Organometallic selenolates. Part 2. [1] A new synthesis of dimeric (selenolato) tetracarbonylmanganese(I) complexes. Crystal structures of [Mn(CO)$_4$SeR]$_2$; R = CH$_2$Ph, C(O)Ph and CO$_2$Me [2]

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Abstract

Dimeric selenolato-carbonyl manganese(I) complexes [Mn(CO)$_4$SeR]$_2$ (R = CH$_2$Ph, C(O)Ph, CO$_2$Ph, CO$_2$Me) have been synthesised via reaction of elemental selenium with NaMn(CO)$_5$ and subsequent reaction with the corresponding organohalides in one-pot syntheses. They have been characterised by spectroscopic methods (^{1}H, ^{13}C, ^{77}Se) and the chemical shifts have been compared with the assumed reaction intermediate [Mn(CO)$_4$Se]$_2$Na$_2$. Additionally, X-ray crystal structure analyses have been performed for [Mn(CO)$_4$(SeR)]$_2$ (R = CH$_2$Ph, C(O)Ph, CO$_2$Me).

Keywords: Manganese; Selenolates; X-ray structure

1. Introduction

Organoselenolato transition metal complexes are of current interest because of their potential use in material science and, in the case of homoleptic complexes, as volatile single-source precursors [2].

Apart from various syntheses of transition-metal selenolates, only a few general methods for the preparation of neutral selenolato manganese complexes have been reported. Thus the reaction of Mn(CO)$_5$X (X = Cl, Br) with organotin selenides or the reaction of Mn(CO)$_5$H with various aliphatic diselenides leads directly to the dimeric selenolate manganese complexes [Mn(CO)$_4$(SeR)]$_2$, whereas the reaction of Mn[N(SiMe$_3$)$_2$]$_2$ with a highly sterically hindered selenol leads to the homoleptic dimeric compound [Mn(SeR)$_2$]$_2$ (R = 2,4,6-^{i}Pr$_3$-C$_6$H$_2$) [3,4]. Additionally, the remarkable deep blue radical cpMn(CO)$_2$SePh has been prepared by reacting the unsaturated complex fragment cpMn(CO)$_2$THF with PhSeH, PhSeO$_2$H or Ph$_2$Se$_2$ in moderate yields [5]. Similar manganese complexes are

precursors for organomanganese "inidine" complexes such as [{(η^5-MeC$_5$H$_4$)(CO)$_2$Mn}$_2$SeMes]$^+$ [5b].

Recently we developed a new route to organometallic selenolates via the insertion of selenium into metal–lithium bonds or its reaction with sodium transition-metal carbonylates, and subsequent reactions with organohalides [1]. Here we report on an application of this method to the synthesis of the dimeric (selenolato)tetracarbonylmanganese(I) complexes [Mn(CO)$_4$(SeR)]$_2$ (R = PhCH$_2$, PhC(O), PhCO$_2$, MeCO$_2$).
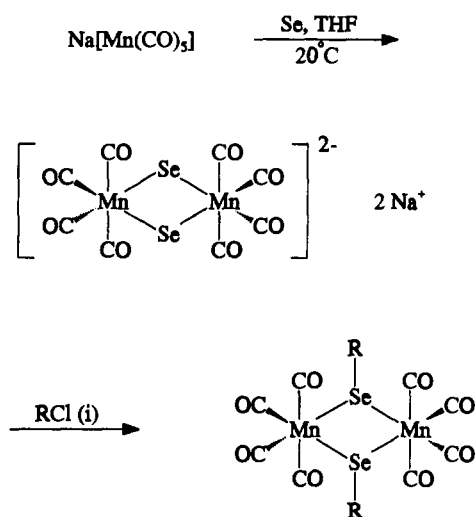
2. Results and discussion

Grey selenium reacts readily with alkali-metal manganese carbonylates in tetrahydrofuran (THF) solutions to form selenocarbonylate manganese anions. Subsequent reactions with organohalides lead to neutral dimeric (selenolato)tetracarbonylmanganese(I) complexes (Scheme 1).

