

Organoselenium Derivatives of Metal Carbonyls. Part II.¹ Dimeric and Monomeric Derivatives of Iron Carbonyl

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Dodecacarbonyltri-iron reacts with dimethyl and diethyl diselenides and with the corresponding bisperfluoroalkyl diselenides to afford the respective selenoalkyl and perfluoroalkyl iron tricarbonyl dimers, $[\text{Fe}(\text{CO})_3\text{Se}(\text{R})]_2$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{CF}_3, \text{or } \text{C}_2\text{F}_5$), while the *i*- C_3H_7 derivative is obtained by the reaction of the same iron carbonyl with perfluoroisopropylselenol. The two compounds of the type $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})\text{Se}(\text{R})]_2$ ($\text{R} = \text{C}_2\text{H}_5$ or *n*- C_3H_7) resulted from the reaction between the cyclopentadienyl iron dicarbonyl dimer, $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$, and the appropriate dialkyl diselenide.

The only monomeric derivatives in this group of compounds, $(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Se}(\text{R}_F)$ ($\text{R}_F = \text{CF}_3, \text{C}_2\text{F}_5, \text{or } \text{C}_3\text{F}_7$), were obtained by the reaction of cyclopentadienyl iron dicarbonyl dimer and the respective bisperfluoroalkyl diselenide.

The mechanism of the above reactions is discussed and the properties of the new compounds are described.

NUMEROUS derivatives of transition-metal carbonyls or cyclopentadienyl carbonyls also containing organo-sulphur bridges have been prepared; most of these compounds are either binuclear²⁻⁸ or polynuclear.⁸⁻¹³ However, some derivatives with terminal organosulphur groups are also known.^{7,14-17} Surprisingly, few such

derivatives with organo-selenium or -tellurium bridges are found in the literature.^{1,13-21} A study was, therefore, undertaken to elucidate the mechanism by which these complexes are formed. During this study several

† The symbol R_F is used throughout this paper to denote a perfluoroalkyl group.

¹ Part I, N. Welcman and I. Rot, *J. Chem. Soc.*, 1965, 7515.

² W. Hieber and W. Beck, *Z. anorg. Chem.*, 1960, **305**, 265.

³ R. B. King, P. M. Treichel, and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1961, **83**, 3600.

⁴ P. M. Treichel, J. H. Morris, and F. G. A. Stone, *J. Chem. Soc.*, 1963, 720.

⁵ R. B. King, *J. Amer. Chem. Soc.*, 1963, **85**, 1584.

⁶ J. K. Ruff and R. B. King, *Inorg. Chem.*, 1969, **8**, 180.

⁷ R. B. King and N. Welcman, *Inorg. Chem.*, 1969, **8**, 3540.

⁸ A. R. Dias and M. L. H. Green, *J. Chem. Soc. (A)*, 1971, 1951.

⁹ E. Klumpp, G. Bor, and L. Markó, *Chem. Ber.*, 1967, **100**, 1451.

¹⁰ C. R. Jenkins, *J. Organometallic Chem.*, 1968, **15**, 441.

¹¹ G. R. Crooks, B. F. G. Johnson, J. Lewis, and I. G. Williams, *J. Chem. Soc. (A)*, 1969, 798.

¹² E. Klumpp, L. Markó, and G. Bor, *Chem. Ber.*, 1967, **97**, 926.

¹³ J. A. de Beer and R. J. Haines, *Chem. Comm.*, 1970, 288.

¹⁴ M. Ahmad, R. Bruce, and G. R. Knox, *J. Organometallic Chem.*, 1966, **6**, 1.

¹⁵ H. Behrens, E. Lindner, and S. Birkle, *Z. anorg. Chem.*, 1969, **369**, 131.

¹⁶ R. B. King and M. B. Bisnette, *Inorg. Chem.*, 1965, **4**, 482.

¹⁷ A. G. Osborne and F. G. A. Stone, *J. Chem. Soc. (A)*, 1966, 1143.

¹⁸ E. W. Abel, B. C. Crosse, and G. V. Hutson, *J. Chem. Soc. (A)*, 1967, 2014.

¹⁹ N. Welcman and A. Josef, *Israel J. Chem.*, 1968, **6**, 33p.

²⁰ E. D. Schermer and W. H. Baddley, *J. Organometallic Chem.*, 1971, **27**, 83.

²¹ E. D. Schermer and W. H. Baddley, *J. Organometallic Chem.*, 1971, **30**, 67.

alkyl- and perfluoroalkyl selenide derivatives of iron carbonyl and cyclopentadienyl iron carbonyl have been prepared.

