Notes

Selenium-Bridged Clusters. Synthesis and Structural Characterization of the μ_4-Se Twin Cluster $[(\mu\text{-BuSe})Fe_2(CO)_6]_2(\mu_4\text{-Se})$

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*Summary: The unusual tetranuclear cluster $[(\mu\text{-BuSe})Fe_2(CO)_6]_2(\mu_4\text{-Se})$ (**1**) has been obtained from the reaction of a monoanion, derived from $Fe_2(\mu\text{-Se}_2)(CO)_6$ and n-BuLi, with 1,3-dibromopropane. Compound **1** has been characterized by IR and ^1H, ^{13}C, and ^{77}Se NMR spectroscopy. It has been structurally characterized by single-crystal X-ray diffraction methods. The structure consists of two $[(\mu\text{-BuSe})Fe_2(CO)_6]$ units bridged by a pseudotetrahedral Se atom.*

Introduction

The use of chalcogen atoms as bridging ligands in transition-metal cluster compounds continues to attract attention.[1] While earlier work concentrated on the use of sulfur as a ligand for cluster growth and stabilization purposes, in recent times interest has been extended to the usage of selenium and tellurium.[2,3] Seyferth has reported the formation of the monoanion and dianion of $Fe_2(CO)_6(\mu\text{-Se}_2)$ using organolithium reagents and lithium triethylborohydride, respectively, and their reactions with various types of electrophiles.[4] Similarly, organolithium or Grignard reagents have been reported to cleave the S−S bond of $Fe_2(CO)_6(\mu\text{-S}_2)$ to give monoanionic intermediates that undergo alkylation, mercuration, protonation, acylation, and conjugated addition with α,β-unsaturated substrates.[5] At room temperature, the reaction also produced Fe−S cluster complexes in which a central sulfur atom bridges four Fe atoms. In this report we describe the formation of an analogous cluster complex in which a μ_4-Se ligand serves to bridge two Fe_2 units.[6]

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of prepurified nitrogen in well-dried glassware. Solvents were rigorously dried before use. Infrared spectra were obtained using Nicolet Impact-400 infrared FT spectrometer. NMR spectra were recorded on a Varian XL-300 NMR spectrometer. Chemical shifts are reported in δ units (ppm) downfield from internal tetramethylsilane for the ^1H NMR spectrum and for the ^{13}C NMR spectrum. Me_2Se was used as an internal standard for the ^{77}Se NMR spectrum. $Fe_2(\mu\text{-Se}_2)(CO)_6$ was prepared as previously reported.[7] *n*-Butyllithium was purchased from Aldrich Chemical Co.

Preparation of $[(\mu\text{-BuSe})Fe_2(CO)_6]_2(\mu_4\text{-Se})$ (1). In a 100 mL three-necked Schlenk flask equipped with a serum cap and a magnetic stirring bar was placed $Fe_2(\mu\text{-Se}_2)(CO)_6$ (0.5 g, 1.14 mmol) in THF (50 mL), and the red solution was cooled to −78 °C. A 1.6 M hexane solution of *n*-butyllithium (1 mL, 2.28 mmol) was added by syringe over a period of 15 min with stirring, causing a color change of the solution from red to dark green. The mixture was stirred for 20 min, and then $Br(CH_2)_3Br$ (0.19 mL, 2.28 mmol) was added. The reaction mixture was warmed slowly to room temperature, and it was stirred for a further 6 h. The solution was filtered through Celite, and the solvent was evaporated. The residue was dissolved in petroleum ether and this solution subjected to chromatographic workup on a silica gel column using petroleum ether

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Scheme 1

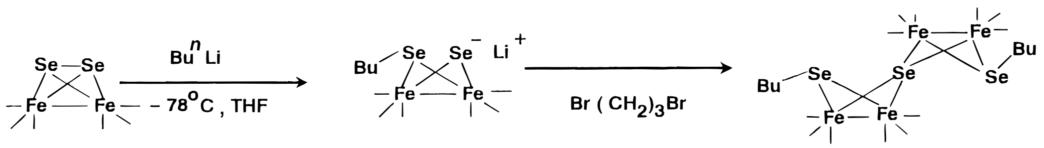

Table 1. Crystal Data and Structure Refinement for 1

compd	$C_{12}H_{18}O_{12}Fe_4Se_3$
mol wt	910.6
space group	*Pbca*
a, Å	16.014(3)
b, Å	19.137(4)
c, Å	39.244(9)
V, Å^3	12014(6)
molecules/unit cell	16
ρ_{calcd}, Mg/m^3	2.014
μ_{calcd}, mm^{-1}	5.583
radiation	Mo Kα
cryst size, mm	0.25 × 0.15 × 0.10
temp, K	220
scan type	ω
scan width, deg	1.20 plus Kα separation
2θ range, deg	3.5−42.0
std rflns	3 measd every 260 rflns
decay of standards	no
no. of rflns collected	6122
no. of rflns obsd, $F > 6.0\sigma(F)$	1693
no. params varied	383
GOF	1.63
R	0.082
R_w	0.090

