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SELENIUM—SELENIUM BOND REACTIONS OF μ-(DISELENIUM)BIS(TRICARBONYLIRON), AN INORGANIC MIMIC OF ORGANIC DISELENIDES

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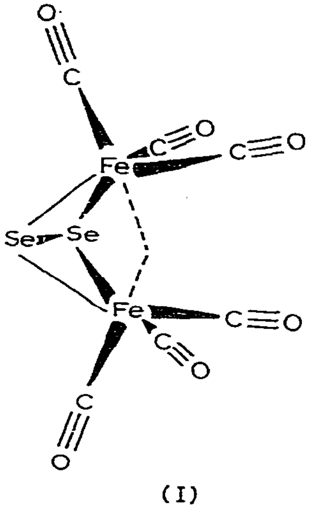
Summary

μ-(Diselenium)bis(tricarbonyliron), $(\mu\text{-}Se_2)Fe_2(CO)_6$, has been found to have reactivity typical of organic diselenides, RSeSeR. Reaction with two molar equivalents of $LiBEt_3H$ converts $(\mu\text{-}Se_2)Fe_2(CO)_6$ to the dianion, $(\mu\text{-}LiSe)_2Fe_2(CO)_6$. Organolithium reagents, RLi, cleave its Se—Se bond, giving $(\mu\text{-}LiSe)(\mu\text{-}RSe)Fe_2(CO)_6$. Low valent transition metal species, e.g., $(Ph_3P)_2Pt$, insert into the Se—Se bond. $(\mu\text{-}Se_2)Fe_2(CO)_6$ is fragmented by the action of dicobalt octacarbonyl, giving $(\mu_3\text{-}Se)FeCo_2(CO)_9$.

Introduction

μ-(Diselenium)bis(tricarbonyliron), I, was first reported in 1958 by Hieber and Gruber [1]. By analogy with μ-(dithio)bis(tricarbonyliron), whose structure had been determined by Dahl [2], and on the basis of infrared spectroscopic studies [3], it was assumed that $(\mu\text{-}Se_2)Fe_2(CO)_6$ had the structure as shown. This was confirmed in 1979 with the report of an X-ray structural investigation of this compound [4]. In spite of its novel structure, which features potentially reactive Se—Se and Fe—Fe bonds, the chemical reactivity of $(\mu\text{-}Se_2)Fe_2(CO)_6$ has been virtually unexplored, with the exception of some CO ligand substitutions [5]. During the course of the past two years we have been investigating the reactivity of $(\mu\text{-}S_2)Fe_2(CO)_6$ [6—9] and, in terms of its chemistry, have found it to be an inorganic mimic of organic disulfides. In view of the interesting $(\mu\text{-}S_2)Fe_2(CO)_6$ chemistry which our work uncovered, we initiated a similar program of investigation of the chemical reactivity of $(\mu\text{-}Se_2)Fe_2(CO)_6$. We report here the results of these studies.

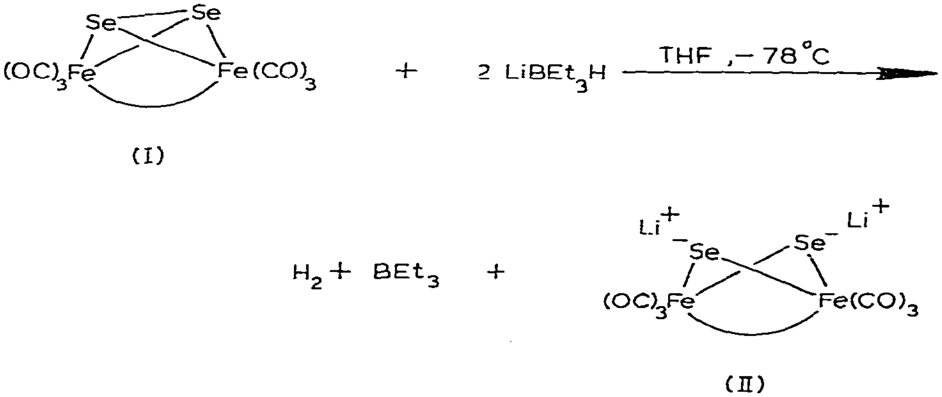


(I)

Results and discussion

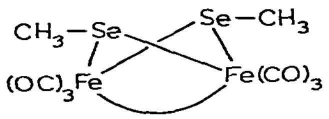
μ-(Diselenium)bis(tricarbonyliron), an air-sensitive, deep ruby-red, crystalline solid, mp 39—40.5°C, was prepared in 20% (pure) yield by the method used by Hieber and Gruber [1] for $(\mu\text{-}S_2)Fe_2(CO)_6$.

