), Fe1–Se1–Fe2 64.90(4), Se1–Fe2–Se2 88.61(4), Fe1–Se2–Fe2 64.65(4), Fe1–Se1–C7 114.7(2), Fe2–Se1–C7 109.7(2), Fe1–Se2–C14 113.4(2), Fe2–Se2–C14 116.6(2).



Fig. 4 Molecular structure of $[Fe_2(CO)_6(\mu\text{-SeFecp}(CO)_2)_2]$ (5) in the crystal (20% probability ellipsoids, H atoms omitted for clarity)^[a]

 $^{[a]}$ Selected bond lengths [pm] and angles [°]: Fe1–Fe2 256.26(10), Fe1–Se1 237.09(9), Fe1–Se2 239.89(9), Fe2–Se1 236.42(8), Fe2–Se2 240.74(9), Se1…Se2 305.99(7), Se1–Fe3 240.56(9), Se2–Fe4 244.01(8); Se1–Fe1–Se2 79.81(3), Fe1–Se1–Fe2 65.53(3), Se1–Fe2–Se2 79.77(3), Fe1–Se2–Fe2 64.44(3), Fe1–Se1–Fe3 126.05(3), Fe2–Se1–Fe3 122.10(3), Fe1–Se2–Fe4 117.18(3), Fe2–Se2–Fe4 122.15(3).

the iron atoms are 79.81(3)° (Se1–Fe1–Se2) and 79.77(3)° (Se1–Fe2–Se2), respectively. The Fe–Se bond lengths differ slightly and lie in the range 236.42(8) pm (Se1–Fe2) to 244.01(8) pm (Se2–Fe4). Comparable values were found in $[(CO)_6Fe_2Se_2(\mu-Fe_7Fe_7Fe_2Se_2)Se_2Fe_2(CO)_6]^{2-}$ [13 a, b] and $[(CO)_9Fe_3(\mu_3-Se)_2]$ [14]. The observed Fe–Fe bond length of 256.26(10) pm lies in the above mentioned range of Fe–Fe single bonds in related complexes. All other bond distances and angles are similar to those observed in **1**, **3** and **4**.

Experimental Section

All manipulations were carried out under a dry nitrogen atmosphere using conventional Schlenk techniques. – NMR: Bruker AC 200 (¹H 200 Mhz, ¹³C 50.3 Mhz, ⁷⁷Se 38.2 Mhz). The spectra were recorded using CDCl₃ or [D₆]acetone as solvents. Standards: ¹H, ¹³C TMS internal; ⁷⁷Se Me₂Se external. – IR: Biorad FTS 165. – MS: Finnigan MAT 8430. Tetrahydrofuran (THF) was dried over sodium in nitrogen atmosphere and distilled prior to use. KB[CH(CH₃)C₂H₅]₃H, NaBEt₃H, KBEt₃H (1 m solutions in THF), grey Se and Fe(CO)₅ were purchased from Aldrich and used as received. Fe₃(CO)₁₂, Ru₃(CO)₁₂ and cpFe(CO)₂Cl were prepared according to literature methods [15, 16, 17].

General synthesis procedure

Route A: 0.5 ml Fe(CO)₅ (3.8 mmol) in 30 ml THF was transformed into a solution of $K_2Fe(CO)_4$ using 7.6 ml KB[CH(CH₃)C₂H₅]₃H (7.6 mmol) according to the proce-

dure of Gladysz. 0.6 g Se (7.6 mmol) was then added to the resulting colourless suspension. CO evolution occurred and the Se was consumed within 15 min, affording a deep redbrown solution. After 1 h of stirring the organic electrophile was added (Me₃SiCH₂Cl, p-O₂NC₆H₄CH₂Br: excess; o-C₆H₄(CH₂Br)₂: 0.5 g, 1.9 mmol). The work-up procedure after 18 h of stirring comprised the removal of THF in vacuo, addition of CH₂Cl₂ to the remaining residue, removal of the potassium halogenide via filtration over Celite and column chromatography (20×4 cm) on silica. The separated products were recrystallised from ethanol [1 and 2], toluene/ hexanes (3) or hexanes (4) at -60 °C.

Route B: The same as route A employing $0.5 \text{ g Fe}_3(\text{CO})_{12}$ (1 mmol) in 30 ml THF, 6 ml NaBEt₃H (6 mmol) and 0.47 g Se (6 mmol).

