

Diacetylene-bridged clusters: Synthesis and Characterization of $(\text{CO})_6\text{Fe}_2\text{Se}_2\{\mu\text{-HC}=\text{C}(\text{C}\equiv\text{CR})\}$, $\{(\text{CO})_6\text{Fe}_2\text{Se}_2\}_2\{\mu\text{-HC}-\text{C}(\text{C}\equiv\text{CR})\}$ ($\text{R}=\text{Me}$ on $n\text{-Bu}$) and $(\text{CO})_6\text{Fe}_2\text{Se}_2(\mu\text{-HC}=\text{CC}-\text{CCH}_3)\text{Os}_3(\text{CO})_{10}$

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Abstract

The compounds $(\text{CO})_6\text{Fe}_2\text{Se}_2\{\mu\text{-HC}=\text{C}(\text{C}\equiv\text{CR})\}$ ($\text{R}=\text{Me}$ (1) or $n\text{-Bu}$ (2)) and $\{(\text{CO})_6\text{Fe}_2\text{Se}_2\}_2\{\mu\text{-HC}-\text{C}(\text{C}\equiv\text{CR})\}$ ($\text{R}=\text{Me}$ (3) or $n\text{-Bu}$ (4)) have been obtained by room-temperature reactions of $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$ with $\text{HC}\equiv\text{CC}\equiv\text{CR}$. Compound 1 reacts with $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ to give $(\text{CO})_6\text{Fe}_2\text{Se}_2(\mu\text{-HC}=\text{CC}-\text{CCH}_3)\text{Os}_3(\text{CO})_{10}$ (5). The structure of compounds 1, 3 and 5 have been established by single-crystal X-ray diffraction studies.

Keywords: Iron; Carbonyl; Alkyne; Clusters; Crystal structure

1. Introduction

Metal–alkyne chemistry continues to attract considerable interest largely because of the variety of bonding modes observed between alkynes and metal atoms which facilitate a number of interesting transformations [1]. Currently, there is much interest in the transition metal derivatives of diynes [2]. For instance, derivatives of buta-1,3-diyne have been used to obtain novel metal-lacumulenes containing an $\text{R}_2\text{C}=\text{C}=\text{C}=\text{Ru}=\text{C}=\text{C}=\text{CR}_2$ unit [3]. Complexes containing unsaturated C_4 and partly unsaturated C_6 chains as bridging groups between two rhodium centres have also been reported recently [4]. Metal–diyne complexes are also of interest in the context of obtaining novel polynuclear complexes [5]. Complexes in which one alkyne $\text{C}\equiv\text{C}$ triple bond is uncoordinated may be of use as starting materials for preparation of new heterometallic compounds. In general, the alkynes can be incorporated into metal clusters under thermolytic conditions, which often gives numerous products with low yields, or by use of only weakly stabilized or activated clusters. The chemistry of clusters which are stabilized by main group ligands is well documented [6]. The main group ligand aids the cluster

growth and also helps to maintain the cluster nuclearity. The use of the heavy Group 16 elements as ligands for cluster growth purposes is now fairly well established [7]. Useful starting materials for various types of cluster growth reaction are the compounds $\text{Fe}_2(\text{CO})_6(\mu\text{-E}_2)$ where $\text{E}=\text{S}, \text{Se}$ or Te [8]. A characteristic feature of these compounds is the presence of a reactive $\text{E}-\text{E}$ bond which readily undergoes insertion of various types of inorganic and organic moieties. The butterfly Fe_2E_2 core is a fairly flexible unit, and insertion of small groups such as CH_2 [9] and of large cluster units such as $\text{M}_3(\text{CO})_{11}$ ($\text{M}=\text{Ru}$ or Os) can take place under mild conditions [10]. Recent emphasis has been on exploring the differences in the structures and reactivities of complexes containing bridging Se and Te ligands, as well as on studying the chemistry of the mixed-chalcogenide complexes $\text{Fe}_2(\text{CO})_6(\mu\text{-EE}')$ ($\text{E}, \text{E}'=\text{S}, \text{Se}$ or Te ; $\text{E}\neq\text{E}'$) in respect of cluster growth [11]. We recently reported the use of $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$ as a starting material for the synthesis of the mixed-metal clusters $\text{Fe}_2\text{M}(\text{CO})_{10}(\mu_3\text{-Se})_2$ ($\text{M}=\text{Mo}$ or W) [12] and for the stepwise reduction of the acetylenic $\text{C}\equiv\text{C}$ triple bond of phenylacetylene on the Fe_2Se_2 framework [13]. The cluster $\text{Cp}_2\text{Mo}_2\text{Fe}_2\text{Se}_3(\text{CO})_6$ has been prepared by reaction of the phenylacetylene adduct of $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$, $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC}(\text{Ph})=\text{C}(\text{H})\text{Se}\}$ with $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ [14].

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In seeking to extend the chemistry of the acetylenic derivatives of $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$, we have studied the reactions of the diynes, $\text{HC}\equiv\text{CC}\equiv\text{CR}$ ($\text{R} = \text{Me}$ or $n\text{-Bu}$) with $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$. Our interest in such reactions is directed towards the possibility of using the diyne derivative of $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$ for reaction with reactive metal species. In this paper we describe the addition of $\text{HC}\equiv\text{CC}\equiv\text{CR}$ ($\text{R} = \text{Me}$ or $n\text{-Bu}$) to $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$ to give $(\text{CO})_6\text{Fe}_2\text{Se}_2\{\mu\text{-HC}=\text{C}(\text{C}\equiv\text{CR})\}$ ($\text{R} = \text{Me}$ (**1**) or $n\text{-Bu}$ (**2**)) and $\{(\text{CO})_6\text{Fe}_2\text{Se}_2\}_2\{\mu\text{-HC}=\text{C}(\text{C}\equiv\text{CR})\}$ ($\text{R} = \text{Me}$ (**3**) or $n\text{-Bu}$ (**4**)) and the addition of the $\text{Os}_3(\text{CO})_{10}$ moiety to **1** to form the novel heterometallic cluster $(\text{CO})_6\text{Fe}_2\text{Se}_2(\mu\text{-HC}=\text{CC}-\text{CCH}_3)\text{-Os}_3(\text{CO})_{10}$ (**5**).

2. Experimental section

Reactions and manipulations were carried out under argon by means of standard Schlenk techniques. Solvents were deoxygenated immediately prior to use. IR spectra were recorded on a Nicolet 5DXB Fourier transform spectrometer. NMR spectra were obtained on a Varian XL-300 spectrometer at 25°C. The compounds $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$ [12], $\text{HC}\equiv\text{CC}\equiv\text{CR}$ ($\text{R} = \text{Me}$ or $n\text{-Bu}$) [15] and $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ [16] were prepared as previously described.

