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Synthesis of single and double butterfly iron carbonyl complexes by reactions of [(μ-RSe)(μ-CO)Fe$_2$(CO)$_6$]$^-$ anions. Crystal structures of (μ-*p*-MeC$_6$H$_4$Se)[μ-PhCH$_2$N(H)C=S]Fe$_2$(CO)$_6$ and [(μ-PhSe)(μ-MeAs)Fe$_2$(CO)$_6$]$_2$

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Abstract

The in situ reactions of the [Et$_3$NH]$^+$ and [MgBr]$^+$ salts of [(μ-RSe)(μ-CO)Fe$_2$(CO)$_6$]$^-$ (**1**) anions with PhC(Cl)=NPh gave single butterfly complexes (μ-RSe)(μ-PhC=NPh)Fe$_2$(CO)$_6$ (**2**, R = Ph; **3**, R = *p*-MeC$_6$H$_4$; **4**, R = Et), whereas those of the [Et$_3$NH]$^+$ salts of **1** with R′N=C=S afforded single butterfly complexes (μ-RSe)[μ-R′N(H)C=S]Fe$_2$(CO)$_6$ (**5**, R = Ph, R′ = Ph; **6**, R = *p*-MeC$_6$H$_4$ R′ = Ph; **7**, R = *p*-MeC$_6$H$_4$, R′ = PhCO; **8**, R = *p*-MeC$_6$H$_4$, R′ = PhCH$_2$). Compound **8** could also be prepared by reaction of the [MgBr]$^+$ salt of **1** (R = *p*-MeC$_6$H$_4$) with PhCH$_2$NCS followed by treatment with CF$_3$CO$_2$H. More interestingly, while the [Et$_3$NH]$^+$ salt of **1** (R = Ph) reacted with Et$_3$OBF$_4$ to give a carbyne ligand-bridged single butterfly complex (μ-PhSe)(μ-EtOC)Fe$_2$(CO)$_6$ (**9**), reaction of the [Et$_3$NH]$^+$ salt of **1** (R = Ph) with MeAsI$_2$ produced a MeAs–AsMe ligand-bridged double butterfly complex [(μ-PhSe)(μ-MeAs)Fe$_2$(CO)$_6$]$_2$ (**10**). All the new complexes, **2**–**10**, were characterized by elemental analysis and various spectroscopic methods, for complexes **8** and **10**, the structures were also confirmed by X-ray diffraction techniques. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: RSe-bridged anions; CO-bridged anions; Electrophiles; In situ reactions; Butterfly iron carbonyl complexes; X-ray structures

1. Introduction

Reactions of anions of type [(μ-RSe)(μ-CO)Fe$_2$(CO)$_6$]$^-$ (**1**) with electrophiles are of great interest and have been utilized in the synthesis of various butterfly iron carbonyl complexes containing one or more (μ-RSe)Fe$_2$(CO)$_6$ structural moieties [1,2]. On the basis of our recent studies on this type of anions [3–5], we investigated its reactions with electrophiles PhC(Cl)=NPh, R′N=C=S, Et$_3$OBF$_4$ and MeAsI$_2$, in order to know the reaction modes systematically and to synthesize the corresponding new butterfly iron carbonyl complexes. Herein we report the synthesis and spectroscopic characterization of some new single and double butterfly iron complexes obtained from the studied reactions, as well as the molecular structures of (μ-*p*-MeC$_6$H$_4$Se)[μ-PhCH$_2$N(H)C=S]Fe$_2$(CO)$_6$ and [(μ-PhSe)(μ-MeAs)Fe$_2$(CO)$_6$]$_2$ determined by X-ray diffraction techniques.

2. Results and discussion

2.1. *Reactions of [(μ-RSe)(μ-CO)Fe$_2$(CO)$_6$]$^-$ (1) with PhC(Cl)=NPh leading to (μ-RSe)(μ-PhC=NPh)Fe$_2$(CO)$_6$ (2–4; R = Ph, p-MeC$_6$H$_4$, Et)*

We found that the [Et$_3$NH]$^+$ salts of anions (**1**;

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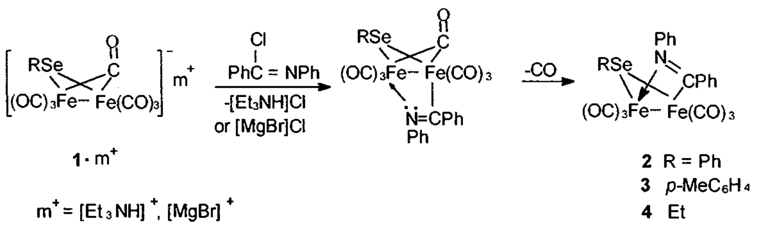


Scheme 1.

R = Ph, *p*-MeC_6H_4) (prepared from RSeH, $Fe_3(CO)_{12}$ and Et_3N [4]) reacted in situ with ca. an equimolar amount of PhC(Cl)=NPh in THF at −78°C to room temperature to give iminoacyl-bridged single butterfly complexes **2** and **3** in 22% yield, whereas the $[MgBr]^+$ salt of anion (**1**; R = Et) (prepared from an insertion reaction of Grignard reagent EtMgBr with elemental selenium followed by treatment of the intermediate EtSeMgBr with $Fe_3(CO)_{12}$ [3]) reacted with PhC(Cl)=NPh under similar conditions to afford iminoacyl-bridged single butterfly complex **4** in 17% yield (Scheme 1).

