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# Reaction of $[Et_3NH][(\mu\text{-}RE)(\mu\text{-}CO)Fe_2(CO)_6]$ (E = S, Se) with azides. Synthesis of $(\mu\text{-}RE)(\mu\text{-}p\text{-}R^1C_6H_4N_3H)Fe_2(CO)_6$ and crystal structure of $(\mu\text{-}Bu^tS)(\mu\text{-}PhN_3H)Fe_2(CO)_6$

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## Abstract

The reaction of $[Et_3NH][(\mu\text{-}RE)(\mu\text{-}CO)Fe_2(CO)_6]$ (E = S, Se) (**1**) with aryl azides gives bridging triazenido complexes $(\mu\text{-}RE)(\mu\text{-}p\text{-}R^1C_6H_4N_3H)Fe_2(CO)_6$ (**2**–**8**) (**2**, RE = $Bu^tS$, $R^1$ = H; **3**, RE = PhS, $R^1$ = H; **4**, RE = $Bu^tS$, $R^1$ = Cl; **5**, RE = $Bu^tS$, $R^1$ = MeO; **6**, RE = PhS, $R^1$ = MeO; **7**, RE = PhSe, $R^1$ = H; **8**, RE = PhSe, $R^1$ = Cl). These complexes were characterized by elemental analyses and $^1H$-NMR and IR spectroscopy. The structure of complex **2**, established by single-crystal X-ray diffraction analysis, shows that the triazenido ligand binds to two iron centers in a bridging bidentate fashion. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Iron; Selenium; Sulfur; Triazenido ligand; Complex; Structure

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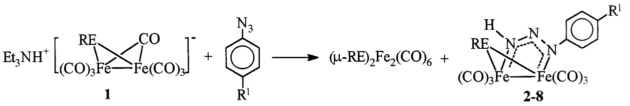
## 1. Introduction

The anionic complexes $[(\mu\text{-}RE)(\mu\text{-}CO)Fe_2(CO)_6]^-$ (E = S, Se) have been studied extensively and shown to be versatile reagents for the synthesis of Fe–E cluster complexes containing a great variety of organic and inorganic bridging groups [1–18]. In most cases, the anions act as iron-centered nucleophiles. For example, reactions with acid chlorides [2], with allyl chloride [12], and with $Ph_2PCl$ [13] yield neutral products in which the organic group or $Ph_2P$ group has replaced the μ-CO ligand of the anion as a bridging group, while reactions with $CS_2$, with RNCS, and with $(\mu\text{-}S_2)Fe_2(CO)_6$ result in formation of anionic initial products [15,19]. Furthermore, the reactivity of azides toward nucleophiles such as RLi is well known, forming triazenido compounds [20]. Triazenido ligand readily binds to the main group and transition metals in monodentate, bidentate and bridging fashions [21–26]. To further investigate the reactivity of $[(\mu\text{-}RE)(\mu\text{-}CO)Fe_2(CO)_6]^-$, we initiated a study on the reaction of $[(\mu\text{-}RE)(\mu\text{-}CO)Fe_2(CO)_6]^-$ (E = S, Se) with $ArN_3$. The expected products would be triazenido diiron complexes. Apparently, the coordination modes of triazenido ligand on diiron are also of considerable interest.

## 2. Results and discussion

When $ArN_3$ (Ar = Ph, $p$-$ClC_6H_4$, $p$-$MeOC_6H_4$) was added to a solution of $[Et_3NH][(\mu\text{-}RE)(\mu\text{-}CO)Fe_2(CO)_6]$ (E = S, Se) at room temperature, a reaction ensued, with gas evolution and slowly color change from brown–red to red–orange. After chromatographic work-up, two products, $(\mu\text{-}RE)_2Fe_2(CO)_6$ and $(\mu\text{-}RE)(\mu\text{-}ArN_3H)Fe_2(CO)_6$, were obtained (see Eq. (1)). Mechanistically, the formation of complexes **2**–**8** could be through the nucleophilic iron atoms of **1** attacking



| | **2** | **3** | **4** | **5** | **6** | **7** | **8** | |
|---|---|---|---|---|---|---|---|---|
| RE = | $Bu^tS$ | PhS | $Bu^tS$ | $Bu^tS$ | PhS | PhSe | PhSe | (1) |
| $R^1$ = | H | H | Cl | OMe | OMe | H | Cl | |