These reactions can be performed advantageously as one-pot syntheses under mild conditions in moderate to good yields. Decacarbonyldimanganese Mn$_2$(CO)$_{10}$ and (pentacarbonyl)halomanganese(I) Mn(CO)$_5$X (X = Cl, Br, I) are both possible starting materials, since these complexes can easily be transformed into the corre-

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[1] For Part 1 see Ref. [1].
[2] Dedicated to Professor H.W. Roesky on the occasion of his 60th birthday.

Na[Mn(CO)₅] $\xrightarrow[20°C]{Se, THF}$

RCl (i) $\longrightarrow$

(i) R: 1 = PhCH₂   2 = PhC(O)

3 = PhCO₂   4 = MeCO₂

Scheme 1. Synthesis of the dimeric selenolato manganese(I) complexes [Mn(CO)₄(SeR)]₂.

sponding alkali-metal carbonylates by reduction with commercially available standardised THF solutions of M[BEt₃H] (M = Li, Na or K) [6]. Adding equimolar

amounts of grey selenium to the deep red manganese carbonylate solutions leads to spontaneous formation of dimeric selenocarbonylate manganese anion under instantaneous CO gas evolution. The assumed product $Na_2[Mn(CO)_4Se]_2$ forms deep red–brown solutions and shows less pronounced sensitivity towards oxygen than the corresponding manganese carbonylates. Attempts to precipitate this selenocarbonylate anion with large cations (e.g. $[Ph_3PNPPh_3]^+$) failed, leading instead to decomposition of the reaction mixture; it may contain other species besides the assumed $Na_2[Mn(CO)_4Se]_2$. In contrast to these observations, we have found that ionic manganese carbonylates with large cations (e.g. $[Ph_3PNPPh_3]^+[Mn(CO)_5]^-$) do not react with grey or red selenium under the same conditions. This suggests that the reaction mechanism may not be simply ionic. Further studies are in progress in this respect.

The reactions of the selenocarbonylate manganese anion with organohalides proceed under mild conditions (ambient temperature, reaction time usually 1 h). The resulting complexes are air- and moisture-stable crystalline solids, soluble in halogenoalkanes and many other polar solvents such as acetone, dimethylformamide (DMF) and ethyl acetate.

We conclude that we have found an elegant method of introducing the RSe⁻-group into transition-metal complexes. For manganese, the hitherto reported syntheses suffer from serious disadvantages, such as the

Table 1
Physical and analytical [a] data of the new complexes

Complex	M.p. (°C)	Yield	M⁺ [b]	Analysis (%)	
				C	H
1 [Mn(CO)₄(SeCH₂Ph)]₂	156	47	670	39.1 (39.2)	2.0 (2.1)
2 [Mn(CO)₄(SeC(O)Ph)]₂	142	61	704	36.9 (37.6)	1.5 (1.4)
3 [Mn(CO)₄(SeCO₂Ph)]₂	116	34	736	35.1 (36.0)	1.3 (1.4)
4 [Mn(CO)₄(SeCO₂Me)]₂	142	30	612	23.3 (23.7)	0.9 (1.0)

[a] Required values are given in parentheses. [b] Molecular ion peak.