Although the Se—Se and the Fe—Fe bonds of $(\mu\text{-}Se_2)Fe_2(CO)_6$ both are potential sites for attack by lithium triethylborohydride, a reagent known to cleave both Se—Se bonds [10] and metal—metal bonds [11], this hydride reacted to give the selenium-centered dianion, II, as the sole product (eq. 1).



(1)

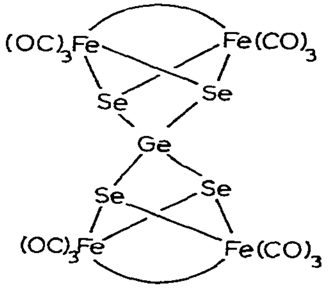
The starting complex dissolves in THF to give a red-purple solution; when dianion II has been formed, the solution is dark red-brown. The reactivity of the dianion parallels that of its $[S_2Fe_2(CO)_6]^{2-}$ analog. Thus, its reaction with iodomethane gave $(\mu\text{-}CH_3Se)_2Fe_2(CO)_6$, an air-stable, ruby-red, malodorous solid, in 87% yield. The ^1H NMR spectrum of this product showed a single resonance at δ 2.10 ppm, which is indicative of the *syn* isomer III. This compound has been reported previously, having been prepared by the reaction of dimethyl selenide with $Fe_3(CO)_{12}$ [12]. Although the proton NMR resonance of our



(III)

product matches that reported for this compound [12], the IR spectra do not match exactly and the melting point of our product is considerably higher (134—135°C) than that reported [12] earlier (84°C). Samples of $(\mu\text{-CH}_3\text{Se})_2\text{Fe}_2(\text{CO})_6$ which we prepared by two other procedures (see below) also had melting points of 134—135°C.

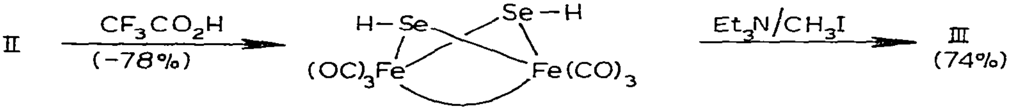
Addition of one-half molar equivalent of germanium tetrachloride to the $[\text{Se}_2\text{Fe}_2(\text{CO})_6]^{2-}$ solution produced the germanium tetraselenide IV in 65% yield.



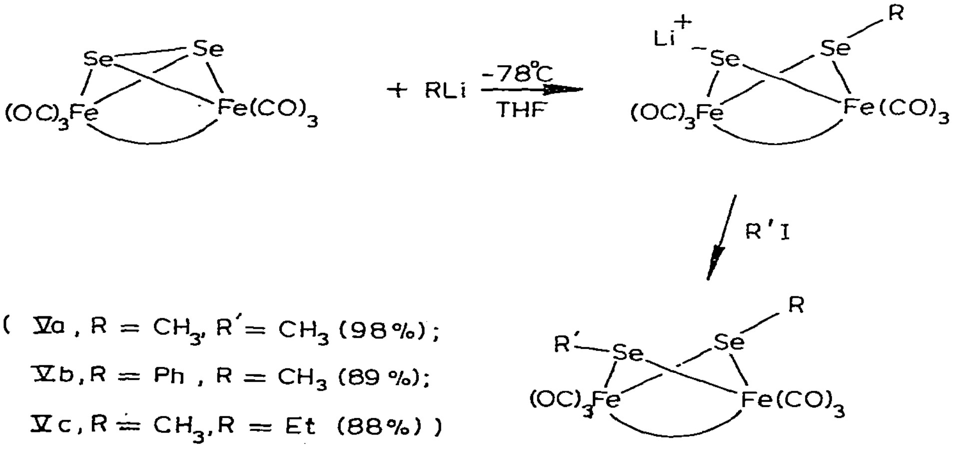
(IV)

The $[\text{Se}_2\text{Fe}_2(\text{CO})_6]^{2-}$ dianion also could be prepared by the action of triethylamine on $(\mu\text{-HSe})_2\text{Fe}_2(\text{CO})_6$, which was generated in situ by treatment of II with trifluoroacetic acid (eq. 2).

