1370. *Organoselenium Derivatives of Metal Carbonyls. Part I. Complexes Derived from Manganese Pentacarbonyl Hydride*

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Several organoselenium derivatives of manganese carbonyl of the dimeric structure $[Mn(CO)_4SeR]_2$, where R = CH_3, C_2H_5, and C_3H_7, and also CF_3, C_2F_5, and C_3F_7, were prepared by the interaction of manganese pentacarbonyl hydride and the appropriate diselenide. Some of the physical properties of these new compounds are described.

Several organosulphur derivatives of iron, cobalt, and manganese are known from recent literature.[1] In these binuclear complexes the sulphur atoms are known to serve as bridging atoms between the two metal atoms.

We now report several organoselenium manganese compounds of the general formula $[Mn(CO)_4SeR]_2$, where R = CH_3, C_2H_5, C_3H_7, and also CF_3, C_2F_5, and C_3F_7. Both the alkyl- and perfluoroalkyl-selenium derivatives were prepared by the action of the appropriate diselenide on manganese pentacarbonyl hydride.

The new alkylselenium compounds, like their sulphur analogues are crystalline solids, stable to atmospheric conditions; they are orange-brown and soluble in common organic solvents, such as carbon tetrachloride, chloroform, and pentane.

The selenium–manganese bond in the alkyl complexes is apparently different from the bond in the perfluoroalkyl complexes, because in the latter complexes the donor properties of the selenium atom are bound to be considerably weakened by the electron-withdrawing perfluoroalkyl group attached to it. Nevertheless, the perfluoroalkyl complexes were stable in air, and were solids which could be recrystallised from several organic solvents. It is suggested that the stability of these new perfluoroalkyl complexes is largely due to back-co-ordination of the non-bonding 3*d*-electrons on the metal atom to vacant *d*-orbitals of the donor atom, a phenomenon known to occur in some metal carbonyls.[2]

The infrared spectra of the new compounds show stretching frequencies of terminal carbonyls only, and the spectra of the perfluoroalkyl complexes show bands in the region 1350—1000 cm.$^{-1}$ due to carbon–fluorine stretching vibrations.[3] The proton magnetic resonance spectra of the alkyl compounds are similar to those found for related substances.[1b]

Experimental

The starting materials for the preparation of dialkyl diselenides[4] for the alkyl-seleno-complexes were commercial selenium metal powder, sodium formaldehyde sulphoxylate, and the respective dialkyl sulphate. Dimethyl and diethyl sulphate were available, but dipropyl sulphate had to be prepared.[5] Manganese pentacarbonyl hydride was prepared by a known procedure,[6] and the preparation of the bisperfluoroalkyl diselenides was accomplished by a method described elsewhere.[7]

All experiments were conducted in a vacuum system of conventional design with removable fractionation bulbs.

Molecular weights were determined by use of an Atlas CH-4 mass spectrometer.

Preparation of Alkyl Selenium Derivatives.—(*a*) $[Mn(CO)_4SeCH_3]_2$. Manganese pentacarbonyl hydride (0·85 g., 4·3 mmoles) and methyl diselenide (1·2 g., 6·4 mmoles) were distilled in the vacuum system into an evacuated, liquid-air-cooled Pyrex reaction bulb of 300-ml.

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[1] (*a*) R. B. A. King, P. M. Treichel, and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1961, **83**, 3600; (*b*) P. M. Treichel, J. H. Morris, and F. G. A. Stone, *J.*, 1963, 720; (*c*) R. B. A. King, *J. Amer. Chem. Soc.*, 1963, **85**, 1584.

[2] (*a*) S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.*, 1958, **12**, 265; (*b*) L. E. Orgel, *Chem. Soc. Special Publ.*, No. 13, 1959, p. 93.

[3] E. Pitcher and F. G. A. Stone, *Spectrochim. Acta*, 1962, **18**, 585.

[4] M. L. Bird and F. Challenger, *J.*, 1942, 570.

[5] C. M. Suter and H. L. Gerhart, *Org. Synth.*, 1946, **2**, 112.

[6] R. B. A. King and F. G. A. Stone, *Inorg. Synth.*, 1963, **7**, 198.

[7] (*a*) H. J. Emeléus and N. Welcman, *J.*, 1963, 1268; (*b*) N. Welcman and H. Regev, preceding paper.

capacity, and the bulb was sealed. On warming to room temperature, gas evolution was observed in the reaction mixture and the solution turned brown. On standing for 12 hr. at room temperature, orange-brown crystals appeared and then the reaction bulb was opened to the vacuum system and the volatile products, *i.e.*, excess methyl diselenide, carbon monoxide, and other unidentified products, were removed from the bulb. The remaining orange-brown *solid* (0·65 g., 1·24 mmoles) (58%) was recrystallised from pentane (Found: C, 23·2; H, 1·15; O, 24·55%; *M*, 522. $C_{10}H_6Mn_2O_8Se_2$ requires C, 23·0; H, 1·15; O, 24·5%; *M*, 522). The compound decomposes without melting when heated to 110°.

All other reactions were performed in a manner similar to (*a*), the corresponding diselenide being taken in all cases in considerable excess.

