Acetylenic Bond Reduction on $Fe_2(CO)_6(\mu\text{-}Se_2)$ and Synthesis of the Double-Butterfly Complex $[\{(CO)_6Fe_2(\mu\text{-}Se)_2\}_2C(Ph){-}C(H)]$

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Summary: Room-temperature reaction of $[Fe_2(CO)_6\{\mu\text{-}SeC(Ph){=}C(H)Se\}]$ *(1) with* $Fe_2(CO)_6(\mu\text{-}Se_2)$ *gives the double-butterfly complex* $[\{(CO)_6Fe_2(\mu\text{-}Se)_2\}_2C(Ph){-}C(H)]$ *(2). The structures of 1 and 2 have been determined by single-crystal X-ray diffraction studies 1:* $P2_1/a$, $a = 14.561(1)$ Å, $b = 6.666(1)$ Å $c = 17.475(1)$ Å, $\beta = 91.22(1)°$, $V = 1695.8(4)$ Å^3, $Z = 4$, $R = 3.98\%$, *and* $R_w = 4.59\%$. *2: monoclinic,* $P\bar{1}$, $a = 8.913(1)$ Å, $b = 9.115(1)$ Å, $c = 17.556(1)$ Å, $\alpha = 74.97(1)°$, $\beta = 84.96(1)°$, $\gamma = 86.09(1)°$, $V = 1367.5(4)$ Å^3, $Z = 2$, $R = 4.69\%$, and $R_w = 4.89\%$. *Structural analysis shows the systematic reduction of the acetylenic C≡C bond on the* Fe_2Se_2 *frameworks of 1 and 2.*

Introduction

Bonding and reactivity studies of alkynes attached to metal centers is of current interest because of the potential of the coordinated alkynes to be transformed into useful organic species[1] and because metal–alkyne complexes may be models of intermediates in the overall reduction of acetylene by nitrogenase.[2] Recently we reported a convenient method of preparing $[Fe_2(CO)_6(\mu\text{-}Se_2)]$ and its reaction with $[M(CO)_5(THF)]$ (M = Mo, W)[3] and the synthesis of $[Fe_2(CO)_6\{\mu\text{-}SeC(Ph){=}C(H)Se\}]$ (1) from the reaction of $[Fe_2(CO)_6(\mu\text{-}Se_2)]$ and phenylacetylene.[4] Here we report on the synthesis of the double-butterfly complex $[\{(CO)_6Fe_2(\mu\text{-}Se)_2\}_2C(Ph){-}C(H)]$ (2). In order to compare the acetylenic bond reduction, a structure determination of $[Fe_2(CO)_6\{\mu\text{-}SeC(Ph){=}C(H)Se\}]$ and $[\{(CO)_6Fe_2(\mu\text{-}Se)_2\}_2C(Ph)\text{-}C(H)]$ by X-ray diffraction methods was undertaken.

Results and Discussion

X-ray single-crystal structure analysis shows that 1 has the structure illustrated in Figure 1. It can be described as an Fe_2Se_2 butterfly core, and the phenylacetylene molecule is attached to the wingtip Se atoms of the butterfly. Each iron atom has three carbonyl ligands. Compound 1 and its Te analog have been prepared previously from the thermal activation of phenylacetylene and $[Fe_3(CO)_9(\mu_3\text{-}E)_2]$ (E = Se, Te), and the crystal structure of the Te compound $[Fe_2(CO)_6\{\mu\text{-}TeC(Ph){=}C(H)Te\}]$ has been reported.[5] Overall the structure of 1 is similar to that of $[Fe_2(CO)_6\{\mu\text{-}TeC(Ph){=}C(H)Te\}]$. The acetylenic C—C distance in 1 is 1.331(7) Å, whereas in the Te compound it is 1.34(1) Å.

