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Carbon–selenium bond cleavage in the double butterfly complex $[\{(CO)_6Fe_2(\mu\text{-}Se)_2\}_2\{C(Ph)-C(H)\}]$ and the synthesis and X-ray structural analysis of its dppe-substituted derivative

Pradeep Mathur and Md. Munkir Hossain
Chemistry Department, Indian Institute of Technology, Powai, Bombay 400 076 (India)

Mary F. Mahon
School of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY (UK)

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Abstract

At room temperature, the double butterfly complex $[\{(CO)_6Fe_2(\mu\text{-}Se)_2\}_2(C(Ph)-C(H)]$ reacted with $Pt(C_2H_4)(PPh_3)_2$ to give $[(CO)_6Fe_2(\mu\text{-}SeC(Ph)C(H)Se)]$, $[(CO)_6Fe_2Pt(PPh_3)_2\{\mu\text{-}SeC(Ph)C(H)Se\}]$ and $[(CO)_6Fe_2(\mu_3\text{-}Se)_2Pt(PPh_3)_2]$. It reacted with dppe to form the substituted derivative $[\{(CO)_5Fe_2(\mu\text{-}Se)_2\}_2C(Ph)C(H)(\mu\text{-dppe})]$, which was subjected to an X-ray diffraction analysis. The crystal of $[\{(CO)_5Fe_2(\mu\text{-}Se)_2\}_2C(Ph)C(H)(\mu\text{-dppe})]$ is triclinic with the space group $P\bar{1}$, $a = 12.969(1)$, $b = 13.032(1)$, $c = 18.669(1)$ Å, $\alpha = 76.81(1)$, $\beta = 72.74(1)$, $\gamma = 63.99(1)°$, $Z = 2$. The structure was refined by the block-matrix least squares method. The final R and R_w values were 0.0435 and 0.0492 respectively.

Key words: Iron; Selenium; X-ray diffraction

1. Introduction

Transition metal–alkyne complexes continue to attract attention in view of the potential of the coordinated alkyne to be transformed into useful organic species [1]. In recent years, complexes containing ligands other than the traditional carbonyl and cyclopentadienyl ligands, such as alkoxide, siloxide, aryloxide and related oxygen donor ligands as supporting groups have been examined in the context of alkyne activation and metathesis reactions [2]. The heavier group 16 elements have also been used in cluster growth reactions, and an important starting material for such reactions has been the class of compounds, $Fe_2(CO)_6(\mu\text{-}E_2)$ where E = Se or Te [3]. The characteristic chemistry of $Fe_2(CO)_6(\mu\text{-}Se_2)$ is dominated by the presence of a reactive Se–Se bond and this property has been exploited for the addition of numerous types of coordinatively unsaturated metal species. Recently, phenylacetylene was found to readily add across the Se–Se bond of $Fe_2(CO)_6(\mu\text{-}Se_2)$ and the stepwise reduction of the acetylenic triple bond to a single bond on the $Fe_2(CO)_6Se_2$ framework was demonstrated [4]. The addition of a $Pt(PPh_3)_2$ group to the coordinated phenylacetylene in $[(CO)_6Fe_2(\mu\text{-}SeC(Ph)C(H)Se)]$ has also been reported [5]. Here we report a facile Se–C bond cleavage in $[\{(CO)_6Fe_2(\mu\text{-}Se)_2\}_2(C(Ph)-C(H)]$ and the synthesis and X-ray structural analysis of the dppe-substituted derivative of the double-butterfly complex $[\{(CO)_6Fe_2(\mu\text{-}Se)_2\}_2(C(Ph)-C(H)]$ (**1**).

2. Results and discussion

Compound **1** was obtained in 14% yield from the reaction of phenylacetylene with $Fe_2(CO)_6(\mu\text{-}Se_2)$ at room temperature. This compound has previously been prepared by the reaction of $[(CO)_6Fe_2(\mu\text{-}SeC(Ph)C$-

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Correspondence to: Dr. P. Mathur.