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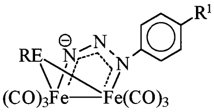
at the terminal nitrogen atom of $ArN_3$, followed by coordination of the lone electron pair of the nitrogen attached to aryl group and concomitant loss of the μ-CO ligand to generate a nitrogen-centered anion **9**, which is further protonated by the proton of the counterion $Et_3NH^+$.



**9**

It is worth pointing out that the products of the type (μ-RE)(μ-$ArN_3H$)$Fe_2(CO)_6$ were isolated even in reactions in which iodomethane was added to the reaction mixture at the time when it was assumed that the anionic product **9** would be present. It would appear that anion **9** reacts rapidly to deprotonate the $Et_3NH^+$ counterion, so that only the neutral product (μ-RE)(μ-$ArN_3H$)$Fe_2(CO)_6$ is present when the MeI is added. In addition, the reaction of *p*-$NO_2C_6H_4N_3$ with [$Et_3NH$][(μ-RS)(μ-CO)$Fe_2(CO)_6$] produced only (μ-RS)$_2Fe_2(CO)_6$. Treatment of [$Et_3NH$][(μ-Bu$^t$S)(μ-CO)$Fe_2(CO)_6$] with $Me_3SiN_3$ gave (μ-Bu$^t$S)$_2Fe_2(CO)_6$ and an instable species.

Complexes (μ-RS)$_2Fe_2(CO)_6$ ($R = Bu^t$, Ph) and (μ-PhSe)$_2Fe_2(CO)_6$ are known and have been identified by comparison of their melting points, IR and ${}^1$H-NMR spectra with those of authentic samples [27–29].

Complexes **2**–**8** are air-stable red solids and have been characterized by elemental analyses, ${}^1$H-NMR and IR spectra. Their ${}^1$H-NMR spectra exhibited respective organic group resonance signals, but NH signals have not been observed. The ${}^1$H-NMR spectra of complexes **2**, **4** and **5** also indicated that each of them exists only one conformer, i.e. equatorial Bu$^t$ group isomer. The ${}^1$H-NMR spectra of **3** and **6**–**8** showed complicated multiplets for their phenyl groups attached to E atoms, which did not provide any useful information for the identification of their isomers. In addition, the ${}^1$H-NMR spectra of complexes **6** and **8** showed the presence of cyclohexane in the crystalline solids, being consistent with their elemental analytical results. The cyclohexane molecules may come from crystallizing solvent petroleum ether. Their IR spectra showed four to six terminal carbonyl absorption bands in the range of 2078–1961 $cm^{-1}$. For each of complexes **3**–**8** the weak absorption band of NH group was also observed. It is noteworthy that the IR spectrum of complex **2** recorded in the solid state as a KBr disc gave two weak NH absorption bands in the region of lower frequencies, 3299 and 3256 $cm^{-1}$, respectively, while the spectrum recorded as $CCl_4$ solution showed only one NH absorption band at 3355 $cm^{-1}$. This is ascribed to the presence of intermolecular hydrogen bonds in the solid state.