(*b*) $[Mn(CO)_4SeC_2H_5]_2$. Manganese pentacarbonyl hydride (0·5 g., 2·6 mmoles) reacted with diethyl diselenide (0·8 g., 3·7 mmoles), to give the brown-red *complex* (0·5 g., 0·86 mmole) (71% yield based on the hydride) (Found: C, 26·5; H, 2·0; O, 23·15%; *M*, 550. $C_{12}H_{10}Mn_2O_8Se_2$ requires C, 26·2; H, 1·8; O, 23·25%; *M*, 550). The compound decomposes without melting above 135°.

(*c*) $[Mn(CO)_4SeC_3H_7]_2$. Manganese pentacarbonyl hydride (0·4 g., 2·0 mmoles) reacted with di-n-propyl diselenide (1·0 g., 4·62 mmoles), to give the *complex* (0·5 g., 0·83 mmole) (83%), m. p. 77—78° (Found: C, 29·15; H, 2·5; O, 22·1%. *M*, 578. $C_{14}H_{14}Mn_2O_8Se_2$ requires C, 29·5; H, 2·4; O, 22·15%; *M*, 578).

Preparation of Perfluoroalkyl Selenium Derivatives.—(*a*) $[Mn(CO)_4SeCF_3]_2$. Manganese pentacarbonyl hydride (0·7 g., 3·6 mmoles) reacted with bistrifluoromethyl diselenide (1·0 g., 4·1 mmoles), to give the *complex* (0·6 g., 0·95 mmole) (53%), m. p. 96—97° (Found: C, 19·5%; *M*, 630. $C_{10}H_6Mn_2O_8Se_2$ requires C, 19·05%; *M*, 630).

(*b*) $[Mn(CO)_4SeC_2F_5]_2$. Manganese pentacarbonyl hydride (0·8 g., 4·1 mmoles) reacted with bispentafluoroethyl diselenide (1·2 g., 3·1 mmoles), to give brown, needle-like crystals (0·8 g., 1·1 mmoles) (54%) of the *complex*, m. p. 78—80° (Found: C, 19·85%; *M*, 730. $C_{12}F_{10}Mn_2O_8Se_2$ requires C, 19·7%; *M*, 730).

(*c*) $[Mn(CO)_4SeC_3F_7]_2$. Manganese pentacarbonyl hydride (0·8 g., 4·1 mmoles) reacted with bisheptafluoropropyl diselenide (1·6 g., 3·3 mmoles), to give brown needle-like crystals (0·85 g., 1·0 mmole) (59% yield based on the hydride) of the *complex*, m. p. 97—99° (Found: C, 20·8%; *M*, 830. $C_{14}F_{14}Mn_2O_8Se_2$ requires C, 20·25%; *M*, 830).

Infrared Spectra.—These were recorded in pressed KBr discs using a Perkin-Elmer model 21 double-beam or model 237 grating spectrophotometer. The main frequencies are listed below:

Compound	CO stretching frequencies	Other frequencies
$[Mn(CO)_4SeCH_3]_2$	2050vs, 2010vs, 1985vs, 1970vs, 1950vs	2918w, 1422m, 1270w, 905w, 895w
$[Mn(CO)_4SeC_2H_5]_2$	2065vs, 2002vs, 1980vs, 1932vs	2980m, 2940m, 1647m, 1620m, 1450s, 1435w, 1383w, 1226m, 1040w, 964w
$[Mn(CO)_4SeC_3H_7]_2$	2060vs, 2010vs, 1975vs, 1940vs	2960m, 2930m, 2870m, 1634m, 1465m, 1428m, 1382w, 1330w, 1205m, 1085w, 1025w, 735w
$[Mn(CO)_4SeCF_3]_2$	2100vs, 2060vs, 2020vs, 1955vs	2440w, 1640w, 1620m, 1140vs, 1093vs, 1053vs, 740s
$[Mn(CO)_4SeC_2F_5]_2$	2090vs, 2040vs, 2020vs, 1990vs	1643w, 1420w, 1320vs, 1290s, 1265m, 1218vs, 1210vs, 1118vs, 1090vs, 1010m, 925vs, 742s
$[Mn(CO)_4SeC_3F_7]_2$	2095vs, 2035vs, 2010vs, 2000vs	1335s, 1322m, 1240vs, 1200vs, 1118vs, 1098m, 1020m, 932m, 825s, 738s

Nuclear Magnetic Resonance Spectra.—These were recorded on a Varian A-60 spectrometer; the samples were run in carbon tetrachloride solution with tetramethylsilane as internal standard. The proton magnetic resonance spectra showed the following features (chemical shifts are given in τ values; the spin–spin coupling constants are given in parentheses): $[Mn(CO)_4SeCH_3]_2$ 8·08; $[Mn(CO)_4SeC_2H_5]_2$ 7·28 (quartet, $J_{H1,2} = 7{\cdot}5$ c./sec.); and 8·78 (triplet, $J_{H1,2} = 7{\cdot}5$ c./sec.); $[Mn(CO)_4SeC_3H_7]_2$ 7·3 (triplet, $J_{H1,2} = 7{\cdot}5$ c./sec.), 8·5 (multiplet) and 9·0 (triplet).

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