ELSEVIER

Journal of Organometallic Chemistry 491 (1995) 291–294

Journal of Organometallic Chemistry

Synthesis and crystal structure of $[(CO)_6Fe_2(\mu\text{-}SeCH_3)_2]$

Pradeep Mathur *[a], Rajiv Trivedi [a], Munkir Hossain Md. [a], S.S. Tavale [b], Vadavati G. Puranik [b]

[a] *Department of Chemistry, Indian Institute of Technology, Powai, Bombay 400 076, India*
[b] *National Chemical Laboratories, Pune - 411 008, India*

Received 10 October 1994

Abstract

The synthesis and crystal structure of $(CO)_6Fe_2(\mu\text{-}SeMe)_2$ (**1**) is reported. The dianion $[Fe_2(CO)_6(\mu\text{-}SeMe)_2]^{2-}$, obtained by the reaction of $Fe_2(CO)_6(\mu\text{-}Se_2)$ with ^nBuLi, reacted with iodomethane to give **1**. Compound **1** has been characterised by IR, ^1H and ^{13}C NMR spectroscopy and elemental analysis. Its structure has been elucidated by X-ray crystallography. The compound belongs to the orthorhombic space group $PC2_1n$ with $a = 7.202(1)$, $b = 10.544(1)$, $c = 18.344(3)$ Å, $Z = 4$. The structure was solved by direct methods and refined by full-matrix least-squares methods using NRCVAX programs, correcting for extinction, to $R = 0.067$ and $R_w = 0.073$ for 854 observed reflections. The structure consists of an Fe_2Se_2 open butterfly core with each Fe atom containing three terminal carbonyl groups and each Se atom having a CH_3 group bonded to it at the equatorial sites.

Keywords: Iron; Selenium

1. Introduction

Although $Fe_2(CO)_6(\mu\text{-}Se_2)$ was first reported in 1958 by Hieber and Gruber [1], its reaction chemistry has remained much less investigated than those of its S and Te analogues. We have in recent times used $Fe_2(CO)_6(\mu\text{-}Se_2)$ as a starting material for facile cluster growth reactions and for the purpose of acetylene activation [2]. By analogy with the formation of $[Fe_2(CO)_6Te_2]^{2-}$ and its reaction with electrophiles [3], we have investigated the formation of the $[Fe_2(CO)_6(Se_2)]^{2-}$ dianion and tested its reactivity with iodomethane to form a neutral compound containing Se—CH_3 groups. We report here the results of these investigations.

2. Results and discussion

The homo-chalcogen compound $Fe_2(CO)_6(\mu\text{-}Se_2)$ was prepared by the reaction of a basic methanolic solution of $Fe(CO)_5$ with an aqueous solution of the oxy anion Na_2SeO_3, followed by acidification, treatment with NaOMe and chromatographic work-up [4].

2.1. Reaction of $Fe_2(CO)_6(\mu\text{-}Se_2)$ with ^nBuLi

The addition of 1 mol equiv. of n-butyllithium to the red THF solution of $Fe_2(CO)_6(\mu\text{-}Se_2)$ caused an immediate colour change to deep green. When a second equivalent of butyllithium was added, the solution remained green on formation of the dianion $[Fe_2(CO)_6(\mu\text{-}Se_2)]^{2-}$. The reaction proceeds in two steps; the first corresponds to the formation of the monoanionic species and the second to that of the dianion. A similar two-step process has been reported for the formation of $[Fe_2(CO)_6(\mu\text{-}S_2)]^{2-}$ and $[Fe_2(CO)_6(\mu\text{-}Te_2)]^{2-}$ from the reactions of $Fe_2(CO)_6(\mu\text{-}S_2)$ [5] and $Fe_2(CO)_6(\mu\text{-}Te_2)$ [3], respectively, with lithium triethylborohydride at low temperatures.