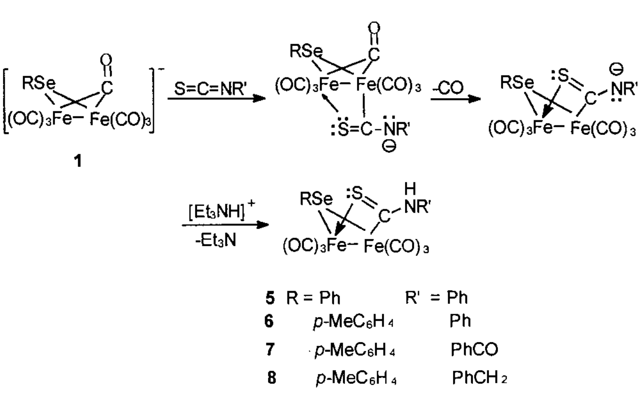
It is noteworthy that the above-mentioned reactions of **1** with the electrophiles always gave single butterfly compounds of type $(\mu\text{-RSe})_2Fe_2(CO)_6$ in 47–70% yields. While these compounds, similar to their Te analogs $(\mu\text{-RTe})_2Fe_2(CO)_6$) [6], could be regarded as derived from decomposition of **1** to give fragments $(\mu\text{-RSe})Fe(CO)_3$ followed by their dimerization, products **2**–**4**, similar to their Te and S analogs (μ-RE)(μ-PhC=NPh)$Fe_2(CO)_6$ (E = S and Te) [3,7], could be regarded as produced through a single S_N2 process with attack of an Fe-centered anion at the imino carbon and subsequent bridging of the iminoacyl ligand by the nitrogen lone electron pair with the concomitant loss of the μ-CO ligand (Scheme 1).

Products **2**–**4** are the first examples of μ-RSe-bridged complexes of this type, and have been characterized by combustion analysis and spectroscopy. For example, the IR spectra of **2**–**4**, similar to their μ-RTe and μ-RS analogs [3,7] showed one medium absorption band in the range 1543–1558 cm^{-1} for the C=N double bond coordinated to one of the two Fe atoms through the lone electron pair of nitrogen atom. In principle, products **2**–**4** may have two isomers, one with an equatorial R (denoted as e(R) hereafter) and the other with an axial R (denoted as a(R) hereafter) [3,7,8]. In fact, **4** is a mixture of the two isomers, since its ^{1}H-NMR spectrum is unlike that of single isomer (μ-EtSe)(μ-Ph_2As)$Fe_2(CO)_6$ which shows a triplet and a quartet for its ethyl group [3], but instead showed two multiplets in the range 1.50–2.97 ppm for its ethyl group. However, **2** and **3** have proved each to be a single isomer, since their ^{77}Se-NMR spectra exhibited only one singlet at 479.74 and 433.89 ppm, respectively. Unfortunately, at present we cannot establish **2** and **3** as the e(R) or a(R) isomer, due to lack of the comparable ^{77}Se-NMR data associated with this assignment and particularly lack of the suitable single crystals for determining their molecular structures.

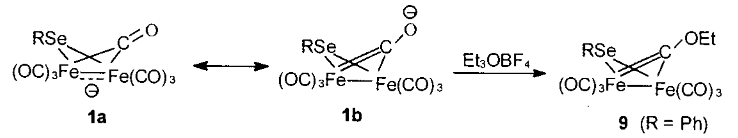
*2.2. Reactions of $[(\mu\text{-RSe})(\mu\text{-CO})Fe_2(CO)_6]^-$ (**1**) with R′NCS leading to (μ-RSe)[μ-R′N(H)C=S]$Fe_2(CO)_6$ (**5**–**8**, R = Ph, p-MeC_6H_4; R′ = Ph, PhCO, $PhCH_2$)*

We further found that the $[Et_3NH]^+$ salts of anions (**1**, R = Ph, *p*-MeC_6H_4) reacted in situ with ca. an equimolar quantity of R′NCS (R′ = Ph, PhCO, $PhCH_2$) in THF at room temperature to afford R′N(H)C=S-bridged single butterfly complexes **5**–**8** in 21–56% yields, along with corresponding $(\mu\text{-RSe})_2Fe_2(CO)_6$ in 32–59% yields (Scheme 2).

Mechanistically, these R′N(H)C=S-bridged complexes, similar to N-methylated derivative of **6** [3], might be viewed as yielded through two major steps. First, the nucleophilic Fe atom attacks at the heterocumulene carbon of R′NCS followed by coordination of the lone electron pair of S atom and concurrent loss of the μ-CO ligand to generate a N-centered anion. Then, this N-centered anion is protonated inter- or intramolecularly by counterion $[Et_3NH]^+$ to give final products (Scheme 2). It is worthy to note that these R′N(H)C=S-bridged complexes can be also prepared by using $[MgX]^+$ salts of the anions **1**. However, in this case an extra electrophile is needed to protonate the



Scheme 2.



Scheme 3.

intermediate N-centered anion. For instance, when the $[MgBr]^+$ salt of **1** (R = *p*-MeC_6H_4) reacted with isothiocyanate $PhCH_2NCS$, followed by treatment of CF_3CO_2H, complex **8** could be obtained in 21% yield, along with (μ-*p*-$MeC_6H_4Se)_2Fe_2(CO)_6$ in 31% yield.