RESULTS AND DISCUSSION

The first monomeric transition-metal compound with a non-bridging methylthio-group was $(C_5H_5)Fe(CO)_2(SCH_3)$, prepared in poor yield¹⁶ by irradiation of either $(C_5H_5)Fe(CO)_2(CH_2CH_2SCH_2)$ or a mixture of $[(C_5H_5)Fe(CO)_2]_2$ and dimethyl disulphide. It was eventually synthesized, also in poor yield, by more conventional methods from dimethyl disulphide and cyclopentadienyl-iron carbonyl hydride in tetrahydrofuran solution.¹⁶

Two other mononuclear complexes of the type $(C_5F_5)SM(CO)_5$ ($M = Mn$ or Re) were prepared by the reaction of the respective metal pentacarbonyl hydride with pentafluorobenzenethiol.¹⁷ The mononuclear anion $[Cr(CO)_5SC_6H_4(CH_3-p)]^-$ has also been prepared from $Na_2[Cr_2(CO)_{10}]$ and *p*-thiocresol.¹⁵

It has been suggested¹⁷ that formation of the binuclear carbonyl complexes with organosulphur bridges occurs in two stages. First the monomer is produced and then the lone electron pair on the sulphur atom, acting as a Lewis base, displaces carbon monoxide from another monomeric species to give the dimer. The problem of preparing monomeric compounds is thus reduced to preventing the second step from taking place. This could be achieved either by reducing the donor properties of the sulphur atom of the SR group by replacing the alkyl or aryl group R with a strongly electronegative perfluoro-alkyl or -aryl group, or, alternatively, by substituting a less-electronegative selenium for the sulphur atom; of course, both measures could be applied simultaneously. Furthermore, the metal-ligand bond cannot be viewed as derived solely from the donation of electron pairs from the ligand to the metal atom. Back coordination of doubly-filled *d* orbitals on the metal atom to empty *d* orbitals of the ligand also contributes to the stability of complex compounds.²² It was stipulated that weakening of this 'back donation' would stabilize the monomer.

The results of this study, as illustrated by the following four series of new complexes (Table 1), are consistent with the two-step mechanism.

TABLE 1

Series A	Series B
(I) $[Fe(CO)_3Se(CH_3)]_2$	(IV) $[Fe(CO)_3Se(CF_3)]_2$
(II) $[Fe(CO)_3Se(C_2H_5)]_2$	(V) $[Fe(CO)_3Se(C_2F_5)]_2$
(III) $[Fe(CO)_3Se(i-C_3H_7)]_2$	
Series C	Series D
(VI) $[(C_5H_5)Fe(CO)Se(C_2H_5)]_2$	(VIII) $(C_5H_5)Fe(CO)_2Se(CF_3)$
(VII) $[(C_5H_5)Fe(CO)Se(n-C_3H_7)]_2$	(IX) $(C_5H_5)Fe(CO)_2Se(C_2F_6)$
	(X) $(C_5H_5)Fe(CO)_2Se(C_3H_7)$

The mere replacement of the sulphur by a selenium atom [compounds (I), (II), and (III)] is not sufficient to prevent the second reaction step, and even substituting the R group with an R_F group does not inhibit the form-

ation of the binuclear compound. As a final measure a step was taken to weaken the 'back-donation' power of the central iron atom, by replacing two carbonyls with the electron-withdrawing cyclopentadienyl. And, indeed, this substitution stabilized the monomers [compounds (VIII), (IX), and (X)] although only after having an R_F group, not an R group, [see compounds (VI) and (VII)] attached to the selenium atom.

All complexes were obtained in fairly good yield (just over 35%) the monomers notwithstanding, but several differences were observed between the four series of compounds (see Table 1). The selenoalkyl derivatives (Series A) are red, foul-smelling solids, soluble in most organic solvents, but pronouncedly less soluble in pentane. Proton n.m.r. studies on the methyl moiety show only a single methyl peak at 2.1 p.p.m. (at a lower field relative to Me_4Si) indicating two identical methyl groups, *i.e.* only one of two possible isomers was obtained as compared with the sulphur analogue.²³ On the other hand, the fragmentation of these complexes in the mass spectrometer is identical with that of the sulphur analogues.^{24,25} The selenoperfluoroalkyl derivatives (Series B) are, in general, similar in their properties to the alkyl analogues; however, they are light-sensitive, less stable in air, and were obtained with greater difficulty as demonstrated by the much longer reaction time.

In contrast, the cyclopentadienyl derivatives of selenoalkyl iron carbonyl (Series C) are very stable towards the influence of air, moisture, and light; in fact, they are the most stable compounds in these series.