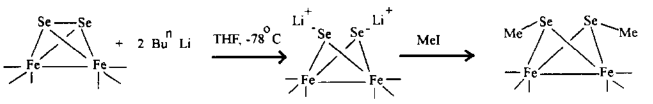
2.2. Iodomethane quench

Addition of 2 equiv. of CH_3I to the dianion $[Fe_2(CO)_6(\mu\text{-}Se_2)]^{2-}$ changed the colour of the reaction mixture from green to red (Scheme 1). Chromato-

---

* Corresponding author.

Elsevier Science S.A.
SSDI 0022-328X(94)05265-4



Scheme 1. Formation of compound **1**.

graphic work-up on a silica gel column yielded three bands. Of these, only the orange coloured third band could be obtained in sufficient amount for characterisation purposes. On the basis of IR, NMR and elemental analysis, the third band has been identified as $Fe_2(CO)_6(\mu\text{-SeMe})_2$ (**1**). It displayed an IR spectrum in the carbonyl region which is similar to that of the recently reported $Fe_2(CO)_6(\mu\text{-TeMe})_2$, with a shift of the corresponding carbonyl stretching frequencies to higher values (Fig. 1). The ^1H NMR spectrum of **1** shows a single peak for the CH_3 protons at δ 2.09 ppm. The ^1H-decoupled ^{13}C NMR spectrum of **1** shows a singlet at δ 7.96 ppm (Fig. 2). The ^1H-coupled ^{13}C NMR spectrum of **1** shows a quartet centred at δ 8.0 ppm (δ 5.15–10.85 ppm) ($^1J_{C-H} = 143.4$ Hz) for the CH_3 group and a single peak at δ 209 ppm due to the carbonyl groups (Fig. 2 inset).

Seyferth and Henderson [5] have reported the formation of the dianionic species $[Fe_2(CO)_6(\mu\text{-}S_2)]^{2-}$ and $[Fe_2(CO)_6(\mu\text{-}Se_2)]^{2-}$, and their reactions with various electrophiles. On treatment of $[Fe_2(CO)_6(\mu\text{-}S_2)]^{2-}$ with excess iodomethane, they were able to isolate two geometric isomers. During the chromatographic work-up of our reaction mixture resulting from the addition of iodomethane to $[Fe_2(CO)_6(\mu\text{-}Se_2)]^{2-}$, three bands were observed. These would correspond to the three geometrical isomers ae, aa and ee (Fig. 3), of which only one isomer could be isolated in characterisable amounts.

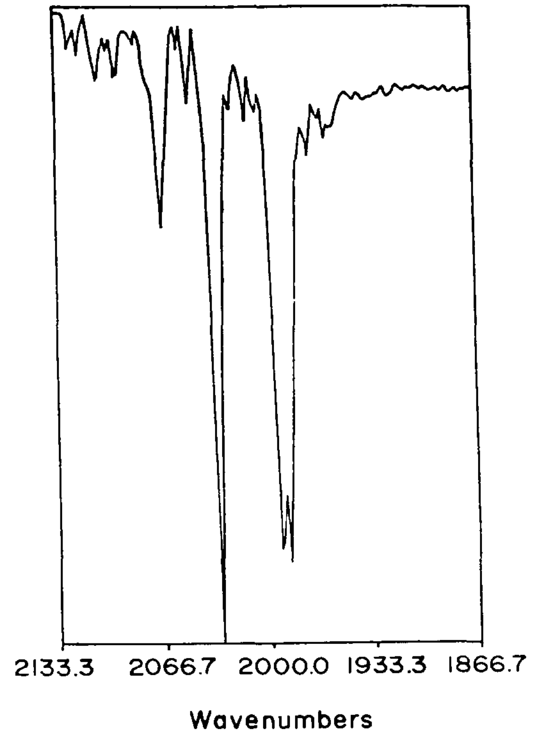


Fig. 1. IR spectrum of $Fe_2(CO)_6(\mu\text{-SeMe})_2$ in the CO region.

