



# Acetylenic derivatives of $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$ : synthesis and spectroscopic characterization of $[(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(H)=C(H)Se}\}]$ and $[(\text{CO})_6\text{Fe}_2\text{Se}_2]_2\{\mu\text{-C(H)-C(H)}\}$

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## Abstract

The new acetylenic derivatives  $[(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(H)=C(H)Se}\}]$  and  $[(\text{CO})_6\text{Fe}_2\text{Se}_2]_2\{\mu\text{-C(H)-C(H)}\}$  have been isolated from the room-temperature reaction of  $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$  with acetylene in methanol solvent containing sodium acetate. The products have been characterized by IR and  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{77}\text{Se}$  NMR spectroscopy. The NMR spectroscopic features of the related phenylacetylene derivatives  $[(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(Ph)=C(H)Se}\}]$  and  $[(\text{CO})_6\text{Fe}_2\text{Se}_2]_2\{\mu\text{-C(Ph)-C(H)}\}$  are also reported.

**Keywords:** Iron; Selenium

## 1. Introduction

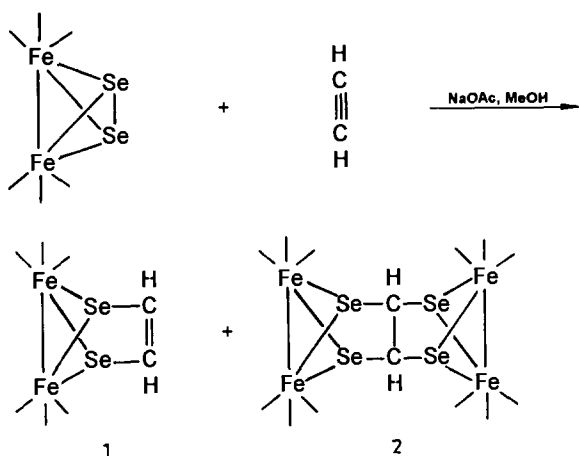
There is continuing interest in transition metal alkyne chemistry because of the potential of the coordinated alkyne to be transformed into useful organic species [1]. Most of the studies on such complexes have centred on compounds in which the alkyne is directly attached to the transition metal atoms. Recent successes in the area of incorporating single atom ligands derived from certain main groups of the periodic table in transition metal carbonyl complexes [2] has evoked interest in studies on the role of these ligands to act as sites of addition of alkynes. It has been shown that  $(\mu_3\text{-X})_2\text{Fe}_3(\text{CO})_9$  compounds (X = RP, Se or Te) add alkynes upon photochemical or thermal activation such that the ligands derived from the main group elements bridge the alkyne and the iron carbonyl cluster units [3]. Direct addition of phenylacetylene to the Se–Se bond of  $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$  [4] and of the diacetylene  $\text{CH}_3\text{C}_4\text{H}$  to the S–Te bond of  $\text{Fe}_2(\text{CO})_6(\mu\text{-STe})$  has been shown [5]. In the complex  $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(Ph)=C(H)Se}\}$  the reactive sites are blocked and addition of organometallic group across the Fe–Fe bond is facilitated as a preliminary step

in the formation of Se-bridged mixed-metal cluster  $\text{Cp}_2\text{Mo}_2\text{Fe}_2(\text{CO})_6(\mu_4\text{-Se})(\mu_3\text{-Se})_2$  [6]. Structural characterization of  $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(Ph)=C(H)Se}\}$  and  $[(\text{CO})_6\text{Fe}_2\text{Se}_2]_2\{\mu\text{-C(Ph)-C(H)}\}$  reveals the corresponding acetylenic bond reduction as a result of coordination of the phenylacetylene molecule to one or two  $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$  units respectively [4]. Here we report the addition of  $\text{HC}_2\text{H}$  to  $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$  and the characterization of the products by IR spectroscopy and by  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{77}\text{Se}$  NMR spectroscopy. The  $^{77}\text{Se}$  NMR spectroscopic features of  $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(Ph)=C(H)Se}\}$  and  $[(\text{CO})_6\text{Fe}_2\text{Se}_2]_2\{\mu\text{-C(Ph)-C(H)}\}$  are also reported.