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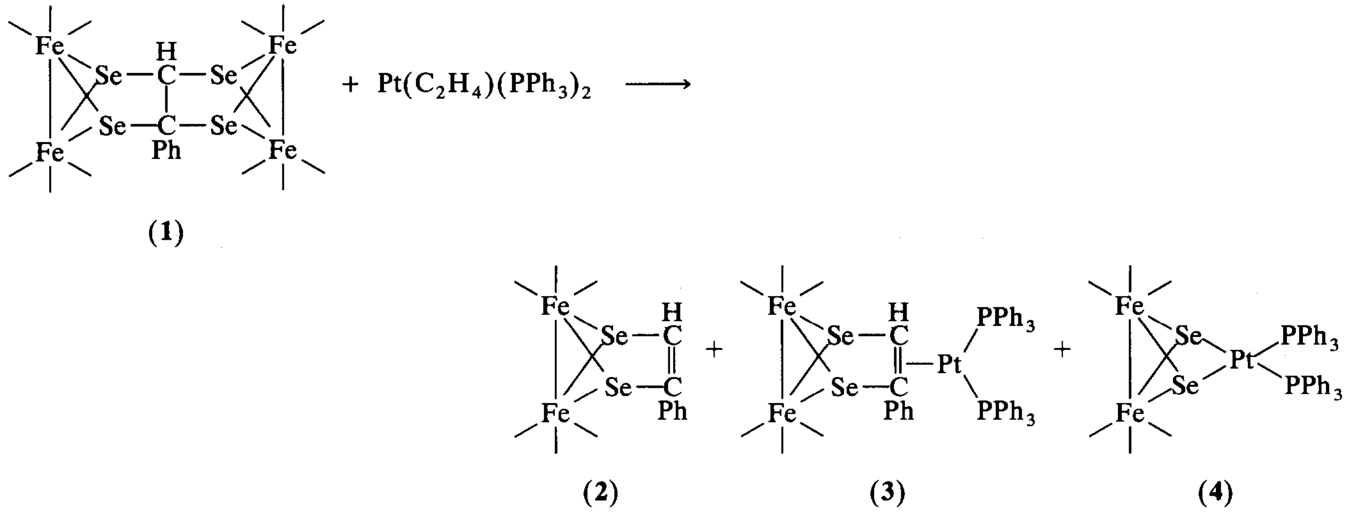
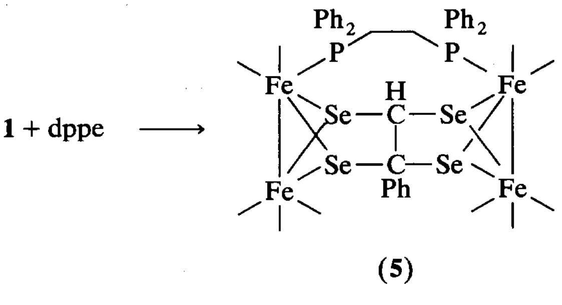


Scheme 1.

(H)Se)] (**2**) with $Fe_2(CO)_6(\mu\text{-}Se_2)$, and has been structurally characterised by single crystal X-ray diffraction analysis [4]. When a benzene solution containing **1** and $Pt(C_2H_4)(PPh_3)_2$ was stirred at room temperature, the following compounds were formed and isolated: $[(CO)_6Fe_2(\mu\text{-}SeC(Ph)C(H)Se)]$ (**2**), $[(CO)_6Fe_2Pt(PPh_3)_2\{\mu\text{-}SeC(Ph)C(H)Se\}]$ (**3**) and $[(CO)_6Fe_2(\mu_3\text{-}Se)_2Pt(PPh_3)_2$ (**4**) (Scheme 1). Compounds **2–4** were identified on the basis of comparison of their IR and NMR spectroscopic data with that reported earlier [4, 6]. Although the mechanistic details have not yet been established, the formation of these three products formally involves the scission of a pair of C–Se bonds to form $Fe_2(CO)_6Se_2$ and $Fe_2(CO)_6Se_2C(Ph)C(H)$ units. The coordinatively unsaturated $Pt(PPh_3)_2$ groups then add to these two units to form compound **4** and compound **3** respectively. The scission of the C–Se bonds is accompanied by the C–C single bond becoming a double bond in the coordinated C(Ph)C(H) group.

When a solution containing compound **1** and dppe was stirred in the presence of trimethylamine oxide, a single product was formed (see Scheme 2). It was isolated and characterised as $[\{(CO)_5Fe_2(\mu\text{-}Se)_2\}_2C(Ph)C(H)(\mu\text{-}dppe)]$ (**5**). Compound **5** was characterised by IR, ^1H NMR and ^{31}P NMR spectroscopy. The IR spectrum of **5** in the carbonyl region shows five bands between 2067 and 1912 cm^{-1}, indicating the presence of only terminally bonded carbonyl groups. The frequencies of the bands are lower than the frequencies of the bands observed in the parent compound **1** (2076–2002 cm^{-1}), consistent with the replacement of carbonyl groups by stronger donor and weaker π-acceptor ligand. The ^1H and ^{31}P NMR spectra of **5** confirm the presence of the dppe ligand. Suitable crystals of **5** were grown and an X-ray structural analysis was undertaken. An ORTEP drawing of the molecular structure of **5** is shown in Fig. 1. The structure of **5** can be described as consisting of two Fe_2Se_2 butterfly units attached to each other by means of a phenylacetylene molecule, which is bonded to all the Se atoms. A dppe group is attached to one Fe atom of each Fe_2Se_2 unit. The Fe atoms associated with the dppe group have two terminal carbonyl groups bonded to them each while the remaining two Fe atoms have three terminal groups bonded to each of them. Essentially, the heavy atom core of **5** is similar to that of **1**. The Fe–Fe bond distances in **1** and **5** are similar (in **1** the average Fe–Fe bond length is 2.527(2) Å, while in **1** the two Fe–Fe bond lengths are 2.527(2) and 2.530(4) Å). The average Fe–Se bond distance in **5** (2.394 Å) is somewhat longer than the average Fe–Se distance in **1** (2.368 Å). It is of interest to note that each Fe atom associated with dppe forms longer bonds to one of the two Se atoms with which it is bonded (Fe(1)–Se(1)