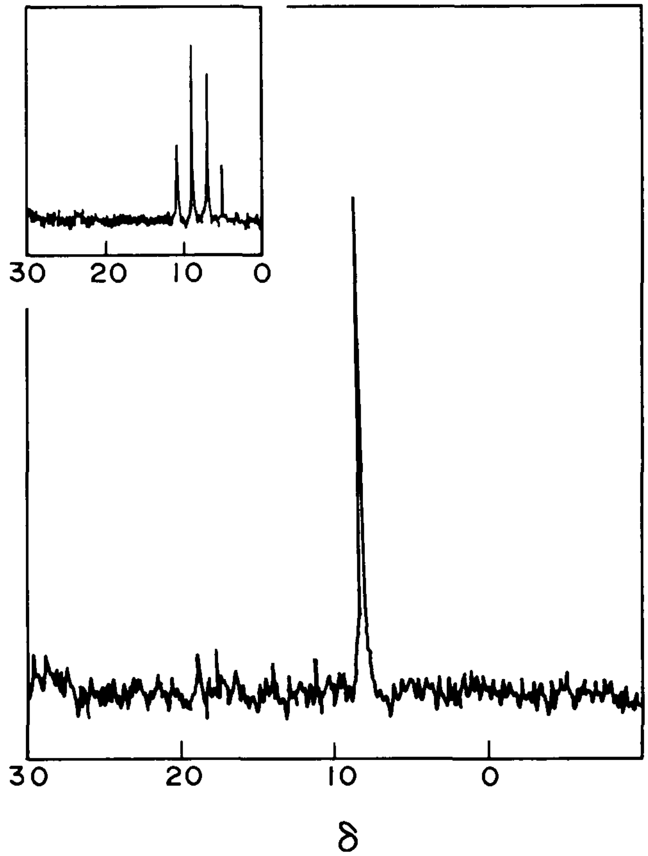


Fig. 2. Proton-decoupled and -coupled (inset) ^{13}C NMR spectra of compound **1**.

3. Molecular structure of $Fe_2(CO)_6(\mu\text{-SeMe})_2$

Dark red crystals of **1** were obtained from hexane/dichloromethane solution at −10°C and an X-ray diffraction study was undertaken. A PLUTO dia-

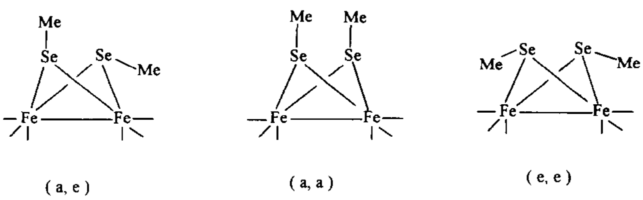


Fig. 3. The three isomers for $Fe_2(CO)_6(\mu\text{-SeMe})_2$.

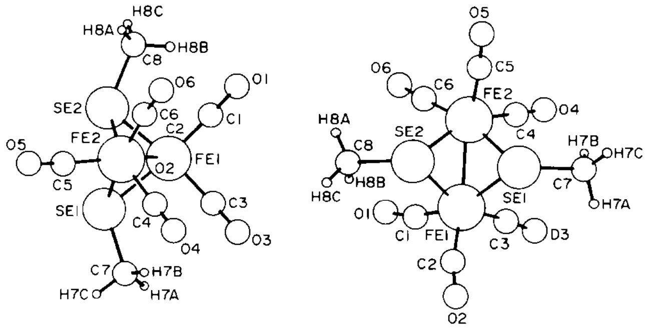


Fig. 4. Two views of the molecular structure of $Fe_2(CO)_6(\mu\text{-}SeMe)_2$.