as eluant. A single orange band of **1** eluted (106 mg, 20% yield based on $Fe_2(\mu\text{-}Se_2)(CO)_6$). **1**: IR ($\nu$(CO), cm^{-1}) 2078 (w), 2051 (s), 2039 (vs), 2004 (w), 1990 (vs); ^{1}H NMR δ 0.96 (t, J = 7.2 Hz) (C*H*$_3$), 1.46 (m, J = 7.5 Hz) (C*H*$_2$), 1.73 (m, J = 7.5 Hz) (C*H*$_2$), 2.66 (t, J = 7.5 Hz) (Se−C*H*$_2$); ^{13}C (^{1}H decoupled) NMR δ 13.6 (s) (*C*H$_3$), 22.9 (s) (*C*H$_2$), 31.4 (s) (*C*H$_2$), 34.4 (s) (*C*H$_2$), 208.6, 209.2 (*C*O); ^{77}Se NMR δ 316.2 (s) (μ_4-*Se*), 170.7 (m) (*Se*-CH$_2$). Mp: 94−96 °C. Anal. Calcd (found) for $C_{20}H_{18}Fe_4O_{12}Se_3$: C, 26.4 (26.8); H, 1.99 (2.12).

Crystal Structure Determination of 1. An orange platelike crystal of the title compound was mounted on a Siemens R3m/V diffractometer under a low-temperature nitrogen stream. Crystal structure and refinement details are given in Table 1. The structure was solved by the heavy-atom method and subsequent difference Fourier syntheses using the SHELXTL-Plus package.[8] Two discrete molecules were found in an independent unit. Scattering factors, as well as anomalous dispersion corrections for Fe and Se atoms, were taken from ref 9. Full-matrix refinements were performed. Fe and Se atoms were anisotropically refined, while C and O atoms were treated isotropically. H atoms were placed at geometrically idealized positions. The weight had the form $w = [\sigma^2(F_o) + 0.001(F_o)^2]^{-1}$. Final cycles of refinement converged at $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.082$ and $R_w = [\Sigma w(||F_o| - |F_c|)^2|/\Sigma w(F_o)^2]^{1/2} = 0.090$ for 1693 observed reflections ($F > 6.0\ \sigma(F)$). The maximum and minimum residuals found on the final ΔF map were 1.45 and −1.01 e/Å^3, respectively.

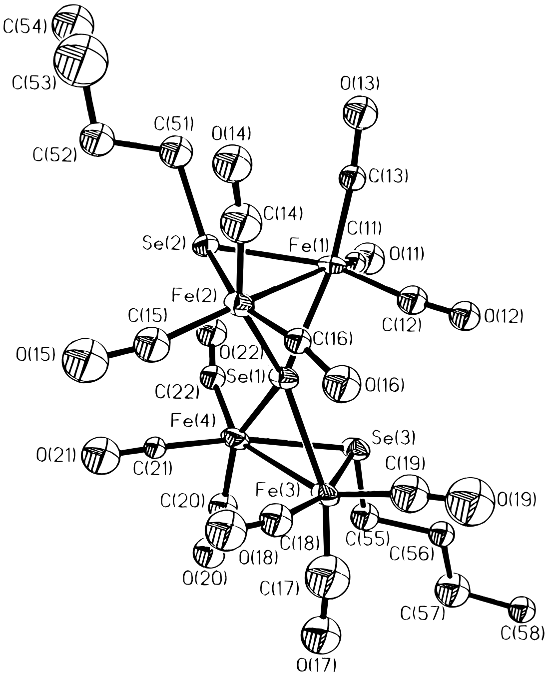

Figure 1. ORTEP drawing of the molecular structure of **1** with thermal ellipsoids drawn at 50% probability. Selected bond distances (Å) and bond angles (deg) for one of the molecules of **1**: Fe(1)−Se(1), 2.373(10); Fe(3)−Se(1), 2.371(10); Fe(1)−Se(2), 2.410(10); Fe(3)−Se(3), 2.416(11); Fe(2)−Se(2), 2.386(11); Fe(2)−Se(1), 2.349(10); Fe(4)−Se(1), 2.322(11); Fe(4)−Se(3), 2.426(10); Fe(1)−Fe(2), 2.618(12); Fe(3)−Fe(4), 2.616(12); Fe(1)−Se(1)−Fe(2), 67.3(3); Fe(3)−Se(1)−Fe(4), 67.7(3); Fe(1)−Se(2)−Fe(2), 66.2(3); Fe(3)−Se(3)−Fe(4), 65.4(3); Fe(1)−Se(1)−Fe(3), 138.6(4); Fe(2)−Se(1)−Fe(4), 135.8(4).