Table 2
Spectroscopic data for 1–4

Complex	¹H [a]	¹³C [a]	⁷⁷Se (ppm) [a,b]	ν(CO) (cm⁻¹) [c,d]
1	3.84 (2H, s, br, CH₂), 7.26 (5H, s, br, Ph)	26.4 (s, br, CH₂), 138.5 (s, br, Ph), 210.2 (s, br, CO)	−442.6 (s, br)	2060 s, 1980 vs, 1954 vs
2	7.43 (2H, t, J(HH) = 7 Hz, m-Ph), 7.59 (1H, t, J(HH) = 7 Hz, p-Ph), 7.82–7.87 (2H, m, o-Ph)	134.0, 135.8 (s, Ph) 193.0 (s, C(O)), 211.3, 214.5 (s, CO)	−170.4 (s)	2065 m, 1992 s, 1918 s, 1780 m [C(O)]
3	7.19–7.47 (m, 5H, Ph)	120.7, 126.8, 129.8 (s, Ph), 160.2 (s, CO₂), 209.7, 214.4 (s, br, CO)	−212.9 (s)	2082 vs, 2007 vs, 1972 vs, 1733 s [C(O)]
4	3.93 (s, 6H, CH₃)	55.4 (s, CH₃), 160.5 (s, CO₂), 210.8, 214.4 (s, br, CO)	−232.9 (s)	2078 vs, 2007 vs 1969 vs, 1713 s [C(O)]

[a] Solvent CDCl₃. [b] Saturated solutions. [c] Solid in KBr. [d] $Na_2[SeMn(CO)_4]_2$ (solution, THF) 2049 s, 2042 s, 1985 vs, 1966 vs, 1913 vs, 1892 vs.
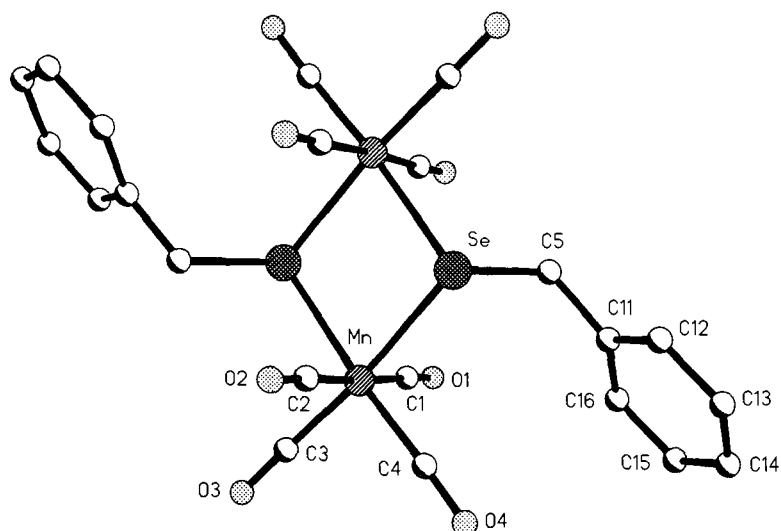
Fig. 1. Molecular structure of 1; radii are arbitrary; H-atoms omitted for clarity.

use of malodorous and toxic organic selenium compounds (e.g. PhSeH, [Me$_3$Sn]$_2$Se), or multi-step reactions with moderate yields. As also shown in the system LiMcp(CO)$_3$/Se (M = Mo, W), the reaction intermediates are strongly nucleophilic and further reactions proceed under mild conditions without the necessity of using organoselenium compounds [1]. Since elemental selenium is cheap and can be handled without precautions, the moderate yields in some cases can be tolerated.

For analytical and physical data of the new complexes see Table 1.

The NMR data are listed in Table 2. With the exception of compound 2 most of the signals are broad, probably due to paramagnetic impurities, but from ^{1}H and ^{13}C NMR data the functional groups can be as-