Scheme 2.

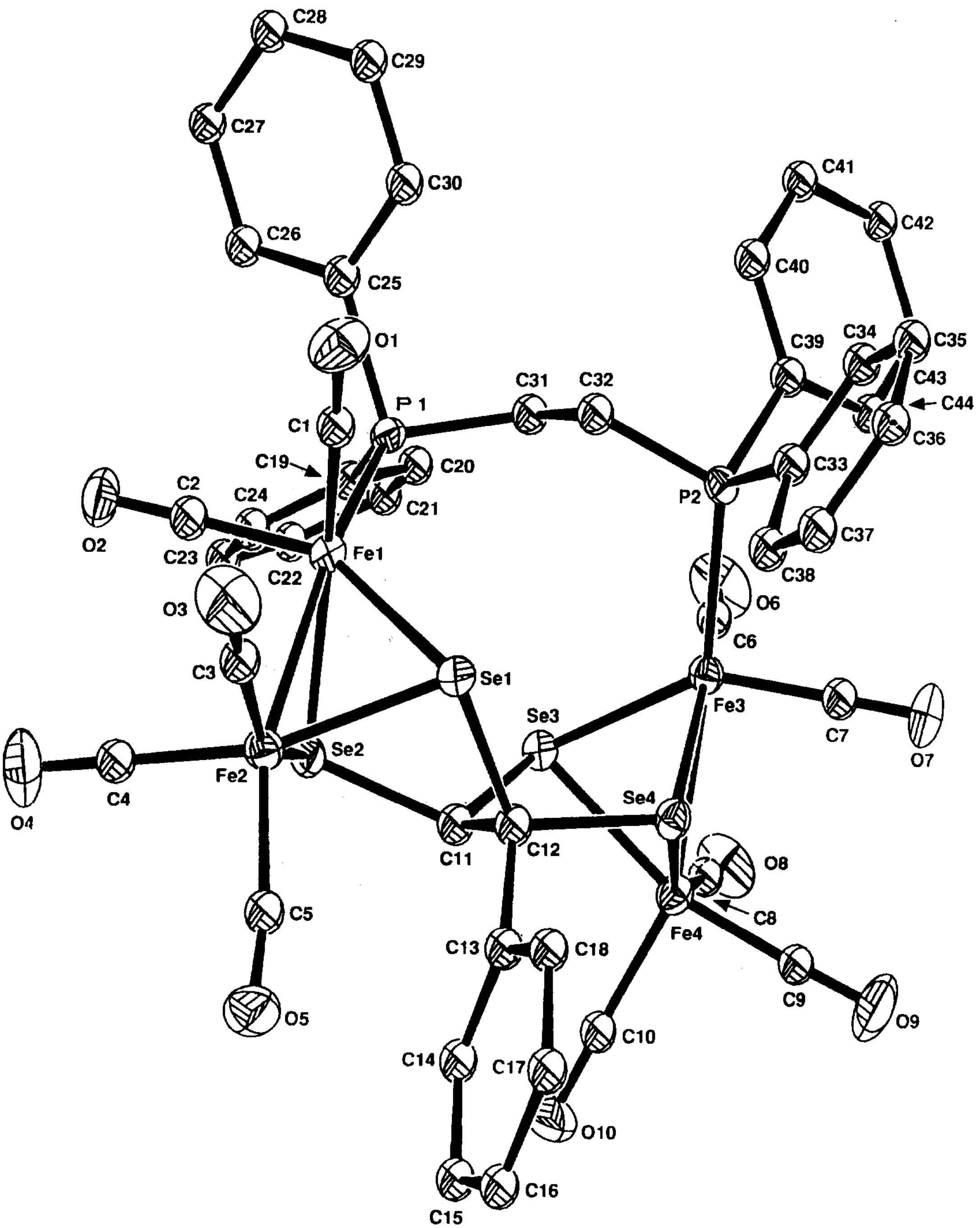


Fig. 1.