Products **5**–**8** have been characterized by elemental analysis and spectroscopic methods. For example, the ^{1}H-NMR spectra of **5**–**8** displayed one broad peak in the range 7.51–10.15 ppm for their NH groups and the order of chemical shifts for these NH groups (**7** > **6** ≈ **5** > **8**) is consistent with the decreasing order of the electron-withdrawing effects of substituents R′ in **5**–**8** (PhCO > Ph > $PhCH_2$). In addition, the ^{1}H-NMR spectrum of **8** showed an octet pattern around 7.19 ppm, which can be assigned to its CH_2 group. This is because the two protons in CH_2 group are magnetically different and can be coupled not only to each other (giving an AB quartet) but also with the proton of the adjacent NH group (to give an octet). Finally, it should be noted that although **5**–**8** may theoretically have a(R) and e(R) two isomers, they have proved to exist as only one isomer, since their ^{77}Se-NMR spectra showed only one singlet at 430.52–480.84 ppm. Fortunately, we have successfully determined the crystal molecular structure of **8** by X-ray crystal diffraction techniques, indicating it as e(R) isomer (vide infra).

*2.3. Reactions of $[(\mu\text{-}RSe)(\mu\text{-}CO)Fe_2(CO)_6]^-$ (**1**, R = Ph) with Et_3OBF_4 or $MeAsI_2$ leading to $(\mu\text{-}PhSe)(\mu\text{-}EtOC)Fe_2(CO)_6$ (**9**) and $[(\mu\text{-}PhSe)(\mu\text{-}MeAs)Fe_2(CO)_6]_2$ (**10**)*

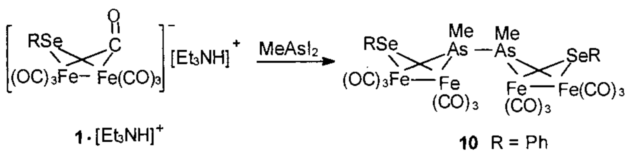
As previously reported [1–5], the reactions of **1** with electrophiles can be best rationalized in terms of their action as Fe-centered anions; however, we have found that **1** can also be regarded as O-centered anions in the reaction with electrophile Et_3OBF_4. For example, when ca. an equimolar amount of **1** (R = Ph) as its $[Et_3NH]^+$ salt was reacted with Et_3OBF_4 in THF at room temperature for 2 h, the O-alkylation product **9** was obtained in 61% yield (Scheme 3).

So, anions **1** are similar to their μ-RS analogs [9] to have ambident nature. This nature can be readily understood upon consideration of the two resonance forms: Fe-centered anions **la** and O-centered anions **lb** (Scheme 3).

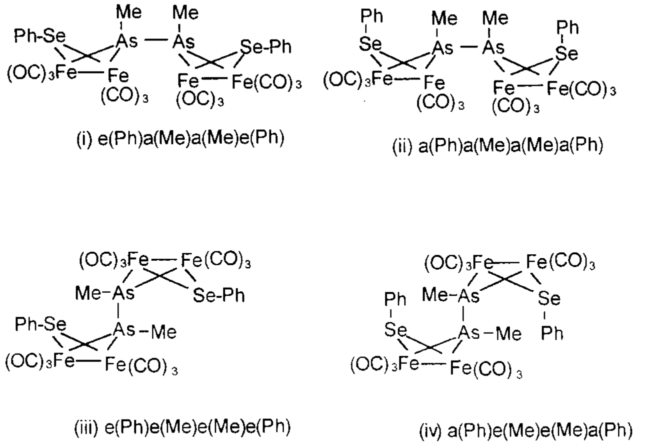
Product **9** is the first example containing a carbyne ligand of this type, which has been characterized by elemental analysis, IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy. Since **9** contains the same carbyne ligand EtOC as its sulfur analog (μ-*t*-BuS)(μ-EtOC)$Fe_2(CO)_6$ [9], the spectroscopic data of these two complexes relating to this ligand are almost the same, for instance, they all showed a singlet at ca. 380 ppm for the carbyne C in their ^{13}C-NMR spectra.

In previous papers [10,11] we described an unexpected reaction of $[(\mu\text{-RS})(\mu\text{-CO})Fe_2(CO)_6]^-$ anions with electrophile $MeAsI_2$ to give a series of double Fe_2SAs butterfly iron carbonyl complexes. In order to show the generality for this type of reactions, a reaction of the $[Et_3NH]^+$ salt of **1** (R = Ph) with ca. an equimolar amount of $MeAsI_2$ in THF at room temperature was carried out. As a result, from this reaction the expected double Fe_2SeAs butterfly complex **10** was obtained in 5% yield, along with $(\mu\text{-PhSe})_2Fe_2(CO)_6$ in 60% yield (Scheme 4).

Product **10** was characterized by elemental analysis, IR and ^{1}H-NMR spectra. In general, **10** may exist, similar to its μ-RS analogs [10,11], as a mixture of several stereoisomers, in terms of the axial or equatorial orientations of the substituents Ph and Me attached to bridged Se and As atoms. However, according to the ^{1}H-NMR spectrum of **10** (it showed only one signal for its two methyl groups and one set of signals for its two phenyl groups), it is believed that **10** would exist as only one of the four stereoisomers (i)–(iv) (Scheme 5). This is because that only these isomers each contain two Me and two Ph groups attached to Se and As atoms by the same e-type or same a-type of bonds, respectively. In addition, on steric grounds, **10** exists most likely as one of the two stereoisomers (i) and (iii), since the other two, i.e. (ii) and (iv) all involve strong steric repulsions in each butterfly unit between two axially bonded substituents, namely, Me and Ph in (iii), and Ph and butterfly unit (μ-MeAs)(μ-PhSe)$Fe_2(CO)_6$. Fortunately, we have successfully carried out the X-ray crystal diffraction analysis for **10** (vide infra) to confirm it to be isomer (iii) in which all the Me and Ph groups are equatorially bonded to Se and As atoms, respectively.