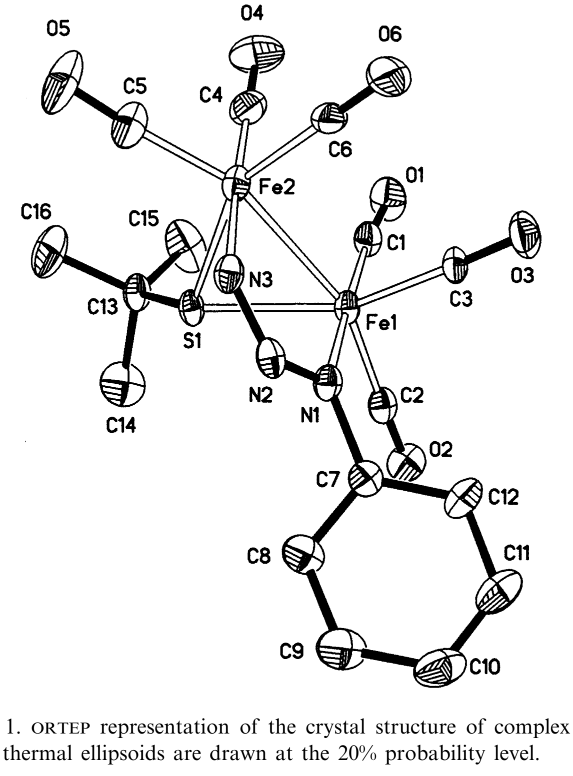


Fig. 1. ORTEP representation of the crystal structure of complex **2**. The thermal ellipsoids are drawn at the 20% probability level.

In order to confirm the coordination modes of $ArN_3H$ ligands and the structures of the complexes, a single crystal X-ray diffraction study for **2** was undertaken. The structure is presented in Fig. 1, the unit cell is in Fig. 2 and selected bond lengths and bond angles are listed in Table 1. The crystal structure showed that two enantiomeric molecules exist in an independent unit and the corresponding bond lengths and angles are almost equivalent. Fig. 1 showed that complex **2** is a diiron hexacarbonyl complex with both an 2-methyl-2-propanethiolate and 1-phenyltriazenido ligand bridging the two metals. The two metal atoms [Fe(1)Fe(2)] and the three nitrogen atoms [N(1)N(2)N(3)] lie approximately in one plane and the angle between this plane and Fe(1)Fe(2)S(1) plane is 94.3°. The plane of phenyl substituent is skewed considerably with respect to the plane of the triazenido-group, and the angle between the two planes is 50.8°. The thiolate ligand is bound almost symmetrically across the metals and the Fe–S bond lengths [2.2553(10) Å for Fe(1)–S(1), 2.2565(12) Å for Fe(2)–S(1)] are unexceptional [12]. The Fe(1)–Fe(2) distance of 2.6004(8) Å is in normal range for diiron hexacarbonyl complexes, however, shorter than that in bridging allyl hexacarbonyldiiron complex (μ-EtS)(μ-$CH_2CHCH_2$)$Fe_2(CO)_6$ [2.675(1) Å] [12]. The Fe–N distances [2.009(3) Å for Fe(1)–N(1) and 1.995(3) for Fe(2)–N(3), respectively] are close to those in complex (μ-$RC_6H_4C{=}NNH$)$_2Fe_2(CO)_6$ (R = H, Me) (between 1.99 and 2.02 Å) [30], but longer than those found in complexes (μ-$\eta^2$-$Et_2N_2$)$Fe_2(CO)_6$ (av. 1.88 Å) and ($\mu_3$-