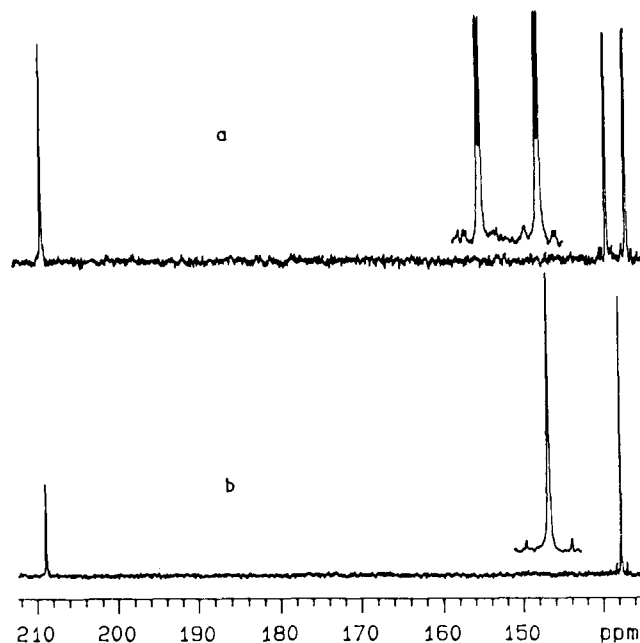
## 2. Results and discussion

When acetylene gas was bubbled through a methanol solution of  $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$  containing sodium acetate, two new compounds were isolated from the reaction medium and characterized as  $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(H)=C(H)Se}\}$  (**1**) (62%) and  $[(\text{CO})_6\text{Fe}_2\text{Se}_2]_2\{\mu\text{-C(H)-C(H)}\}$  (**2**) (24%) (Scheme 1). The IR spectra of **1** and **2** display a carbonyl stretching pattern typically observed in the spectra of compounds containing the  $\text{Fe}_2(\text{CO})_6$  groups. The spectra resemble those of the previously

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Scheme 1. Formation of **1** and **2**.

prepared  $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC}(\text{PH})=\text{C}(\text{H})\text{Se}\}$  and  $[\{(\text{CO})_6\text{Fe}_2\text{Se}_2\}_2\{\mu\text{-C}(\text{Ph})\text{-C}(\text{H})\}]$ . The  $^1\text{H}$  NMR spectrum of **1** shows a single peak at  $\delta = 7.43$  ppm with two pairs of  $^{77}\text{Se}$  satellites ( $^2J_{\text{H-Se}} = 54$  Hz;  $^3J_{\text{H-Se}} = 10$  Hz). Both coupling constants are within the expected range of H–Se coupling observed in compounds containing the Se–C(H)=C(R) (approximately 50–60 Hz) [7] and Se–C(R)=C(H) (approximately 9 Hz) groups respectively [8], and indicative of the presence of SeC(H)=C(H)Se group in **1**. For **2**, the  $^1\text{H}$  NMR spectrum displays a single peak which is 3.12 ppm upfield of the signal observed for **1**. As in **1**, here also two pairs of  $^{77}\text{Se}$  satellites are observed, but with much smaller coupling constants ( $^2J_{\text{H-Se}} = 24$  Hz;  $^3J_{\text{H-Se}} = 6$  Hz), consistent with a decrease in the s character in the acetylenic carbon atoms in **2** compared with **1**. Fig. 1 shows the  $^{13}\text{C}$  NMR spectra of **1** and **2**. The  $^{13}\text{C}({}^1\text{H})$  NMR spectrum of **1** shows a signal at  $\delta = 138$  ppm with  $^1J_{\text{C-H}} = 187$  Hz and  $^2J_{\text{C-H}} = 9$  Hz, and a single peak at  $\delta = 209$  ppm for the carbonyl groups, indicating equivalence of the carbonyl ligands on the NMR time scale at room temperature. The  $^1\text{H}$  decoupled spectrum

Fig. 1.  $^{13}\text{C}$  NMR spectra of **1**: spectrum (a)  $^1\text{H}$  coupled; and spectrum (b)  $^1\text{H}$  decoupled.

