Inorg. Chem. **1995**, *34*, 5088−5090

Transformations of Selenium−Iron Carbonylates in Hieber's Synthesis: Isolation of a Novel Intermediate Complex, $[PhCH_2NMe_3]_2[Se_6Fe_6(CO)_{12}]$

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Received February 27, 1995

The first hybrid main group−transition metal element carbonyl clusters were reported by Hieber and co-workers in the 1950s.[1] This methodology was general for the synthesis of heavier main group element containing iron carbonyl clusters utilizing a wide range of main group compounds with the anionic species $[HFe(CO)_4]^-$ and $[Fe(CO)_4]^{2-}$. In the case of iron chalcogenides, the useful cluster-building dichalcogen compounds $E_2Fe_2(CO)_6$ and $E_2Fe_3(CO)_9$ (E = Se, Te) can be obtained from the reaction of the oxyanion of selenium(IV) or tellurium(IV) with $Fe(CO)_5$/KOH in methanol solution.[1c,2,3] The recent study reveals that a number of interesting anionic species are isolated or observed as intermediates from the modified Hieber's preparations.[4−6] However, the mechanistic relationships of these anionic species are not well-known due to the complex transformations involved. To understand the mechanistic features in the Se−Fe carbonyl system, we investigated the details of the reaction of K_2SeO_3 and $Fe(CO)_5$/KOH. In this study, we successfully isolated a novel Se−Fe carbonylate, $[Se_6Fe_6(CO)_{12}]^{2-}$ (**I**), as one intermediate in the Hieber's synthesis, and the structural transformations of other anionic intermediate species observed in this system are as well demonstrated. The results account for the formation of $Se_2Fe_2(CO)_6$ and $Se_2Fe_3(CO)_9$ in the Hieber's synthesis and aid in elucidating the relevance of the Se−Fe carbonyl complexes found in this system.

Experimental Section

All reactions were performed under an atmosphere of pure nitrogen by using standard Schlenk line techniques.[7] Solvents were purified, dried, and distilled under nitrogen prior to use. K_2SeO_3 (Strem), $Fe(CO)_5$ (Aldrich), and $[PhCH_2NMe_3]Cl$ (Aldrich) were used as received. Infrared spectra were recorded on a Jasco 700 IR spectrometer using CaF_2 liquid cells. All NMR spectra were taken on a Bruker AC-300 instrument. Elemental analyses were performed at the NSC Regional Instrumentation Center at National Taiwan University, Taipei, Taiwan.

Table 1. Selected Crystallographic Data for $[PhCH_2NMe_3]_2[Se_6Fe_6(CO)_{12}]$ ($[PhCH_2NMe_3]_2$[**I**])

empirical formula	$Se_6Fe_6C_{32}H_{32}O_{12}N_2$	V, Å^3	1175.3(5)
		Z	1
fw	1445.44	D(calc), Mg m^{-3}	2.042
crystal system	triclinic	abs coeff, mm^{-1}	6.46
space group	$P\bar{1}$	diffractometer	Nonius CAD-4
a, Å	9.687(2)		
b, Å	10.540(3)	λ(Mo Kα), Å	0.709 30
c, Å	12.936(3)	temp, °C	25
α, Å	103.47(2)	T_{min}/T_{max}	0.31/1.00
β, deg	95.57(2)	residuals: R; R_w	0.036; 0.027
γ, deg	111.00(2)		

[a] The functions minimized during least-squares cycles were $R = \Sigma(F_o - F_c)/\Sigma F_o$ and $R_w = [\Sigma w(F_o - F_c)^2/\Sigma w(F_o)^2]^{1/2}$.