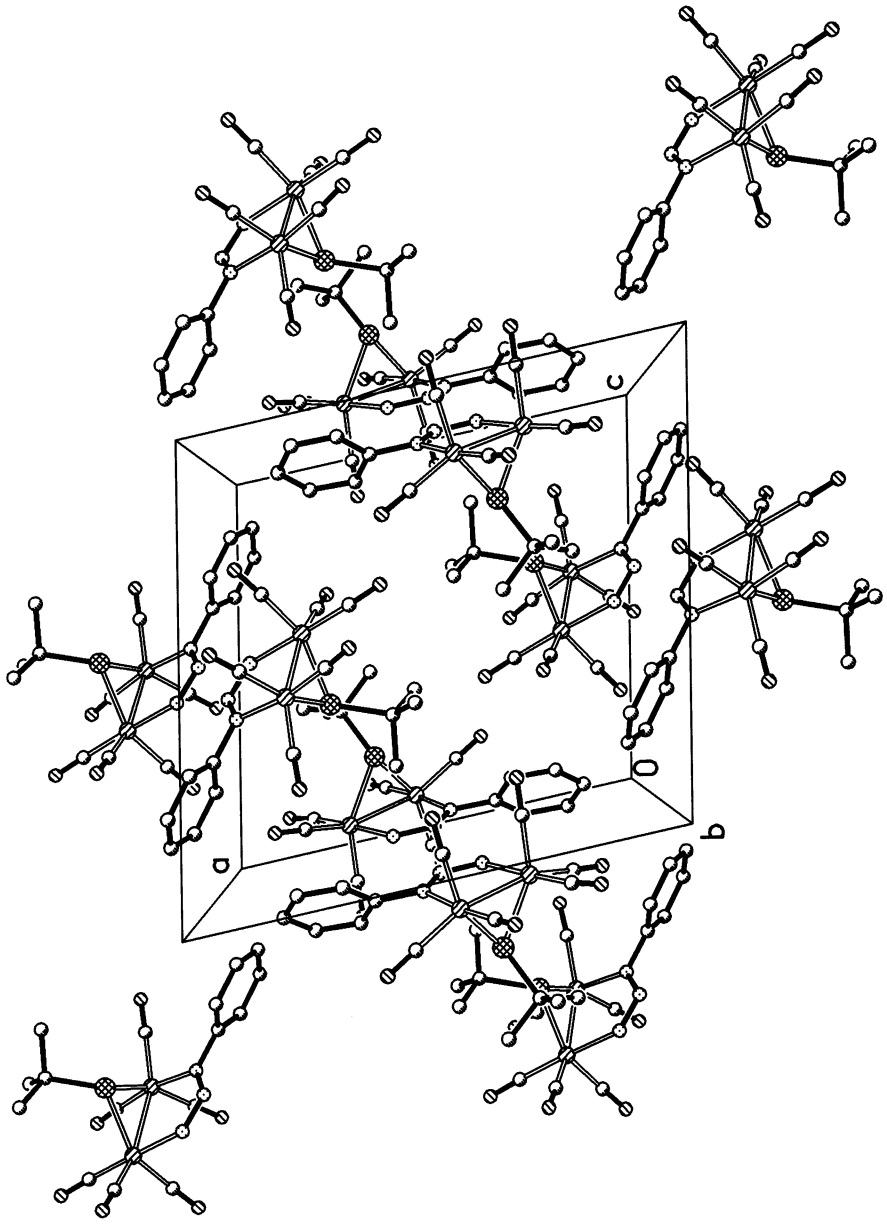


Fig. 2. Unit cell of complex **2**.

$\eta^2$-$Et_2N_2)Fe_3(CO)_9$ (av. 1.93 Å) [31]. The two N–N bonds are nearly equivalent and the N(1)–N(2)–N(3) angle is 118.2° indicating pronounced π-electron delocalization.

In addition, it was noted that the head-to-head arrangement of the molecules makes the $N_3$ ligands of two molecules very close, 3.002 Å between N2 and N3′ (or N3 and N2′), supporting the presence of intermolecular hydrogen bonds (Fig. 3). This is also consistent with its IR spectrum.

## 3. Experimental

All reactions were carried out under nitrogen using standard Schlenk techniques. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. PhSeH [32] and $Fe_3(CO)_{12}$ [33] were obtained by published procedures. $PhN_3$, $p$-$ClC_6H_4N_3$ and $p$-$MeOC_6H_4N_3$ were prepared by reaction of sodium azide with respective diazonium chloride [34]. The solutions of $[Et_3NH][(\mu\text{-}RS)(\mu\text{-}CO)Fe_2(CO)_6]$ and $[Et_3NH][(\mu$-