A monoanion was formed in the cleavage of the Se—Se bond of I by organolithium reagents (eq. 3). The red $\text{Se}_2\text{Fe}_2(\text{CO})_6$ solution in THF turned emerald



(2)

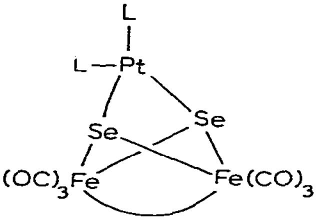


(Ⅴa, R = CH$_3$, R$'$ = CH$_3$ (98%);
Ⅴb, R = Ph , R = CH$_3$ (89 %);
Ⅴc, R = CH$_3$, R = Et (88%))

(3)

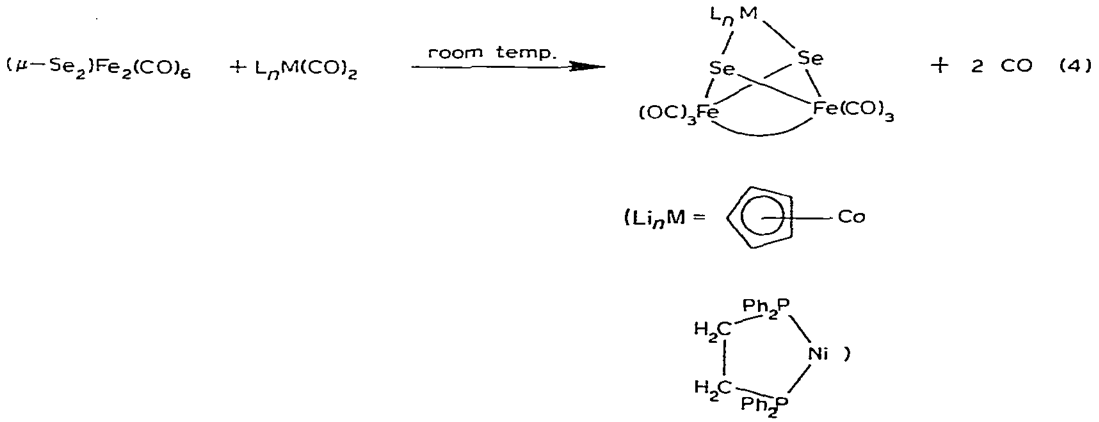
green when exactly one molar equivalent of the organolithium reagent had been added. Addition of the iodoalkane produced a reddish solution again, from which the product (Va, b, c) could be isolated.

μ-(Diselenium)bis(tricarbonyliron), like its sulfur analog, reacts with low valent metal species, giving products derived from insertion of the metal complex into the Se—Se bond. Thus the reaction of (μ-Se_2)$Fe_2(CO)_6$ with tetrakis(triphenylphosphine)platinum(0) in benzene solution in the presence of an excess of iodomethane gave VI in 99% yield. In this reaction, the iodomethane served to scavenge the triphenylphosphine which was released, giving insoluble

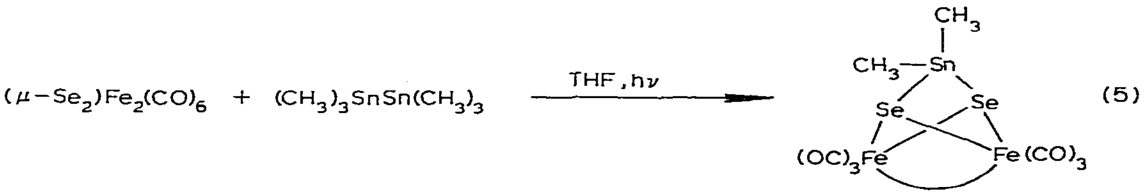


(VI, L = Ph_3P)

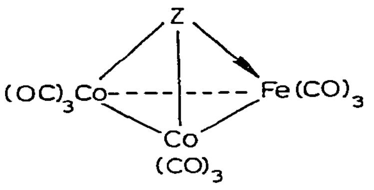
methyltriphenylphosphonium iodide. Two metal dicarbonyls reacted with the selenium compound with concomitant loss of the two carbon monoxide ligands (eq. 4).



The insertion of dimethylstannylene into the Se—Se bond was accomplished using hexamethyldistannane as the Me_2Sn source (eq. 5). An analogous reaction had been found to occur with (μ-S_2)$Fe_2(CO)_6$ [9].



Finally, (μ-Se_2)$Fe_2(CO)_6$ reacted with dicobalt octacarbonyl upon UV irradiation to give the very stable mixed metal cluster VIIa in 95% yield. The sulfur analog, VIIb, had been prepared earlier in 56% yield by the reaction of (μ-S_2)-$Fe_2(CO)_6$ with $Co_2(CO)_8$ at room temperature [13], but we have found that UV irradiation of the reaction mixture (THF solution, quartz flask) leads to an almost quantitative yield of VIIb.