Reaction of K_2SeO_3 with $Fe(CO)_5$/KOH/MeOH. 1. Direct Synthesis of $[PhCH_2NMe_3]_2[Se_6Fe_6(CO)_{12}]$ ($[PhCH_2NMe_3]_2$[I]). To a solution prepared from 0.40 mL (3.00 mmol) of $Fe(CO)_5$ and 0.40 g (10 mmol) of KOH in MeOH was added 0.62 g (3.00 mmol) of K_2SeO_3 in 10 mL of deionized H_2O. After being stirred for 5 h at room temperature, the solution was filtered and an aqueous solution of 0.70 g (3.77 mmol) of $[PhCH_2NMe_3]Cl$ added dropwise, precipitating the product. This crude product was collected by filtration, washed with H_2O, and dried under vacuum. Recrystallization from THF/ether system gave 0.68 g (0.47 mmol, 94% based on Se) of $[PhCH_2NMe_3]_2[Se_6Fe_6(CO)_{12}]$ ($[PhCH_2NMe_3]_2$[**I**]). IR (ν_{CO}, MeCN) for $[PhCH_2NMe_3]_2$[**I**]: 2035 s, 2006 s, 1961 m, br cm^{-1}. ^{1}H NMR (DMSO-d_6, ppm): 7.52 (s, 5H), 4.50 (s, 2H), 3.00 (s, 9H). ^{13}C NMR (DMSO-d_6, ppm): 219.5 (12CO), 132.6, 130.2, 128.8, 128.2 (Ph), 67.9 (CH_2), 51.7 (CH_3). Anal. Calcd (found) for $[PhCH_2NMe_3]_2$[**I**]: C, 26.59 (27.15); H, 2.23 (2.11); N, 1.94 (1.54). Crystals suitable for X-ray diffraction were grown from THF/MeOH solution.

2. Observation of Other Intermediates. To a solution prepared from 0.40 mL (3.00 mmol) of $Fe(CO)_5$ and 0.40 g (10 mmol) of KOH in 10 mL of MeOH was added 0.62 g (3.00 mmol) of *solid* K_2SeO_3. After the mixture was stirred in MeOH for 30 min, the first observed species was shown to be $[Se\{Fe(CO)_4\}_3]^{2-}$ (IR (ν_{CO}, MeOH) 1992 s, 1919 s, br cm^{-1}; lit.[6] IR for $[Te\{Fe(CO)_4\}_3]^{2-}$ (ν_{CO}, MeOH): 2024 w, 1992 s, 1920 sh, 1908 vs); then continued stirring for 5 h formed the previously characterized cluster $[SeFe_3(CO)_9]^{2-}$ (isolated as the $[PPN]^+$ salt) (IR (ν_{CO}, MeCN) 1996 m, 1928 vs, 1901 s, 1873 m cm^{-1}; lit.[5] IR (ν_{CO}, CH_2Cl_2) 1996 m, 1928 vs, 1901 s, 1875 m cm^{-1}) and an as yet unidentified reactive species proposed to be $[(Se_2)_2Fe_2(CO)_6]^{2-}$, which can be isolated as the $[PPN]^+$ salt by using THF/hexane (4/1, v/v) as the extraction solvent (IR (ν_{CO}, CH_2Cl_2) 2034 m, 2014 m, 1992 vs, 1951 s cm^{-1}; lit.[8] IR for $Na_2[(Te_2)_2Fe_2(CO)_6]$ (ν_{CO}, THF) 2025 m, 2018m, 1984 vs, 1945 s cm^{-1}). Following the same procedure, prolonged stirring of the reaction solution led to formation of $[I]^{2-}$ in about the same yield as obtained from the direct path mentioned above.

Acidification of $[PhCH_2NMe_3]_2$[I]. To a solution of 0.63 g (0.43 mmol) of $[PhCH_2NMe_3]_2$[**I**] in 10 mL of THF and 5 mL of MeOH was added dropwise 12 mL of 4 M HCl(aq) in an ice/water bath. The mixed solution was allowed to stir at room temperature for 1 h, the solution was filtered, and the solvent was removed under vacuum. The residue was then extracted into 20 mL of CH_2Cl_2 to give 0.17 g (0.38 mmol) of $Se_2Fe_2(CO)_6$ (44% based on the $Se_2Fe_2(CO)_6$ units present in $[PhCH_2NMe_3]_2$[**I**]).

X-ray Structural Characterization of $[PhCH_2NMe_3]_2$[I]. A summary of selected crystallographic data is given in Table 1. Data collection was carried out on a Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation at 25 °C. Atomic scattering