Table 1
Selected bond distances (Å) and angles (°) for complex **2**

| | | | |
|---|---|---|---|
| *Bond length* | | | |
| Fe(1)–N(1) | 2.0086(16) | Fe(3)–N(4) | 2.0138(17) |
| Fe(1)–S(1) | 2.2551(6) | Fe(3)–S(2) | 2.2599(6) |
| Fe(1)–Fe(2) | 2.6000(5) | Fe(3)–Fe(4) | 2.6092(5) |
| Fe(2)–N(3) | 1.9922(17) | Fe(4)–N(6) | 1.9667(19) |
| Fe(2)–S(1) | 2.2566(7) | Fe(4)–S(2) | 2.2464(6) |
| N(1)–N(2) | 1.290(2) | N(4)–N(5) | 1.304(2) |
| N(1)–C(7) | 1.441(3) | N(5)–N(6) | 1.280(3) |
| N(2)–N(3) | 1.280(3) | | |
| *Bond angles* | | | |
| N(1)–Fe(1)–S(1) | 84.20(5) | N(4)–Fe(3)–S(2) | 82.95(5) |
| N(1)–Fe(1)–Fe(2) | 85.27(5) | N(4)–Fe(3)–Fe(4) | 85.95(5) |
| S(1)–Fe(1)–Fe(2) | 54.837(19) | S(2)–Fe(3)–Fe(4) | 54.377(17) |
| N(3)–Fe(2)–S(1) | 82.81(5) | N(6)–Fe(4)–S(2) | 83.13(5) |
| N(3)–Fe(2)–Fe(1) | 83.00(5) | N(6)–Fe(4)–Fe(3) | 81.99(5) |
| S(1)–Fe(2)–Fe(1) | 54.783(17) | S(2)–Fe(4)–Fe(3) | 54.862(17) |
| Fe(1)–S(1)–Fe(2) | 70.38(2) | Fe(4)–S(2)–Fe(3) | 70.761(18) |
| N(2)–N(1)–C(7) | 109.46(16) | N(5)–N(4)–C(23) | 110.62(16) |
| N(2)–N(1)–Fe(1) | 125.36(13) | N(5)–N(4)–Fe(3) | 123.81(14) |
| C(7)–N(1)–Fe(1) | 124.95(13) | C(23)–N(4)–Fe(3) | 124.71(13) |
| N(3)–N(2)–N(1) | 117.07(16) | N(6)–N(5)–N(4) | 116.38(17) |
| N(2)–N(3)–Fe(2) | 129.16(13) | N(5)–N(6)–Fe(4) | 131.41(13) |

PhSe)(μ-CO)Fe$_2$(CO)$_6$] were prepared by the methods described in the literature [8,12]. Infrared spectra were obtained by using a VECTOR22 spectrometer. $^1$H-NMR spectra were recorded on either a Varian EM360L or a JEOL FX-90Q spectrometer. Elemental analyses were performed with a 240C analyzer.

### 3.1. Preparation of (μ-RS)(μ-p-R$^1$C$_6$H$_4$N$_3$H)Fe$_2$(CO)$_6$ (2, R = Bu$^t$, R$^1$ = H; 3, R = Ph, R$^1$ = H; 4, R = Bu$^t$, R$^1$ = Cl; 5, R = Bu$^t$, R$^1$ = MeO; 6, R = Ph, R$^1$ = MeO)