2.416(1) Å, Fe(1)–Se(2) 2.368(2) Å, Fe(3)–Se(3) 2.413(2) Å, Fe(3)–Se(4) 2.348(1) Å). The remaining two Fe atoms form bonds of almost equal length to the Se atoms (Se(4)–Fe(4) 2.393(2), Se(1)–Fe(2) 2.403(2) Å). The Se(1)–C(12)–Se(4) and the Se(2)–C(11)–Se(3) angles in **5** (113.9(5)° and 112.7(3)°) are longer than the corresponding angles in the parent molecule, **1** (106.0(3)° and 109.5(4)°). The presence of dppe leads to a tilting of the two Fe_2Se_2 butterfly units such that the wing tip atoms Fe(1) and Fe(3) move apart and the Fe(2) and Fe(4) move closer together. This results in an increase in the Se(1)–C(12)–Se(4) and Se(2)–C(11)–Se(3) angles. Also, due to the increased proximity of the two $Fe(CO)_3$ groups, one of the metal car-

TABLE 1. Fractional atomic coordinates and thermal parameters (Å)

Atom	x	y	z	U_{iso} or U_{eq}	*
Se1	0.16332(7)	0.41118(7)	0.14313(4)	0.0352(5)	*
Se2	0.16864(8)	0.59127(7)	0.22131(5)	0.0404(5)	*
Se3	−0.00758(8)	0.49152(7)	0.35868(5)	0.0374(5)	*
Se4	0.10654(8)	0.25087(7)	0.30851(5)	0.0382(5)	*
Fe1	0.07052(11)	0.61854(10)	0.12549(6)	0.0357(7)	*
Fe2	0.29139(11)	0.51194(11)	0.10522(7)	0.0410(7)	*
Fe3	−0.09366(11)	0.36404(10)	0.35211(7)	0.0383(7)	*
Fe4	0.05424(12)	0.30730(11)	0.43202(7)	0.0434(8)	*
P1	−0.1203(2)	0.7103(2)	0.1775(1)	0.036(1)	*
P2	−0.1833(2)	0.3976(2)	0.2583(1)	0.035(1)	*
O1	0.0279(7)	0.6015(6)	−0.0151(4)	0.080(5)	*
O2	0.1027(6)	0.8302(5)	0.0620(4)	0.064(5)	*
O3	0.3270(7)	0.4759(8)	−0.0500(4)	0.093(6)	*
O4	0.3771(7)	0.6949(7)	0.0617(5)	0.092(6)	*
O5	0.5285(6)	0.3444(7)	0.1183(4)	0.077(5)	*
O6	−0.3037(7)	0.5127(7)	0.4503(4)	0.090(6)	*
O7	−0.1339(8)	0.1552(7)	0.4104(5)	0.110(7)	*
O8	−0.1239(7)	0.3962(8)	0.5673(4)	0.096(6)	*
O9	0.0857(9)	0.0706(7)	0.4948(5)	0.120(7)	*
O10	0.2577(7)	0.3065(8)	0.4710(4)	0.101(6)	*
O11	0.45370	0.75310	0.40970	0.175(12)	*
C45	0.39450	0.98130	0.41375	0.167(17)	*
C46	0.38150	0.87160	0.43250	0.365(50)	*
C47	0.43800	0.87340	0.49660	0.205(20)	*
C48	0.14400	0.91460	0.35250	0.139(14)	*
C49	0.18910	0.85310	0.29940	0.271(32)	*
O12	0.24020	0.87600	0.20344	0.185(14)	*
C50	0.29910	0.91230	0.21660	0.403(51)	*
C51	0.42840	0.84730	0.18310	0.343(40)	*
C1	0.0429(8)	0.6085(8)	0.0403(5)	0.050(2)	
C2	0.0885(8)	0.7498(8)	0.0873(5)	0.045(2)	
C3	0.3135(9)	0.4925(9)	0.0110(6)	0.061(3)	
C4	0.3431(9)	0.6250(9)	0.0795(6)	0.058(3)	
C5	0.4343(9)	0.4051(8)	0.1191(5)	0.056(2)	
C6	−0.2210(9)	0.4549(9)	0.4104(6)	0.059(3)	
C7	−0.1190(9)	0.2383(9)	0.3880(6)	0.060(3)	
C8	−0.0543(9)	0.3627(8)	0.5150(6)	0.056(2)	
C9	0.0749(9)	0.1630(9)	0.4707(6)	0.063(3)	
C10	0.1812(10)	0.3063(9)	0.4551(6)	0.061(3)	
C11	0.1524(7)	0.4542(6)	0.2894(4)	0.036(2)	
C12	0.1901(7)	0.3527(7)	0.2497(4)	0.036(2)	
C14	0.3916(5)	0.2709(5)	0.2840(3)	0.053(2)	
C15	0.5058(5)	0.1870(5)	0.2802(3)	0.070(3)	
C16	0.5484(5)	0.0985(5)	0.2353(3)	0.079(3)	
C17	0.4768(5)	0.0938(5)	0.1942(3)	0.069(3)	
C18	0.3627(5)	0.1777(5)	0.1980(3)	0.060(3)	
C13	0.3201(5)	0.2663(5)	0.2429(3)	0.042(2)	
C20	−0.2527(5)	0.8120(5)	0.3120(4)	0.065(3)	
C21	−0.2812(5)	0.8847(5)	0.3657(4)	0.078(3)	
C22	−0.2140(5)	0.9474(5)	0.3582(4)	0.078(3)	
C23	−0.1184(5)	0.9373(5)	0.2970(4)	0.084(4)	
C24	−0.0899(5)	0.8646(5)	0.2433(4)	0.074(3)	
C19	−0.1571(5)	0.8020(5)	0.2508(4)	0.041(2)	
C26	−0.2084(5)	0.9208(5)	0.0875(3)	0.050(2)	
C27	−0.2696(5)	0.9945(5)	0.0332(3)	0.065(3)	
C28	−0.3257(5)	0.9565(5)	−0.0018(3)	0.065(3)	
C29	−0.3206(5)	0.8448(5)	0.0176(3)	0.080(3)	
C30	−0.2594(5)	0.7710(5)	0.0719(3)	0.067(3)	
C25	−0.2033(5)	0.8090(5)	0.1069(3)	0.041(2)	
C31	−0.2073(7)	0.6236(7)	0.2229(4)	0.041(2)	
C32	−0.1666(7)	0.5131(7)	0.1874(4)	0.038(2)	
C34	−0.2223(4)	0.2639(5)	0.1788(3)	0.064(3)	
C35	−0.1861(4)	0.1814(5)	0.1303(3)	0.080(3)	
C36	−0.0664(4)	0.1180(5)	0.1036(3)	0.060(3)	
C37	0.0172(4)	0.1370(5)	0.1254(3)	0.063(3)	
C38	−0.0190(4)	0.2195(5)	0.1739(3)	0.059(3)	
C33	−0.1388(4)	0.2830(5)	0.2006(3)	0.036(2)	
C40	−0.4177(6)	0.5282(5)	0.2444(3)	0.060(3)	
C41	−0.5396(6)	0.5634(5)	0.2684(3)	0.079(3)	
C42	−0.5878(6)	0.5125(5)	0.3362(3)	0.090(4)	
C43	−0.5142(6)	0.4263(5)	0.3801(3)	0.081(3)	
C44	−0.3924(6)	0.3910(5)	0.3561(3)	0.066(3)	
C39	−0.3441(6)	0.4420(5)	0.2883(3)	0.049(2)	