Bis(μ -trimethylsilylmethylselenolato)-(hexacarbonyl)di-iron(I) 1: Chromatography using hexanes as eluent afforded one red band of 1. Route A: 0.5 g (41%, based on Fe(CO)₅); Route B: 0.48 g (52%, based on Fe₃(CO)₁₂). M. p. 41 °C, red crystals.

¹H NMR (CDCl₃): $\delta = 0.15$ ppm (s, 18 H, CH₃), 1.78 (s, 4 H, CH₂). – ¹³C NMR (CDCl₃): $\delta = -1.5$ ppm (s, CH₃), 14.2 (s, CH₂), 209.9, 210.7 (s, CO). – ⁷⁷Se NMR (CDCl₃): $\delta = 90.4$ ppm (s). – IR (CH₂Cl₂): v = 2061, 2026, 1983 (CO). – MS (70 eV); m/z (%): 614(30) [M⁺], 530(53) [M⁺–3 CO], 446(100) [M⁺–6 CO].

 $C_{14}H_{22}Fe_2O_6Se_2Si_2\ (612.1):\ C\ 27.46\ (calc.\ 27.47);\ H\ 3.62\ (3.62)\%.$

 $Bis(\mu$ -benzylselenolato)-(hexacarbonyl)di-iron(I) **2**: Route A: Chromatography using hexanes as eluent afforded four bands with traces of orange by-products. The fifth red band contained 0.525 g (44%, based on Fe(CO)₅) of **2**. Route B: A mixture of toluene/hexanes 1:9 as eluent afforded a violet and an orange band with traces of by-products. The third red band contained 0.432 g (46%, based on Fe₃(CO)₁₂) of **2**. M. p. 85 °C (dec.), red crystals.

¹H NMR ([D₆] acetone): δ = 3.59, 4.01, 4.03 ppm (s, Σ 4 H, CH₂), 7.30 (m, 10 H, Ph). – ¹³C NMR (CDCl₃): δ = 27.6 ppm (s, CH₂), 32.8 (s, CH₂), 126.7, 127.8, 128.5, 128.8, 129.0 (s, *o*-, *m*- und *p*-C₆H₅), 139.1, 139.2 (s, *ipso*-C, C₆H₅), 210.4 (s, CO). – ⁷⁷Se NMR (CDCl₃): δ = +222.6 ppm (s), +273.0 (s), +295.5 (s). – IR (CH₂Cl₂): *v* = 2062, 2029, 1987 (CO). – MS (70 eV); *m/z* (%): 622(14) [M⁺], 538(25) [M⁺–3 CO], 454(72) [M⁺–6 CO].

C₂₀H₁₄Fe₂O₆Se₂ (619.9): C 38.64 (calc. 38.75), H 2.44 (2.28)%.

$Bis(\mu$ -p-nitrobenzylselenolato)-(hexacarbonyl)di-iron(I) \cdot

1/2 toluene **3**: The nitrobenzyl complex was prepared following route A. The chromatographic work-up using toluene/ hexanes 7:3 as eluent afforded four red-brown bands with traces of by-products. The fifth red band contained 0.684 g (47%, based on Fe(CO)₅) of **3**. M. p. 117 °C, red crystals.

¹H NMR ([D₆ acetone]: δ = 2.31 ppm (s, CH₃, toluene) 3.73 (s, 2 H, CH₂), 4.16 (s, 2 H, CH₂), 7.19 (m, C₆H₅, toluene), 7.47 (d, ³J = 8.7 Hz, 2 H, 3,5-O₂NC₆H₄), 7.81 (d, ³J = 8.8 Hz, 2 H, 3,5-O₂NC₆H₄), 8.15 (d, ³J = 8.7 Hz, 2 H, 2,6-O₂NC₆H₄), 8.31 (d, ³J = 8.8 Hz, 2 H, 2,6-O₂NC₆H₄), - ¹³C NMR (CDCl₃): δ = 16.6, 31.9 ppm (s, CH₂), 21.5 (s, CH₃, toluene), 124.3, 124.6, 128.3, 129.1, 129.4, 130.0 (s, *o*-, *m*- und *p*-O₂NC₆H₄), 146.3, 146.5 (s, *ipso*-O₂NC₆H₄), 208.8 (s, CO). - ⁷⁷Se NMR (CDCl₃): δ = +274.8 ppm (s), +309.5 (s). - IR (CH₂Cl₂): 2066, 2035, 1995 (CO). - MS (70 eV); *m/z* (%): 712(9) [M⁺], 628(18) [M⁺-3 CO], 544(21) [M⁺-6 CO].