(VIIa, Z = Se;
VIIb, Z = S)

Although the mechanism of the (μ-Z_2)$Fe_2(CO)_6$ (Z = S, Se)/$Co_2(CO)_8$ reaction remains unknown, it seems certain that attack at the chalcogen—chalcogen bond, not at the iron—iron bond, is involved. In support of this idea is the fact that no reaction occurs between (μ-CH_3S)$_2Fe_2(CO)_6$, which has an Fe—Fe bond but no S—S bond, and $Co_2(CO)_8$. After a THF solution of these two compounds (1 : 2.3 molar ratio) had been irradiated (quartz flask, 350 nm Rayonet photochemical reactor) for 20 h, the iron complex was recovered in 80% yield and there was no evidence of the formation of a new product.

Enough of an overview of the reactivity of (μ-Se_2)$Fe_2(CO)_6$ has been obtained in this brief study to show that it is very similar to that of (μ-S_2)Fe_2-$(CO)_6$. Furthermore, a comparison with the reactions of organic diselenides, RSeSeR (R = alkyl and aryl), shows that (μ-Se_2)$Fe_2(CO)_6$ mimics the chemistry of the wholly organic systems. Thus, organic diselenides are cleaved by complex hydrides and by organolithium reagents [14], and low valent transition metal complexes have been shown to insert into the Se—Se bond of RSeSeR compounds [15].

Experimental

General comments

All reactions were carried out under an atmosphere of pre-purified nitrogen in well-dried glassware. Solvents were rigorously dried before use. Precautions to exclude air during all operations were particularly important in the preparation and isolation of the starting material, (μ-Se_2)$Fe_2(CO)_6$. The progress of the reactions which are reported was monitored by thin layer chromatography (J.T. Baker Silica Gel 1B). Since all reactions yielded a single product, full-scale column chromatography was not required. Instead, filtration chromatography, in which the reaction products were dissolved in a suitable solvent and poured on top of a bed of Mallinckrodt 100 mesh silicic acid (ca. 200 ml) in a 350 ml glass-frit filter funnel, was used in most cases. The eluting solvent then was passed through with suction filtration. In general, the selenium compounds involved in this study are particularly malodorous and some, if not all, probably are toxic as well. Consequently, all operations were carried out in a good hood. Most of the products reported are air-stable for short periods of time but usually decomposed slowly over a period of a few weeks. Their solutions are less stable to air.

Infrared spectra were obtained using a Perkin-Elmer Model 457A double-beam grating infrared spectrophotometer. Proton NMR spectra were recorded on either a Varian Associates T60 or a Hitachi-Perkin-Elmer R-20B spectrometer. Chemical shifts are reported in δ units, ppm downfield from internal tetramethylsilane. Chloroform or dichloromethane generally were used as internal standards. Mass spectra were obtained with a Varian MAT-44 instrument operating at 70 eV. Melting points are uncorrected.

Preparation of $(\mu\text{-}Se_2)Fe_2(CO)_6$

We provide full details of this preparation since its synthesis was indicated only in a footnote in ref. 1. All operations were performed under nitrogen.

A one-liter, three-necked, round-bottomed flask fitted with a serum cap, mechanical stirrer and a nitrogen inlet tube was flame-dried and flushed with nitrogen and charged with 60 ml of degassed methanol and 10.5 ml (75 mmol) of iron pentacarbonyl. The solution was cooled to 0° C and 24 ml of 50% aqueous KOH was added. The serum cap was replaced with a solids addition funnel and, under a brisk counterflow of nitrogen, 40.3 g (0.51 mol as "Se") of elemental selenium was added, followed by rapid addition of 30 g (0.125 mol) of $Na_2S \cdot 9\,H_2O$ in 120 ml of water. (The serum cap was replaced.) The solution immediately turned dark red and brisk CO evolution commenced. The reaction mixture was stirred for about 1 h and then was acidified by cautious addition of about 120 ml of 15% hydrochloric acid, at such a rate that the vigorous evolution of H_2Se could be controlled. A brown solid precipitated, leaving a light pink supernatant solution. Filtration was followed by washing of the solid with water and drying in vacuo. The dry solid was extracted with pentane (three 600 ml portions). The extracts were evaporated at reduced pressure to leave a brown solid. The latter was purified by filtration chromatography on silicic acid. Pentane elute a red band. The solid isolated was chromatographed again * to give 3.284 g (20% yield, based on $Fe(CO)_5$) of $(\mu\text{-}Se_2)Fe_2(CO)_6$ as an air-sensitive, deep metallic ruby-red solid, mp 39—40.5° C (lit. [1] mp 40.4° C). Its mass spectrum showed the molecular ion and fragment ions corresponding to the successive loss of six CO ligands. IR (in pentane, cm^{-1}): 2081s, 2041vs, 2004vs, 1989m, 1964w, 1954w.