A solution of the triethylammonium salt of [(μ-Bu$^t$S)(μ-CO)Fe$_2$(CO)$_6$]$^-$ was generated by reacting 0.50 g (0.99 mmol) of Fe$_3$(CO)$_{12}$, 0.12 ml (1.06 mmol) of Bu$^t$SH and 0.15 ml (1.07 mmol) of Et$_3$N in 20 ml of THF at room temperature (r.t.). To the solution was added 0.12 g (1.01 mmol) of PhN$_3$ with stirring for 40 min. Subsequently 0.30 ml (1.93 mmol) of iodomethane was added to the mixture. After stirring overnight, the solvent was removed at reduced pressure and the residue extracted with petroleum ether (60–90°C). After removal of the solvent, the material remaining was subjected to filtration chromatography (silica gel). Petroleum ether eluted a first band which gave, after recrystallization from petroleum ether (60–90°C), 0.07 g (31%) of (μ-Bu$^t$S)$_2$Fe$_2$(CO)$_6$ [30] as red crystals. Further elution with 3:7 (v/v) CH$_2$Cl$_2$–petroleum ether followed by evaporation of the solvent gave 0.18 g (37%) of red solid **2**, m.p. 109–111°C. Anal. Found: C, 38.94; H, 3.14; N, 8.51. Calc. for $C_{16}H_{15}Fe_2N_3O_6S$: C, 39.29; H, 3.09; N, 8.59%. $^1$H-NMR (CDCl$_3$): $\delta$ (ppm) 1.45 (s, 9H, Bu$^t$), 6.80–7.30 (m, 5H, Ph). IR (KBr disc): $\nu$ (cm$^{-1}$) 3299 w, 3256 w (NH); 2071 s, 2032 vs, 1996 vs, 1980 vs (Fe–CO). IR (CCl$_4$): $\nu$ (cm$^{-1}$) 3355 w (NH); 2072 vs, 2034 vs, 1997 vs, br (Fe–CO).

The reaction was also carried out according to the same procedure and scale as above but absence of MeI. After work-up, complex **2** was obtained.

#### 3.1.1. Compound 3

The same procedure as for **2** was followed, but PhSH was used instead of Bu$^t$SH. After work-up, (μ-PhS)$_2$Fe$_2$(CO)$_6$ (57%) [31] and **3** (36%) were obtained. **3**, red crystals, m.p. 114–116°C. Anal. Found: C, 42.42; H, 2.34; N, 7.99. Calc. for $C_{18}H_{11}Fe_2N_3O_6S$: C, 42.47; H, 2.18; N, 8.25%. $^1$H-NMR (CDCl$_3$): $\delta$ (ppm) 6.40–6.75 (m, 2H, Ph), 7.05–7.45 (m, 8H, Ph). IR (KBr disc): $\nu$ (cm$^{-1}$) 3343 w (NH); 2078 s, 2031 vs, 2014 s, 2000 vs, 1991 s, 1980 s (Fe–CO).

#### 3.1.2. Compound 4

The same procedure as for **2** was followed, but *p*-ClC$_6$H$_4$N$_3$ was used instead of PhN$_3$. After similar work-up, (μ-Bu$^t$S)$_2$Fe$_2$(CO)$_6$ (60%) and complex **4** (34%) were obtained. **4**, red crystals, m.p. 126–128°C.

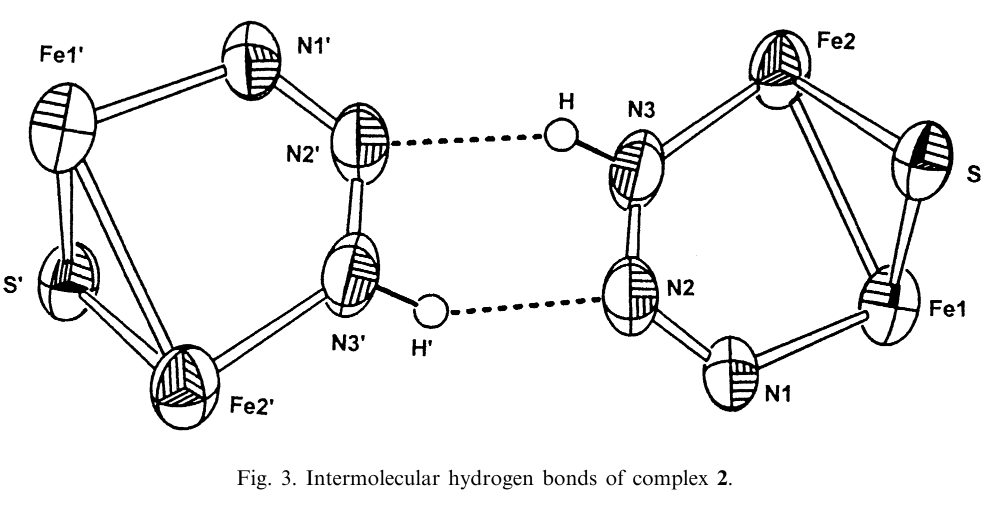


Fig. 3. Intermolecular hydrogen bonds of complex **2**.

