Inorganic Quadricyclanes: Synthesis and Characterization of Novel Sulfur- and Selenium-Bridged Mixed Cr/Fe Clusters, $CrFe_2(CO)_{10}E_4$ (E = S, Se). Crystal Structure of $CrFe_2(CO)_{10}Se_4$

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Summary: The new clusters $CrFe_2(CO)_{10}E_4$ (E = S, ***1****; E = Se,* ***2****) have been isolated from the room-temperature reactions of $Fe_2(CO)_6(\mu\text{-}E_2)$ and $Cr(CO)_5(THF)$, and the structure of $CrFe_2(CO)_{10}Se_4$ has been established by single-crystal X-ray diffraction methods.*

Introduction

Clusters with unique structural features and unusual reactivities have been obtained by using chalcogen atoms as bridging ligands.[1] Chalcogen ligands display a wide variety of bonding modes when these are incorporated in transition metal carbonyl cluster frameworks. The compounds $Fe_2(CO)_6(\mu\text{-}E_2)$ (E = S, Se, Te) have been used as convenient starting materials for several cluster growth reactions.[2] Depending on which chalcogen atom is present and the nature of the adding metal unit, several different types of cluster core geometries are observed (Figure 1). For instance, CpCo(CO) and CpRh(CO) groups add to $Fe_2(CO)_6(\mu\text{-}Te_2)$, to give clusters of structure types A−C whereas they add to $Fe_2(CO)_6(\mu\text{-}S_2)$ or $Fe_2(CO)_6(\mu\text{-}Se_2)$ to form only the closed structure type B or C.[3] The selenium-bridged compound $Fe_2(CO)_6(\mu\text{-}Se_2)$ readily adds molybdenum and tungsten carbonyl groups to form $Fe_2M(CO)_{10}(\mu_3\text{-}Se)_2$ (M = Mo, W) (structure type C), but the tellurium analogue, $Fe_2(CO)_6(\mu\text{-}Te_2)$, adds only the tungsten carbonyl unit to form $Fe_2W(CO)_{10}(\mu_3\text{-}Te)_2$.[4] Some clusters possessing type B structures readily add metal carbonyl groups to form clusters with octahedral core geometries (structure type D).[2a,5] Recently, easy preparative routes to the mixed-chalcogenide compounds $Fe_2(CO)_6(\mu\text{-}EE')$ (E ≠ E′) have provided opportunity to investigate addition of organic and inorganic moieties across the very reactive E−E′ bonds.[6] An “hourglass” cluster geometry (structure type E) is observed in the formation of $[\{Fe_2(CO)_6(\mu_3\text{-}Se)(\mu_3\text{-}Te)\}_2Mo(CO)_2]$ from the reaction of $Fe_2(CO)_6(\mu\text{-}SeTe)$ with $Mo(CO)_5(THF)$.[7] In continuation of our investigations on the influence of different metal atoms on the structures and reactivity of chalcogen-stabilized mixed-metal clusters, we report here the synthesis and characterization of S- and Se-stabilized mixed Cr/Fe carbonyl clusters possessing an unusual Cr/Fe/Se core structure.

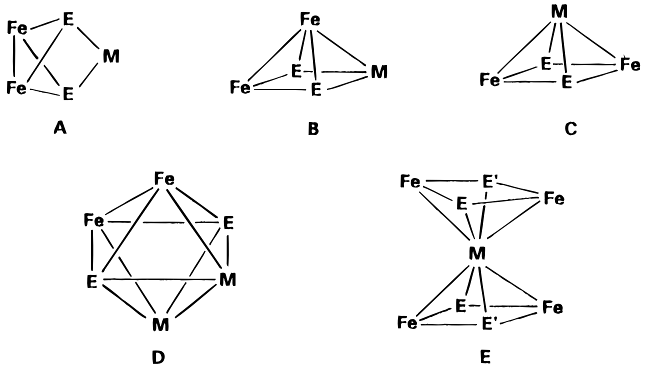

Figure 1. Core geometries of clusters constructed from $Fe_2(CO)_6(\mu\text{-}E_2)$ and $Fe_2(CO)_6(\mu\text{-}EE')$.