Scheme 4.


(i) e(Ph)a(Me)a(Me)e(Ph)

(ii) a(Ph)a(Me)a(Me)a(Ph)

(iii) e(Ph)e(Me)e(Me)e(Ph)

(iv) a(Ph)e(Me)e(Me)a(Ph)

Scheme 5.

Table 1
Selected bond lengths (Å) and angles (°) for **8**

Bond lengths			
Fe(1)–Fe(2)	2.6207(9)	Fe(1)–Se	2.3766(9)
Fe(2)–Se	2.3558(7)	Fe(2)–S	2.317(1)
Fe(1)–C(7)	1.958(4)	N–C(7)	1.329(5)
S–C(7)	1.691(4)	N–C(8)	1.465(6)
Se–C(21)	1.938(4)		
Bond angles			
S–Fe(2)–Se	82.10(3)	S–C(7)–Fe(1)	113.7(2)
Fe(1)–Se–Fe(2)	67.25(3)	Se–Fe(1)–Fe(2)	56.00(2)
Fe(1)–C(7)–N	125.7(3)	C(7)–N–C(8)	125.6(4)
Se–Fe(1)–C(6)	97.6(2)	Se–Fe(2)–C(5)	103.8(1)
S–C(7)–N	120.5(3)	N–C(8)–C(11)	113.8(4)

2.4. Crystal structures of **8** and **10**

To confirm unambiguously the structures of single and double butterfly complexes **8** and **10**, the X-ray

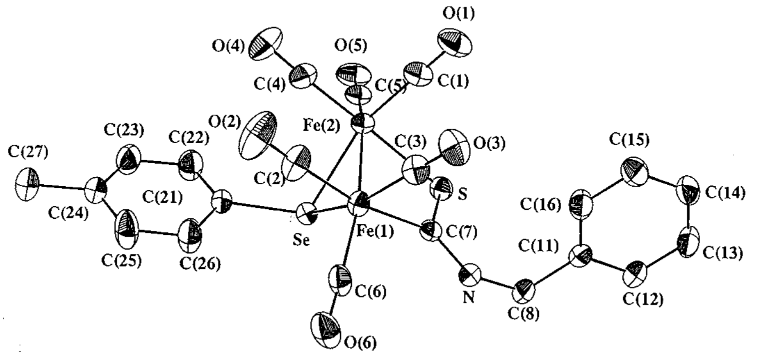


Fig. 1. Molecular structure of **8** showing the atom labeling scheme.

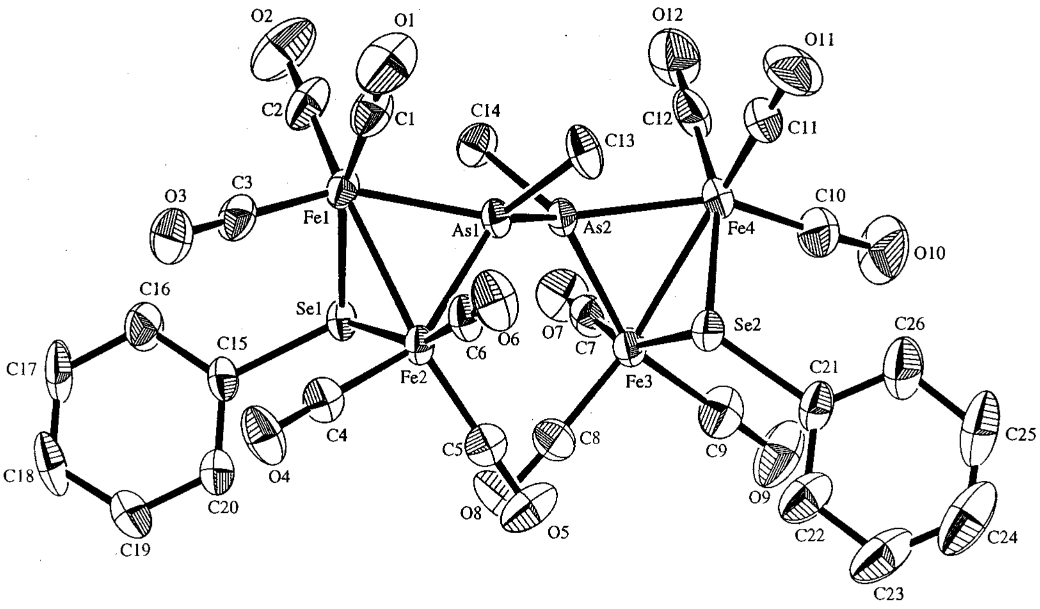


Fig. 2. Molecular structure of **10** showing the atom labeling scheme.

crystal diffraction analyses for **8** and **10** were performed. The ORTEP drawings of molecular structures of **8** and **10** are shown in Figs. 1 and 2; Tables 1 and 2 list their bond lengths and angles, respectively.