of **1** shows the presence of  $^{77}\text{Se}$  satellites ( $J = 98$  Hz). The  $^{13}\text{C}({}^1\text{H})$  NMR spectrum of **2** displays a signal at  $\delta = 53$  ppm with a reduced  $^1J_{\text{C-H}}$  coupling of 159 Hz, consistent with a reduction in s character on the CH atom. Long-range C–H coupling is not observed in the spectrum of **2**. The C–Se satellites are not observed in the  $^1\text{H}$ -decoupled spectrum of **2**. Two peaks are seen in the carbonyl region, at  $\delta = 208$  and 209 ppm. Table 1 gives a comparison of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral features of ethylene with **1**, and of ethane with **2** [9]. A formal substitution of two H atoms by an  $\text{Fe}_2(\text{CO})_6\text{Se}_2$  group to form **1** leads to a downfield shift in the signals of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. There is an increase in the  $J_{\text{C-H}}$  values on the formal conversion of ethylene to **1**. The downfield shift of the signals is more apparent

Table 1  
 $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral comparison of ethylene and ethane with **1** and **2**

Structure	$^1\text{H}$ NMR, $\delta$ (ppm)	$^{13}\text{C}$ NMR, $\delta$ (ppm)
	5.25	123 ( $^1J_{\text{C-H}} = 156$ Hz; $^2J_{\text{C-H}} = 2.4$ Hz)
	7.43	138 ( $^1J_{\text{C-H}} = 187$ Hz; $^2J_{\text{C-H}} = 8.5$ Hz)
	0.86	57 ( $^1J_{\text{C-H}} = 125$ Hz; $^2J_{\text{C-H}} = 4.5$ Hz)
	4.31	53 ( $^1J_{\text{C-H}} = 159$ Hz)

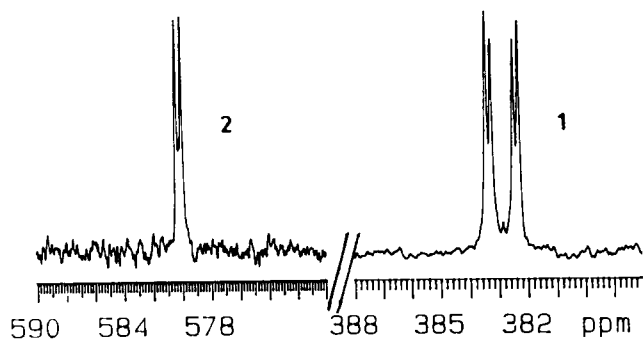


Fig. 2.  $^{77}\text{Se}$  NMR spectra of **1** and **2**.

when the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of ethane are compared with those of **2**, which can be thought of as being formed by a formal replacement of four H atoms of ethane by two  $\text{Fe}_2(\text{CO})_6\text{Se}_2$  groups. The  $^{77}\text{Se}$  NMR spectra of **1** and **2** display signals centred at  $\delta = 383$  and 580 ppm respectively (Fig. 2). In the spectrum of **1**, both short-range and long-range Se–H coupling are observed (54 Hz and 10 Hz respectively) while, in the spectrum of **2**, only the short-range coupling of 24 Hz is seen. The  $^{77}\text{Se}$  NMR spectral features of **1** compares well with those of the phenylacetylene derivative  $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC}(\text{Ph})=\text{C}(\text{H})\text{Se}\}$  ( $\delta = 371$  ppm,  $^2J_{\text{Se-H}} = 54$  Hz;  $\delta = 448$  ppm,  $^3J_{\text{Se-H}} = 6.9$  Hz). Because of poor solubility, it has not been possible to obtain a  $^{77}\text{Se}$  NMR spectrum of  $[\{(\text{CO})_6\text{Fe}_2\text{Se}_2\}_2\{\mu\text{-C}(\text{Ph})\text{-C}(\text{H})\}]$ .

The formation of **1** involves a straightforward addition of the Se–Se bond of  $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$  to the  $\text{C}\equiv\text{C}$  of acetylene. The formation of **2** can likewise be thought of as involving a simultaneous addition of Se–Se bonds of two  $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$  molecules across the  $\text{C}\equiv\text{C}$  bond of acetylene. The  $\text{Fe}_2(\text{CO})_6\text{Se}_2$  affects the reactivity of the  $\text{C}\equiv\text{C}$  bond in phenylacetylene and in acetylene in contrasting ways. For instance, formation of  $[\{(\text{CO})_6\text{Fe}_2\text{Se}_2\}_2\{\mu\text{-C}(\text{Ph})\text{-C}(\text{H})\}]$  occurs by the addition of  $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$  to  $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC}(\text{Ph})=\text{C}(\text{H})\text{Se}\}$ , whereas the formation of **2** from the reaction of  $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$  with **1** was not observed. Further investigations are currently in progress to study the contrasting effect of the Se-bridged metal carbonyl compounds on acetylenic species.