Experimental Section

General Procedures. All reactions and manipulations were performed using standard Schlenk techniques under an atmosphere of prepurified dry argon. Solvents were purified, dried, and distilled under an argon or nitrogen atmosphere prior to use. Infrared spectra were recorded on a Nicolet Impact 400 FT spectrometer as hexane solutions in 0.1 mm path length NaCl cells. ^{77}Se NMR spectra were obtained on a Varian VXR-300S spectrometer in $CDCl_3$. The ^{77}Se NMR

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Table 1. Crystal Data and Structure Refinement for 2

formula	$C_{10}CrFe_2O_{10}Se_4$
fw	759.64
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	6.596(1)
b, Å	17.500(3)
c, Å	17.090(3)
β, deg	96.74(1)
V, Å^3	1959.2(6)
Z	4
D(calc), g cm^{-3}	2.576
μ(Mo Kα), cm^{-1}	94.82
F(000)	1408
θ range, deg	2.33−22.50
T, K	233(2)
reflcns collcd	3608
indepdt reflcns	2560
data/restraints/params	2558/0/245
goodness-of-fit on F^2	0.995
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0323$, w$R2 = 0.0689$
R indices (all data)	$R1 = 0.0486$, w$R2 = 0.0730$
largest diff peak and hole, e Å^{-3}	0.694 and −0.538
extinction coeff	0.001 08(13)

measurement was made at an operating frequency of 57.23 MHz using 90° pulses with 1.0 s delay and 1.0 s acquisition time and referenced to Me_2Se ($\delta = 0$). Elemental analyses were performed on a Carlo-Erba automatic analyzer. $Fe_2(CO)_6(\mu\text{-}S_2)$[3b] and $Fe_2(CO)_6(\mu\text{-}Se_2)$[4] were prepared by established procedures. $Cr(CO)_6$ was purchased from Aldrich Chemical Co. and used as such. Photochemical reactions were carried out in a water-cooled double-walled quartz vessel having a 125 W immersion type mercury lamp manufactured by Applied Photophysics Ltd.

Preparation of $CrFe_2(CO)_{10}S_4$ (1) and $CrFe_2(CO)_{10}Se_4$ (2). A THF solution (120 mL) of $Cr(CO)_6$ (0.16 g, 0.73 mmol, for **1**; 0.187 g, 0.85 mmol, for **2**) was irradiated with 366 nm UV light for 10 min under a constant argon purge. The yellow-orange solution of $Cr(CO)_5(THF)$ was added to a hexane solution (50 mL) containing $Fe_2(CO)_6(\mu\text{-}S_2)$ (0.5 g, 1.45 mmol) or $Fe_2(CO)_6(\mu\text{-}Se_2)$ (0.75 g, 1.71 mmol). The reaction mixture was stirred at room temperature for 2 h. The solvent was removed *in vacuo*, and the residue was dissolved in hexane and subjected to chromatographic workup on a silica gel column. Using hexane as eluant, unreacted $Fe_2(CO)_6(\mu\text{-}E_2)$ (50%) eluted first followed by a maroon band of $CrFe_2(CO)_{10}E_4$ (E = S, **1**, 0.09 g, 22% based on $Fe_2(CO)_6(\mu\text{-}S_2)$ consumed; E = Se, **2**, 0.19 g, 29% based on $Fe_2(CO)_6(\mu\text{-}Se_2)$ consumed). **1**: IR (ν(CO), cm^{-1}) 2100 (w), 2080 (vs), 2043 (s), 2035 (vs), 2013 (m), 1957 (s), 1943 (s), 1932 (m); mp 103−105 °C (dec). Anal. Calcd (found) for $C_{10}O_{10}Fe_2CrS_4$: C, 21.0 (21.3). **2**: IR (ν(CO), cm^{-1}) 2090 (w), 2070 (vs), 2033 (s), 2025 (vs), 2011 (m), 1958 (s), 1946 (s), 1936 (m); ^{77}Se NMR δ 249.7 (s, Se−Cr), 880.2 (s, Se−Fe) ppm; mp 120−122 °C (dec). Anal. Calcd (found) for $C_{10}O_{10}Fe_2CrSe_4$: C, 15.8 (16.0).

Crystal Structure Determination of $CrFe_2(CO)_{10}Se_4$ (2). A single crystal of approximate dimensions 0.45 × 0.40 × 0.35 mm^3 was mounted on a thin glass fiber with epoxy. Crystal data and structure refinement details are given in Table 1. The data were measured on a Siemens P4 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Semi-empirical absorption corrections were applied. The structure was solved by direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. Final cycles of refinement converged at $R1 = \sum|(F_o - F_c)|/\sum(F_o) = 0.0323$ and $wR2 = \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2} = 0.0689$ for 1958 observed reflections [$I > 2\sigma(I)$]. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors are contained in the SHELXTL (5.3) program library (Sheldrick, G. M. Siemens XRD, Madison, WI). Atomic coordinates are given in the Supporting Information; selected bond lengths and bond angles are listed in Table 2.