As can be seen from Fig. 1, **8** has two ligands μ-*p*-MeC_6H_4Se and μ-$PhCH_2N(H)C{=}S$, which are bridged to two Fe atoms of the two $Fe(CO)_3$ units to form the iron carbonyl complex with a single butterfly $SeFe_2CS$ skeleton. In fact, the structure of **8** is very similar to that of $(\mu\text{-}PhSe)(\mu\text{-}PhCH_2SC{=}S)Fe_2(CO)_6$ (denoted as PPF hereafter) [12]. For example, in **8** the bond lengths of Fe(1)–Fe(2) (2.6207(9) Å), Fe(1)–Se (2.3766(9) Å), Fe(2)–Se (2.3558(7) Å), Fe(2)–S (2.317(1) Å), Fe(1)–C(7) (1.958(4) Å) and C(7)–S (1.691(4) Å) involved in the butterfly skeleton are very close to corresponding those in PPF (2.648(3), 2.380(2), 2.368(3), 2.307(5), 1.978(7) and 1.63(1) Å) [12], respectively. The bond length of thiocarbonyl C(7)=S (1.691(4) Å) in **8** is much longer than a typical C=S double bond in CS_2 (1.554 Å) [13]. This is apparently due to its coordination to Fe(1) and Fe(2). In addition, that the bond length of Fe(1)–C(7) is much shorter than that of Fe(2)–S, which means that the thiocarbonyl C(7)=S is bonded to Fe(1) via a σ bond with a carbene character and to Fe(2) via the donation of an unshared electron pair from S atom [12,14]. It is worth pointing out that the angle C(21)–Se···C(7) (150.0°) reveals that the substituent *p*-MeC_6H_4 is attached to Se atom by an equatorial bond, namely, **8** belongs to an e-type isomer.

Fig. 2 shows that the structure of **10** is totally similar to those of its sulfur analogs $[(\mu\text{-}t\text{-}BuS)(\mu\text{-}MeAs)Fe_2(CO)_6]_2$ (denoted as BMF hereafter) [10] and $[(\mu\text{-}i\text{-}PrS)(\mu\text{-}MeAs)Fe_2(CO)_6]_2$ (denoted as PMF hereafter) [11], which consists of two butterfly-shaped structural units $[(\mu\text{-}PhSe)(\mu\text{-}MeAs)Fe_2(CO)_6]_2$, dimerized via an As–As bond. The bond length of As(1)–As(2) is 2.446(1) Å, which is almost the same as corresponding those in BMF (2.435(1) Å) and PMF (2.4346(8) Å) [10,11] and very close to the normal As–As single bond length (ca. 2.4 Å) [15]. In complex **10** the average lengths of the two Fe–Fe bonds (2.606 Å) and the four Fe–As bonds (2.332 Å) are also very close to the corresponding those in BMF (2.591 Å for Fe–Fe and 2.339 Å for Fe–As) [10] and PMF (2.585 Å for Fe–Fe and 2.336 Å for Fe–As) [11], respectively. In addition, since the angles of As(1)···Se(1)–C(15) = 155.1°, As(2)···Se(2)–C(21) = 156.7°, Se(1)–C(15) = 155.1°, Se(1)···As(1)–As(2) = 81.6°, the two phenyl groups are bound to selenium by e-bonds and the two arsenic atoms bound to each other by a-bonds (thus the two methyl groups are inevitably bound to As by e-bonds). It follows that complex **10**, similar to its two sulfur analogs BMF and PMF [10,11], belongs to isomer e(Ph)e(Me)e(Me)e(Ph), namely, isomer (iii) shown in Scheme 5.

Table 2
Selected bond lengths (Å) and angles (°) for **10**

Bond lengths			
Fe(1)–Fe(2)	2.603(2)	Fe(3)–Fe(4)	2.608(2)
As(1)–As(2)	2.446(1)	As(1)–Fe(1)	2.327(2)
As(1)–Fe(2)	2.335(1)	As(2)–Fe(3)	2.329(1)
As(2)–Fe(4)	2.338(2)	Se(1)–Fe(1)	2.393(1)
Fe(2)–Se(1)	2.392(2)	Fe(3)–Se(2)	2.388(2)
Bond angles			
Fe(1)–Se(1)–Fe(2)	65.91(5)	As(2)–As(1)–Fe(1)	119.13(5)
Fe(1)–As(1)–Fe(2)	67.86(5)	As(1)–As(2)–Fe(3)	121.94(5)
As(1)–As(2)–Fe(4)	119.55(5)	Se(1)–Fe(1)–As(1)	78.24(5)
Se(1)–Fe(1)–Fe(2)	57.04(4)	As(1)–Fe(1)–Fe(2)	56.21(4)
Se(1)–Fe(2)–Fe(1)	57.05(4)	As(1)–Fe(2)–Fe(1)	55.92(5)

3. Experimental

All reactions were carried out under an atmosphere of highly purified nitrogen using standard Schlenk and vacuum-line techniques. Tetrahydrofuran (THF) and benzene were distilled under nitrogen from sodium/benzophenone ketyl, Et_3N from KOH. Se powder, PhNCS, $PhCH_2NCS$, CF_3CO_2H were commercially available and used without further purification. $Fe_3(CO)_{12}$ [16], PhSeH [17], *p*-MeC_6H_4SeH [17], Grignard reagent EtMgBr [18], PhC(Cl)=NPh [19], PhCONCS [20], Et_3OBF_4 [21], $MeAsI_2$ [22] were prepared according to the literature. The products were separated by TLC ($20 \times 25 \times 0.25$ cm^3, silica gel G) and further purified by recrystallization from mixed CH_2Cl_2–hexane solvent. IR spectra were recorded on a Nicolet 170 SX FTIR spectrophotometer, and ^1H-NMR spectra on a Bruker AC-P200 NMR spectrometer. ^{77}Se-NMR spectra were recorded on a Unity plus-400 spectrometer with Ph_2Se_2 as an external standard and the chemical shifts were referenced to Me_2Se (δ 0 ppm). C/H analyses were performed on a Yanaco CHN Corder MT-3 analyzer. Melting points were determined on a Yanaco MP-500 apparatus.