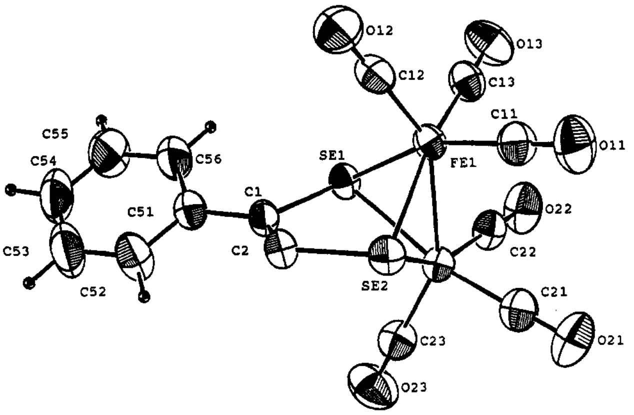
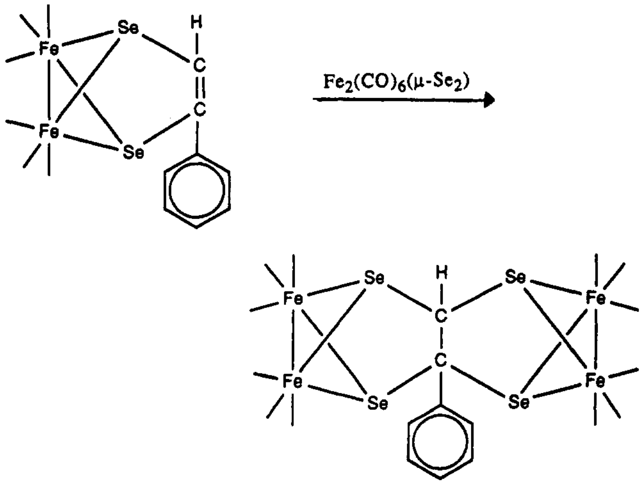


Figure 1. ORTEP representation of 1 and the atom-numbering scheme.

Scheme I



At room temperature, 1 reacts with $[Fe_2(CO)_6(\mu\text{-}Se_2)]$ to form the double-butterfly complex $[\{(CO)_6Fe_2(\mu\text{-}Se)_2\}_2C(Ph)\text{-}C(H)]$ (2) (Scheme I). Its structure, as determined by an X-ray single-crystal analysis, is shown in Figure 2. The structure can be envisaged as two Fe_2Se_2 butterfly units which are linked to each other through a bridging PhC—CH group. Each iron atom contains three carbonyl groups. Both 1 and 2 contain essentially similar $Fe_2(CO)_6Se_2$ units, with almost identical parameters. The most important difference is the elongation of the acetylenic C—C bond in 2 to 1.48(1) Å. The structure of 2 can be compared with that of the methylene-bridged, double-butterfly complex $[(\mu\text{-}CH_3Te)Fe_2(CO)_6]_2[\mu\text{-}(CH_2)Te]$, which was obtained from the reaction of $[Fe_3(CO)_9(\mu_3\text{-}Te)_2]$ and excess diazomethane.[6] The most notable difference between 2 and the methylene-bridged complex is that in 2 both the Se atoms in each Fe_2Se_2 butterfly are attached to phenylacetylene, which forms a bridge between the two $Fe_2(CO)_6Se_2$ units, whereas in the methylene-

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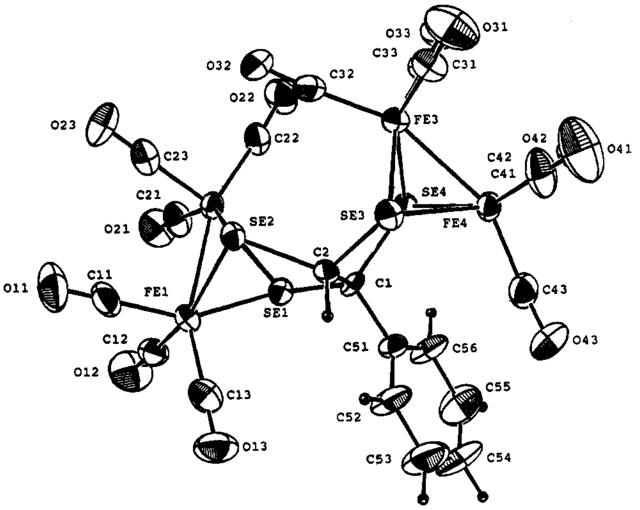

Figure 2. ORTEP representation of 2 and the atom-numbering scheme.