gram of the molecular structure of **1** is shown in Fig. 4. The geometry of **1** can be described as that of an open Fe_2Se_2 tetrahedron. The open edge of Fe_2Se_2 has one CH_3 group bonded to each Se atom at the equatorial position. There are three terminal carbonyl groups bonded to each Fe atom. Overall, the structure of **1** is similar to the reported structure for $Fe_2(CO)_6(\mu\text{-}TeMe)_2$ [6]. The average Fe—Se bond distance in **1** (2.377 Å) is similar to the average Fe—Se bond distance in $\{(CO)_6Fe_2(\mu\text{-}Se)_2\}_2C(Ph){—}C(H)$ (2.3705 Å) but slightly shorter than the average Fe—Se bond distance in $Fe_2(CO)_6\{\mu\text{-}SeC(Ph){=}C(H)Se\}$ (2.3836 Å). The average Se—C bond length in **1** (2.00 Å) is longer than the average Se—C bond distance in $Fe_2(CO)_6\{\mu\text{-}SeC(Ph){=}C(H)Se\}$ (1.94 Å) but similar to the average Se—C bond distance in $\{(CO)_6Fe_2(\mu\text{-}Se)_2\}_2C(Ph){—}C(H)$ (2.016 Å). The average Fe—Se—Fe angle in **1** (65.1°) is similar to the corresponding angles in $\{(CO)_6Fe_2(\mu\text{-}Se)_2\}_2C(Ph){—}C(H)$ (64.4°) and in $Fe_2(CO)_6\{\mu\text{-}SeC(Ph){=}C(H)Se\}$ (63.6°), indicating a similar extent of opening of the Fe_2Se_2 butterfly in **1** as in the closed geometries of the latter two structures. All other bond distances and angles are unexceptional.

4. Experimental details

4.1. General comments

All reactions were carried out under an atmosphere of pre-purified nitrogen in well-dried glassware. Solvents were rigorously dried before use. Infrared spectra were recorded on a Nicolet 5DXB infrared FT spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Varian XL-300 NMR spectrometer. Chemical shifts are reported in δ units ppm downfield from tetramethylsilane. $CDCl_3$ was used as solvent. Melting points are uncorrected. $Fe_2Se_2(CO)_6$ was prepared as previously reported [4]. ^nBuLi was purchased from the Aldrich Chemical Co.

Table 1
Crystal data

Empirical formula	$Fe_2(\mu\text{-}SeMe)_2(CO)_6$
Colour, habit	dark red, plate
Crystal system	orthorhombic
Space group	$PC2_1n$
Unit cell dimensions	
a (Å)	7.202(1)
b (Å)	10.544(1)
c (Å)	18.344(3)
Volume, V (Å^3)	1392.9(3)
Z	4
Formula weight	467.74
Calculated density, D_c, g cm^{-3}	2.23
Absorption coefficient, μ, mm^{-1}	7.27
F(000)	888

4.2. Reaction of $Fe_2Se_2(CO)_6$ with ^nBuLi followed by MeI quenching

To a 100 ml three-necked, Schlenk flask equipped with a serum cap and a magnetic stirring bar was added $Fe_2Se_2(CO)_6$ (1 g, 2.28 mmol) in 50 ml of THF and the resulting red solution was cooled to −78°C. Subsequently, a hexane solution containing 1.6 M n-butyllithium (2 ml, 4.7 mmol) was added by means of a syringe over 15 min to the solution, causing a colour change from red to dark green. The mixture was stirred for a further 20 min and then iodomethane (0.28 ml,