 $C_{20}H_{12}Fe_2N_2O_{10}Se_2\cdot 1/2\,C_6H_5CH_3\ (756.00);\ C\ 37.46\ (calc.\ 37.33),\ H\ 2.28\ (2.13),\ N\ 3.65\ (3.71)\%.$

 μ -(o-Xylylselenolato)-(hexacarbonyl)di-iron (I) **4**: The workup procedure via route A with toluene/hexanes 1:4 as eluent afforded an orange band with a trace of Fe(CO)₅. The second red band contained 0.348 g of **4** (34%, based on Fe(CO)₅). Route B led to only one red mobile fraction using the same eluent. It contained 0.12 g (15%, based on Fe₃(CO)₁₂) of **4**. M. p. 165 °C, red crystals.

¹H NMR (CDCl₃): $\delta = 3.52$ ppm (d, ²J = 11.7 Hz, CH₂, H_A), 3.86 (d, ²J = 11.7 Hz, CH₂, H_B), 7.04 (m, 4 H, C₆H₄). – ¹³C NMR (CDCl₃): $\delta = 25.3$ ppm (s, CH₂), 128.0, 129.4 (s, C₆H₄), 139.1 (s, ipso-C, C₆H₄), 207.4, 207.9 (s, CO). – ⁷⁷Se NMR (CDCl₃): $\delta = +221.3$ ppm (s). – IR (CH₂Cl₂): $\nu = 2066$, 2032, 1991 (CO). – MS (70 eV); m/z (%): 544(25) [M⁺], 460(22) [M⁺–3 CO], 376(100) [M⁺–6 CO].

 $C_{14}H_8Fe_2O_6Se_2~(541.8);\ C~31.23~(calc.~31.03),\ H~1.50~(1.49)\%.$

Synthesis of $[Fe_2(CO)_6(\mu$ -SeFecp $(CO)_2)_2]$ 5: The solution of K₂Se₂Fe₂(CO)₆ in THF was prepared according to route A employing 0.5 ml Fe(CO)₅ (3.8 mmol), 7.6 ml KB[CH(CH₃)C₂H₅]₃H (7.6 mmol) and 0.6 g Se (7.6 mmol). 1.58 g cpFe(CO)₂Cl (7.6 mmol) was added with strirring in one portion. After 1 h stirring at ambient temperature, the solvent was removed in vacuo. The work-up procedure was the same as described above using CH₂Cl₂/hexanes as eluent. After one yellow and one orange band with traces of by-products, the third red-brown band contained 0.97 g (64%, based on Fe(CO)₅) of **5**. M. p. 102 °C (dec.), redbrown crystals.

¹H NMR ([D₆]acetone): δ = 5.20, 5.28, 5.35 ppm (s, Σ 10 H, cp). – ¹³C NMR ([D₆]acetone): δ = 87.35 ppm (s, cp), 87.55 (s, cp), 87.59 (s, cp), 213.08, 214.17, 214.47, 216.62 (s, CO). – ⁷⁷Se NMR (CDCl₃): δ = +29.9 ppm (s), +258.7 (s), +305.3 (s). – IR (CH₂Cl₂): ν = 2053, 2024, 2016, 2008, 1989, 1964 (CO).

 $C_{20}H_{10}Fe_4O_{10}Se_2$ (791.6): C 30.08 (calc. 30.35); H 1.24 (1.27)%.

$[p-O_2NC_6H_4CH_2Se]_2$ from

 $K_2Ru(CO)_4/2 Se/p-O_2NC_6H_4CH_2CH_2Br: 0.5 g Ru_3(CO)_{12}$ (0.79 mmol) were dissolved in 30 ml THF. 4.7 ml $KB[CH(CH_3)C_2H_5]_3H$ solution (4.7 mmol) were added via a syringe and the mixture was refluxed for 4 hrs, during which the orange solution was transformed into a fawn-coloured suspension. After cooling to room temperature, 0.37 g Se (4.7 mmol) was added with stirring. After 15 min the selenium had been consumed and the colour turned to redbrown. Addition of 1.3 g p-O₂NC₆H₄CH₂Br (6 mmol) and stirring for additional 15 hrs afforded a deep-red solution, which then was evaporated to dryness. KBr was removed via addition of 20 ml CH₂Cl₂ and filtration over Celite. A chromatographic work-up procedure on silica $(40 \times 3 \text{ cm};$ CH₂Cl₂/acetone 2:3) afforded a colourless band with traces of p-O₂NC₆H₄CH₂Br, a yellow-orange band with traces of an unknown by-product and as the third orange band [p-O₂NC₆H₄CH₂Se]₂ as the main product of the reaction, as spectroscopically characterised by comparison with an authentic sample [18]. Yield: 0.695 g (1.61 mmol, 69%). The fourth orange band contained Ru₃(CO)₁₂ as sole detectable material.