2.1. Preparation of 1–4

A solution of $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$ (2.7 mmol), anhydrous sodium acetate (0.25 g) and $\text{HC}\equiv\text{CC}\equiv\text{CMe}$ (0.2 g, 3.12 mmol) in 20 ml of methanol was stirred at room temperature for 12 h. The solvent was removed in

vacuo, the residue was redissolved in dichloromethane and the solution filtered through Celite. The filtrate was dried and the residue was subjected to chromatographic work-up on a silica-gel column with hexane as eluent. The following compounds were obtained in order of elution: $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$ (trace amount), **1** (0.5 g (37%)) and **3** (0.29 g (23%)).

Analytical and spectral data for **1**: IR (hexane): $\nu(\text{CO})$ 2073(m), 2038(vs), 2000(vs) cm^{-1} . ^1H NMR (CDCl_3): δ 7.2 (s, 1H), 1.95 (s, 3H) ppm. ^{13}C NMR (CDCl_3): δ 5.5 (CH_3), 75.4 ($\equiv\text{CCH}_3$), 105.0 ($\text{C}\equiv\text{CCH}_3$), 135.0 ($\text{C}=\text{CH}$), 136.5 (CH), 208.6 (CO) ppm. M.p., 97–99°C. Anal. Found: C, 26.4; H, 0.83. Calc. C, 26.3; H, 0.79%.

Analytical and spectral data for **3**: IR (hexane) $\nu(\text{CO})$ 2078(m), 2064(vs), 2039(vs), 2031(m), 2008(vs), 1997(s), 1982(w, sh) cm^{-1} . ^1H NMR (CCl_4): 7.31 (s, 1H), 2.13 (s, 3H) ppm. ^{13}C NMR (CDCl_3): δ 4.9 (CH_3), 57.3 (CH), 61.1 (CCH), 82.2 (CCH_3), 92.6 ($\text{C}\equiv\text{CCH}_3$), 208.1 (CO), 209.0 (CO) ppm. M.p., 161°C (decomposition). Anal. Found: C, 21.8; H, 0.51. Calc.: C, 21.7; H, 0.42%.

By the same procedures, **2** and **4**, with yields of 43% and 19% respectively were obtained from the reaction of $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$ with $\text{HC}\equiv\text{CC}\equiv\text{C}-n\text{-Bu}$ in the presence of sodium acetate.

Analytical and spectral data for **2**: IR (hexane) $\nu(\text{CO})$ 2071(m), 2039(vs), 2001(vs) cm^{-1} . ^1H NMR (CDCl_3): δ 7.18 (s, 1H), 2.30 (t, 2H), 1.49 (m, 2H), 1.37 (m, 2H), 0.90 (t, 3H) ppm. ^{13}C NMR (CDCl_3): δ 13.5 (CH_3), 20.13 (CH_2CH_3), 22.0 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 30.0 ($\equiv\text{CCH}_2$), 76.5 ($\equiv\text{CCH}_2$), 109.5 ($\text{C}\equiv\text{CCH}_2$); 135.0 ($=\text{C}(\text{Se})-\text{C}$), 136.0 (CH), 208.6 (CO) ppm. M.p., 127–129°C. Anal. Found: C, 30.6; H, 2.01. Calc.: C, 30.9; H, 1.83%.

Table 1
Crystal data for **1**, **3** and **5**

	1	3	5
Formula	$\text{C}_{11}\text{H}_4\text{Fe}_2\text{O}_6\text{Se}_2$	$\text{C}_{17}\text{H}_4\text{Fe}_4\text{O}_{12}\text{Se}_4\text{-C}_4\text{H}_8\text{O}$	$\text{C}_{21}\text{H}_4\text{Fe}_2\text{O}_{16}\text{Os}_3\text{Se}_2$
Formula weight	501.8	1011.5	1352.5
Space group	$P2_1/n$	$P\bar{1}$	$Pcca2_1$
a (Å)	6.999(2)	11.281(2)	17.751(10)
b (Å)	18.701(6)	11.952(2)	9.953(4)
c (Å)	12.065(3)	12.614(2)	16.925(7)
α (°)	—	88.69(2)	—
β (°)	104.19(2)	64.95(1)	—
γ (°)	—	67.10(2)	—
V (Å ³)	1531.0(6)	1395.5(5)	2990(2)
Z	4	2	4
$D(\text{calc})$ (g cm ⁻³)	2.177	2.407	3.006
μ (Mo K α) (cm ⁻¹)	66.69	73.20	161.54
Temperature (K)	295	295	297
T (max)/ T (min)	1.16	2.34	1.77
Radiation		Mo K α ($\lambda = 0.71073$ Å)	
$R(F)$ (%)	4.58	5.13	5.12
$R(wF)$ (%)	5.37	5.97	5.62

Analytical and spectral data for **4**: IR (hexane): $\nu(\text{CO})$ 2078(m), 2064(s), 2040(vs), 2032(m), 2008(vs), 1997(s), 1982(w, sh) cm^{-1} . ^1H NMR (CCl_4): δ 7.33 (s, 1H), 2.42 (t, 2H), 1.70–1.60 (m, 4H), 1.13 (t, 3H) ppm. ^{13}C NMR (CDCl_3): δ 13.5 (CH_3), 19.5 (CH_2CH_3), 22.1 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 22.6 ($\equiv\text{CCH}_2$), 57.4 (CH), 61.7 (CCH), 83.0 (CCH_2), 97.1 ($\text{C}\equiv\text{CCH}_2$), 208.1 (CO), 209.0 (CO) ppm. M.p. 172°C (decomposition). Anal. Found: C, 24.7; H, 1.31. Calc.: C, 24.4; H, 1.02%.

2.2. Preparation of **5**

A benzene solution (50 ml) of $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ (0.1 g, 0.11 mmol) and **1** (0.075 g, 0.15 mmol) was stirred at room temperature for 3 h. The solvent was removed in vacuo and chromatographic work-up on a silica-gel column with hexane as eluent yielded a single orange band of **5** (0.059 g (29%)). IR (KBr) $\nu(\text{CO})$ 2101(m), 2068(vs), 2058(s), 2037(m), 2025(sh), 2017(m), 2014(m), 1992(s), 1984(sh), 1976(m), 1963(m), 1943(m) cm^{-1} . IR (hexane): $\nu(\text{CO})$ 2100(m), 2067(vs), 2057(s), 2036(s), 2028(s), 2011(sh), 2001(vs), 1964(sh), 1953(w), 1854(w) cm^{-1} . ^1H NMR (CDCl_3): δ 6.37 (s, 1H), 2.42 (s, 3H) ppm. ^{13}C NMR (CDCl_3): δ 38.7(CH_3), 121.2 (CCH_3), 135.3 (CH), 144.8 (CCH), 167.3 (CC_2H_3), 208.1 (CO) ppm. M.p., 149°C (decomposition). Anal. Found: C, 18.8; H, 0.31. Calc.: C, 18.6; H 0.29%.