Table 2
Bond lengths (Å) and bond angles (°) for $Fe_2(CO)_6(\mu\text{-}SeMe)_2$

Se(1)–Fe(1)	2.398(9)	Fe(2)–C(4)	1.88(3)
Se(1)–Fe(2)	2.371(9)	Fe(2)–C(5)	1.84(3)
Se(1)–C(7)	1.99(2)	Fe(2)–C(6)	1.79(4)
Se(2)–Fe(1)	2.365(10)	O(1)–C(1)	1.22(5)
Se(2)–Fe(2)	2.388(9)	O(2)–C(2)	1.17(4)
Fe(1)–Fe(2)	2.563(5)	O(3)–C(3)	1.09(8)
Se(2)–C(8)	2.01(5)	O(4)–C(4)	1.07(4)
Fe(1)–C(1)	1.76(3)	O(5)–C(5)	1.10(4)
Fe(1)–C(2)	1.81(3)	O(6)–C(6)	1.12(5)
Se(1)–Se(2)	2.971(3)	Fe(1)–C(3)	1.84(8)
Fe(1)–Se(1)–Fe(2)	65.0(2)	Se(1)–Fe(2)–Se(2)	77.2(1)
Fe(1)–Se(1)–C(7)	111.2(8)	Se(1)–Fe(2)–C(4)	91.9(10)
Fe(2)–Se(1)–C(7)	110.1(7)	Se(1)–Fe(2)–C(5)	96.5(15)
Fe(1)–Se(2)–Fe(2)	65.3(2)	Se(1)–Fe(2)–C(6)	163.9(15)
Fe(1)–Se(2)–C(8)	108.0(13)	Se(2)–Fe(2)–C(4)	153.7(8)
Fe(2)–Se(2)–C(8)	113.9(15)	Se(2)–Fe(2)–C(5)	104.3(15)
Se(1)–Fe(1)–Se(2)	77.18(15)	Se(2)–Fe(2)–C(6)	91.7(13)
Se(1)–Fe(1)–C(1)	159.3(9)	C(4)–Fe(2)–C(5)	101(2)
Se(1)–Fe(1)–C(2)	103 (2)	C(4)–Fe(2)–C(6)	93(2)
Se(1)–Fe(1)–C(3)	93.4(15)	C(5)–Fe(2)–C(6)	98(2)
Se(2)–Fe(1)–C(1)	91.5(10)	Fe(1)–C(1)–O(1)	166(3)
Se(2)–Fe(1)–C(2)	97(2)	Fe(1)–C(2)–O(2)	167(8)
Se(2)–Fe(1)–C(3)	158(2)	Fe(1)–C(3)–O(3)	173(5)
C(1)–Fe(1)–C(2)	96(2)	Fe(2)–C(4)–O(4)	178(3)
C(1)–Fe(1)–C(3)	91(2)	Fe(2)–C(5)–O(5)	174(5)
C(2)–Fe(1)–C(3)	104(3)	Fe(2)–C(6)–O(6)	171(4)
Se(1)–Fe(1)–Fe(2)	57.0(3)	Se(2)–Fe(1)–Fe(2)	57.8(3)
Se(1)–Fe(2)–Fe(1)	58.0(3)	Se(2)–Fe(2)–Fe(1)	56.9(3)

4.7 mmol) was added. The reaction mixture was allowed to warm to room temperature and was stirred for another 6 h. The solution was filtered through Celite and the solvent was removed in vacuo. The residue was subjected to chromatographic work-up on silica gel column. Using petroleum ether as eluant, the ruby red coloured compound **1** (11 mg, 23%) was obtained as the major band. Recrystallisation from hexane gave air-stable, ruby red crystals, m.p. 134–135°C. Anal. Found: C, 20.62; H, 1.34%, $C_8H_6O_6Se_2Fe_2$ Calc.: C, 20.54; H, 1.29%. ^1H NMR δ: 2.09 (s) ppm. ^{13}C NMR: proton-decoupled δ: 7.96 (s) ppm; proton-coupled δ: 5.15–10.85 (q) ppm. IR (CO region) (hexane) (cm^{-1}): 2064 (m); 2031 (vs); 1991 (s); 1986 (s).

4.3. *Crystallographic analysis of* $(CO)_6Fe_2(\mu\text{-}SeMe)_2$

The crystal was prepared as described above and crystallised at −10°C from petroleum ether solutions. Crystal data are collected in Table 1. Selected bond lengths (Å) and angles (°) are listed in Table 2. The atomic coordinates and equivalent isotropic displacements for $Fe_2(CO)_6(\mu\text{-SeMe})_2$ are listed in Table 3. The structure was solved by direct methods and refined by full-matrix least-squares methods using NRCVAX programs to $R = 0.067$ and $R_w = 0.073$ for 854 ($|F_o| > 3\sigma|F_o|$) reflections from a 1095 unique data set collected on a CAD 4 diffractometer. Final ΔF syntheses showed no features above 1.24 e Å^{-3}.