Table 2
Crystal data and refinement for complex **2**

| | |
|---|---|
| Formula | $C_{16}H_{14}Fe_2N_3O_6S$ |
| Molecular weight | 488.06 |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| $a$ (Å) | 13.6361(18) |
| $b$ (Å) | 24.092(3) |
| $c$ (Å) | 13.0367(17) |
| $\beta$ (°) | 102.015(3) |
| $V$ (Å$^3$) | 4189.0(10) |
| $Z$ | 8 |
| Crystal size (mm) | 0.18 × 0.16 × 0.12 |
| Radiation $\lambda$ (Å) | 0.71073 |
| Temperature (K) | 293(2) |
| Scan type | $\phi$–$\omega$ |
| $2\theta_{max}$ (°) | 55.16 |
| Total reflections | 26 920 |
| Independent reflections | 9617<br>($R_{int} = 0.0914$) |
| Reflections with $I > 2\sigma(I)$ | 4172 |
| Goodness-of-fit on $F^2$ | 0.749 |
| Final $R$ indices [$I > 2\sigma(I)$] | |
| $R_1$ [a] | 0.0564 |
| $wR_2$ [b] | 0.1269 |
| Largest differences peak and hole (e Å$^{-3}$) | 0.892 and −0.597 |

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

Anal. Found: C, 37.10; H, 2.92; N, 8.11. Calc. for $C_{16}H_{14}ClFe_2N_3O_6S$: C, 36.71; H, 2.70; N, 8.03%. $^1$H-NMR ($CCl_4$): $\delta$ (ppm) 1.46 (s, 9H, Bu$^t$), 7.05 (q, $J = 8.0$ Hz, 4H, $C_6H_4$). IR (KBr disc): $\nu$ (cm$^{-1}$) 3333 w (NH); 2071 s, 2033 vs, 1994 vs, 1979 s, 1961 s (Fe–CO).

### *3.1.3. Compound **5***

The same procedure as for **2** was followed, but $p$-$MeOC_6H_4N_3$ was used instead of $PhN_3$. After similar work-up, (μ-Bu$^t$S)$_2$Fe$_2$(CO)$_6$ (53%) and complex **5** (40%) were obtained. **5**, red crystals, m.p. 132–134°C. Anal. Found: C, 39.46; H, 3.66; N, 8.12. Calc. for $C_{17}H_{17}ClFe_2N_3O_7S$: C, 39.34; H, 3.30; N, 8.10%. $^1$H-NMR ($CCl_4$): $\delta$ (ppm) 1.50 (s, 9H, Bu$^t$), 3.75 (s, 3H, Me), 6.20–7.10 (m, 4H, $C_6H_4$). IR (KBr disc): $\nu$ (cm$^{-1}$) 3316 w (NH); 2068 s, 2029 vs, 2002 vs, 1984 s (Fe–CO).

### *3.1.4. Compound **6***

The same procedure as for **3** was followed, but $p$-$MeOC_6H_4N_3$ was used instead of $PhN_3$. After similar work-up, (μ-PhS)$_2$Fe$_2$(CO)$_6$ (33%) and **6**·0.2$C_6H_{12}$ (31%) were isolated. **6**·0.2$C_6H_{12}$, red crystals, m.p. 110–112°C. Anal. Found: C, 43.81; H, 2.83; N, 7.53. Calc. for $C_{19}H_{13}Fe_2N_3O_7S\cdot 0.2C_6H_{12}$: C, 43.64; H, 2.79; N, 7.56%. $^1$H-NMR ($CDCl_3$): $\delta$ (ppm) 1.40 (s, 2.4H, $C_6H_{12}$), 3.70 (s, 3H, Me), 6.20–7.40 (m, 9H, Ph + $C_6H_4$). IR (KBr disc): $\nu$ (cm$^{-1}$) 3322 w (NH); 2076 vs, 2034 vs, 1996 s, 1984 s, br (Fe–CO).