Table I. Crystallographic Data for 1 and 2

formula	$C_{14}H_6Fe_2Se_2O_6$ (**1**)	$C_{20}H_6Fe_4Se_4O_{12}$ (**2**)
fw	539.80	977.48
cryst syst	monoclinic	triclinic
space group	$P2_1/a$	$P\bar{1}$
a, Å	14.561(1)	8.913(1)
b, Å	6.666(1)	9.115(1)
c, Å	17.475(1)	17.556(1)
α, deg		74.97(1)
β, deg	91.22(1)	84.96(1)
γ, deg		86.09(1)
V, Å^3	1695.8(4)	1367.5(4)
Z	4	2
D_{calcd}, g cm^{-3}	2.12	2.37
$F(000)$	1032	924
corrections	Lorentz–polarizn, linear decay (from 1.000 to 1.005 on I), rfln averaging (agreement on I = 2.1%), empirical absorption (from 47.37 to 9.90 on I)	Lorentz–polarizn, rfln averaging (agreement on I = 3.1%)
$2\theta_{max}$, deg	60.9	54.0
T, K	294	294
hkl ranges	h = –20 to 20, k = –9 to 0, l = 0–24	h = –11 to 0, k = –11 to +11, l = 22 to +22
esd of observn of unit wt	1.44	1.52
convergence, largest shift	1.68	0.42
minimization factor	$w(\lvert F_o\rvert - \lvert F_c\rvert)$	$w(\lvert F_o\rvert - \lvert F_c\rvert)$
least-squares wts	$4F_o/\sigma(F_o)$	$4F_o/\sigma(F_o)$
instrument instability factor	0.040	0.040
high peak in final diff map, e Å^{-3}	1.09(13)	1.09(16)
low peak in final diff map, e Å^{-3}	0.00(13)	0.00(16)

bridged complex, only one Te atom in each Fe_2Te_2 unit is attached to the bridging CH_2 group, giving overall a more open structure.

Transition-metal–alkyne complexes are often prepared by displacement of labile ligands by alkynes.[7] In di- and polynuclear complexes, the use of certain main-group, single-atom bridging ligands can provide additional sites of reactivity. The three elements S, Se, and Te are now ubiquitous bridging ligands in di- and polynuclear metal carbonyl chemistry.[8] Their ability to stabilize the metal framework against fragmentation and their utility in facile cluster synthesis arise from their versatile bonding modes; the S ligand can bridge up to five metal atoms,[9] while the Se and Te ligands have been shown to bridge four metal atoms.[10] Strain inherent in the FeFeEE ring in the $[Fe_2(CO)_6(\mu\text{-}E_2)]$ complexes, where E = S, Se, Te, facilitates easy addition of various coordinatively unsaturated metal carbonyl species across the E—E bond as the first step in cluster growth reactions. Seyferth has reported on the reactions of $[Fe_2(CO)_6(\mu\text{-}S_2)]$ with alkenes and alkynes in presence of base[11] and on the formation and reactivity of the dianions $[Fe_2(CO)_6E_2]^{2-}$ (E = S, Se).[12] Similar dianion formation and its reactivity toward metal dihalides has been reported for the Te compound $[Fe_2(CO)_6(\mu\text{-}Te_2)]$.[13] In general, the possibility of using bridging Se atoms as