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Table 2. Selected Atomic Coordinates and Isotropic Displacement Coefficients for $[PhCH_2NMe_3]_2[Se_6Fe_6(CO)_{12}]$ ($[PhCH_2NMe_3]_2$[**I**])

	x	*y*	*z*	B_{iso}, Å^2
Se(1)	0.67592(6)	0.81065(6)	0.21721(5)	3.63(3)
Se(2)	0.65314(6)	0.51299(6)	0.26731(5)	3.57(3)
Se(3)	0.31460(6)	0.47390(7)	0.04137(6)	4.06(4)
Fe(1)	0.85962(8)	0.74173(9)	0.30288(7)	3.33(4)
Fe(2)	0.61334(9)	0.71758(9)	0.36769(8)	3.60(5)
Fe(3)	0.57285(8)	0.56756(9)	0.10628(7)	3.45(5)
C(1)	0.9625(7)	0.7080(7)	0.2012(5)	4.4(3)
C(2)	0.9669(7)	0.9268(7)	0.3558(5)	4.4(4)
C(3)	0.9500(7)	0.6939(7)	0.4051(6)	4.3(4)
C(4)	0.6532(7)	0.8950(8)	0.4421(6)	4.8(4)
C(5)	0.6532(7)	0.6692(7)	0.4865(6)	4.6(4)
C(6)	0.4109(8)	0.6465(7)	0.3457(6)	5.0(4)
O(1)	1.0346(5)	0.6858(5)	0.1397(4)	7.1(3)
O(2)	1.0356(5)	1.0465(5)	0.3880(4)	6.5(3)
O(3)	1.0089(5)	0.6633(6)	0.4694(4)	6.9(3)
O(4)	0.6804(6)	1.0093(5)	0.4894(5)	7.5(4)
O(5)	0.6800(6)	0.6415(5)	0.5646(4)	6.8(4)
O(6)	0.2815(5)	0.6013(6)	0.3314(5)	7.8(4)

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $[PhCH_2NMe_3]_2[Se_6Fe_6(CO)_{12}]$ ($[PhCH_2NMe_3]_2$[**I**])

	(A) Distances		
Se(1)−Se(2)	3.285(1)	Se(1)−Fe(1)	2.417(1)
Se(1)−Fe(2)	2.411(1)	Se(1)−Fe(3)	2.408(1)
Se(2)−Fe(1)	2.424(1)	Se(2)−Fe(2)	2.424(1)
Se(2)−Fe(3)	2.416(1)	Se(3)−Se(3)′	3.736(1)
Se(3)−Fe(3)	2.318(1)	Se(3)−Fe(3)′	2.321(1)
Fe(1)−Fe(2)	2.552(1)	Fe(3)−Se(3)′	2.321(1)
Fe(3)−Fe(3)′	2.750(2)		
	Carbonyl Range		
C−O	1.134(8)−1.149(8)		
	(B) Angles		
Se(1)−Fe(3)−Se(2)	85.84(4)	Se(1)−Fe(3)−Se(3)	114.57(5)
Se(2)−Fe(3)−Se(3)′	118.24(4)	Se(3)−Fe(3)−Se(3)′	107.28(5)
Fe(1)−Se(1)−Fe(2)	63.83(3)	Fe(1)−Se(2)−Fe(2)	63.54(4)
Fe(3)−Se(3)−Fe(3)′	72.72(4)	Fe(3)′−Fe(3)−Se(3)′	53.60(3)

factors were taken from ref 9, and data reduction and structural refinement were performed using the NRCC-SDP-VAX packages.[10]

A brown crystal of $[PhCH_2NMe_3]_2$[**I**] with dimensions 0.20 × 0.40 × 0.40 mm^3 was selected for X-ray analysis. The crystal was mounted with epoxy on the tip of a glass fiber. Cell parameters were obtained from 25 reflections with 2θ angles in the range 22.76−32.54°. Systematic absences and intensity statistics indicated that the space group is $P\bar{1}$. A total of 5379 unique reflections were collected, and the data were corrected for decay and absorption.[10] A total of 3413 reflections with $I > 2.5\sigma(I)$ were used in the refinement. The structure was solved by the heavy-atom method and refined by least-squares cycles. All the non-hydrogen atoms were refined with anisotropic temperature factors. Full-matrix least-squares refinement led to convergence with $R = 3.6\%$ and $R_w = 2.7\%$.

Selected atomic coordinates and isotropic displacement coefficients are given in Table 2, and selected bond distances and angles are listed in Table 3. Additional crystallographic data are available as Supporting Information.