The only monomeric complexes prepared were the three cyclopentadienyl selenoperfluoroalkyl iron dicarbonyls (Series D). They are low-melting solids (the perfluoropropyl derivative is a liquid at 20 °C), very unstable in atmospheric conditions. They decompose rapidly above 70–80 °C so that their molecular weights could not be determined by mass spectrometric measurements and were found cryoscopically instead.

TABLE 2

Infrared data for the new compounds

Compound	C—O Stretching frequencies (cm^{-1})	C—F Stretching frequencies (cm^{-1})
$[Fe(CO)_3Se(CH_3)]_2$	2060vs, 2010vs, 1955vs	
$[Fe(CO)_3Se(C_2H_5)]_2$	2060vs, 2020vs, 1985vs	
$[Fe(CO)_3Se(i-C_3H_7)]_2$	2060vs, 2025vs, 1950vs	
$[Fe(CO)_3Se(CF_3)]_2$	2095vs, 2055vs, 2010vs	1140s, 1075vs
$[Fe(CO)_3Se(C_2F_5)]_2$	2095vs, 2060vs, 2010vs	1330vs, 1215vs, 1105vs
$[(C_5H_5)Fe(CO)Se(C_2H_5)]_2$	1920s	
$[(C_5H_5)Fe(CO)Se(n-C_3H_7)]_2$	1935s	
$(C_5H_5)Fe(CO)_2Se(CF_3)$	2050vs, 1990vs	1090vs, 1060vs
$(C_5H_5)Fe(CO)_2Se(C_2F_6)$	2045vs, 1995vs	1320vs, 1195vs, 1115s, s
$(C_5H_5)Fe(CO)_2Se(C_3H_7)$		1335s, 1175s, 1105s
$(C_5H_5)Fe(CO)_2Se(C_3F_7)$	2055vs, 2010vs	

The main frequencies of the i.r. spectra of the new compounds are summarized in Table 2.

²² L. E. Orgel, 'An Introduction to Transition-Metal Chemistry,' Methuen, London, 1960, p. 133.

²³ R. B. King, *J. Amer. Chem. Soc.*, 1962, **84**, 2460.

²⁴ K. Edgar, B. F. G. Johnson, J. Lewis, I. G. Williams, and J. M. Wilson, *J. Chem. Soc. (A)*, 1967, 379.

²⁵ E. W. Abel and B. C. Crosse, *J. Chem. Soc. (A)*, 1966, 1141.

EXPERIMENTAL

Vacuum techniques were used for the treatment of substances that are volatile and poisonous. Non-volatile compounds were handled under nitrogen; certain light-sensitive complexes were handled in darkness. All volatile materials were purified in trap-to-trap distillation; solids were purified by recrystallization from different solvents and/or vacuum sublimation. Infrared spectra were recorded in the frequency range 4000—650 cm^{-1} on a Perkin-Elmer spectrometer, model 237 in 10 cm gas cell, in chloroform solution or potassium bromide disc. Molecular weights were determined on an Atlas CH-4 mass spectrograph or cryoscopically in benzene solution.

Melting and decomposition points were determined in sealed capillaries and are uncorrected.

Dialkyl diselenides were prepared by known methods;^{26,27} dodecacarbonyltri-iron and cyclopentadienyldicarbonyliron dimer were prepared by the method of King and Stone^{28a,b} and bisperfluoroalkyl diselenides were prepared by published procedures.^{29,30}

Analytical data are summarized in Table 3.

TABLE 3
Analytical data

	M.p.	Found (%)				Required (%)			
		C	H	Fe	M	C	H	Fe	M
$[\text{Fe}(\text{CO})_3\text{Se}(\text{CH}_3)]_2$	84°	20.55	1.35	23.7	468	20.5	1.3	23.9	468
$[\text{Fe}(\text{CO})_3\text{Se}(\text{C}_2\text{H}_5)]_2$ *	35	24.2	2.15		496	24.2	2.0		496
$[\text{Fe}(\text{CO})_3\text{Se}(\text{i-C}_3\text{H}_7)]_2$	97	27.7	3.1	21.2	524	27.5	2.65	21.35	524
$[\text{Fe}(\text{CO})_3\text{Se}(\text{CF}_3)]_2$	64	17.05		19.45	576			19.45	576
$[\text{Fe}(\text{CO})_3\text{Se}(\text{C}_2\text{F}_5)]_2$	54—55	17.8		17.35	676	17.75		16.57	676
$[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})\text{Se}(\text{C}_2\text{H}_5)]_2$	93—94	37.45	3.8	21.5	514	37.4	3.9	21.8	514
$[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})\text{Se}(\text{n-C}_3\text{H}_7)]_2$	52—54	39.8	4.35	20.9	542	39.85	4.4	20.65	542
$(\text{C}_6\text{H}_5)\text{Fe}(\text{CO})_2\text{Se}(\text{CF}_3)$	28	29.5	1.55	17.05	336 †	29.55	1.55	17.2	325
$(\text{C}_6\text{H}_5)\text{Fe}(\text{CO})_2\text{Se}(\text{C}_2\text{F}_5)$	39—40	28.9	1.5	15.05	362 †	28.8	1.35	14.95	375
$(\text{C}_6\text{H}_5)\text{Fe}(\text{CO})_2\text{Se}(\text{C}_3\text{F}_7)$		28.3	1.55	13.65		28.25	1.2	13.2	