### *3.2. Preparation of (μ-PhSe)(μ-p-R$^1$C$_6$H$_4$N$_3$H)Fe$_2$(CO)$_6$ (**7**, R$^1$ = H; **8**, R$^1$ = Cl)*

To a solution of [Et$_3$NH][(μ-PhSe)(μ-CO)Fe$_2$(CO)$_6$] generated from 0.92 g (1.83 mmol) of $Fe_3(CO)_{12}$, 0.20 ml (1.88 mmol) of PhSeH and 0.26 ml (1.82 mmol) of $Et_3N$ in about 30 ml of THF was added 0.22 g (1.85 mmol) of $PhN_3$ and stirred overnight at r.t.

The solvent was removed at reduced pressure and the residue extracted with petroleum ether (60–90°C). After removal of the solvent, the material remaining was subjected to filtration chromatography (silica gel). Elution with petroleum ether (60–90°C) yielded, after recrystallization from petroleum ether(60–90°C), 0.39 g (72%) of red crystalline (μ-PhSe)$_2$Fe$_2$(CO)$_6$ [32]. Further elution with 3:7 (v/v) $CH_2Cl_2$–petroleum ether followed by evaporation of the solvent and recrystallization from petroleum ether (60–90°C) gave 0.24 g (24%) of red crystalline **7**, m.p. 106–108°C. Anal. Found: C, 38.87; H, 2.17; N, 7.47. Calc. for $C_{18}H_{11}Fe_2N_3O_6Se$: C, 38.89; H, 1.99; N, 7.56%. $^1$H-NMR ($CDCl_3$): $\delta$ (ppm) 6.30–7.70 (m, 10H, Ph). IR (KBr disc): $\nu$ (cm$^{-1}$) 3346 w (NH); 2073 s, 2031 vs, 2012 s, 1984 s (Fe–CO).

### *3.2.1. Compound **8***

The same procedure as for **7** was followed, but $p$-$ClC_6H_4N_3$ was used instead of $PhN_3$. After similar work-up, (μ-PhSe)$_2$Fe$_2$(CO)$_6$ (15%) and **8**·0.33$C_6H_{12}$ (22%) were obtained. 8·0.33$C_6H_{12}$, red crystals, m.p. 92–94°C. Anal. Found: C, 38.61; H, 2.67; N, 6.64. Calc. for $C_{18}H_{10}ClFe_2N_3O_6Se\cdot 0.33C_6H_{12}$: C, 38.84; H, 2.28; N, 6.79%. $^1$H-NMR ($CDCl_3$): $\delta$ (ppm) 1.42 (s, 4H, $C_6H_{12}$), 6.25–7.40 (m, 9H, Ph + $C_6H_4$). IR (KBr disc): $\nu$ (cm$^{-1}$) 3331 w (NH); 2073 s, 2031 vs, 1999 s, 1989 vs (Fe–CO).

The reaction was also carried out according to similar procedure to above, but $p$-$ClC_6H_4N_3$ was added to the anion **1** (RE = PhSe) at −78°C. After stirring overnight at r.t. and then work-up, complex **8** was obtained in 23% yield.

### *3.3. Crystal data and structure determination of complex **2***

Red–black crystals of complex **2** were grown from petroleum ether–$CH_2Cl_2$ solution at r.t. Data were collected on a Siemens P4 four-circle diffractometer using graphite-monochromated Mo–K$_\alpha$ radiation. Absorption correction was applied using SADABS. Structure was solved by direct method and refined by full-matrix least-squares on $F^2$ with anisotropic thermal parameters for non-hydrogen atoms on a PC using SHELXTL software package. A summary of crystal data and refinement parameters is given in Table 2.

## 4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre. CCDC no. 136084. 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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