signed exactly. In order to examine the electronic influences of the organic group bonded at selenium, ^{77}Se NMR spectra were recorded. The reaction intermediate sodium selenocarbonylate manganese was measured as a concentrated THF solution with an internal CDCl$_3$ capillary. The resulting signal is a very broad singlet at −255.4 ppm (half-width 16000 Hz), suggesting unpaired electrons in the anion. This value is comparable with those of complexes 1–4, although the chemical shifts in ^{77}Se NMR spectra show a marked solvent dependence [7]. For [Mn(CO)$_4$(SeCH$_2$Ph)]$_2$ (1) the signal is shifted upfield, whereas the signals of compounds 2–4, with more electron-withdrawing organic substituents at selenium, are slightly shifted downfield. The values indicate that the bridging organoselenolate groups remove electron density from the electron-rich man-
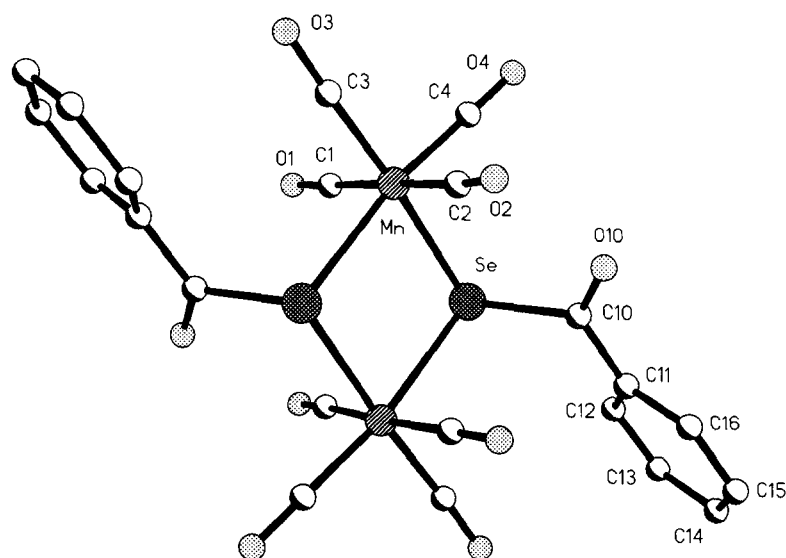

Fig. 2. Molecular structure of 2; radii are arbitrary; H-atoms omitted for clarity.

Table 3
Selected bond lengths (Å) and angles (°) for compound 1

Se–Mn	2.4926(4)	Se–C(5)	1.985(2)
Mn–C(1)	1.853(2)	Mn–C(2)	1.859(2)
Mn–C(3)	1.816(2)	Mn–C(4)	1.819(2)
O(1)–C(1)	1.138(2)	O(2)–C(2)	1.135(2)
O(3)–C(3)	1.142(2)	O(4)–C(4)	1.142(2)
Mn–Se#1	2.4985(4)	C(5)–C(11)	1.498(2)
C(5)–Se–Mn	109.49(6)	C(5)–Se–Mn#1	104.79(5)
Mn–Se–Mn#1	97.446(13)	C(3)–Mn–C(4)	92.44(8)
C(3)–Mn–C(1)	90.59(9)	C(4)–Mn–C(1)	92.11(9)
C(3)–Mn–C(2)	91.15(8)	C(4)–Mn–C(2)	89.75(8)
C(1)–Mn–C(2)	177.39(7)	C(3)–Mn–Se	173.94(6)
C(4)–Mn–Se	93.08(6)	C(1)–Mn–Se	91.69(6)
C(2)–Mn–Se	86.39(6)	C(3)–Mn–Se#1	92.00(6)
C(4)–Mn–Se#1	175.30(6)	C(1)–Mn–Se#1	86.30(6)
C(2)–Mn–Se#1	91.70(5)	Se–Mn–Se#1	82.554(13)
O(1)–C(1)–Mn	178.6(2)	O(2)–C(2)–Mn	177.8(2)
O(3)–C(3)–Mn	179.0(2)	O(4)–C(4)–Mn	177.3(2)
C(11)–C(5)–Se	112.43(13)	C(12)–C(11)–C(5)	120.7(2)

Symmetry transformation used to generate equivalent atoms: #1, −x + 1, −y, −z + 1.

ganese. Unfortunately, no comparable NMR data for other selenolato manganese complexes are yet available. The IR data are typical of this class of compounds [3]. The IR spectrum of $Na_2[SeMn(CO)_4]_2$ recorded in THF solution shows six bands in the carbonyl region, which implies a lower than ideal symmetry.