Table 2

Atomic coordinates and equivalent isotropic displacement coefficients for **1**

	<i>x</i> ($\times 10^{-4}$)	<i>y</i> ($\times 10^{-4}$)	<i>z</i> ($\times 10^{-4}$)	U_{eq}^a ($\times 10^{-3} \text{ \AA}^2$)
Se(1)	1970(13)	8772.1(5)	3385(7)	40(1)
Se(2)	6032(1)	8774.6(5)	2741.8(7)	35(1)
Fe(1)	3348(2)	7951.3(7)	2285(1)	38(1)
Fe(2)	2907(2)	9249.2(6)	1766(1)	32(1)
O(1)	5002(12)	6819(4)	3916(7)	87(4)
O(2)	-575(12)	7338(5)	1414(8)	95(4)
O(3)	4645(14)	7499(4)	263(7)	82(4)
O(4)	3974(11)	9236(4)	-441(5)	64(3)
O(5)	-1270(10)	9292(4)	582(6)	72(3)
O(6)	3622(10)	10765(4)	2351(6)	58(3)
C(1)	4383(14)	7252(5)	3284(8)	48(4)
C(2)	983(15)	7582(6)	1758(9)	56(4)
C(3)	4176(14)	7661(5)	1067(8)	46(4)
C(4)	3594(13)	9243(5)	425(8)	40(3)
C(5)	363(14)	9256(5)	1034(8)	45(3)
C(6)	3315(14)	10187(5)	2131(7)	41(3)
C(7)	4262(14)	9005(5)	4558(7)	45(3)
C(8)	5987(13)	8997(4)	4329(7)	34(3)
C(9)	7839(14)	9168(5)	5117(7)	41(3)
C(10)	9306(14)	9258(5)	5811(8)	46(4)
C(11)	11093(13)	9376(6)	6711(8)	59(4)

^a Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3

Selected bond distances (\AA) and angles ($^\circ$) for **1**

Bond distances			
Se(1)–Fe(1)	2.382(2)	Se(1)–Fe(2)	2.381(2)
Se(2)–Fe(2)	2.386(2)	Se(2)–Fe(1)	2.386(2)
Se(1)–C(7)	1.912(8)	Se(2)–C(8)	1.967(8)
Fe(1)–Fe(2)	2.507(2)	C(7)–C(8)	1.303(14)
C(8)–C(9)	1.443(11)	C(9)–C(10)	1.167(12)
C(10)–C(11)	1.457(12)		
Bond angles			
Fe(1)–Se(1)–Fe(2)	63.5(1)	Fe(1)–Se(1)–C(7)	100.3(3)
Fe(2)–Se(1)–C(7)	99.9(3)	Fe(1)–Se(2)–Fe(2)	63.4(1)
Fe(1)–Se(2)–C(8)	99.3(3)	Fe(2)–Se(2)–C(8)	99.8(2)
Se(1)–Fe(1)–Se(2)	81.9(1)	Se(1)–Fe(1)–Fe(2)	58.2(1)
Se(2)–Fe(1)–Fe(2)	58.3(1)	Se(1)–Fe(2)–Se(2)	81.9(1)
Se(1)–Fe(2)–Fe(1)	58.3(1)	Se(2)–Fe(2)–Fe(1)	58.3(1)
Fe(1)–C(1)–O(1)	178.7(10)	Fe(1)–C(2)–O(2)	180.0(15)
Se(1)–C(7)–C(8)	119.5(7)	Se(2)–C(8)–C(7)	116.5(6)
Se(2)–C(8)–C(9)	117.5(7)	C(7)–C(8)–C(9)	125.9(8)
C(8)–C(9)–C(10)	174.3(10)	C(9)–C(10)–C(11)	177.7(12)

2.3. Crystal structure determinations for **1**, **3** and **5**

Crystallographic data are collected in Table 1. All three samples were subjected to a preliminary photographic characterization which revealed that **1**, **3** and **5** had $2/m$, 1 and mmm Laue symmetry respectively. The space group for **1** was unambiguous from systematic absences in the data, for **3** the centrosymmetric alternative was preferred, and for **5** the absence of a molecular mirror plane allowed only the non-centrosymmetric alternative. All were semiempirically corrected for absorption using 216 ψ scan data for each. In all cases, solutions were obtained by direct methods. The crystal structure of **3** also contains a slightly distorted molecule of tetrahydrofuran (THF) for each Fe_4 cluster. All non-hydrogen atoms for **1** were refined anisotropically. For **3** all except those in the THF molecule were similarly treated. For **5**, owing to the limited number of data observed, only the Os, Fe and Se atoms were anisotropically refined. In all cases, hydrogen atoms were treated as idealized isotropic contributions. All computations used the SHELXTL-PC (4.2) program library [17]. Tables 2 gives the atomic coordinates and Table 3 the selected bond distances and angles for **1**, Tables 4 and 5 the corresponding values for **3** and Tables 6 and 7 those for **5**. Tables of hydrogen atom coordinates and anisotropic thermal parameters and complete lists of bond lengths and angles have been deposited at the Cambridge System Data Centre.

3. Results and discussion

At room temperature, $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$ adds the diynes, $\text{HC}\equiv\text{CC}\equiv\text{CR}$ ($\text{R} = \text{Me}$ or $n\text{-Bu}$) to give the

compounds $\text{Fe}_2(\text{CO})_6\text{Se}_2\{\mu\text{-HC}=\text{C}(\text{C}\equiv\text{CR})\}$ ($\text{R} = \text{Me}$ (**1**) or $n\text{-Bu}$, (**2**)) and $\{(\text{CO})_6\text{Fe}_2\text{Se}_2\}_2\{\mu\text{-HC}=\text{C}(\text{C}\equiv\text{CR})\}$ ($\text{R} = \text{Me}$ (**3**) or $n\text{-Bu}$ (**4**)) (Scheme 1). Compounds **1–4** have been characterized by IR, ^1H NMR and ^{13}C NMR spectroscopy. The IR spectra of **1** and **2** and **3** and **4** are almost identical in the carbonyl stretching region. For all four compounds, only terminally bonded carbonyl stretching frequencies are observed. The NMR spectroscopy data confirms the presence of the diyne units in **1–4**. Purple air-stable crystals of **1** were obtained by slow evaporation of a CH_2Cl_2 –hexane solution and an X-ray diffraction study was undertaken. An ORTEP draw-

Table 4
Atomic coordinates and equivalent isotropic displacement coefficients for **3**

