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Supporting Information

Sulphur-Sulphur, Sulphur-Selenium, Selenium-Selenium and Selenium-Carbon Bond Activation Using Fe₃(CO)₁₂: An Unexpected Formation of a Fe₂(CO)₆ Complex Containing a μ^2 , κ^3 -C,O,Se-Ligand

Ralf Trautwein,^a Hassan Abul-Futouh,^b Helmar Görls,^a Wolfgang Imhof,^c Laith R. Almazahreh^{d*}, Wolfgang Weigand^{a*}

^a Institut für Anorganische und Analytische Chemie, Friedrich-Schiller-Universität Jena, Humboldt Str. 8, 07743 Jena, Germany. E-Mail: wolfgang.weigand@uni-jena.de

^b Department of Pharmacy, Al-Zaytoonah University of Jordan, P.O. Box 130, Amman 11733, Jordan

^c Institut für Integrierte Naturwissenschaften, Universität Koblenz-Landau, Universitätsstr. 1, D-56070 Koblenz, Germany

^d ERCOSPLAN Ingenieurbüro Anlagentechnik GmbH, Arnstädter Straße 28, 99096 Erfurt, Germany. (The current address), E-mail: laithmazahreh81@gmail.com

Synthesis of 5-Bromomethyl-5-acetylthiomethyl-2,2-dimethyl-1,3-dioxane (A)

In a schlenk flask, 5.00 g (16.56 mmol) of 5,5-bis (bromomethyl)-2,2-dimethyl-1,3-dioxane were dissolved in 40 ml of dry THF under a nitrogen atmosphere. Then, 1.89 g (15.56 mmol) of a potassium thioacetate solution (freshly prepared by reacting an equimolar amount of KOH and thioacetic acid in 20 mL of ethanol) was added, and the reaction mixture was stirred at room temperature for three days followed by refluxing for three hours. After addition of water to solution, it has extracted three times with CH₂Cl₂, washing the combined organic phases with water and drying with Na₂SO₄. After that the solvent was removed and the residue purified by column chromatography (eluent: CH₂Cl₂ / hexane 5:1). Yield 1.28 g (4.31 mmol, 26.0%). Elemental analysis: C10H17BrO3S: calc.: C 40.41, H 5.77, S 10.79, Br 26.88 found: C 40.75, H 5.78, S 11.32, Br 26.46. ¹HMR (400 MHz, CDCl₃, 24°C): δ = 3.74 (d, ²*J*_{H-H} = 11.92 Hz, 2H, OC*H*₂), 3.68 (d, ²*J*_{H-H} = 11.92 Hz, 2H, OC*H*₂), 3.59 (s, 2H, C*H*₂Br), 3.01 (s, 2 H, SC*H*₂), 2.34 (s, 3H, C(O)C*H*₃), 1.40 (s, 3H, CH₂OCC*H*₃), 1.36 (s, 3H, CH₂OCC*H*₃). ¹³C {¹H}</sup> NMR (101 MHz, CDCl₃, 24°C): δ = 194.52 (s, *C*=O), 98.57 (s, OCO), 65.04 (s, OCH₂), 37.32 (s, CCH₂), 37.01 (s, CH₂Br), 31.28 (s, SCH₂), 30.58 (s, C(O)CH₃), 26.21 (s, CH₂OCCH₃), 20.82 (s, CH₂OCCH₃). DEI-MS: *m*/*z* = 297 [M+H]⁺.

In addition to the desired product (pale yellow oil), the doubly substituted dithioacetate derivative, 5,5-Bis(acetylthiomethyl)-2,2-dimethyl-1,3-dioxan, could also be isolated as a yellow solid. Yield 0.46 g (1.57 mmol, 9.5%). ¹H NMR (400 MHz, CDCl₃, 24°C): δ = 3.62 (s, 4H, OCH₂), 3.05 (s, 4H, SCH₂), 2.33 (s, 6H, C(O)CH₃), 1.37 (s, 6H, CH₂OCCH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃, 24°C): δ = 194.78 (s, *C*=O), 98.41 (s, OCO), 65.81 (s, OCH₂), 36.88 (s, CCH₂), 31.46 (s, SCH₂), 30.59 (s, C(O)CH₃), 23.61 (s, CH₂OCCH₃). DEI-MS: *m*/*z* = 293 [M+H]⁺, 249 [M-COCH₃]⁺.

Synthesis of 5-Selenocyanatomethyl-5-acetylthiomethyl-2,2-dimethyl-1,3-dioxane (B)

In a Schlenk vessel 1.08 g (7.50 mmol) KSeCN were dissolved in 40 mL of dry acetone under nitrogen atmosphere. To this solution an acetone solution of 5-bromomethyl-5-acetylthiomethyl-2,2-dimethyl-1,3-dioxane (A, 1.12 g, 3.75 mmol) was added and the resulting mixture was stirred under reflux for three days. After cooling to room temperature, water was added to the reaction mixture, extracted three times with CH₂Cl₂ and then the combined organic phases were washed with water, dried with Na₂SO₄ and the solvent was removed in vacuo. Column