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

Bond Lengths			
Se(1)−Fe(1)	2.442(13)	Se(2)−Se(4)	2.362(11)
Se(1)−Fe(2)	2.411(13)	Se(3)−Cr	2.411(2)
Se(1)−Se(3)	2.362(11)	Se(3)−Fe(2)	2.435(12)
Se(2)−Fe(1)	2.410(13)	Se(4)−Cr	2.429(14)
Se(2)−Fe(2)	2.433(12)	Se(4)−Fe(1)	2.440(13)
Bond Angles			
Fe(2)−Se(1)−Fe(1)	95.3(4)	Se(2)−Se(4)−Fe(1)	60.2(4)
Se(3)−Se(1)−Fe(1)	108.7(4)	Cr−Se(4)−Fe(1)	118.7(5)
Se(3)−Se(1)−Fe(2)	61.3(4)	Se(2)−Se(4)−Cr	111.3(5)
Fe(1)−Se(2)−Fe(2)	95.6(4)	Se(2)−Fe(1)−Se(1)	83.8(4)
Se(4)−Se(2)−Fe(1)	61.5(4)	Se(4)−Fe(1)−Se(1)	95.9(4)
Se(4)−Se(2)−Fe(2)	109.8(4)	Se(2)−Fe(1)−Se(4)	58.3(4)
Se(1)−Se(3)−Fe(2)	60.3(3)	Se(1)−Fe(2)−Se(2)	84.0(4)
Cr−Se(3)-Fe(2)	120.2(5)	Se(2)−Fe(2)−Se(3)	95.2(4)
Se(1)−Se(3)−Cr	111.9(5)	Se(3)−Cr−Se(4)	91.4(5)

Results and Discussion

When a THF solution containing $Cr(CO)_5(THF)$ was added to a hexane solution of $Fe_2(CO)_6(\mu\text{-}S_2)$ or $Fe_2(CO)_6(\mu\text{-}Se_2)$, and the mixture was stirred for 2 h at room temperature, a single product was isolated in each case and characterized as $CrFe_2(CO)_{10}E_4$ (E = S, **1**; E = Se, **2**). The infrared spectra of **1** and **2** display identical but complex carbonyl stretching pattern indicating the presence of only terminally bonded carbonyl groups. The stretching frequencies of **1** are 2−10 cm^{-1} greater than the frequencies of the corresponding bands in the spectrum of **2**. The ^{77}Se NMR spectrum of **2** shows two signals at δ 249.7 and 880.2 ppm, indicating the presence of two types of selenium atoms in the molecule. On the basis of comparison with the ^{77}Se NMR spectra of previously reported compounds $Fe_2W(CO)_{10}(\mu_3\text{-}Se)_2$ (δ 372.2 ppm), $Fe_2W(CO)_{10}(\mu_3\text{-}S)(\mu_3\text{-}Se)$ (δ 301.9 ppm), and $Fe_2W(CO)_{10}(\mu_3\text{-}Se)(\mu_3\text{-}Te)$ (δ 442.8 ppm) and $Fe_3(CO)_9(\mu_3\text{-}Se)_2$ (δ 778.5 ppm), $Fe_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}Se)$ (δ 679.7 ppm), and $Fe_3(CO)_9(\mu_3\text{-}Se)(\mu_3\text{-}Te)$ (δ 867.1 ppm),[8] the upfield signal can be assigned to selenium atoms attached with chromium atom and the downfield signal to the selenium atoms attached with iron atoms arranged in the four-membered base of the molecule.