### 3. Experimental details

Reactions and manipulations were carried out under an inert atmosphere of argon by means of standard Schlenk techniques. Solvents were deoxygenated immediately prior to use.  $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$  was prepared as reported earlier [10]. IR spectra were recorded on a Nicolet Impact 400 Fourier transform spectrometer in NaCl cells of 0.1 mm path length as hexane solutions. Elemental analysis was performed on a Carlo Erba automatic analyser.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{77}\text{Se}$  NMR spectra were

recorded on a Varian VXR-300S spectrometer. The  $^{77}\text{Se}$  NMR signals are referenced to  $\text{Me}_2\text{Se}$  ( $\delta = 0$  ppm). The spectra were obtained at an operating frequency of 57.23 MHz using a pulse width of 15  $\mu\text{s}$  and a delay of 2 s.

#### 3.1. Reaction of $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$ with acetylene

To a methanol solution (15 ml) containing freshly prepared  $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$  (0.54 g, 1.23 mmol) and anhydrous sodium acetate (0.25 g) was bubbled acetylene gas at a slow rate with constant stirring at room temperature for 24 h. The solvent was evaporated in vacuo, and the residue was redissolved in 5 ml of dichloromethane. The solution was filtered through Celite to remove insoluble material. After removal of the solvent, the residue was redissolved in 5 ml of hexane and subjected to chromatographic work-up on a silica gel column. Using hexane as eluant, the following two compounds were obtained, in order of elution: orange  $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC}(\text{H})=\text{C}(\text{H})\text{Se}\}$  (**1**) (yield, 0.35 g (62%)) and yellow  $[\{(\text{CO})_6\text{Fe}_2\text{Se}_2\}_2\{\mu\text{-C}(\text{H})\text{-C}(\text{H})\}]$  (**2**) (yield 0.14 g (24%)).

**1**: melting point (m.p.) 101–102°C. IR:  $\nu$  2074 (vs), 2039 (s), 2001 (vs), 1987 (m), 1965 (m)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.43 (CH,  $^2J_{\text{H-Se}} = 54$  Hz,  $^3J_{\text{H-Se}} = 10$  Hz) ppm.  $^{13}\text{C}$  ( $^1\text{H}$ ) NMR ( $\text{CDCl}_3$ ):  $\delta$  138 (CH,  $^1J_{\text{C-H}} = 188$  Hz,  $^2J_{\text{C-H}} = 9$  Hz), 209 (CO) ppm.  $^{13}\text{C}$  ( $^1\text{H}$ -decoupled) NMR ( $\text{CDCl}_3$ ):  $\delta$  138 ( $J_{\text{C-Se}} = 98$  Hz), 209 (CO) ppm.  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  383 ( $^2J_{\text{Se-H}} = 54$  Hz,  $^3J_{\text{Se-H}} = 10$  Hz) ppm. Anal. Found: C, 20.8; H, 0.55.  $\text{C}_8\text{H}_2\text{O}_6\text{Fe}_2\text{Se}_2$  calc.: C, 20.7; H, 0.43%.

**2**: m.p. 158°C (decomposition). IR:  $\nu$  2074 (vs), 2067 (s), 2040 (vs), 2010 (m), 2002 (s)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  4.31 (CH,  $^2J_{\text{H-Se}} = 24$  Hz,  $^3J_{\text{H-Se}} = 6$  Hz) ppm.  $^{13}\text{C}$  ( $^1\text{H}$ ) NMR ( $\text{CDCl}_3$ ):  $\delta$  53 (CH,  $J_{\text{C-H}} = 159$  Hz), 208, 209 (CO) ppm.  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  580 ( $^2J_{\text{Se-H}} = 24$  Hz) ppm. Anal. Found: C, 18.8; H, 0.39.  $\text{C}_{14}\text{H}_2\text{O}_{12}\text{Fe}_4\text{Se}_4$  calc.: C, 18.6; H, 0.22%.

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