3.1. Preparation of $(\mu\text{-}PhSe)(\mu\text{-}PhC{=}NPh)Fe_2(CO)_6$ (**2**)

A 100-ml three-necked flask equipped with a magnetic stir-bar, a N_2 inlet tube and a serum cap was charged with 1.00 g (2.0 mmol) of $Fe_3(CO)_{12}$, 20 ml of THF, 0.22 ml (2.1 mmol) of PhSeH and 0.32 ml (2.3 mmol) of Et_3N. The mixture was stirred at room temperature (r.t.) for 0.5 h to give a brown–red solution, which was cooled to −78°C. To this solution was slowly added 0.431 g (2.0 mmol) of PhC(Cl)=NPh in 10 ml of THF (also cooled to −78°C). The mixture was stirred for 15 min at −78°C and for 12 h at r.t. The resulting mixture was filtered and the filtrate was condensed under reduced pressure. The residue was subjected to TLC separation using CH_2Cl_2–petroleum ether (v/v = 1:10) as an eluent. From the first red band was obtained 0.416 g (70%) of $(\mu\text{-PhSe})_2Fe_2(CO)_6$, which was identified by comparison of its melting point and ^{1}H-NMR spectrum with those of an authentic sample [23]. From the second band was obtained 0.267 g (22%) of **2** as a red solid; m.p. 147°C (dec.). Anal. Found: C, 48.93; H, 2.40; N, 2.44. Calc. for $C_{25}H_{15}Fe_2NO_6Se$: C, 48.72; H, 2.44; N, 2.27%. IR (KBr disk, cm^{-1}): ν(C=N) 1543m; terminal C≡O, 2069s, 2020vs, 1991vs, 1975s, 1970s, 1944s. ^{1}H-NMR ($CDCl_3$): δ 6.57–7.51 (m, 15H, $3C_6H_5$). ^{77}Se-NMR ($CDCl_3$, Me_2Se): δ 479.74 (s).

*3.2. Preparation of (μ-p-MeC_6H_4Se)(μ-PhC=NPh)$Fe_2(CO)_6$ (**3**)*

The procedure for preparation of **3** is similar to that of **2**, but using 0.360 g (2.1 mmol) of μ-*p*-MeC_6H_4SeH instead of PhSeH. The first red band afforded 0.343 g (55%) of $(\mu\text{-}p\text{-}MeC_6H_4Se)_2Fe_2(CO)_6$, which was identified by comparison of its melting point and ^{1}H-NMR spectrum with those of an authentic sample [12]. The second band gave 0.275 g (22%) of **3** as a red solid; m.p. 138°C (dec.). Anal. Found: C, 49.37; H, 2.72; N, 2.43. Calc. for $C_{26}H_{17}Fe_2NO_6Se$: C, 49.55; H, 2.70; N, 2.22%. IR (KBr disk, cm^{-1}): ν(C=N), 1548m; terminal C≡O, 2077s, 2053s, 2025vs, 1990s, 1977s, 1960s. ^{1}H-NMR (acetone-d_6): δ 2.28 (s, 3H, CH_3), 6.71–7.47 (m, 14H, C_6H_4, $2C_6H_5$). ^{77}Se-NMR ($CDCl_3$, Me_2Se): δ 433.89 (s).

*3.3. Preparation of (μ-EtSe)(μ-PhC=NPh)$Fe_2(CO)_6$ (**4**)*

The flask described above was charged with 0.158 g (2.0 mmol) of Se powder, and 20 ml of THF. To this stirred suspension was slowly added 2.0 mmol of EtMgBr–Et_2O solution. The mixture was further stirred until Se powder was disappeared. Then, 1.00 g (2.0 mmol) of $Fe_3(CO)_{12}$ was added and the mixture was stirred for 0.5 h. After cooling this mixture to −78°C, 0.216 g (1.0 mmol) of PhC(Cl)=NPh in 5 ml of THF (also cooled to −78°C) was added. The resulting mixture was filtered and condensed under reduced pressure. The residue was subjected to TLC separation using CH_2Cl_2–petroleum ether (v/v = 1:20) as eluent. From the first red band was obtained 0.217 g (47%) of $(\mu\text{-EtSe})_2Fe_2(CO)_6$, which was identified by comparison of its melting point and ^{1}H-NMR spectrum with those of an authentic sample [24]. From second band was obtained 0.093 g (17%) of **4** as a red solid; m.p. 170°C (dec.). Anal. Found: C, 44.45; H, 2.76; N, 2.20. Calc. for $C_{21}H_{15}Fe_2NO_6Se$: C, 44.39; H, 2.64; N, 2.47%. IR (KBr disk, cm^{-1}): ν(C=N), 1558m; terminal C≡O, 2065s, 2015vs, 1991s, 1975s, 1966s, 1948s. ^{1}H-NMR (acetone-d_6): δ 1.50–1.61 (m, 3H, CH_3), 2.86–2.97 (m, 2H, CH_2), 6.65–7.33 (m, 10H, $2C_6H_5$).