Formation and reactions of the $[(\mu\text{-}Se_2)Fe_2(CO)_6]^{2-}$ *anion*

A 200 ml one-necked round-bottomed flask equipped with a magnetic stir-bar and a serum cap was flame-dried and flushed with nitrogen, and then was charged with 0.70 g (1.60 mmol) of $(\mu\text{-}Se_2)Fe_2(CO)_6$ and 75 ml of THF. The red solution was cooled to −78° C. Over a 30 min period 3.2 ml (3.2 mmol) of 1.0 *M* $LiBEt_3H$ in THF was added by syringe. The solution darkened in color (to deep purple or dark red-brown). It was stirred for 10 min longer and then 1 ml (an excess) of iodomethane was added. The reaction mixture was stirred at −78° C for 1 h and then was allowed to warm to room temperature; it was

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* Alternatively, it may be sublimed at 35° C at 0.1 mm Hg after the initial filtration chromatography.

stirred at room temperature for an additional hour. Subsequently, volatiles were removed at reduced pressure, leaving a brown solid residue which was chromatographed (silicic acid/pentane) to give 0.655 g (87% yield, based on (μ-Se_2)$Fe_2(CO)_6$) of (μ-$CH_3Se)_2Fe_2(CO)_6$, mp 134—135°C (sealed capillary). ^1H NMR ($CDCl_3/CHCl_3$): δ 2.10 ppm (s). IR ($CHCl_3$, cm^{-1}) 2066s, 2032vs, 1990vs (CO region); 2945w, 1420w, 1273m, 900w, 615m, 580m and 560m.

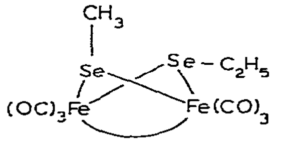
In another experiment, (μ-$LiSe)_2Fe_2(CO)_6$ was prepared on the same scale using the same procedure and then was treated, at —78°C, with 0.092 ml (0.80 mmol) of $GeCl_4$. The resulting solution was stirred for 30 min at —78°C and then was allowed to warm to room temperature. Solvent was removed at reduced pressure, leaving a dark solid which was purified by filtration chromatography on silicic acid. Diethyl ether eluted a dark red band. The eluate was evaporated to give 0.478 g (63%) of Ge[(μ-$Se)_2Fe_2(CO)_6]_2$, IV, a dark ruby-red solid, mp ~130°C (dec). Anal. Found: C, 15.20; $C_{12}O_{12}GeSe_4Fe_4$ calcd.: C, 15.20%. The mass spectrum showed the molecular ion and fragment ions corresponding to the successive loss of CO ligands, $[M - n\ CO]^+$, with n = up to 12. IR (in CH_2Cl_2, cm^{-1}): 2070s, 2043vs, 2005vs.

The [(μ-$Se_2)Fe_2(CO)_6]^{2-}$ ion also was generated from (μ-$HSe)_2Fe_2(CO)_6$ by the triethylamine procedure. A THF solution of (μ-$LiSe)_2Fe_2(CO)_6$ was prepared at —78°C, as above, from 1.00 g (2.28 mmol) of (μ-$Se)_2Fe_2(CO)_6$. To this solution was added, at —78°C, all at once, 0.39 ml (5 mmol) of CF_3CO_2H, which caused a color change from red-brown to red-purple. Iodomethane (1.0 ml. 16 mmol) then was added, followed immediately by triethylamine (1.59 ml, 11.4 mmol), which was added portionwise, in 0.5 ml aliquots every 5 min. The reaction mixture was stirred at —78°C for 30 min, and then was allowed to warm to room temperature. After another 30 min period of stirring at room temperature, a red solution containing a white precipitate was present. Filtration was followed by evaporation of the filtrate at reduced pressure. The residual brown solid was purified by filtration chromatography (silicic acid/pentane) to give 0.785 g (74%) of (μ-$CH_3S)_2Fe_2(CO)_6$, mp 134—135°C (sealed capillary), whose IR and NMR spectra were identical with those of the sample prepared directly from (μ-$LiSe)_2Fe_2(CO)_6$.