bonyl bonds becomes slightly bent (Fe(2)–C(5)–O(5) 170.7(9)°). The carbon–carbon bond of the bridging C(Ph)C(H) unit remains unchanged as a result of dppe substitution.

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. $Fe_2(CO)_6(\mu\text{-}Se_2)$ was prepared as reported earlier [4]. Infrared spectra were recorded on a Nicolet 5DXB FT spectrometer as dichloromethane solutions in 0.1 mm pathlength NaCl cells. ^1H NMR spectra were obtained on a Varian XL-300 spectrometer with chemical shifts reported in ppm referenced to $SiMe_4$. ^{31}P NMR spectra were recorded on a Varian FT-80A spectrometer at 32.2 MHz with chemical shifts reported in ppm referenced to external H_3PO_4.

3.1. Preparation of 1

To a solution of $Fe_2(CO)_6(\mu\text{-}Se_2)$ (1.14 mmol) in methanol (25 ml) was added phenylacetylene (0.15 g, 1.5 mmol) and solid anhydrous sodium acetate (0.5 g). The mixture was stirred at room temperature for 48 h. The solvent was evaporated and the mixture was redissolved in dichloromethane. The solution was filtered through Celite to remove insoluble impurities and chromatographic work-up in a silica gel column using a 40/60 dichloromethane/petroleum ether mixture as eluent yielded the following two compounds in order of elution **2** (0.14 g, 23%) and **1** (0.08 g, 14%).

3.2. Reaction of 1 with $Pt(C_2H_4)(PPh_3)_2$

To a solution of **1** (0.04 g, 0.04 mmol) in benzene (50 ml) was added solid $Pt(C_2H_4)(PPh_3)_2$ (0.06 g, 0.08 mmol) and the mixture was stirred at room temperature for 7 h. Evaporation of the solvent and chromatographic work-up on silica gel TLC plates using 20/80 dichloromethane/petroleum ether gave the following compounds in order of elution: **2** (3.7 mg, 17%), **3** (2.6 mg, 5%) and **4** (20.9 mg 22%).