*3.4. Preparation of (μ-PhSe)[μ-PhN(H)C=S]$Fe_2(CO)_6$ (**5**)*

The flask described above was charged with 1.00 g (2.0 mmol) of $Fe_3(CO)_{12}$, 20 ml of THF, 0.22 ml (2.1 mmol) of PhSeH and 0.32 ml (2.3 mmol) of Et_3N. The mixture was stirred for 0.5 h at r.t. to give a brown–red solution. To the solution was added 0.24 ml (2.0 mmol) of PhNCS and the mixture was stirred for 16 h. Solvent was removed under reduced pressure. The residue was subjected to TLC separation using CH_2Cl_2–petroleum ether (v/v = 1:3) as eluent. From the first red band was obtained 0.187 g (32%) of $(\mu\text{-PhSe})_2Fe_2(CO)_6$. From the second band was obtained 0.505 g (44%) of **5** as a red solid; m.p. 111°C (dec.). Anal. Found: C, 39.66; H, 1.98; N, 2.35. Calc. for $C_{19}H_{11}Fe_2NO_6SSe$: C, 39.85; H, 1.92; N, 2.45%. IR (KBr disk, cm^{-1}): ν(N–H), 3339m; terminal C≡O, 2063s, 2020vs, 2005vs, 1975s, 1952s. .^{1}H-NMR ($CDCl_3$): δ 7.24–7.49 (m, 10H, $2C_6H_5$), 8.85 (broad s, 1H, NH). ^{77}Se-NMR ($CDCl_3$, Me_2Se): δ 480.84 (s).

*3.5. Preparation of (μ-p-MeC_6H_4Se)[μ-PhN(H)C=S]$Fe_2(CO)_6$ (**6**)*

The procedure for the preparation of **6** is similar to that of **5**, but using 0.306g (2.1 mmol) of μ-*p*-MeC_6H_4SeH instead of PhSeH. The first band afforded 0.385 g (59%) of $(\mu\text{-}p\text{-}MeC_6H_4Se)_2Fe_2(CO)_6$. The second band gave 0.477 g (41%) of **6** as a red solid; m.p. 110°C (dec.). Anal. Found: C, 40.84; H, 2.35, N, 2.45. Calc. for $C_{20}H_{13}Fe_2NO_6SSe$: C, 40.95; H, 2.39; N, 2.22%. IR (KBr disk, cm^{-1}): ν(N–H), 3341m; terminal C≡O, 2060s, 2015vs, 1989vs, 1977vs, 1964s. ^{1}H-NMR ($CDCl_3$): δ 2.29 (s, 3H, CH_3), 7.03–7.34 (m, 9H, C_6H_4, C_6H_5), 8.86 (broad s, 1H, NH).

*3.6. Preparation of (μ-p-MeC_6H_4Se)[μ-PhCON(H)C=S]$Fe_2(CO)_6$ (**7**)*

The procedure for preparation of **7** is similar to that of **5**, but 0.360 g (2.1 mmol) of μ-*p*-MeC_6H_4SeH and 0.27 ml (2.0 mmol) of PhCONCS were used instead of PhSeH and PhNCS, respectively. The first red band afforded 0.196 g (32%) of $(\mu\text{-}p\text{-}MeC_6H_4Se)_2Fe_2(CO)_6$. The second band gave 0.253 g (21%) of **7** as a red solid; m.p. 72–74°C. Anal. Found: C, 40.95; H, 2.04; N, 2.46. Calc. for $C_{21}H_{13}Fe_2NO_7SSe$: C, 41.06; H, 2.12; N, 2.28%. IR (KBr disk, cm^{-1}): ν(N–H) 3418m; terminal C≡O, 2066s, 2023vs, 1997s, 1975s; C=O, 1716m. ^{1}H-NMR ($CDCl_3$): δ 2.29 (s, 3H, CH_3), 7.02, 7.06, 7.32, 7.36 (4s, 4H, C_6H_4), 7.55–7.89 (m, 5H, C_6H_5), 10.15 (broad s, 1H, NH). ^{77}Se-NMR ($CDCl_3$, Me_2Se): δ 430.52 (s).

3.7. Preparation of (μ-*p*-MeC_6H_4Se)[μ-$PhCH_2N(H)C{=}S$]$Fe_2(CO)_6$ (**8**)

Method (i). The procedure for the preparation of **8** is similar to that of **5**, but 0.360 g (2.1 mmol) of μ-*p*-MeC_6H_4SeH and 0.27 ml (2.0 mmol) of $PhCH_2NCS$ were used instead of PhSeH and PhNCS, respectively. Using CH_2Cl_2–petroleum ether (v/v = 1:5) as eluent, the first band afforded 0.198 g (32%) of (μ-*p*-$MeC_6H_4Se)_2Fe_2(CO)_6$. The second band gave 0.670 g (56%) of **8** as a red solid; m.p. 108–109°C. Anal. Found: C, 42.01; H, 2.52; N, 2.20. Calc. for $C_{21}H_{15}Fe_2NO_6SSe$: C, 42.02; H, 2.50; N, 2.33%. IR (KBr disk, cm^{-1}): ν(N–H) 3353m; terminal C≡O, 2061s, 2016vs, 1995vs, 1979vs, 1964s, 1952s. ^{1}H-NMR ($CDCl_3$): δ 2.29 (s, 3H, CH_3), 4.62 (octet, $^2J = 14.6$, $^3J = 4.2$ Hz, 2H, CH_2), 7.00–7.38 (m, 9H, C_6H_4, C_6H_5), 7.51 (broad s, 1H, NH). ^{77}Se-NMR ($CDCl_3$, Me_2Se): δ 476.70 (s).