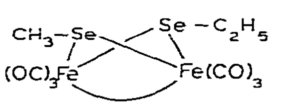
Organolithium cleavage of (μ-$Se_2)Fe_2(CO)_6$

(a) *Methyllithium.* A 200 ml one-necked, round-bottomed flask equipped with a magnetic stir-bar and a serum cap was flame-dried, flushed with nitrogen and charged with 0.70 g (1.60 mmol) of (μ-$Se_2)Fe_2(CO)_6$ and 75 ml of THF. The solution was cooled to —78°C, and over a period of 15 min 1.0 ml of 1.6 M CH_3Li/LiBr (1.60 mmol) in diethyl ether was added by syringe. At the molar equivalence point the solution turned instantly from deep red to emerald green. The reaction mixture was stirred at —78°C for 10 min, and then ca. 1 ml (an excess) of iodomethane was added. The resulting red solution was stirred at —78°C for 1 h, and then was allowed to warm to room temperature. Removal of solvent at reduced pressure left a brown solid which was purified by filtration chromatography (silicic acid/pentane) to give 0.739 g (98%) of air-stable, ruby red (μ-$CH_3Se)_2Fe_2(CO)_6$, mp 134—135°C (sealed capillary). Anal. Found: C, 20.48; H, 1.39. $C_8H_6O_6Se_2Fe_2$ calcd.: C, 20.54; H, 1.29%. The IR and proton NMR spectra of the product were identical with those of samples of this compound prepared by the other two routes described above.

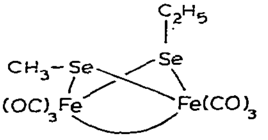
In another experiment, (μ-LiSe)(μ-CH_3Se)$Fe_2(CO)_6$ was prepared as described above from 1.0 g (2.28 mmol) of (μ-Se_2)$Fe_2(CO)_6$ and 2.3 mmol of CH_3Li/LiBr in 1.35 ml of THF at —78° C. To this solution was added 1 ml (an excess) of iodoethane. The resulting mixture was stirred at —78° C for 2 h. No reaction appeared to occur (no color change), so the mixture was warmed to room temperature and stirred for 2 more hours. The green-to-red color change was observed. Removal of solvent at reduced pressure left a brown oil which was chromatographed on silicic acid (pentane) to give 0.967 g (2.01 mmol, 88%) of (μ-CH_3Se)(μ-C_2H_5Se)$Fe_2(CO)_6$, a dark-red, air-sensitive oil of which could be short-path distilled (bp 100° C at 0.14 mm Hg). Anal. Found: C, 22.62; H, 1.72. $C_9H_8O_6Se_2Fe_2$ calcd.: C, 22.44; H, 1.67%. IR (in pentane, cm^{-1}): 2067s, 2032vs, 1995vs, 1989vs. The proton NMR spectrum indicated the presence of at least two isomers, Vc-i and Vc-ii or Vc-iii, or all three isomers. NMR ($CDCl_3$/$CHCl_3$): δ 1.20 (t, CH_3 of Et), 1.43 (t, CH_3 of Et), 1.65 (s, CH_3Se), 2.13 (s, CH_3Se), 2.35 (q, CH_2 of Et) and 2.68 ppm (q, CH_2 of Et), J(HH) 7.5 Hz).



(Vc-i)

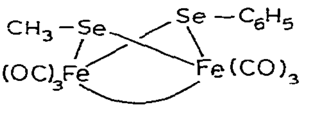


(Vc-ii)

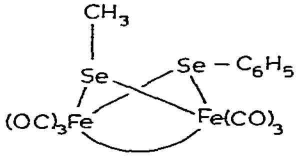


(Vc-iii)

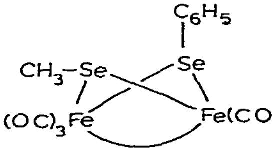
(b) Phenyllithium. To a solution of 1.60 mmol of (μ-Se_2)$Fe_2(CO)_6$ in 75 ml of THF was added, at —78° C, over a period of 15 min, 1.11 ml of 1.44 *M* C_6H_5Li (1.60 mmol) in diethyl ether. The resulting emerald green solution was stirred for 10 min at —78° C, and then 1 ml (an excess) of iodomethane was added. The reaction mixture was stirred at —78° C for 1 h and 1 h at room temperature. Removal of solvent from the red solution at reduced pressure left a brown oil which was chromatographed on a pad of silicic acid. Elution with 30% dichloromethane-pentane yielded a red band which, after removal of solvent, gave 0.758 g (89%) of (μ-CH_3Se)(μ-C_6H_5Se)$Fe_2(CO)_6$, a slightly air-sensitive, viscous red oil which could be short-path distilled (bp 120°C at 0.15 mm Hg). Anal. Found: C, 29.29; H, 1.62. $C_{13}H_8O_6Se_2Fe_2$ calcd.: C, 29.47; H, 1.52%. The mass spectrum showed the molecular ion and fragment ions corresponding to successive loss of CO ligands. IR (in CH_2Cl_2, cm^{-1}) (CO region): 2068s, 2032vs, 1991vs. ^1H NMR ($CDCl_3$/$CHCl_3$): δ 1.74, 2.05, 2.18 (singlets, CH_3Se) and 7.11—7.48 ppm (C_6H_5). The presence of three CH_3Se singlets is indicative of the presence of three isomers, Vb-i, Vb-ii and Vb-iii.