	<i>x</i> ($\times 10^{-4}$)	<i>y</i> ($\times 10^{-4}$)	<i>z</i> ($\times 10^{-4}$)	U_{eq} ($\times 10^{-3} \text{ \AA}^2$)
Se(1)	4455(1)	8931(1)	9412(1)	31(1) ^a
Se(2)	5085(1)	6348(1)	8312(1)	38(1) ^a
Se(3)	7609(1)	6936(1)	6178(1)	34(1) ^a
Se(4)	7775(1)	8612(1)	7893(1)	34(1) ^a
Fe(1)	3413(1)	7535(1)	10258(1)	36(1) ^a
Fe(2)	3376(1)	8328(1)	8390(1)	36(1) ^a
Fe(3)	7463(1)	8991(1)	6177(1)	35(1) ^a
Fe(4)	9622(1)	7170(1)	6156(1)	34(1) ^a
O(11)	1962(9)	5893(7)	10727(7)	77(5) ^a
O(12)	669(8)	9567(7)	11791(7)	68(4) ^a
O(13)	4435(9)	6842(8)	12058(7)	77(5) ^a
O(21)	1158(8)	10863(7)	9208(7)	76(5) ^a
O(22)	1404(8)	7243(8)	8495(7)	73(5) ^a
O(23)	4398(8)	8507(8)	5856(6)	67(4) ^a
O(31)	8184(10)	8687(9)	3643(7)	87(6) ^a
O(32)	8582(8)	10855(7)	6059(7)	67(4) ^a
O(33)	4476(7)	10895(7)	7061(8)	77(4) ^a
O(41)	11602(8)	8216(8)	6131(7)	68(4) ^a
O(42)	11284(7)	6327(7)	3588(6)	65(4) ^a
O(43)	10749(10)	4886(8)	7022(8)	89(6) ^a
C(1)	6831(8)	6666(7)	7849(7)	33(4) ^a
C(2)	6544(8)	7715(7)	8717(7)	29(3) ^a
C(3)	6933(9)	7294(8)	9654(7)	36(4) ^a
C(4)	7409(10)	6914(8)	10338(8)	48(5) ^a
C(5)	7979(13)	6394(12)	11179(10)	79(7) ^a
C(11)	2558(11)	6507(9)	10519(9)	55(6) ^a
C(12)	1752(10)	8777(9)	11208(8)	46(5) ^a
C(13)	4122(10)	7069(9)	11322(9)	49(5) ^a
C(21)	2004(10)	9876(9)	8893(8)	47(5) ^a
C(22)	2164(10)	7670(9)	8447(9)	50(5) ^a
C(23)	4061(10)	8444(9)	6830(9)	44(5) ^a
C(31)	7883(10)	8823(9)	4628(9)	51(5) ^a
C(32)	8181(9)	10121(9)	6072(8)	45(4) ^a
C(33)	5623(10)	10115(8)	6741(8)	47(5) ^a
C(41)	10795(10)	7819(9)	6169(8)	46(5) ^a
C(42)	10642(9)	6637(8)	4570(8)	42(4) ^a
C(43)	10342(10)	5777(10)	6688(9)	52(5) ^a
O(51)	3875(31)	5181(32)	6216(26)	67(13)
C(51)	5432(36)	4648(34)	5552(29)	196(20)
C(52)	6011(35)	5410(35)	4277(31)	105(16)
C(53)	5395(50)	5625(40)	4051(36)	106(20)
C(54)	3999(28)	4869(25)	4832(23)	73(12)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 5
Selected bond distances and angles for **3**

<i>Bond distances</i>			
Se(1)–Fe(1)	2.381(2)	Se(1)–Fe(2)	2.389(2)
Se(1)–C(2)	2.019(7)	Se(2)–Fe(1)	2.397(1)
Se(2)–Fe(2)	2.368(1)	Se(2)–C(1)	1.989(10)
Se(3)–Fe(3)	2.391(2)	Se(3)–Fe(4)	2.382(2)
Se(3)–C(1)	1.985(8)	Se(4)–Fe(3)	2.344(2)
Se(4)–Fe(4)	2.370(1)	Se(4)–C(2)	2.009(9)
Fe(1)–Fe(2)	2.529(2)	Fe(3)–Fe(4)	2.545(2)
C(1)–C(2)	1.522(13)	C(2)–C(3)	1.443(14)
C(3)–C(4)	1.193(16)	C(4)–C(5)	1.470(18)
<i>Bond angles</i>			
Fe(1)–Se(1)–Fe(2)	64.0(1)	Fe(1)–Se(1)–C(2)	97.8(3)
Fe(2)–Se(1)–C(2)	107.4(3)	Fe(1)–Se(2)–Fe(2)	64.1(1)
Fe(1)–Se(2)–C(1)	105.7(2)	Fe(2)–Se(2)–C(1)	101.1(2)
Fe(3)–Se(3)–Fe(4)	64.5(1)	Fe(3)–Se(3)–C(1)	108.3(3)
Fe(4)–Se(3)–C(1)	95.7(3)	Fe(3)–Se(4)–Fe(4)	65.4(1)
Fe(3)–Se(4)–C(2)	104.3(3)	Fe(4)–Se(4)–C(2)	102.8(2)
Se(1)–Fe(1)–Se(2)	80.7(1)	Se(1)–Fe(1)–Fe(2)	58.1(1)
Se(1)–Fe(1)–C(11)	163.6(4)	Se(2)–Fe(1)–C(11)	89.2(3)
Se(3)–Fe(3)–Se(4)	81.4(1)	Se(3)–Fe(3)–Fe(4)	57.6(1)
Se(4)–Fe(3)–Fe(4)	57.8(1)	Se(3)–Fe(4)–Se(4)	81.1
Se(3)–Fe(4)–Fe(3)	57.9(1)	Se(4)–Fe(4)–Fe(3)	56.8(1)
Se(2)–C(1)–Se(3)	111.7(5)	Se(2)–C(1)–C(2)	111.2(5)
Se(3)–C(1)–C(2)	112.5(6)	Se(1)–C(2) = Se(4)	108.6(4)
Se(1)–C(2)–C(1)	110.1(7)	Se(4)–C(2)–C(1)	110.6(5)
Se(1)–C(2)–C(3)	110.2(4)	Se(4)–C(2)–C(3)	104.0(7)
C(1)–C(2)–C(3)	113.2(7)	C(2)–C(3)–C(4)	172.7(9)
C(3)–C(4)–C(5)	177.2(13)		