Results and Discussion

An aqueous K_2SeO_3 solution treated with 1 equiv of $Fe(CO)_5$/KOH in methanol immediately forms brown solutions whose infrared data indicate the existence of an anionic carbonyl species. The unstable species decomposes in solution to form $Se_2Fe_2(CO)_6$ and can be isolated as the $[PhCH_2NMe_3]^+$ salt ($[PhCH_2NMe_3]_2$[**I**]). On the basis of analyses, spectroscopic data, and X-ray analysis, $[PhCH_2NMe_3]_2$[**I**] is shown to be $[PhCH_2NMe_3]_2[Se_6Fe_6(CO)_{12}]$. As shown in Figure 1, the core geometry of **I** can be viewed as two $Se_2Fe_2(CO)_6$ clusters asymmetrically attached each to the two Fe atoms of the central anion $[Se_2Fe_2]^{2-}$, which lies on a crystallographic inversion center, and Se(3) and Se(3)′ are nonbonded ($d_{Se-Se} = 3.736$ (1) Å).[11] The bond lengths for Se−Fe average 2.384 Å, which is close to those in other related clusters, such as $[Fe(Se_4)_2(CO)_2]^{2-}$ (2.436 Å)[12] and $[Fe_2(\mu\text{-}Se)_2(Se_5)_2]^{2-}$ (2.374 Å).[13] While the Fe(1)−Fe(2) distance of 2.552(1) Å is comparable to that found in $Se_2Fe_2(CO)_6$ (2.575(2) Å)[14] and $Se_2Fe_3(CO)_9$ (2.65 Å, average),[15] the Fe(3)⋯Fe(3)′ distance of 2.750 (2) Å, close to that (2.787 Å) found for $[Fe_2(\mu\text{-}Se)_2(Se_5)_2]^{2-}$,[13] which is somewhat long but is still within the range of significant Fe−Fe interaction.

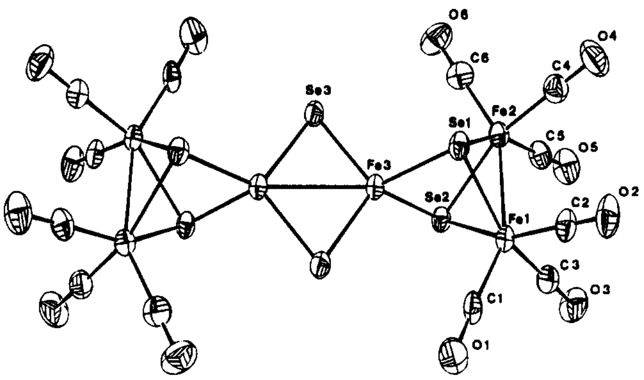

Figure 1. ORTEP diagram showing the structure and atom labeling for the dianion **I**.

The structural features of the dianion **I** are unprecedented in the iron−chalcogen carbonyl system but can be compared to the iron selenide, $[Fe_2(\mu\text{-}Se)_2(Se_5)_2]^{2-}$,[13,16] which consists of two Fe(III) centers tetrahedrally coordinated by two Se^{2-} anions and two Se_5^{2-} polyselenides. The formation of **I** arises from the oxidation of the anionic species $[Fe(CO)_4]^{2-}/[HFe(CO)_4]^-$ with the oxyanion SeO_3^{2-}. The dianion **I** is best to be viewed to contain two Fe(III) centers bridged by two Se^{2-} anions, and the coordination of each Fe(III) atom is completed by bonding to one $[Se_2Fe_2(CO)_6]^{2-}$ cluster. In this case, each selenium atom in the end butterfly is formally assigned a −II oxidation state, and each butterfly iron atom a +I state. For the iron atoms, the central iron is in a +III state whereas the butterfly iron obeys the conventional 18-electron count. These different electronic demands may be in part the cause of the instability of the dianion **I** in solution.

It is reported by Hieber and other workers[1c,2a] that a mixture of $Se_2Fe_2(CO)_6$ and $Se_2Fe_3(CO)_9$ is obtained from the reaction of SeO_3^{2-} with basic $Fe(CO)_5$ solution followed by acidification. Complex **I** is an intermediate for the formation of $Se_2Fe_2(CO)_6$, as the latter can be obtained by acidification of the dianion **I** in the methanol solution. The mechanism for the formation of $Se_2Fe_2(CO)_6$ is not clear but may involve the loss of the central Se_2Fe_2 fragment of the dianion **I** to afford $Se_2Fe_2(CO)_6$. Furthermore, we found that the reaction of an aqueous K_2SeO_3 solution with 3 equiv of $Fe(CO)_5$/KOH in methanol produced the previously characterized compound, $[SeFe_3(CO)_9]^{2-}$,[3b,5,6] and