(Vb-i)



(Vb-ii)



(Vb-iii)

The 1.74 ppm resonance can be assigned to the methyl protons of isomer Vb-ii using the assignments made in the case of the sulfur analogs, $(\mu\text{-}CH_3S)_2Fe_2(CO)_6$, as a guide [16].

Insertion reactions

(a) η^5-Cyclopentadienylcobalt dicarbonyl. A 200 ml one-necked, round-bottomed flask equipped with a magnetic stir-bar and a serum cap was charged with 1.00 g (2.28 mmol) of $(\mu\text{-}Se_2)Fe_2(CO)_6$, 0.822 g (4.56 mmol) of $C_5H_5Co(CO)_2$ and 75 ml of THF. The resulting solution was stirred under nitrogen at room temperature for 20 h. Solvent then was removed at reduced pressure and the black solid which remained was purified by chromatography on a pad of silicic acid. Pentane eluted some of both starting materials. A purple band then was eluted with 20% dichloromethane-pentane. On removal of solvent 0.715 g (1.27 mmol, 56%) of $(\mu\text{-}C_5H_5CoSe_2)Fe_2(CO)_6$ was obtained. Recrystallization from pentane gave black, air-stable crystals, mp ~155°C (dec)(sealed capillary). Anal. Found: C, 23.57; H, 1.00. $C_{11}H_5O_6Se_2CoFe_2$ calcd.: C, 23.52; H, 0.90%. IR (in CH_2Cl_2, cm^{-1}) (CO region): 2060s, 2034vs, 1985vs. ^1H NMR ($CDCl_3/CHCl_3$): δ 5.84 ppm (s, C_5H_5). The mass spectrum showed the molecular ion and fragment ions corresponding to the successive loss of the six CO ligands and then of the C_5H_5 ligand.

(b) 1,2-bis(Diphenylphosphino)ethanenickel dicarbonyl. In a glove box, a 100 ml one-necked, round-bottomed flask equipped with a magnetic stir-bar and a serum cap was charged with 0.876 g (2.0 mmol) of $(\mu\text{-}Se_2)Fe_2(CO)_6$ and 1.177 g (2.29 mmol) of $(Ph_2PCH_2CH_2PPh_2)Ni(CO)_2$ (Strem). Benzene (50 ml) was added by syringe and the resulting solution was stirred for 24 h at room temperature. The solvent then was removed at reduced pressure and the residual brown-black solid was purified by filtration chromatography on silicic acid. Pentane eluted a trace of $(\mu\text{-}Se_2)Fe_2(CO)_6$ and dichloromethane subsequently eluted a brown-red band. Evaporation of solvent from the latter gave 1.488 g (1.66 mmol, 83%) of $[\mu\text{-}(Ph_2PCH_2CH_2PPh_2)NiSe_2]Fe_2(CO)_6$. Recrystallization from dichloromethane/pentane yielded air-stable, brown-black crystals, mp 192—194°C (sealed capillary). Anal. Found: C, 42.73; H, 2.79. $C_{32}H_{24}O_6P_2Se_2NiFe_2$ calcd.: C, 42.95; H, 2.70%. IR (in CH_2Cl_2, cm^{-1}) (CO region): 2045s, 2004vs, 1967s, 1957(sh). ^1H NMR (CD_2Cl_2/CH_2Cl_2): δ 2.19 (d, J 17 Hz, PCH_2) and 7.35—7.95 ppm (m, C_6H_5P).

(c) Tetrakis(triphenylphosphine)platinum(0). The usual reaction flask was charged with 0.481 g (1.10 mmol) of $(\mu\text{-}Se_2)Fe_2(CO)_6$, 50 ml of benzene and 2.5 ml of iodomethane. This solution was cannulated into another similar reaction flask (nitrogen pressure) which contained 0.531 g (0.427 mmol) of $(Ph_3P)_4Pt$ (Strem). The reaction mixture was stirred at room temperature under nitrogen overnight. Subsequent filtration removed a white precipitate ($[CH_3Ph_3P]I$) which had formed. Evaporation of the filtrate at reduced pressure left a dark red oil which was purified by filtration chromatography (silicic acid). Pentane eluted at trace of $(\mu\text{-}Se_2)Fe_2(CO)_6$; dichloromethane then eluted a red band which was isolated and rechromatographed. The product, $[\mu\text{-}(Ph_3P)_2PtSe_2]Fe_2(CO)_6$, was thus obtained; 0.448 g (0.422 mmol, 99%). Recrystallization from CH_2Cl_2/pentane gave material of mp ~205°C (dec) (sealed capillary) as crystals. Anal. Found: C, 43.57; H, 2.67. $C_{42}H_{30}O_6P_2Se_2PtFe_2$ calcd.: C, 43.59; H, 2.61%. IR (in CH_2Cl_2, cm^{-1}) (CO region): 2043s,

2003vs, 1965s, 1955(sh). NMR ($CDCl_3/CHCl_3$): δ 7.05—7.60 ppm (broad m).