ing of the molecular structure of **1** is shown in Fig. 1. The structure can be described as consisting of an Fe_2Se_2 butterfly unit and an $\text{HC}=\text{CC}\equiv\text{CCH}_3$ group attached to the two Se atoms through the two olefinic carbon atoms. Each Fe atom has three terminally bonded carbonyl groups. The Fe–C–O angles lie in the range $176.8(8)$ – $180.0(15)^\circ$. The Fe–Fe distance of $2.507(2) \text{ \AA}$ in **1** is shorter than that of $2.575(2) \text{ \AA}$ in $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$ [18], but is comparable with that of $2.512(1) \text{ \AA}$ in $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC}(\text{Ph})=\text{C}(\text{H})\text{Se}\}$ [13a] and $2.587(2) \text{ \AA}$ in $\text{Fe}_2(\text{CO})_6\{\mu\text{-Te}(\text{CH}_2)\text{Te}\}$ [9]. The Se–Fe distances in **1** are in the range 2.381 – 2.386 \AA and are longer than that of 2.363 \AA observed in $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$ but similar to those of 2.379 – 2.39 \AA in $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC}(\text{Ph})=\text{C}(\text{H})\text{Se}\}$. The bond distances between each Se atom and the two Fe atoms are equal in **1**, unlike in $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC}(\text{Ph})=\text{C}(\text{H})\text{Se}\}$ and $(\text{CO})_6\text{Fe}_2\text{Pt}(\text{PPh}_3)_2\{\mu\text{-SeC}(\text{Ph})\text{C}(\text{H})\text{Se}\}$ in which each Se atom forms one short and one long bond to each of the two Fe atoms. The average Se–Fe–Se angle in **1** is 81.9° , which is similar to the average Se–Fe–Se angle of 81.4° in $(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC}(\text{Ph})=\text{C}(\text{H})\text{Se}\}$ but larger than the average Se–Fe–Se angle of 58° in $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$, in keeping with opening of the Fe_2Se_2 butterfly core to accommodate the HC_4CH_3 molecule. The acetylenic carbon atoms C(7) and C(8) which are attached to the Se atoms are separated by $1.303(14) \text{ \AA}$, indicating an

Table 6
Atomic coordinates and equivalent isotropic displacement coefficients for **5**

	<i>x</i> ($\times 10^{-4}$)	<i>y</i> ($\times 10^{-4}$)	<i>z</i> ($\times 10^{-4}$)	<i>U</i> _{eq} ($\times 10^{-3}$ Å ²)
Os(1)	563.5(7)	4448.4(10)	5636	22.4(4) ^a
Os(2)	658.9(7)	4894.6(15)	4050.1(12)	24.5(4) ^a
Os(3)	2019.6(6)	4658.9(16)	4959.0(12)	22.6(4) ^a
Fe(1)	2796(3)	-38(5)	6696(4)	29(2) ^a
Fe(2)	1461(3)	19(6)	7224(4)	34(2) ^a
Se(1)	1784(2)	-1014(4)	5987(3)	30(1) ^a
Se(2)	2026(2)	1896(3)	6567(3)	24(1) ^a
O(6)	-1050(13)	3555(26)	5732(16)	44(5)
O(7)	104(14)	7387(29)	5912(18)	56(6)
O(8)	664(13)	3837(27)	7421(17)	47(5)
O(9)	-1019(14)	4965(27)	3950(20)	54(5)
O(10)	747(15)	7926(29)	3914(21)	64(6)
O(11)	868(17)	4270(30)	2312(20)	61(6)
O(12)	3493(13)	3271(27)	5343(16)	45(5)
O(13)	2093(15)	5763(28)	6676(20)	56(6)
O(14)	2630(16)	7428(30)	4404(19)	64(6)
O(15)	2360(17)	3769(30)	3257(20)	67(6)
O(16)	3688(18)	1255(36)	7916(24)	87(7)
O(17)	3258(16)	-2587(32)	7399(20)	69(6)
O(18)	3878(17)	168(32)	5385(21)	70(6)
O(19)	1771(24)	1158(44)	8798(30)	134(7)
O(20)	-98(19)	771(34)	6963(22)	82(7)
O(21)	1218(18)	-2638(35)	7878(23)	87(7)
C(1)	1500(16)	407(32)	5296(20)	26(6)
C(2)	1555(15)	1641(30)	5491(19)	19(5)
C(3)	1334(18)	2931(33)	5113(21)	32(6)
C(4)	688(14)	3009(28)	4577(18)	13(5)
C(5)	133(19)	1886(37)	4458(23)	44(6)
C(6)	-430(16)	3880(30)	5695(23)	27(6)
C(7)	248(18)	6272(34)	5900(21)	28(6)
C(8)	675(18)	4032(34)	6729(23)	29(6)
C(9)	-392(17)	4995(33)	3955(24)	30(6)
C(10)	717(21)	6780(40)	3956(28)	52(7)
C(11)	756(18)	4462(36)	2975(24)	33(6)
C(12)	2928(18)	3800(34)	5199(21)	32(6)
C(13)	1966(18)	5261(35)	6046(24)	34(6)
C(14)	2414(17)	6423(33)	4627(20)	23(6)
C(15)	2093(20)	4077(37)	3860(26)	42(6)
C(16)	3284(22)	798(41)	7425(26)	50(7)
C(17)	3090(21)	-1583(38)	7085(26)	46(7)
C(18)	3478(29)	81(46)	5943(33)	72(7)
C(19)	1619(23)	685(41)	8192(28)	54(7)
C(20)	524(23)	514(43)	7033(28)	57(7)
C(21)	1269(25)	-1541(47)	7582(30)	71(7)

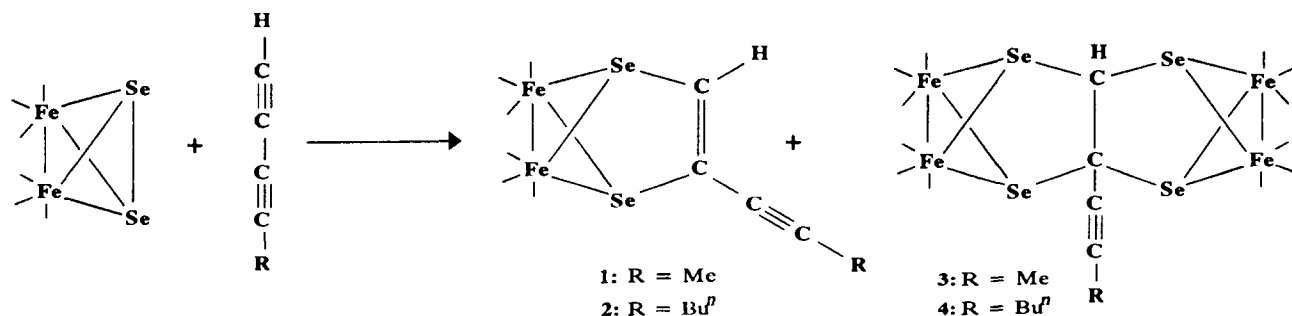
^a Equivalent isotropic *U* defined as one third of the trace of the orthogonalized *U*_{*ij*} tensor.