* Found: O, 19.5%; reqd., 19.35%. † Cryoscopically from benzene.

Preparation of $[\text{Fe}(\text{CO})_3\text{Se}(\text{CH}_3)]_2$.—Dodecacarbonyl tri-iron (5.0 g, 9.3 mmol) was dissolved in light petroleum (100 ml). Dimethyl selenide (5.5 g, 29.2 mmol) was added dropwise under constant magnetic stirring to the boiling solution; refluxing was continued for 5 h. The colour of the solution turned from green to red. The cool mixture was filtered and solvent was removed under reduced pressure. The resultant brown-red oily residue was crystallized from dichloromethane-pentane solution in a solid CO_2 -acetone bath. After recrystallization from pentane foul-smelling red crystals of $[\text{Fe}(\text{CO})_3\text{Se}(\text{CH}_3)]_2$ were obtained [2.1 g, 1.48 mmol, 31% based on $\text{Fe}_3(\text{CO})_{12}$].

Preparation of $[\text{Fe}(\text{CO})_3\text{Se}(\text{C}_2\text{H}_5)]_2$.²—Dodecacarbonyl tri-iron (4.0 g, 7.9 mmol) in light petroleum (100 ml) was treated in a similar manner to that described above with diethyl diselenide (5.0 g, 29.1 mmol); and red, crystalline $[\text{Fe}(\text{CO})_3\text{Se}(\text{C}_2\text{H}_5)]_2$ (2.55 g, 5.05 mmol, 43%) was obtained.

Preparation of $[\text{Fe}(\text{CO})_3\text{Se}(\text{i-C}_3\text{H}_7)]_2$.—Dodecacarbonyl tri-iron (4.0 g, 7.9 mmol) in refluxing benzene (100 ml) was treated with perfluoroisopropylselenol (1.0 g, 8.1 mmol). After 10 min the dark green colour of the solution due to the carbonyl turned to red-brown. The stirring was continued at room temperature for 24 h. The solvent was then removed and the remaining red residue was crystallized from

dioxan to give red crystals of $[\text{Fe}(\text{CO})_3\text{Se}(\text{i-C}_3\text{H}_7)]_2$ (0.84 g, 1.6 mmol, 40%).

Preparation of $[\text{Fe}(\text{CO})_3\text{Se}(\text{CF}_3)]_2$.—Dodecacarbonyl tri-iron (1.5 g, 2.98 mmol) was dissolved in benzene (50 ml). The solution was warmed to 47—50°, and bistrifluoromethyl diselenide (2.5 g, 8.45 mmol) was added to it; the mixture was stirred vigorously at this temperature for 48 h. During this period the solution changed colour gradually from green to red. The mixture was then cooled to room temperature and filtered. The solvent was removed from the solution at 25°/20 mmHg to leave a red residue; this was crystallized from pentane at -78°. The dark red, obnoxiously smelling feathery crystals were sublimed in high vacuum to give $[\text{Fe}(\text{CO})_3\text{Se}(\text{CF}_3)]_2$ (0.82 g, 1.43 mmol, 32%).

Preparation of $[\text{Fe}(\text{CO})_3\text{Se}(\text{C}_2\text{F}_5)]_2$.—Dodecacarbonyl tri-iron (1.5 g, 2.98 mmol) and bispentafluoroethyl diselenide (2.0 g, 5.05 mmol) were dissolved in benzene (50 ml). The solution was then heated at 45—50° with constant stirring for 64 h. The cool mixture was filtered and the solvent evaporated from the filtrate at 25°/20 mmHg. The resultant red, oily residue was crystallized from pentane to

give red malodorous crystals. After sublimation at 45°/0.1 mm the yield of $[\text{Fe}(\text{CO})_3\text{Se}(\text{C}_2\text{H}_5)]_2$ was 0.85 g (28%).