(d) Hexamethylditin. A 150 ml one-necked quartz flask equipped with a magnetic stir-bar and a serum cap was flushed with nitrogen and charged with 1.00 g (2.28 mmol) of $(\mu\text{-}Se_2)Fe_2(CO)_6$, 2.24 g (6.84 mmol) of $(CH_3)_6Sn_2$ and 50 ml of THF. The mixture was photolyzed for 10 h in a 350 nm Rayonet photochemical reactor. Subsequently, the volatiles were removed at reduced pressure, leaving a red solid which was purified by filtration chromatography on silicic acid (CH_2Cl_2) to give 0.713 g of $[\mu\text{-}(CH_3)_2SnSe_2]Fe_2(CO)_6$ (53% yield), air-stable red needles, mp ~95°C (dec). Anal. Found: C, 16.52; H, 1.08. $C_8H_6O_6Se_2SnFe_2$ calcd.: C, 16.39; H, 1.03%. IR (in CH_2Cl_2, cm^{-1}) (CO region): 2066s, 2027vs, 1990s. ^1H NMR ($CDCl_3/CHCl_3$): δ 1.30 (s, CH_3Sn, $J(^{117}Sn—^1H)$ 50 Hz, $J(^{119}Sn—^1H)$ 52 Hz). The mass spectrum showed the molecular ion and fragment ions corresponding the the successive loss of the CO ligands and then both methyl groups.

Reaction of $(\mu\text{-}Se_2)Fe_2(CO)_6$ with dicobalt octacarbonyl

A 150 ml one-necked quartz flask equipped as in the experiment above was flushed with nitrogen and charged with 1.00 g (2.26 mmol) of $(\mu\text{-}Se_2)Fe_2(CO)_6$, 1.71 g (5 mmol) of $Co_2(CO)_8$ (Strem) and 25 ml of THF. The reaction mixture was photolyzed for 20 h in a 350 nm Rayonet photochemical reactor. Upon completion of the reaction, volatiles were removed at reduced pressure and the black solid which remained was purified by filtration chromatography on silicic acid. Dichloromethane eluted the product which was isolated as air-stable, black crystals, mp 104—106°C; 2.199 g (95% yield based on $(\mu\text{-}Se_2)Fe_2(CO)_6$). An analytical sample was recrystallized from pentane. Anal. Found: C, 21.54. $C_9O_9SeFeCo_2$ calcd.: C, 21.42%. The mass spectrum showed the molecular ion and fragment ions corresponding to the successive loss of the nine CO ligands. IR (in CH_2Cl_2, cm^{-1}): 2104m, 2066vs, 2053vs, 2039s, 2028(sh), 1977m. The similarity to $(\mu_3\text{-}S)FeCo_2(CO)_9$ [13] (preparation, mass spectrum, IR spectrum) suggests the structure $(\mu_3\text{-}Se)FeCo_2(CO)_9$ for this product.

Reaction of $(\mu\text{-}S_2)Fe_2(CO)_6$ with dicobalt octacarbonyl

A 200 ml, one-necked quartz flask equipped as above was flushed with nitrogen and charged with 1.00 g (2.91 mmol) of $(\mu\text{-}S_2)Fe_2(CO)_6$ [1], 2.00 g (5.82 mmol) of dicobalt octacarbonyl and 25 ml of THF. This mixture was photolyzed for 20 h in a 350 nm Rayonet photochemical reactor. Work-up as above gave 2.411 g (90%, based on $(\mu\text{-}S_2)Fe_2(CO)_6$) of $(\mu_3\text{-}S)FeCo_2(CO)_9$, mp ~ 110°C (dec), an air-stable, black crystalline solid. Anal. Found: C, 23.43. $C_9O_9SFeCo_2$ calcd.: C, 23.61%. The mass spectrum showed the molecular ion and fragment ions corresponding to the successive loss of the 9 CO ligands. IR (in CH_2Cl_2, cm^{-1}) (CO region): 2104m, 2067m, 2054vs, 2041s, 2029m, 1973m. Literature [13] data: mp ~112°C (dec); IR (hexane): 2104.5m, 2066vs, 2053.5vs, 2042s, 2029m, 2000w, 1984.5m, 1949.5w.

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