3.3. *Preparation of 5*

To a solution of **1** (0.1 g, 0.1 mmol) and dppe (0.08 g, 0.2 mmol) in dichloromethane (100 ml) was added dropwise a solution of N-trimethylamineoxide (0.015 g, 0.2 mmol) in dichloromethane (2 ml). The mixture was stirred at room temperature for 12 h. Evaporation of the solvent and chromatographic work-up on a silica gel column using a 50/50 dichloromethane/petroleum ether mixture as eluent yielded a single violet band of compound **5** (0.01 g, 12%) Mp:

TABLE 2. Bond lengths (Å)

Se1–Fe1	2.416(1)	Se1–Fe2	2.403(2)
Se1–C12	2.036(8)	Se2–Fe1	2.368(2)
Se2–Fe2	2.415(1)	Se2–C11	1.997(8)
Se3–Fe3	2.413(2)	Se3–Fe4	2.397(1)
Se3–C11	2.006(8)	Se4–Fe3	2.348(1)
Se4–Fe4	2.393(2)	Se4–C12	2.008(9)
Fe1–Fe2	2.527(2)	Fe1–P1	2.237(2)
Fe1–C1	1.775(12)	Fe1–C2	1.784(11)
Fe2–C3	1.755(12)	Fe2–C4	1.790(13)
Fe2–C5	1.817(10)	Fe3–Fe4	2.530(2)
Fe3–P2	2.241(3)	Fe3–C6	1.767(9)
Fe3–C7	1.756(13)	Fe4–C8	1.796(9)
Fe4–C9	1.784(11)	Fe4–C10	1.816(15)
P1–C19	1.841(8)	P1–C25	1.845(6)
P1–C31	1.838(10)	P2–C32	1.808(8)
P2–C33	1.826(7)	P2–C39	1.842(7)
O1–C1	1.138(14)	O2–C2	1.116(13)
O3–C3	1.156(15)	O4–C4	1.123(16)
O5–C5	1.124(12)	O6–C6	1.160(11)
O7–C7	1.145(16)	O8–C8	1.133(11)
O9–C9	1.147(14)	O10–C10	1.118(18)
C11–C12	1.485(13)	C12–C13	1.549(9)
C14–C15	1.395(7)	C14–C13	1.395(11)
C15–C16	1.395(9)	C16–C17	1.395(11)
C17–C18	1.395(7)	C18–C13	1.395(9)
C20–C21	1.395(11)	C20–C19	1.395(8)
C21–C22	1.395(12)	C22–C23	1.395(8)
C23–C24	1.395(11)	C24–C19	1.395(12)
C26–C27	1.395(8)	C26–C25	1.395(9)
C27–C28	1.395(12)	C28–C29	1.395(9)
C29–C30	1.395(8)	C30–C25	1.395(12)
C31–C32	1.535(13)	C34–C35	1.395(10)
C34–C33	1.395(10)	C35–C36	1.395(6)
C36–C37	1.395(10)	C37–C38	1.395(10)
C38–C33	1.395(6)	C40–C41	1.395(9)
C40–C39	1.395(8)	C41–C42	1.395(8)
C42–C43	1.395(8)	C43–C44	1.395(9)
C44–C39	1.395(8)	O11–C46	1.496(1)
C45–C46	1.464(1)	C45–C47	1.875(1)
C46–C47	1.587(1)	C48–C49	1.255(1)
C49–O12	1.721(1)	C49–C50	2.033(1)
O12–C50	1.161(1)	C50–C51	1.515(1)

TABLE 3. Bond angles (°)