chromatographic purification with CH₂Cl₂ as eluent yielded the desired product as a gray-white solid. Yield: (1.43 mmol, 38.1%). Elemental analysis for C₁₁H₁₇NO₃SSe: calculated: C 40.99, H 5.32, N 4.35, S 9.95 found: C 40.11, H 5.47, N 4.31, S 10.47. ¹H NMR (400 MHz, CDCl₃, 24°C): $\delta = 3.77$ (d, ²*J*_{H-H} = 11.96 Hz, 2H, OC*H*₂), 3.70 (d, ²*J*_{H-H} = 11.96 Hz, 2H, OC*H*₂), 3.11 (s with ⁷⁷Se-Satellite, ²*J*_{H-Se} = 14.40 Hz, 2H, C*H*₂Se), 3.07 (s, 2H, C*H*₂S), 2.35 (s, 3H, C(O(C*H*₃), 1.39 (s, 3H, CH₂OCC*H*₃), 1.39 (s, 3H, CH₂OCC*H*₃), 1.39 (s, 3H, CH₂OCC*H*₃), 1.39 (s, 3H, CH₂OCC*H*₃), 1.3C {¹H} NMR (101 MHz, CDCl₃, 24°C): δ = 196.13 (s, *C*=O), 103.25 (s, SeCN), 98.83 (s, OCO), 66.17 (s, OCH₂), 37.36 (s, CCH₂Se), 33.74 (s with ⁷⁷Se-Satellite, ¹*J*_{Se-C} = 59.7 Hz, CH₂Se), 31.48 (s, SCH₂), 30.57 (s, C(O)CH₃), 23.92 (s, CH₂OCCH₃), 22.97 (s, CH₂OCCH₃). ¹H⁷⁷Se HMBC NMR (400 MHz, 76 MHz, CDCl₃, 24°C): δ = 140.27 (s, SeCN). DEI-MS: *m*/*z* = 324 [M+H]⁺, 297 [M-CN]⁺.

Figure S1. Molecular structure (50% probability) of compound **2**. Hydrogen atoms are omitted for clarity.



Figure S2. Molecular structures (50% probability) complex 7. Hydrogen atoms are omitted for clarity.



Figure S3. Cyclic voltammetry of 1.0 mM the first reduction wave of complex **8** in MeCN-[*n*-Bu₄N][PF₄] (0.1 M) solutions at different scan rates using glassy carbon disk (d = 1.6 mm). The arrows indicate the scan direction. The potentials *E* are given in V and referenced to the Fc⁺/Fc couple.







Compound	Structure	HF [a.u.]	NImag
8	Fe(CO) ₃ Fe(CO) ₃ Se	-1401.151132	0
8-	Fe(CO) ₃	-1401.303632	0
8 ²⁻	Fe(CO) ₃	-1401.399732	0
H81	Fe(CO) ₃ Fe(CO) ₃ H	-1401.866178	0
H8 ⁻ _2	Pe(CO) ₃ Se H Fe (CO) ₃	-1401.877471	0
H ₂ 8	Se H Fe(CO) ₃ H Fe(CO) ₃	-1402.317472	0

 Table S1. Calculated energies and numbers of imaginary frequencies

Compound	2	5	6	7	8
formula	$C_8H_{14}O_2Se$	$C_{14}H_{14}Fe_2O_8S_2$	$C_{14}H_{14}Fe_2O_8Se_2$	C ₁₄ H ₁₀ Fe ₂ O ₈ SSe	C ₁₄ H14Fe ₂ O ₈ Se
fw (g·mol ⁻¹)	221.15	486.07	579.87	528.94	500.91
T/°C	-140(2)	-140(2)	-140(2)	-140(2)	-140(2)
crystal system	monoclinic	Triclinic	monoclinic	monoclinic	triclinic
space group	$P 2_1/c$	Ρī	$P 2_1/c$	$P 2_1/c$	P ī
<i>a</i> / Å	15.0541(3)	11.9370(2)	11.3031(2)	11.3209(4)	8.4342(3)
b/ Å	6.0040(1)	12.2072(2)	13.0682(2)	12.9715(6)	8.4688(3)
<i>c</i> / Å	9.8772(2)	13.9728(2)	12.8788(2)	12.7430(4)	14.2380(5)
$\alpha/^{\circ}$	90	87.963(1)	90	90	93.758(2)
$\beta/^{\circ}$	92.705(1)	66.288(1)	95.538(1)	95.542(2)	105.082(2)
γ^{\prime}	90	88.571(1)	90	90	115.498(2)
$V/Å^3$	891.75(3)	1862.89(5)	1893.46(5)	1862.55(12)	867.72(5)
Ζ	4	4	4	4	2
ρ (g·cm ⁻³)	1.647	1.733	2.034	1.886	1.917
μ (cm ⁻¹)	41.61	18.19	54.14	36.61	38.08
measured data	5346	12900	13251	10319	5208
data with $I > 2\sigma(I)$	1884	7959	4060	3751	3703
unique data (R _{int})	2033/0.0231	8450/0.0149	4337/0.0322	4245/0.0389	3876/0.0208
w R_2 (all data, on F^2) ^{a)}	0.0717	0.0586	0.0508	0.0910	0.0588
$R_1 (I > 2\sigma(I))^{a}$	0.0303	0.0261	0.0214	0.0369	0.0239
S ^{b)}	1.026	1.064	1.068	1.120	1.068
Res. dens./e·Å ⁻³	0.760/-0.983	0.409/-0.311	0.406/-0.440	1.029/-0.535	0.533/-0.675
absorpt method	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
absorpt corr	0.5379/0.7456	0.6633/0.7456	0.6420/0.7456	0.6316/0.7456	0.6045/0.7456
CCDC No.	1915755	1915756	1915757	1915758	1915759

Table S2. Crystal data and refinement details for the X-ray structure determinations of compound 2 and complexes 5-8.

a) Definition of the *R* indices: $R_1 = (\Sigma || F_0 || F_c ||) / \Sigma || F_o |; WR_2 = \{\Sigma [w(F_0^2 - F_c^2)^2] / \Sigma [w(F_0^2)^2] \}^{1/2}$ with $w^{-1} = \sigma^2 (F_0^2) + (aP)^2 + bP; P = [2F_c^2 + Max(F_0^2]/3;$ b) $s = \{\Sigma [w(F_0^2 - F_c^2)^2] / (N_0 - N_p) \}^{1/2}$.