Table 7
Selected bond distances and angles for **5**

<i>Bond distances</i>			
Os(1)–Os(2)	2.726(3)	Os(1)–Os(3)	2.835(2)
Os(1)–C(3)	2.221(33)	Os(1)–C(4)	2.306(29)
Os(2)–Os(3)	2.873(3)	Os(2)–C(4)	2.079(28)
Os(3)–C(3)	2.123(33)	Os(3)–C(12)	1.870(33)
Os(1)–C(6)	1.856(30)	Os(1)–C(7)	1.952(34)
Os(1)–C(8)	1.906(38)	Os(2)–C(9)	1.874(30)
Os(2)–C(10)	1.886(40)	Os(2)–C(11)	1.878(40)
Os(3)–C(13)	1.937(40)	Os(3)–C(14)	1.972(32)
Os(3)–C(15)	1.952(43)	Fe(1)–Fe(2)	2.533(8)
Fe(1)–Se(1)	2.368(7)	Fe(1)–Se(2)	2.370(6)
Fe(1)–C(16)	1.723(42)	Fe(2)–Se(1)	2.401(8)
Fe(2)–Se(2)	2.395(7)	Se(1)–C(1)	1.904(33)
Se(2)–C(2)	2.019(32)	C(1)–C(2)	1.275(44)
C(2)–C(3)	1.487(45)	C(3)–C(4)	1.465(43)
C(4)–C(5)	1.503(45)		
<i>Bond angles</i>			
Os(2)–Os(1)–Os(3)	62.2(1)	Os(2)–Os(1)–C(3)	71.4(9)
Os(3)–Os(1)–C(3)	47.8(8)	Os(2)–Os(1)–C(4)	47.9(7)
Os(3)–Os(1)–C(4)	69.2(6)	C(3)–Os(1)–C(4)	37.7(11)
Os(1)–Os(2)–C(4)	55.4(8)	Os(3)–Os(2)–C(4)	71.1(7)
Os(1)–Os(3)–Os(2)	57.0(1)	Se(2)–C(2)–C(1)	112.8(24)
Se(2)–C(2)–C(3)	112.8(22)	C(1)–C(2)–C(3)	134.4(31)
Os(1)–C(3)–Os(3)	81.4(11)	Os(3)–C(15)–O(15)	159.9(32)
Os(1)–C(3)–C(2)	125.4(23)	Os(3)–C(3)–C(2)	126.9(22)
Os(1)–C(3)–C(4)	74.3(17)	Os(3)–C(3)–C(4)	109.2(22)
C(2)–C(3)–C(4)	121.3(27)	Os(1)–C(4)–Os(2)	76.7(9)
Os(1)–C(4)–C(3)	68.0(17)	Os(2)–C(4)–C(3)	109.5(20)
Os(1)–C(4)–C(5)	120.2(21)	Os(2)–C(4)–C(5)	126.7(21)
C(3)–C(4)–C(5)	123.8(27)	Os(3)–C(13)–O(13)	164.7(30)
Fe(2)–Fe(1)–Se(1)	58.6(2)	Fe(2)–Fe(1)–Se(2)	58.4(2)
Se(1)–Fe(1)–Se(2)	81.3(2)	Fe(1)–Fe(2)–Se(1)	57.3(2)
Fe(1)–Fe(2)–Se(2)	57.4(2)	Se(1)–Fe(2)–Se(2)	80.2(3)
Fe(1)–Se(1)–Fe(2)	64.1(2)	Fe(1)–Se(1)–C(1)	102.0(9)
Fe(2)–Se(1)–C(1)	98.9(10)	Fe(1)–Se(2)–Fe(2)	64.2(2)
Fe(1)–Se(2)–C(2)	102.7(9)	Fe(2)–Se(2)–C(2)	98.5(9)
Se(1)–C(1)–C(2)	122.4(26)	Se(2)–C(2)–C(1)	112.8(24)
Se(2)–C(2)–C(3)	112.8(22)	C(1)–C(2)–C(3)	134.4(31)

olefinic bond order, whereas the second acetylenic bond retains its triple bond character with a C(9)–C(10) distance of 1.167(12) Å.

Dark red air-stable crystals of **3** were obtained from a CH₂Cl₂–hexane–tetrahydrofuran (THF) solution at –10°C and subjected to an X-ray diffraction study. An ORTEP drawing of the molecular structure of **3** is shown



Scheme 1.

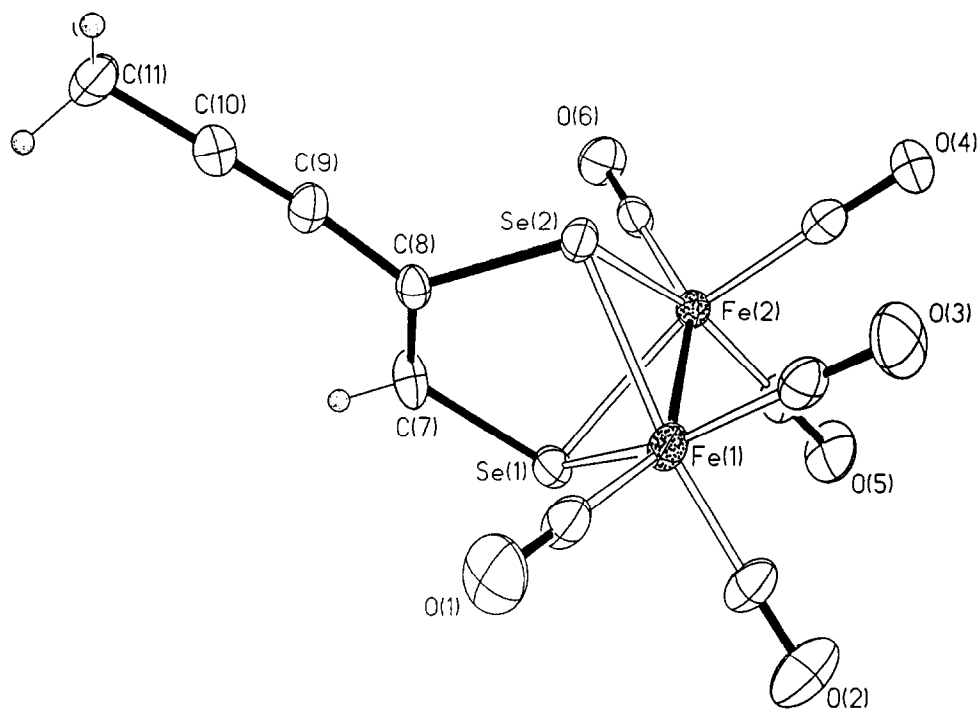


Fig. 1. Molecular structure of **1** with the atom-labelling scheme.

in Fig. 2. The structure of **3** can be described as consisting of two $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$ butterfly groups added to one of the acetylenic bonds of $\text{HC}\equiv\text{CC}\equiv\text{CCH}_3$. The geometry of each $\text{Fe}_2(\text{CO})_6\text{Se}_2$ unit of **3** is similar to that in **1**. The most significant consequence of the addition of a second $\text{Fe}_2(\text{CO})_6\text{Se}_2$ unit to **1** is the conversion of the olefinic bond of **1** to a single bond in **3**, as shown by the $\text{C}(1)\text{--C}(2)$ distance of 1.522 (13) Å. As in **1**, the uncoordinated acetylenic bond retains its

triple bond character with a $\text{C}(3)\text{--C}(4)$ distance of 1.193 (16) Å.