Although the class of the title compounds has been known for 30 years, only one crystal structure has appeared in the literature, namely $[Mn(CO)_4(SeCF_3)]_2$ [8]. Because of their increasing importance, and to examine whether the different electronic effects of the different organoselenolato bridges are reflected in dif-

ferent geometries, the molecular structures of $[Mn(CO)_4(SeCH_2Ph)]_2$ (1), $[Mn(CO)_4\{SeC(O)Ph\}]_2$ (2) and $[Mn(CO)_4(SeCO_2Me)]_2$ (4) have been determined. They are shown in Figs. 1–3; selected bond lengths and angles are listed in Tables 3–5.

All compounds crystallise with crystallographic inversion symmetry, but 4 crystallises with four half-molecules per asymmetric unit. The molecular structures are closely related. The manganese atoms display a distorted octahedral geometry associated from constraints imposed by four-membered Mn_2Se_2 rings. The Se–C bond lengths are comparable with those in [Mn

Table 4
Selected bond lengths (Å) and angles (°) for compound 2

Mn–Se	2.4816(9)	Mn–Se#1	2.5192(8)
Mn–C(1)	1.852(5)	Mn–C(2)	1.874(5)
Mn–C(3)	1.812(5)	Mn–C(4)	1.814(5)
Se–C(10)	1.989(4)	C(1)–O(1)	1.136(5)
C(2)–O(2)	1.134(5)	C(3)–O(3)	1.150(5)
C(4)–O(4)	1.131(5)	C(10)–O(10)	1.197(6)
C(10)–C(11)	1.480(6)		
C(3)–Mn–C(4)	92.9(2)	C(3)–Mn–C(1)	89.0(2)
C(4)–Mn–C(1)	92.2(2)	C(3)–Mn–C(2)	89.2(2)
C(4)–Mn–C(2)	92.1(2)	C(1)–Mn–C(2)	175.4(2)
C(3)–Mn–Se	174.65(14)	C(4)–Mn–Se	88.77(14)
C(1)–Mn–Se	85.87(14)	C(2)–Mn–Se	95.79(13)
C(3)–Mn–Se#1	95.67(14)	C(4)–Mn–Se#1	171.08(14)
C(1)–Mn–Se#1	90.29(13)	C(2)–Mn–Se#1	85.63(13)
Se–Mn–Se#1	82.88(3)	C(10)–Se–Mn	106.75(14)
C(10)–Se–Mn#1	103.28(14)	Mn–Se–Mn#1	97.12(3)
O(1)–C(1)–Mn	177.8(4)	O(2)–C(2)–Mn	173.6(4)
O(3)–C(3)–Mn	178.2(4)	O(4)–C(4)–Mn	179.5(4)
O(10)–C(10)–C(11)	125.2(4)	O(10)–C(10)–Se	120.4(3)
C(11)–C(10)–Se	114.4(3)	C(12)–C(11)–C(10)	122.9(4)
C(16)–C(11)–C(10)	117.2(5)		

Symmetry transformation used to generate equivalent atoms: #1, −x + 1, −y + 1, −z.