Preparation of $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})\text{Se}(\text{C}_2\text{H}_5)]_2$.—A solution of $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})]_2$ (2.0 g, 5.65 mmol) and diethyl diselenide (5.8 g, 26.8 mmol) in methylcyclohexane (50 ml) was heated at 95—100° with vigorous stirring for 20—22 h. The cool mixture was filtered and the brown filtrate was run through a chromatographic column packed with neutral alumina. (The chromatography and the subsequent crystallization were performed in subdued light to avoid decomposition of the light-sensitive product). Elution with benzene gave two bands, the broader one of which contained the product $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})\text{Se}(\text{C}_2\text{H}_5)]_2$. The benzene eluant was evaporated at 20°/25 mmHg leaving an oily solid; this was crystallized from dichloromethane-pentane at -78°C and sublimed at high vacuum.

The shiny-brown malodorous crystals were air- and light-sensitive; 1.1 g (2.14 mmol, 38%) of $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})\text{Se}(\text{C}_2\text{H}_5)]_2$ were obtained.

Preparation of $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})\text{Se}(\text{n-C}_3\text{H}_7)]_2$.— $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})]_2$ (2.0 g, 5.65 mmol) and di-n-propyl diselenide (6.5 g, 26.6 mmol) were treated as in the preceding preparation. Elution with benzene gave one band only. The solvent

²⁶ M. L. Bird and F. Challenger, *J. Chem. Soc.*, 1942, 570.

²⁷ C. M. Suter and H. L. Gerhart, *Org. Synth.*, Coll. Vol. 2, ed. A. H. Blatt, John Wiley and Sons, New York, 1946, p. 112.

²⁸ (a) R. B. King and F. G. A. Stone, *Inorg. Synth.*, 1963, 7, 193; (b) R. B. King and F. G. A. Stone, *ibid.*, p. 99.

²⁹ H. J. Emeléus and N. Welcman, *J. Chem. Soc.*, 1963, 1268.

³⁰ N. Welcman and H. Regev, *J. Chem. Soc.*, 1965, 7511.

was removed (as above) and the remaining brown, oily solid was crystallized from dichloromethane-pentane in an acetone-solid CO₂ bath. Recrystallization from pentane gave brown, shiny, malodorous crystals of [(C₅H₅)Fe(CO)-SeC₃H₇]₂ (1.25 g, 2.3 mmol, 40.7%).

Preparation of (C₅H₅)Fe(CO)₂Se(CF₃).—A solution of [(C₅H₅)Fe(CO)₂]₂ (0.5 g, 1.4 mmol) in methylcyclohexane (50 ml) was heated to 45°. Bistrifluoromethyl diselenide (1.5 g, 5.07 mmol) was then added to the reaction mixture which was then kept at 45–50° for 72 h with constant stirring. Most of the solvent was removed from the cool mixture at 25°/20 mmHg. Recrystallization of the residue from dichloromethane-pentane at –78° and from pentane gave brown malodorous crystals of the monomeric (C₅H₅)Fe(CO)₂-Se(CF₃); the yield was 0.3 g (0.92 mmol, 33%).

Preparation of (C₅H₅)Fe(CO)₂Se(C₂F₅).—[(C₅H₅)Fe(CO)₂]₂ (0.5 g, 1.4 mmol) was treated as in the preceding preparation with bis(pentafluoroethyl) diselenide (2.0 g, 5.05 mmol). After removal of solvent at 25°/20 mmHg the remaining

oily solid was crystallized several times from 1 : 1 dichloromethane-pentane at –78° and then sublimed at 35°/0.1 mmHg to give red, feathery, malodorous crystals of (C₅H₅)Fe(CO)₂Se(C₂F₅) (0.45 g, 1.2 mmol, 42%).

Preparation of (C₅H₅)Fe(CO)₂Se(C₃F₇).—A solution of [(C₅H₅)Fe(CO)₂]₂ (0.5 g, 1.41 mmol) in methylcyclohexane (50 ml) was heated to 50–55° under nitrogen with vigorous stirring. Bisheptafluoropropyl diselenide (2.82 g, 5.7 mmol) was added to the mixture. No change in colour was observed after 3 days under these conditions. Solvent was evaporated at 25°/25 mm. The remaining heavy oily liquid was dissolved in dichloromethane; addition of pentane and cooling to –78° gave (C₅H₅)Fe(CO)₂Se(C₃F₇) as red crystals (0.36 g, 0.85 mmol, 30%). This compound was a liquid at room temperature.

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