Room-temperature stirring of a benzene solution containing **1** and $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ yielded **5** (Scheme 2), which has been characterized by infrared, ^1H NMR and ^{13}C NMR spectroscopy as $(\text{CO})_6\text{Fe}_2\text{Se}_2(\mu\text{-HC}\equiv\text{CC}\text{-CCH}_3)\text{Os}_3(\text{CO})_{10}$. The solid-state IR spectrum of **5** in the carbonyl stretching region shows peaks in the region 2101–1943 cm^{-1} , indicating the presence

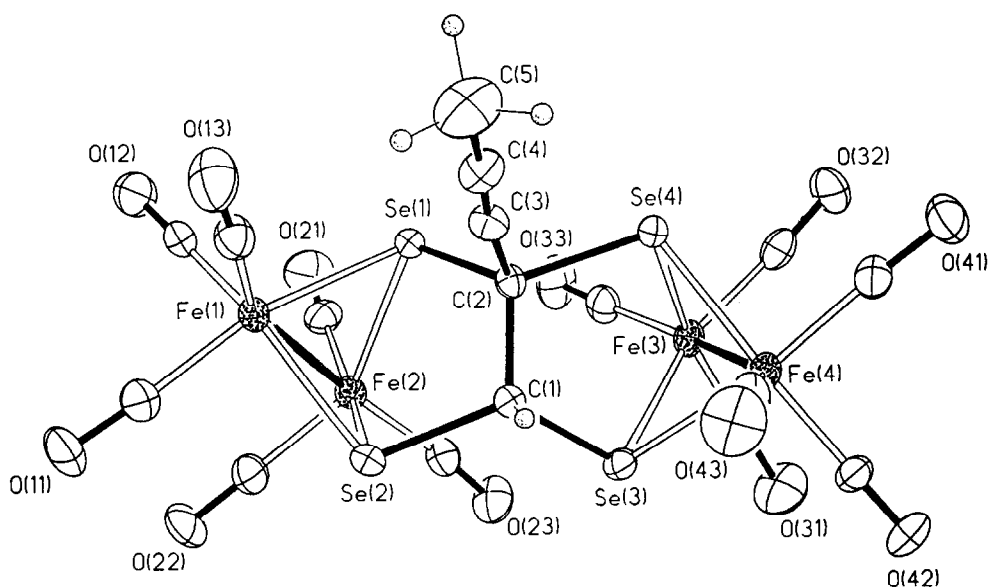
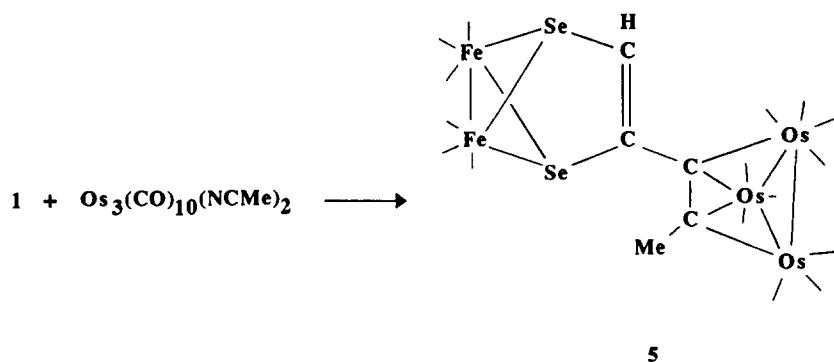


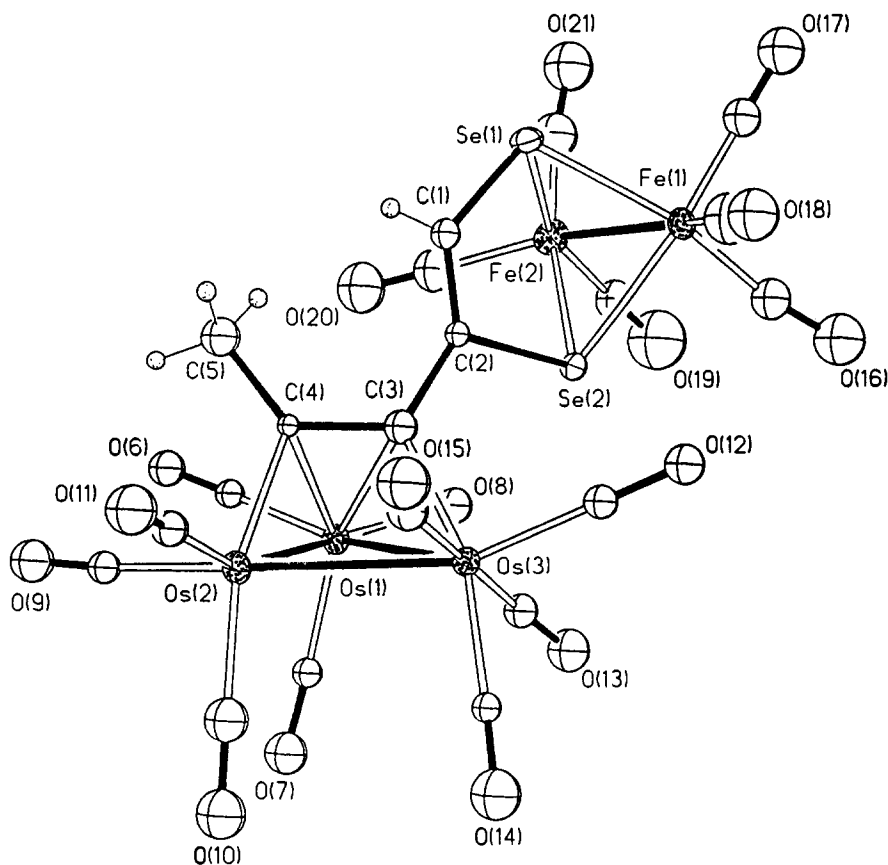
Fig. 2. Molecular structure of **3** with the atom-labelling scheme.