Table 3
Atomic coordinates and equivalent isotropic displacement coefficients (Å$^2 \times 10^3$) for $Fe_2(CO)_6(\mu\text{-SeMe})_2$

Atom	x	y	z	B_{iso}
Se1	0.0885(5)	0.9319(0)	0.0775(2)	3.3(1)
Se2	0.0988(5)	1.2136(3)	0.0776(2)	3.2(1)
Fe1	0.3476(5)	1.0710(13)	0.0586(2)	2.6(4)
Fe2	0.1547(5)	1.0703(13)	0.1760(2)	2.7(3)
O1	0.614(4)	1.272(4)	0.103(3)	14.0(3)
O2	0.359(5)	1.069(7)	−0.103(1)	9.0(2)
O3	0.615(3)	0.869(2)	0.088(1)	4.0(1)
O4	0.365(3)	0.872(2)	0.254(1)	4.0(1)
O5	−0.205(4)	1.056(4)	0.251(1)	6.0(1)
O6	0.316(4)	1.261(3)	0.271(2)	7.0(2)
C1	0.512(4)	1.191(3)	0.076(2)	2.0(1)
C2	0.358(6)	1.085(8)	−0.040(2)	5.0(2)
C3	0.519(8)	0.948(6)	0.080(4)	12.0(4)
C4	0.291(4)	0.944(3)	0.225(1)	2.0(1)
C5	−0.072(5)	1.055(6)	0.221(2)	4.0(2)
C6	0.246(7)	1.195(3)	0.232(2)	6.0(2)
C7	0.173(3)	0.757(2)	0.101(1)	1.0(1)
C8	0.207(7)	1.388(4)	0.093(3)	7.0(3)

Acknowledgements

We are grateful to RSIC, IIT Madras for the single-crystal X-ray analyses. One of us (R.T.) thanks the Department of Atomic Energy for the award of the Dr. K.S. Krishnan fellowship.

References

[1] W. Hieber and J. Gruber, *Z. Anorg. Allg. Chem.*, *296* (1958) 91.

[2] P. Mathur, Md. M. Hossain and A.L. Rheingold, *Organometallics*, *12* (1993) 5029; P. Mathur, Md. M. Hossain and R.S. Rashid, *J. Organomet. Chem.*, *467* (1994) 245; P. Mathur, D. Chakrabarty and I.J. Mavunkal, *J. Cluster. Sci.*, *4* (1993) 351; P. Mathur, Md. M. Hossain and R.S. Rashid, *J. Organomet. Chem.*, *460* (1993) 83; P. Mathur and Md. M. Hossain, *Organometallics*, *12* (1993) 2398; P. Mathur, Md. M. Hossain and R.S. Rashid, *J. Organomet. Chem.*, *448* (1993) 211; P. Mathur, Md. M. Hossain, K. Das and U.C. Sinha, *J. Chem. Soc., Chem. Commun.*, (1993) 46.

[3] P. Mathur and V.D. Reddy, *J. Organomet. Chem.*, *385* (1990) 363.

[4] P. Mathur, D. Chakrabarty, Md. M. Hossain, R.S. Rashid, V. Rugmini and A.L. Rheingold, *Inorg. Chem.*, *31* (1992) 1106.

[5] D. Seyferth and H.S. Henderson, *J. Organomet. Chem.*, *204* (1981) 333; D. Seyferth, R.S. Henderson and L.-C. Song, *Organometallics*, *1* (1982) 125; D. Seyferth, G.B. Womack, R.S. Henderson, M. Cowie and B.W. Hames, *Organometallics*, *5* (1986) 1568; D. Seyferth and G.B. Womack, *Organometallics*, *5* (1986) 2360; D. Seyferth, R.S. Henderson and L.-C. Song, *J. Organomet. Chem.*, *192* (1980) C1; D. Seyferth, R.S. Henderson, L.-C. Song and G.B. Womack, *J. Organomet. Chem.*, *292* (1985) 9.

[6] M. Shieh, F.-D. Mia and M.-H. Shieh, *Organometallics*, *13* (1994) 920.