Method (ii). The flask described above was charged with 0.158 g (2.0 mmol) of Se powder and 20 ml of THF. To this stirred suspension was slowly added 2.0 mmol of *p*-MeC_6H_4MgBr–Et_2O solution. The mixture was further stirred at r.t. until Se powder was disappeared. Then, 1.00 g (2.0 mmol) of $Fe_3(CO)_{12}$ was added and the mixture was stirred at r.t. for 0.5 h to give a brown solution. To this solution was added 0.14 ml (1.0 mmol) of $PhCH_2NCS$ and the mixture was stirred at r.t. for 16 h. Then, 0.16 ml (2.1 mmol) of CF_3CO_2H was added and the mixture was stirred at r.t. for 2 h. By using the same workup as that of method (i), 0.189 g (31%) of (μ-*p*-$MeC_6H_4Se)_2Fe_2(CO)_6$ was obtained from the first band and from the second band was obtained 0.128 g (21%) of **8**.

3.8. Preparation of (μ-PhSe)(μ-EtOC)$Fe_2(CO)_6$ (**9**)

The flask described above was charged with 1.00 g (2.0 mmol) of $Fe_3(CO)_{12}$, 30 ml of benzene, 0.22 ml (2.1 mmol) of C_6H_5SeH and 0.32 ml (2.3 mmol) of Et_3N. The mixture was stirred for 40 min at r.t. to give a bright-red solution. To this solution was added 0.38 g (2.0 mmol) of Et_3OBF_4 and the mixture was stirred at r.t. for additional 6 h. Solvent was removed under reduced pressure. The residue was subjected to TLC separation using petroleum ether as eluent. The orange–yellow band afforded 0.600 g (61%) of **9** as a red oil. Anal. Found: C, 36.48; H, 1.87. Calc. for $C_{15}H_{10}FeO_7Se$: C, 36.55; H, 2.04%. IR (KBr disk, cm^{-1}): ν(terminal C≡O) 2065s, 2032s, 1991s, 1975s. ^{1}H-NMR ($CDCl_3$): δ 1.66 (t, $J = 7.2$ Hz, 3H, CH_3), 4.74 (q, $J = 7.2$ Hz, 2H, CH_2), 7.24 (s, 5H, C_6H_5). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 14.4 (s, CH_3), 87.2 (s, OCH_2), 128.6 (s, 3C of C_6H_5), 132.9 (s, 2C of C_6H_5), 135.7 (s, 1C of C_6H_5), 210.1 (s, carbonyl C's), 378.9 (s, carbyne C).

3.9. Preparation of [(μ-PhSe)(μ-MeAs)$Fe_2(CO)_6$]$_2$ (**10**)

The flask described above was charged with 1.00 g (2.0 mmol) of $Fe_3(CO)_{12}$, 20 ml of THF, 0.22 ml (2.1 mmol) of PhSeH and 0.32 ml (2.3 mmol) of Et_3N. The mixture was stirred at r.t. for 0.5 h to give a brown–red solution. To the solution was added 0.757 g (2.2 mmol) of $MeAsI_2$ and the mixture was stirred at r.t. for 24 h. Solvent was removed under reduced pressure. The residue was subjected to TLC separation using CH_2Cl_2–petroleum ether (v/v = 1:20) as eluent. The first red band afforded 0.354 g (60%) of (μ-$PhSe)_2Fe_2(CO)_6$. The second band gave 0.054 g (5%) of **10** as a red solid; m.p. 185°C (dec.). Anal. Found: C, 29.70; H, 2.01. Calc. for $C_{26}H_{16}As_2Fe_4O_6Se_2$: C, 29.68; H, 1.52%. IR (KBr disk, cm^{-1}): ν(terminal C≡O) 2052s, 2023vs, 1976vs, 1954s. ^{1}H-NMR ($CDCl_3$): δ 2.28 (s, 6H, $2CH_3$), 7.24–7.48 (m, 10H, $2C_6H_5$).

3.10. Single crystal structure determinations of **8** and **10**

Single crystals of **8** and **10** suitable for X-ray diffraction analyses were grown by slow evaporation of their CH_2Cl_2–hexane solutions at about 5°C. The crystal was mounted on an Enraf-Nonius CAD-4 or a Rigaku

Table 3
Crystal data and structural refinements details for **8** and **10**

	8	**10**
Empirical formula	$C_{21}H_{15}Fe_2NO_6Se$	$C_{26}H_{16}As_2Fe_4O_{12}Se_2$
Formula weight	600.07	1051.56
Temperature (K)	296	293
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$(no. 2)	$P2_1/c$ (no. 14)
Unit cell dimensions		
a (Å)	8.0415(8)	10.402(4)
b (Å)	12.140(2)	15.766(7)
c (Å)	13.858(3)	21.224(3)
α (°)	109.86(2)	
β (°)	100.56(2)	93.61(2)
γ (°)	104.70(1)	
V (Å^3)	1176(1)	3473(2)
Z	2	4
D_{calc} (g cm^{-3})	1.695	2.010
F(000)	596	2024
Absorption coefficient (mm^{-1})	2.886	5.678
Wavelength (Å)	0.71069	0.71069
Scan type	ω–2θ	ω–2θ
$2\theta_{max}$ (°)	54.0	50.0
Number of observations, n	4000	4468
Number of variables, p	289	416
R	0.043	0.048
Rw	0.049	0.060
Goodness-of-fit on F^2	1.26	2.29
Largest difference peak and hole (e Å^{-3})	0.41 and −0.52	0.95 and −1.08

AFC5R diffractometer with a graphite monochromator with Mo–K_α radiation ($\lambda = 0.71069$ Å). Details of the crystal data, data collections and structure refinements are summarized in Table 3. The structures were solved by direct methods and expanded by Fourier techniques. The final refinements were accomplished by the full-matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms. The calculations for **8** and **10** were performed using the TEXSAN crystallographic software package of the Molecular Structure Corporation.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 155189 and 155190 for **8** and **10**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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