Table II. Positional Parameters and Their Estimated Standard Deviations for Compound 1

atom	x	y	z	B,[a] Å^2
Se1	0.15710(4)	0.29360(7)	0.27363(3)	2.926(9)
Se2	0.17843(4)	0.73540(7)	0.22005(3)	3.19(1)
Fe1	0.08994(5)	0.4659(1)	0.16714(4)	2.90(1)
Fe2	0.26109(5)	0.4418(1)	0.18601(4)	2.96(1)
O11	0.0839(3)	0.6653(7)	0.0183(2)	6.0(1)
O12	–0.0888(3)	0.5809(7)	0.2270(3)	5.9(1)
O13	0.0345(3)	0.0811(6)	0.1002(3)	5.4(1)
O21	0.3416(3)	0.6546(7)	0.0570(2)	5.7(1)
O22	0.2736(3)	0.0700(6)	0.0992(2)	5.5(1)
O23	0.4250(3)	0.4324(8)	0.2859(3)	6.5(1)
C1	0.1521(3)	0.5034(8)	0.3522(3)	3.2(1)
C2	0.1599(4)	0.6908(8)	0.3270(3)	3.3(1)
C11	0.0859(4)	0.5906(8)	0.0761(3)	3.9(1)
C12	–0.0194(4)	0.5355(8)	0.2035(3)	3.8(1)
C13	0.0572(4)	0.2321(8)	0.1259(3)	3.8(1)
C21	0.3104(4)	0.5733(8)	0.1076(3)	4.0(1)
C22	0.2698(4)	0.2127(8)	0.1349(3)	3.7(1)
C23	0.3612(4)	0.4381(9)	0.2480(3)	4.0(1)
C51	0.1390(4)	0.4413(8)	0.4326(3)	3.5(1)
C52	0.1687(5)	0.562(1)	0.4915(3)	5.2(2)
C53	0.1558(6)	0.514(1)	0.5662(4)	6.8(2)
C54	0.1120(5)	0.338(1)	0.5831(3)	6.5(2)
C55	0.0850(6)	0.213(1)	0.5267(4)	6.8(2)
C56	0.0967(5)	0.265(1)	0.4518(4)	5.5(2)
H52	0.200	0.683	0.480	5.0*
H53	0.177	0.601	0.606	5.0*
H54	0.100	0.306	0.635	5.0*
H55	0.059	0.089	0.540	5.0*
H56	0.076	0.176	0.413	5.0*

[a] Starred values denote atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Table III. Selected Bond Distances (Å) and Angles (deg) for 1

Fe1–Se1	2.3792(9)	Fe2–Se1	2.3901(9)
Fe1–Se2	2.3857(9)	Fe2–Se2	2.3796(9)
Fe1–Fe2	2.512(1)	C1–C2	1.331(7)
Se1–C1	1.963(5)	Se2–C2	1.917(5)
Fe1–Se1–Fe2	63.57	Fe1–Se2–Fe2	63.63(3)
Se1–Fe1–Se2	81.42(3)	Se1–Fe2–Se2	81.32(3)
Se1–C1–C2	115.6(4)	Se2–C2–C1	118.9(4)
Se1–C1–C51	118.2(4)		

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Table IV. Positional Parameters and Their Estimated Standard Deviations for Compound 2