Crystal Structure Determinations [19]: Suitable crystals were obtained from EtOH at $-60 \degree C$ (1), by layering a CH₂Cl₂ solution with hexanes (ambient temperature) (3), from hexanes at $-60 \degree C$ (4) or by cooling a saturated CH₂Cl₂/hexanes solution at $-18 \degree C$ (5). They were mounted on glass fibers in inert oil and transferred to the cold gas stream of the diffractometer (1, 4, 5 Siemens P4 at $-100 \degree C$, 3 Stoe STADI4

Table 1Crystallographic data for 1, 3, 4 and 5

Compound	1	3	4	5
Empirical formula	C14H22Fe2O6Se2Si2	$C_{20}H_{12}Fe_2O_{10}N_2Se_2\cdot CH_2Cl_2$	C14H8Fe2O6Se2	$C_{20}H_{10}Fe_4O_{10}Se_2$
Formula weight/g mol ⁻¹	612.12	794.86	541.82	791.6
Crystal system	monoclinic	triclinic	triclinic	monoclinic
Space group (No.)	$P2_1/c$ (14)	P(-1)(2)	P(-1) (2)	C2/c (15)
a/pm	1261.3(2)	934.2(2)	769.1(2)	1944.6(3)
b/pm	1598.8(2)	935.6(2)	992.0(3)	1841.1(3)
c/pm	1295.0(2)	1570.0(3)	1251.2(3)	1591.8(2)
αl°		87.00(2)	71.52(2)	
β/°	114.457(10)	82.81(2)	72.54(2)	116.605(12)
γ/°		89.11(2)	70.89(2)	
$V/pm^3 \times 10^{-6}$	2377.3(6)	1359.6(5)	834.7(4)	5095.6(13)
$\rho_{\rm calc}/{\rm g}~{\rm cm}^{-3}$	1.71	1.94	2.16	2.06
Z	4	2	2	8
F (000)/e	1208	776	520	3056
μ/cm^{-1}	44.07	39.97	61.25	51.4
Crystal Size/mm	$0.4 \times 0.32 \times 0.32$	$0.6 \times 0.2 \times 0.1$	$0.32 \times 0.2 \times 0.04$	$0.36 \times 0.24 \times 0.18$
$2 \theta_{\rm max}/^{\circ}$	50	50	50	50
T/°C	-100	-130	-100	-100
Measured reflections	4866	4877	2951	7004
Unique reflections	4175	4781	2905	4444
R _{int}	0.0311	0.0103	0.0299	0.0348
No. of parameters	241	353	217	325
No. of restraints	42	0	0	0
T_{min}/T_{max}	0.67/0.79	0.67/1.00	0.58/0.98	0.69/0.93
$R(F), F > 4\sigma(F)$	0.0349	0.0306	0.0391	0.0323
$R_{\rm w}(F^2)$, all refl.	0.052	0.0689	0.0793	0.0449
Weighting parameters (a, b)	0.0143, 0	0.0266, 1.0656	0.0323, 0	0.0102, 0
S	0.79	1.06	0.83	0.78
max. Δ/σ	< 0.001	< 0.001	< 0.001	< 0.001
$\rho_{\rm fin}$ (max/min) (e pm ⁻³)×10 ⁶	0.47/-0.44	0.47/-0.48	0.89/-0.68	0.42/-0.41

at -130 °C) equipped with an LT-2 low-temperature attachment. Mo–K α radiation ($\lambda = 0.71073$ Å, graphite monochromator) was used to collect the intensity data in the ω -scan (1, 4, 5) or in the ω/θ -scan mode (3). Cell constants were refined from setting angles of 62 reflections in the 2θ range 8–23° (1, 4, 5) or from $\pm \omega$ values of 52 reflections in the 2θ range 20–23° (3). Absorption corrections based on ψ -scans were applied. The crystallographic program system used was SHELXL-93 [20]. All structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 . All non-H atoms were refined anisotropically; hydrogen atoms were included using a riding model or as rigid methyls. The final difference Fourier maps were featureless. Additional crystallographic data are presented in Table 1. Selected bond lengths and angles are listed in the Figure captions.

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