Fe1–Se1–Se2	49.4(1)	Fe2–Se1–Se2	50.6(1)
Fe2–Se1–Fe1	63.3(1)	C12–Se1–Se2	66.6(3)
C12–Se1–Fe1	111.2(2)	C12–Se1–Fe2	96.6(3)
Fe1–Se2–Se1	50.8(1)	Fe2–Se2–Se1	50.3(1)
Fe2–Se2–Fe1	63.8(1)	C11–Se2–Se1	64.9(3)
C11–Se2–Fe1	104.9(3)	C11–Se2–Fe2	102.9(2)
Fe3–Se3–Se4	49.1(1)	Fe4–Se3–Se4	50.3(1)
Fe4–Se3–Fe3	63.5(1)	C11–Se3–Se4	65.7(3)
C11–Se3–Fe3	111.4(3)	C11–Se3–Fe4	92.4(2)
Fe3–Se4–Se3	51.0(1)	Fe4–Se4–Se3	50.4(1)
Fe4–Se4–Fe3	64.5(1)	C12–Se4–Se3	66.6(2)
C12–Se4–Fe3	109.5(2)	C12–Se4–Fe4	100.3(3)
Se2–Fe1–Se1	79.7(1)	Fe2–Fe1–Se1	58.1(1)
Fe2–Fe1–Se2	59.0(1)	P1–Fe1–Se1	120.3(1)
P1–Fe1–Se2	104.4(1)	P1–Fe1–Fe2	163.3(1)
C1–Fe1–Se1	88.4(3)	C1–Fe1–Se2	161.5(3)
C1–Fe1–Fe2	102.7(3)	C1–Fe1–P1	93.7(3)
C2–Fe1–Se1	147.0(3)	C2–Fe1–Se2	90.8(4)
C2–Fe1–Fe2	89.8(3)	C2–Fe1–P1	92.6(3)
C2–Fe1–C1	91.6(5)	Se2–Fe2–Se1	79.1(1)
Fe1–Fe2–Se1	58.6(1)	Fe1–Fe2–Se2	57.2(1)
C3–Fe2–Se1	89.4(4)	C3–Fe2–Se2	152.2(3)
C3–Fe2–Fe1	95.1(3)	C4–Fe2–Se1	161.9(3)
C4–Fe2–Se2	90.5(3)	C4–Fe2–Fe1	103.3(3)
C4–Fe2–C3	93.3(5)	C5–Fe2–Se1	105.4(4)
C5–Fe2–Se2	111.0(3)	C5–Fe2–Fe1	160.2(3)
C5–Fe2–C3	96.4(5)	C5–Fe2–C4	92.1(5)
Se4–Fe3–Se3	79.9(1)	Fe4–Fe3–Se3	57.9(1)
Fe4–Fe3–Se4	58.6(1)	P2–Fe3–Se3	119.9(1)
P2–Fe3–Se4	107.1(1)	P2–Fe3–Fe4	165.4(1)
C6–Fe3–Se3	84.9(5)	C6–Fe3–Se4	158.2(5)
C6–Fe3–Fe4	100.1(4)	C6–Fe3–P2	93.9(4)
C7–Fe3–Se3	149.0(4)	C7–Fe3–Se4	89.4(3)
C7–Fe3–Fe4	91.6(4)	C7–Fe3–P2	91.1(4)
C7–Fe3–C6	95.8(5)	Se4–Fe4–Se3	79.4(1)
Fe3–Fe4–Se3	58.6(1)	Fe3–Fe4–Se4	56.9(1)
C8–Fe4–Se3	92.2(3)	C8–Fe4–Se4	150.8(4)
C8–Fe4–Fe3	94.8(4)	C9–Fe4–Se3	162.2(5)
C9–Fe4–Se4	88.8(4)	C9–Fe4–Fe3	103.8(5)
C9–Fe4–C8	91.7(4)	C10–Fe4–Se3	99.7(3)
C10–Fe4–Se4	110.3(3)	C10–Fe4–Fe3	155.0(3)
C10–Fe4–C8	98.6(5)	C10–Fe4–C9	96.8(5)
C19–P1–Fe1	117.3(3)	C25–P1–Fe1	112.0(2)
C25–P1–C19	103.5(3)	C31–P1–Fe1	118.0(2)
C31–P1–C19	102.0(4)	C31–P1–C25	101.9(4)
C32–P2–Fe3	113.4(4)	C33–P2–Fe3	119.1(2)
C33–P2–C32	101.7(4)	C39–P2–Fe3	114.6(2)
C39–P2–C32	103.4(3)	C39–P2–C33	102.5(3)
O1–C1–Fe1	178.4(9)	O2–C2–Fe1	178.0(7)
O3–C3–Fe2	177 (1)	O4–C4–Fe2	178.3(9)
O5–C5–Fe2	170.7(9)	O6–C6–Fe3	178.2(9)
O7–C7–Fe3	178.8(9)	O8–C8–Fe4	178 (1)
O9–C9–Fe4	178 (1)	O10–C10–Fe4	178.3(9)
Se3–C11–Se2	112.7(3)	C12–C11–Se2	114.0(5)
C12–C11–Se3	112.5(7)	Se4–C12–Se1	113.9(5)
C11–C12–Se1	107.8(5)	C11–C12–Se4	110.5(5)
C13–C12–Se1	107.5(4)	C13–C12–Se4	100.6(5)
C13–C12–C11	116.6(8)	C13–C14–C15	120.0(6)
C16–C15–C14	120.0(7)	C17–C16–C15	120.0(5)
C18–C17–C16	120.0(6)	C13–C18–C17	120.0(7)
C14–C13–C12	121.7(6)	C18–C13–C12	118.2(7)
C18–C13–C14	120.0(5)	C19–C20–C21	120.0(7)

TABLE 3 (continued)