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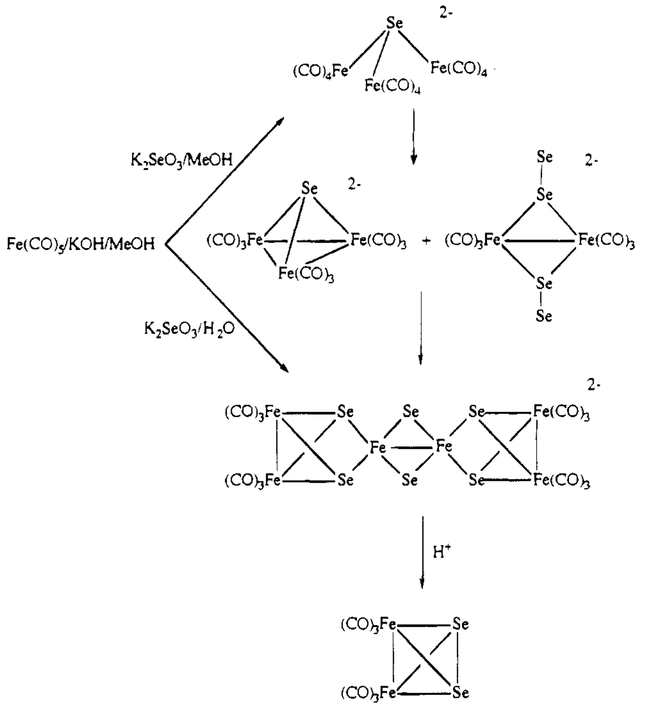
subsequent acidification with 4 M HCl(aq) afforded the major product $Se_2Fe_3(CO)_9$. Our results clearly demonstrate that the ratio of the oxidant SeO_3^{2-} to the reductant $Fe(CO)_5$/KOH is a controlling factor in determining which intermediate anion is formed in the Hieber's synthesis and $Se_2Fe_2(CO)_6$ and $Se_2Fe_3(CO)_9$ are the acidification products of these intermediates.

To probe the transformations of the anionic species in this system, we carried out a reaction by employment of solid K_2SeO_3 and 1 equiv of $Fe(CO)_5$/KOH in methanol solution. The low solubility of K_2SeO_3 in MeOH allows for a gradual increase of SeO_3^{2-} concentration, and the observation of other anionic species in this system is therefore feasible. The reaction mixture formed the open cluster $[Se\{Fe(CO)_4\}_3]^{2-}$ first,[6] which was characterized by its IR spectrum. Continued stirring the reaction mixture produced the tetrahedral complex $[SeFe_3(CO)_9]^{2-}$ and a reactive anionic species proposed to be $[(Se_2)_2Fe_2(CO)_6]^{2-}$,[17] the yields depending on the reaction time. After prolonged stirring, $Fe(CO)_5$ consumed a total amount of 1 equiv of K_2SeO_3 to form the dianion **I** as the ultimately anionic product. As illustrated, this process involves the intermediate formation of several anionic species, and the cluster aggregation in this system is evident. This unique reactivity pattern provides insight into the formation of the dianion **I** and the other anionic carbonyl species, depending on the concentration and reaction conditions.

The dianion **I** exhibits interesting chemistry in the Se–Fe carbonyl system (Scheme 1). The Se–Fe carbonyl system is obviously very rich, and this study allows for the new development of iron–selenide carbonyl chemistry and opens up an avenue to the understanding of the transformations of the anionic species in the related iron–chalcogenide carbonyl systems.

Scheme 1



Acknowledgment. Financial support from the National Science Council of the Republic of China (Grant No. NSC 84-2113-M-003-008) is gratefully acknowledged.

Supporting Information Available: Complete listings of crystallographic data, atomic positional parameters, bond distances and angles, and anisotropic thermal parameters for $[PhCH_2NMe_3]_2[\mathbf{I}]$ (5 pages). Ordering information is given on any current masthead page.

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(17) The IR absorption pattern for this compound is similar to that for the analogous complex $[(Te_2)_2Fe_2(CO)_6]^{2-}$.[8] All attempts at crystallization of this complex for further characterization were unsuccessful and resulted in formation of $Se_2Fe_2(CO)_6$ due to its reactive nature.