Scheme 2.

of only terminal carbonyl groups. The IR spectrum recorded in hexane solution shows a weak broad peak due to the presence of bridging carbonyl group at 1854 cm^{-1} , in addition to the terminal carbonyl peaks. NMR spectroscopy confirms the presence of the HC_4CH_3 moiety. Dark-red air-stable crystals of **5** were obtained from its hexane solution at -10°C and subjected to an X-ray diffraction study. An ORTEP drawing of the molecular structure of **5** is shown in Fig. 3. The structure of **5** may be described as consisting of **1** with an $\text{Os}_3(\text{CO})_{10}$ group added to the second acetylenic bond in a η^2, μ_3 mode. The bond parameters of the

$\text{Fe}_2(\text{CO})_6\text{Se}_2$ part of **5** are almost identical with those in **1** and **3**. Three carbonyl ligands are bonded to each of two osmium atoms Os(1) and Os(2). The third osmium atom Os(3) has four-coordinated carbonyl ligands. The acetylenic bond is π bonded to Os(1) and σ bonded to Os(2) and Os(3). The two osmium atoms that form σ bonds to the acetylenic unit form the longest of the three metal–metal bonds in the Os_3 triangle, with an Os(2)–Os(3) distance of $2.873(3) \text{ \AA}$. The shortest separation between the metal atoms in the Os_3 triangle is the $2.726(3) \text{ \AA}$ observed for the Os(1)–Os(2) bond. This is comparable with a metal–metal separation of $2.711(1)$

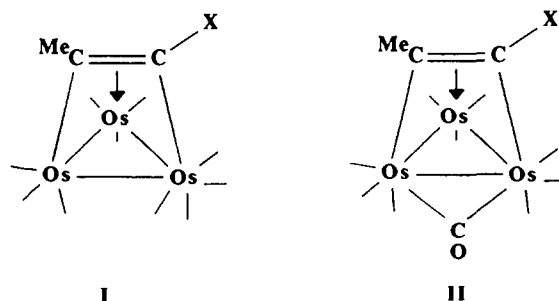
Fig. 3. Molecular structure of **5** with the atom-labelling scheme.

Å reported for $\text{Os}_3(\text{CO})_{10}(\text{PhC}_2\text{Ph})$ [19] and 2.744(2) Å for $\text{Os}_3(\text{CO})_7(\text{C}_4\text{Ph}_4)(\text{PhC}_2\text{Ph})$ [20], but significantly longer than the double-bond value of 2.670(2) Å reported for $\text{H}_2\text{Os}_3(\text{CO})_{10}$ [21]. The formation of **5** from **1** causes the reduction of the second acetylenic bond to below an olefinic bond order, with the C(3)–C(4) bond distance of 1.465(43) Å consistent with the activity of the acetylene ligand as a four-electron donor to the triosmium unit. The Os(1)–C(3) and Os(1)–C(4) bond lengths differ slightly, with values of 2.221(33) and 2.306(29) Å respectively. A similar difference is observed for the π -bonded Os–C lengths of 2.293(9) and 2.188(8) Å in $\text{Os}_3(\text{CO})_{10}(\text{PhC}_2\text{Ph})$ and the corresponding Os–C bond lengths of 2.22(1) and 2.28(2) Å in the metallocyclic complex $\text{Os}_3(\text{CO})_7(\text{C}_4\text{Ph}_4)(\text{PhC}_2\text{Ph})$. The σ bond between the acetylenic ligand and the metal atom Os(3) with the four carbonyl ligands coordinated to it namely, with an Os(3)–C(3) length of 2.123(33) Å, is weaker than the σ bond to the metal atom Os(3) with three carbonyl ligands coordinated to it, with an Os(2)–C(4) length of 2.079(28) Å. A similar pattern is observed in $\text{Os}_3(\text{CO})_{10}(\text{PhC}_2\text{Ph})$, with corresponding bond lengths of 2.182(8) and 2.070(9) Å, and in $\text{Os}_3(\text{CO})_7(\text{C}_4\text{Ph}_4)(\text{PhC}_2\text{Ph})$, with the weak and strong bond lengths of 2.16(2) and 2.08(2) Å respectively. There is some variation in the bonding of the carbonyl groups to the metal atoms. At each metal center, the Os–C bond distances to the carbonyl groups that are approximately *trans* to Os–Os bonds are shorter than those to the carbonyl groups that are approximately *trans* to each other or to those opposite the acetylenic bonds. A significant feature in respect of the carbonyl bonding is found at the metal Os(3) with four carbonyl groups, the Os(3)–C(13)–O(13) and Os(3)–C(15)–O(15) angles being 164.7(30)° and 159.9(32)° respectively. This deviation from linearity may be attributable to semibridging interaction. The two semibridging carbonyl groups are *trans* oriented on the single Os(3) atom. They are directed along the Os(3)–Os(1) and Os(3)–Os(2) bonds, which are longer than the unbridged Os(1)–Os(2) bond. The arrangement of the semibridging carbonyl groups is similar to that in $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ [22] and $\text{Os}_3(\text{CO})_{10}(\text{PhC}_2\text{Ph})$; in both compounds a pair of *trans*-oriented carbonyl groups semibridge two edges of the M_3 triangle.

The stepwise addition of $\text{Fe}_2(\text{CO})_6(\mu\text{-Se}_2)$ to one of the acetylenic bonds of the diynes leads to reduction of the triple bond to an olefinic bond when **1** and **2** are formed, and to a single bond when **3** and **4** are formed. The second acetylenic bond remains inert during the formation of **1**–**4**. By contrast, the reaction of $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ with **1** gives **5** by addition of the $\text{Os}_3(\text{CO})_{10}$ group to the second uncoordinated bond of **1**. The acetylenic unit is attached to the triosmium unit through η^2 , μ_3 bonding, and formally the acetylenic bond acts as a four-electron donor to the triosmium unit.

Conventional electron counting for **5** shows the Os(2) is short of one valence electron while Os(1) is electronically saturated. The third metal atom Os(3) with four-coordinated carbonyl ligands exceeds the optimal 18-valence-electron configuration by one. Since Os(3) possesses two more electrons than Os(2), the Os(2)–Os(3) interaction may be viewed as a donor–acceptor bond between electron-rich Os(3) and electron-deficient Os(2). The formal electronic differences between the Os(1)–Os(3) and Os(2)–Os(3) bonds, however, are not reflected in their bond distances, which remain quite similar, with values of 2.835(2) and 2.873(3) Å respectively. The bonding features of the acetylene ligand and the carbonyl groups are related directly to the electronic dissimilarities at the three Os centers. The bond distance between the electron-rich Os(3) and C(3) is longer than that between the electron-deficient Os(2) and C(4). The most significant carbonyl-bonding feature at the triosmium unit of **5** is the presence of two semibridging carbonyl groups. Semibridging carbonyl ligands are common in clusters with electronically dissimilar metal centers. The two metal–metal bonds associated with the semibridging carbonyl groups Os(1)–Os(3) and Os(2)–Os(3) are longer than the unbridged Os(1)–Os(2) bond. The observation of a bridging carbonyl band at 1854 cm^{-1} in the solution IR spectrum suggests that, the structure I is present in the solid; in solution, some of the isomer with II is present.

In this paper we have described the synthesis of complexes containing the diyne ligands. As expected, facile addition of the reactive $\text{Fe}_2(\text{CO})_6\text{Se}_2$ groups to the acetylenic ligands takes place. The availability of a second acetylenic bond facilitates the addition of other metal carbonyl groups, such as $\text{Os}_3(\text{CO})_{10}$. A feature of these reactions is the ease of addition of the metal groups. Investigations are in progress to extend the scope of such syntheses of mixed-metal polynuclear complexes by taking advantage of the large number of metal–ligand combinations which can participate in η^2 bonding with the $\text{C}\equiv\text{C}$ triple bonds.



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