Results and Discussion

Adding 1,3-dibromopropane to a solution containing *n*-BuLi and $Fe_2(\mu\text{-}Se_2)(CO)_6$ and stirring at room temperature yielded a single isolable product, identified as $[(\mu\text{-}BuSe)Fe_2(CO)_6]_2(\mu_4\text{-}Se)$ (**1**; Scheme 1). Trace amounts of at least two other compounds were also observed, but these could not be isolated in sufficient amounts for characterization. Compound **1** was characterized by IR and ^{1}H, ^{13}C, and ^{77}Se NMR spectroscopy. The IR spectrum showed the presence of only terminally bonded carbonyl groups. ^{1}H and ^{13}C NMR spectra confirmed the presence of an *n*-Bu group, and the proton-coupled ^{77}Se NMR spectrum showed two signals, a singlet at lower field assignable to the μ_4-Se atom and a multiplet for the μ_3-Se atoms which are bonded to the *n*-Bu groups. Elemental analysis confirmed the molecular formula of **1**.

Dark red, air-stable crystals of **1** were grown from CH_2Cl_2/hexane solution at −4 °C, and an X-ray analysis was undertaken. An ORTEP diagram of the molecular structure of **1** is shown in Figure 1, together with the selected bond lengths and bond angles. The molecule consists of two identical $[(\mu\text{-}BuSe)Fe_2(CO)_6]$ moieties joined to a unique selenium atom. In the cluster core, the unique selenium is situated at the center of a distorted tetrahedron with four iron atoms at its apices. The coordination polyhedron around the iron is a distorted tetragonal bipyramid with two carbonyls and two selenium atoms occupying the equatorial positions and the other carbonyl and iron atom at the axial

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positions. The geometry of the μ_4-Se ligand here can be compared with that of μ_4-S found in [(μ-EtS)$Fe_2(CO)_6$]$_2$(μ_4-S),[6] [(μ_2-SMe)$Fe_2(CO)_6$]$_2$(μ_4-S),[10] μ_4-Sn in [$Fe_2(CO)_8$(μ_2-Sn(CH_3)$_2$]$_2$(μ_4-Sn),[11] μ_4-As in [Co_4(η^5-C_5H_5)$_4$(CO)$_4$(μ_4-As)]$^+$,[12] μ_4-CO in [Me_3NCH_2Ph][$Fe_4(CO)_{12}H$(μ_4-CO)],[13] and μ_4-Sb in [$Fe_2(CO)_8$(μ_4-Sb)]$_2$$Fe_2(CO)_6$.[14]

The formation of **1** is analogous to that of several tetranuclear complexes of general formula [$RSFe_2(CO)_6$]$_2$S, obtained from the reaction of Grignard reagent/$Fe_2(CO)_6$(μ-S_2)-derived monoanion with di-acid chlorides.[6] Although several face-capping, μ_4-Se complexes have been reported,[15] the six-electron-donor, tetrahedrally coordinated μ_4-Se in **1** is new. In $Fe_2Ru_3Se_2(CO)_{17}$, one of the Se ligands is reported to adopt tetrahedral coordination, though its structure has not been established by crystallographic methods.[16]

Assuming that the μ_4-Se is a 6-electron-donor ligand, and that the μ_3-Se is a 4-electron ligand, compound **1** is electron precise according to the 18-electron rule. Overall, the formation of **1** involves the abstraction of one Se atom by the dibromopropane. With 1,2-dibromoethane or with 1,4-dibromobutane, although the reaction produced numerous products, **1** was not observed.[17] It is possible that 1,3-dibromopropane reacts in an intramolecular fashion to remove one Se atom. Further studies are currently in progress to establish whether a cyclic intermediate is necessary for the formation of **1**.

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Supporting Information Available: Tables of all bond lengths and angles, fractional atomic coordinates, and isotropic and anisotropic thermal parameters (7 pages). Ordering information is given on any current masthead page.

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