atom	*x*	*y*	*z*	*B*,[a] Å^2
Se4	0.0603(1)	0.3330(1)	0.24529(6)	2.16(2)
Se3	0.3241(1)	0.4476(1)	0.31201(6)	2.03(2)
Se1	0.3167(1)	0.0664(1)	0.24024(5)	1.88(2)
Se2	0.5838(1)	0.2722(1)	0.22164(6)	2.19(2)
Fe(1)	0.5566(2)	0.0552(2)	0.17217(8)	2.26(3)
Fe2	0.5269(2)	0.0471(2)	0.31763(8)	2.15(3)
Fe(3)	0.0889(2)	0.5697(2)	0.27359(8)	2.31(3)
Fe4	0.1073(2)	0.3189(2)	0.37643(8)	2.12(3)
O11	0.527(1)	0.180(1)	0.0029(5)	5.7(3)
O12	0.5062(9)	−0.2594(9)	0.1759(4)	4.0(2)
O13	0.880(1)	−0.008(1)	0.1542(6)	6.8(3)
O21	0.458(1)	−0.270(1)	0.3911(5)	4.6(2)
O22	0.846(1)	−0.022(1)	0.3467(6)	6.2(3)
O23	0.4733(9)	0.1614(9)	0.4588(4)	3.8(2)
O31	0.114(1)	0.758(1)	0.3832(5)	5.1(2)
O32	−0.236(1)	0.635(1)	0.2769(5)	5.4(3)
O33	0.171(1)	0.785(1)	0.1236(5)	4.9(2)
O41	0.1617(9)	−0.0048(9)	0.4507(4)	4.0(2)
O42	−0.218(1)	0.311(1)	0.4186(5)	4.9(2)
O43	0.180(1)	0.399(1)	0.5191(5)	5.1(2)
C1	0.264(1)	0.290(1)	0.1940(5)	1.9(2)
C2	0.381(1)	0.381(1)	0.2137(5)	1.9(2)
C52	0.280(1)	0.450(1)	0.0528(7)	3.6(3)
C53	0.244(2)	0.477(2)	−0.0232(8)	5.4(4)
C54	0.165(2)	0.377(2)	−0.0476(9)	5.6(4)
C55	0.123(2)	0.246(2)	0.0052(8)	4.8(3)
C56	0.155(1)	0.218(1)	0.0823(7)	3.6(3)
C51	0.237(1)	0.319(1)	0.1067(6)	2.5(2)
C11	0.531(1)	0.135(1)	0.0697(7)	3.6(3)
C12	0.527(1)	−0.138(1)	0.1744(6)	2.6(2)
C13	0.755(1)	0.023(1)	0.1610(7)	3.7(3)
C21	0.483(1)	−0.146(1)	0.3634(6)	2.8(2)
C22	0.723(1)	0.005(1)	0.3343(7)	3.7(3)
C23	0.486(1)	0.121(1)	0.4029(6)	2.6(2)
C31	0.105(1)	0.686(1)	0.3395(7)	3.5(3)
C32	−0.109(1)	0.607(1)	0.2741(7)	3.4(3)
C33	0.141(1)	0.701(1)	0.1811(6)	3.0(3)
C41	0.144(1)	0.120(1)	0.4182(6)	2.7(2)
C42	−0.091(1)	0.314(1)	0.4033(6)	3.0(3)
C43	0.151(1)	0.368(1)	0.4634(6)	3.1(3)
H2	0.400	0.478	0.169	4.0*
H52	0.336	0.525	0.070	5.2*
H53	0.274	0.569	−0.062	5.2*
H54	0.141	0.395	−0.103	5.2*
H55	0.068	0.171	−0.013	5.2*
H56	0.123	0.124	0.121	5.2*

[a] See footnote *a* of Table II.

sites of addition of organic species has remained largely unexplored. The stepwise acetylenic bond reduction on 1 and 2 therefore represents an important development in this area.

Experimental Section

General Procedures. Reactions and manipulations were carried out under an inert atmosphere of nitrogen by means of standard Schlenk techniques. Solvents were deoxygenated immediately prior to use. Compound 1 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. NMR spectra were obtained on a Varian XL-300 spectrometer at 25 °C.

Preparation of 2. To a solution of 1[4] (0.5 g, 0.92 mmol) in methanol (15 mL) was added [$Fe_2(CO)_6(\mu\text{-}Se_2)$][14] (0.92 mmol) in methanol (5 mL), and the mixture was stirred at room temperature under N_2 for 72 h. Evaporation of the solvent and chromatographic workup on a silica gel column using a 10/90 dichloromethane/hexane mixture as eluent yielded a single red band of 2 (0.1 g, 12%). Mp: 172 °C dec. IR (CH_2Cl_2; *ν*, cm^{-1}): 2076 m, 2063 s, 2038 vs, 2002 s, br. ^{1}H NMR (CCl_4; *δ*): 7.28–7.44 (m, phenyl protons), 7.94 (s, C*H*). ^{13}C NMR (CCl_4; *δ*): 121.0 (*C*H), 128.7, 129.3, 129.9 (phenyl ring carbons), 132.7 (*C*Ph), 203.8, 207.6, 209.2 (*C*O). Anal. Calcd (found) for $C_{20}H_6Fe_4Se_4$: C, 24.5, (24.6); H, 0.61 (0.60).