C22–C21–C20	120.0(6)	C23–C22–C21	120.0(7)
C24–C23–C22	120.0(7)	C19–C24–C23	120.0(6)
C20–C19–P1	120.9(6)	C24–C19–P1	119.0(4)
C24–C19–C20	120.0(7)	C25–C26–C27	120.0(7)
C28–C27–C26	120.0(6)	C29–C28–C27	120.0(6)
C30–C29–C28	120.0(7)	C25–C30–C29	120.0(6)
C26–C25–P1	120.2(6)	C30–C25–P1	119.8(5)
C30–C25–C26	120.0(6)	C32–C31–P1	114.5(5)
C31–C32–P2	111.2(5)	C33–C34–C35	120.0(4)
C36–C35–C34	120.0(6)	C37–C36–C35	120.0(6)
C38–C37–C36	120.0(4)	C33–C38–C37	120.0(6)
C34–C33–P2	120.9(3)	C38–C33–P2	119.0(6)
C38–C33–C34	120.0(6)	C39–C40–C41	120.0(5)
C42–C41–C40	120.0(5)	C43–C42–C41	120.0(6)
C44–C43–C42	120.0(5)	C39–C44–C43	120.0(5)
C40–C39–P2	120.3(5)	C44–C39–P2	119.7(5)
C44–C39–C40	120.0(6)	C47–C45–C46	55.1(1)
C45–C46–O11	135.5(1)	C47–C46–O11	102.9(1)
C47–C46–C45	75.8(1)	C46–C47–C45	49.2(1)
O12–C49–C48	134.8(1)	C50–C49–C48	109.8(1)
C50–C49–O12	34.8(1)	C50–O12–C49	87.4(1)
O12–C50–C49	57.8(1)	C51–C50–C49	128.0(1)
C51–C50–O12	111.9(1)		

97–99°C. IR (ν, cm^{-1}. 2067 (m), 2036 (vs), 1985 (s, br), 1932 (w), 1912 (W). ^{1}H NMR ($CDCl_3$; δ): 69.67. Anal. Found: C, 42.6; H, 3.31, $C_{55}H_{42}O_{12}P_2Se_4Fe_4$ calc.: C, 42.3; H, 2.90%.

3.4. X-ray diffraction study of 5

A crystal of approximate dimensions 0.2 × 0.2 × 0.15 mm^3 was used for data collection.

Crystal data: $C_{15}H_{42}O_{12}P_2Se_4Fe_4$, $M = 1386.1$, triclinic, $a = 12.969(1)$, $b = 13.032(1)$, $c = 18.669(1)$ Å, $\alpha = 76.78(1)$, $\beta = 72.74(2)$, $\gamma = 63.99(1)°$, $V = 2690.4$ Å^3, space group $P1$, $Z = 2$, $D_c = 1.71$ g cm^{-3}, μ(Mo Kα) = 37.50 cm^{-1}, $F(000) = 1428$. Data were measured at room temperature on a CAD4 automatic four-circle diffractometer in the range $2° < \theta < 24°$; 7867 reflections were collected of which 5109 were unique with $I > 3\sigma(I)$. Data were corrected for Lorentz and polarization effects and for a linear decay of 9% (based on the standard reflection intensities) during data collection. The structure was solved by Patterson methods and refined using the SHELX suite of programs [7,8]. In the final least squares cycles the selenium, iron, phosphorus, oxygen atoms and carbons 45–51 were allowed to vibrate anisotropically. All other atoms were treated isotropically. Hydrogen atoms were included at calculated positions.

The crystals of 5 were grown from CH_2Cl_2/petroleum ether mixtures. Advanced difference electron density maps indicated the presence of 2 solvent moieties per asymmetric unit, which were severely disordered precluding clean refinements. Many models were assessed for each solvent entity, and the most superior fit was for 2 fragments approximating to a molecule of each acetone and diethylether per metal complex. Anisotropic thermal parameters were refined for solvent atoms (O11–12 and C45–51) although positional parameters were not, as the electron density was largely smeared and convergence was not assisted by crystal decay (quite possibly due to solvent loss) in the X-ray beam for these atoms.

Final residuals after 16 cycles of blocked least squares were $R = 0.0435$, $R_w = 0.0492$, for a weighting scheme of $w = 2.3289/[\sigma^2(F) + 0.000883(F)^2]$. Max. final shift/esd was 0.15. The max. and min. residual densities were 0.43 and −0.29 e Å^{-3} respectively in the solvent regions but the area proximate to the metal atoms was clean and devoid of ripples. Final fractional atomic coordinates and isotropic thermal parameters, bond distances and angles are given in Tables 1–3.

Fractional atomic coordinates for the hydrogen atoms, anisotropic thermal parameters, intermolecular distances, intramolecular distances, and the structure factor tables are available from the authors.

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