Black block crystals of **2** were obtained from its hexane and dichloromethane solvent mixture by slow evaporation of the solvents at −5 °C, and its molecular structure was established by single-crystal X-ray methods (Figure 2). Its core structure can be regarded as being an inorganic analogue of the well-known organic compound quadricyclane, fitting well into the concept of isolobal analogy.[9] The four-membered base of **2** consists of an alternate arrangement of two iron and two selenium atoms. Two opposite Fe−Se edges are bridged by a selenium atom each, both of which are also bonded to a chromium atom. The three selenium atoms and the three terminal carbonyl groups bonded to each iron atom give it a distorted octahedral coordination. Similarly, the two selenium atoms and the four terminal carbonyl groups bonded to the chromium atom results in a distorted octahedral coordination around it. The

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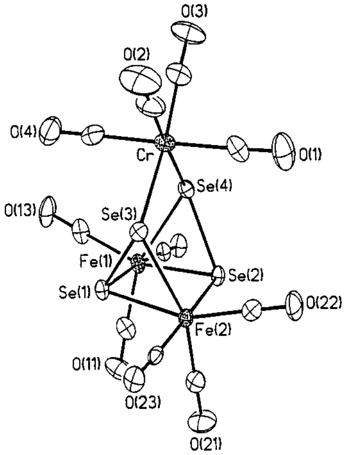

Figure 2. ORTEP diagram of the molecular structure of **2**.

two Cr−Se bond distances are almost equal (2.411(2) and 2.429(14) Å) and shorter than the Cr−Se single bond distances of 2.495(2) and 2.555(2) Å in CpFe(CO)$_2$(μ-Se$_2$)Cr(CO)$_2$Cp,[10] in which a CpFe(CO)$_2$ group is attached to one of the Se atoms of the CrSe$_2$ triangular arrangement. It is also shorter than the Cr−Se distance of 2.530 Å (av) in CpCr(CO)$_2$Se$_2$,[11] which features a CrSe$_2$ triangular core, but longer than the Cr−Se triple bond distances of 2.206(1) and 2.211(1) Å in [CpCr(CO)$_2$]$_2$Se.[12] The Se−Se distance, 2.362 Å (av), is longer than that of Se═Se double bond (2.19 Å).[13] It is also slightly beyond the range reported for μ-η^2-Se$_2$ ligands in other complexes ([W$_2$Cl$_8$Se(Se$_2$)]$^{2-}$, 2.255(8) Å; [(η^5-CH$_3$C$_5$H$_4$)$_2$V$_2$Se$_5$], 2.290(2), 2.295(2) Å; [Fe$_2$(CO)$_6$(μ-Se$_2$)], 2.293(2) Å; [FeW(Se$_2$)(CO)$_8$]$^{2+}$, 2.281(3) Å)[14] but is close to the normal Se−Se single bond distance of 2.336 Å [13] and the average Se−Se bond distance of 2.318 Å observed in [Fe$_3$(Se$_2$)$_2$(CO)$_{10}$][SbF$_6$]$_2$.[15] The two three-membered rings in **2**, Fe(1)−Se(2)−Se(4) and Fe(2)−Se(1)−Se(3), are almost equilateral with the three angles in each triangle being within the range 58−61° and the three edges in each triangle being within the range 2.36−2.44 Å. Assuming that each μ-E$_2$ group in these clusters acts as a 6 e$^-$ donor, the metal atoms achieve the noble gas configuration.

Even when equimolar amounts of Fe$_2$(CO)$_6$(μ-E$_2$) and Cr(CO)$_5$(THF) were used, or longer reaction times were employed, considerable amounts of Fe$_2$(CO)$_6$(μ-E$_2$) were recovered from the reaction mixture and the yields of **1** and **2** formed were low, optimum yields being obtained when a 2:1 ratio of Fe$_2$(CO)$_6$(μ-E$_2$) and Cr(CO)$_5$(THF) was used. Although the exact mechanism of formation of **1** and **2** is not established as yet, it may be visualized as involving the formal loss of one Fe(CO)$_3$ group each from two Fe$_2$(CO)$_6$(μ-E$_2$) molecules and the addition of two Fe(CO)$_3$E$_2$ groups thus formed to one Cr(CO)$_4$ group. Formally, each Fe$_2$(CO)$_6$(μ-E$_2$) molecule undergoes one Fe−Fe and two Fe−E bond scissions and there is an overall formation of four new bonds, two Cr−E and two Fe−E bonds. The structure described in this paper is unique to the case of Cr carbonyl addition; the W and Mo carbonyl groups add to Fe$_2$S$_2$(CO)$_6$ or Fe$_2$Se$_2$(CO)$_6$ to form different cluster cores.[4,16] Further investigations are currently in progress to explore the reactivity of these compounds, in particular of the two three-membered FeE$_2$ rings present in the molecules.

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Supporting Information Available: Tables of complete bond lengths and angles, atomic coordinates, and isotropic and anisotropic thermal parameters (5 pages). Ordering information is given on any current masthead page.

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