Table V. Selected Bond Distances (Å) and Angles (deg) for 2

Fe1–Se1	2.364(1)	Fe2–Se1	2.381(2)
Fe1–Se2	2.391(2)	Fe2–Se2	2.346(1)
Fe3–Se3	2.373(1)	Fe4–Se3	2.372(1)
Fe3–Se4	2.369(2)	Fe4–Se4	2.346(2)
C1–C2	1.48(1)	Se1–C1	2.035(7)
Se2–C2	1.997(8)	Se3–C2	1.990(8)
Se4–C1	2.014(8)	Fe1–Fe2	2.527(2)
Fe1–Se1–Fe2	64.35(5)	Fe1–Se2–Fe2	64.46(5)
Fe3–Se3–Fe4	64.32(4)	Fe3–Se4–Fe4	64.77(5)
Se1–Fe1–Se2	80.51(5)	Se3–Fe4–Se4	81.27(5)
Se1–C1–C51	109.5(6)	Se4–C1–C51	104.1(5)
Se1–C1–Se4	106.0(3)	Se2–C2–Se3	109.5(4)

Crystal Structure Determination of 1. A purple, rectangular crystal of approximate dimensions 0.44 × 0.55 × 0.61 mm^3 was selected for X-ray diffraction study. The data were collected on an Enraf-Nonius CAD4 diffractometer generating Mo Kα radiation at room temperature, using the ω–2θ scan method. The crystallographic data collection parameters are summarized in Table I. A total of 5709 reflections were collected (5145 unique), of which 2884 data (corrected for absorption, Lorentz, and polarization effects with averaging of equivalent reflections) with $F_o > 3\sigma(F_o)$ were used in the refinement. The structure was solved by direct methods (SIR, MolEN), and the hydrogen atoms were located in the Fourier difference maps and refined with B_{iso} = 0.5 Å^2. Least-squares refinement converged to final agreement factors of R = 3.98% and R_w = 4.59% for 217 variables. Final positional and displacement parameters are listed in Table II. Selected bond distances and angles are listed in Table III.

Crystal Structure Determination of 2. A purple, rectangular crystal of approximate dimensions 0.33 × 0.35 × 0.55 mm^3 was selected for the X-ray diffraction study. Data collection, treatment of intensity, data corrections, and solution of the structure were accomplished as described above. A total of 8745 reflections were collected (8267 unique), of which 4099 data (corrected for absorption, Lorentz, and polarization effects with averaging of equivalent reflections) with $F_o > 3\sigma(F_o)$ were used in the refinement. The structure was solved by direct methods (SIR, MolEN), and the hydrogen atoms were located in the Fourier difference maps and refined with B_{iso} = 0.5 Å. Least-squares refinement converged to final agreement factors of R = 4.69% and R_w - 4.84% for 361 variables. The crystallographic data are summarized in Table I. Final positional and displacement parameters are listed in Table IV. Selected bond distances and angles are shown in Table V. Full bond metricals distances and angles and anisotropic displacement for both compounds are included with the supplementary material.

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Supplementary Material Available: For 1 and 2, crystallographic details including complete tables of bond distances and angles and of anisotropic displacement parameters (13 pages). Ordering information is given on any current masthead page.

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(14) Since [$Fe_2(CO)_6(\mu\text{-}Se_2)$] rapidly decomposes in the solid state, a freshly prepared solution has to be used for subsequent study. We find that a quantitative conversion of [$Fe_3(CO)_9(\mu_3\text{-}Se)_2$] to [$Fe_2(CO)_6(\mu\text{-}Se_2)$] occurs when the former is treated with a saturated methanolic solution or NaOMe followed by acidification and chromatographic workup of the solution on a silica gel column using hexane as eluent. The solvent is removed to *almost* complete dryness and the required amount of methanol added, followed by complete removal of the remaining hexane.