Table 5
Selected bond lengths (Å) and angles (°) for compound **4**

Mn(1)–Se(1)#1	2.4842(10)	Mn(1)–Se(1)	2.5041(10)
Mn(2)–Se(2)#2	2.4862(10)	Mn(2)–Se(2)	2.5080(10)
Mn(3)–Se(3)#3	2.4744(8)	Mn(3)–Se(3)	2.4972(9)
Mn(4)–Se(4)#4	2.4862(9)	Mn(4)–Se(4)	2.5034(8)
Mn(1)–C(11)	1.846(4)	Mn(1)–C(12)	1.854(4)
Mn(1)–C(13)	1.812(4)	Mn(1)–C(14)	1.815(4)
Mn(2)–C(21)	1.859(4)	Mn(2)–C(22)	1.865(4)
Mn(2)–C(23)	1.817(4)	Mn(2)–C(24)	1.821(4)
Mn(3)–C(31)	1.843(4)	Mn(3)–C(32)	1.866(4)
Mn(3)–C(33)	1.818(4)	Mn(3)–C(34)	1.818(4)
Mn(4)–C(41)	1.853(4)	Mn(4)–C(42)	1.862(4)
Mn(4)–C(43)	1.813(4)	Mn(4)–C(44)	1.826(4)
Se(1)–C(15)	1.949(5)	Se(2)–C(25)	1.946(4)
Se(3)–C(35)	1.947(4)	Se(4)–C(45)	1.947(4)
C(11)–O(11)	1.126(5)	C(12)–O(12)	1.134(5)
C(13)–O(13)	1.143(5)	C(14)–O(14)	1.140(5)
C(15)–O(15)	1.180(5)	C(15)–O(16)	1.317(5)
C(16)–O(16)	1.457(5)	C(21)–O(21)	1.132(5)
C(22)–O(22)	1.136(5)	C(23)–O(23)	1.139(5)
C(24)–O(24)	1.137(5)	C(25)–O(25)	1.190(5)
C(25)–O(26)	1.327(5)	C(26)–O(26)	1.456(5)
C(31)–O(31)	1.133(5)	C(32)–O(32)	1.132(5)
C(33)–O(33)	1.138(5)	C(34)–O(34)	1.128(5)
C(35)–O(35)	1.182(5)	C(35)–O(36)	1.320(5)
C(36)–O(36)	1.450(5)	C(41)–O(41)	1.134(5)
C(42)–O(42)	1.133(5)	C(43)–O(43)	1.140(5)
C(44)–O(44)	1.136(5)	C(45)–O(45)	1.187(5)
C(45)–O(46)	1.336(5)	C(46)–O(46)	1.452(5)
C(13)–Mn(1)–C(14)	92.9(2)	C(13)–Mn(1)–C(11)	90.3(2)
C(14)–Mn(1)–C(11)	89.6(2)	C(13)–Mn(1)–C(12)	91.7(2)
C(14)–Mn(1)–C(12)	90.7(2)	C(11)–Mn(1)–C(12)	178.0(2)
C(13)–Mn(1)–Se(1)#1	92.83(13)	C(14)–Mn(1)–Se(1)#1	173.59(13)
C(11)–Mn(1)–Se(1)#1	87.45(14)	C(12)–Mn(1)–Se(1)#1	92.00(14)
C(13)–Mn(1)–Se(1)	174.54(13)	C(14)–Mn(1)–Se(1)	92.38(13)
C(11)–Mn(1)–Se(1)	91.13(13)	C(12)–Mn(1)–Se(1)	86.87(14)
Se(1)#1–Mn(1)–Se(1)	81.98(3)	C(23)–Mn(2)–C(24)	91.7(2)
C(23)–Mn(2)–C(21)	91.3(2)	C(24)–Mn(2)–C(21)	90.3(2)
C(23)–Mn(2)–C(22)	90.9(2)	C(24)–Mn(2)–C(22)	91.4(2)
C(21)–Mn(2)–C(22)	177.1(2)	C(23)–Mn(2)–Se(2)#2	93.45(13)
C(24)–Mn(2)–Se(2)#2	173.16(13)	C(21)–Mn(2)–Se(2)#2	85.11(13)
C(22)–Mn(2)–Se(2)#2	92.99(12)	C(23)–Mn(2)–Se(2)	175.02(13)
C(24)–Mn(2)–Se(2)	92.92(13)	C(21)–Mn(2)–Se(2)	90.38(13)
C(22)–Mn(2)–Se(2)	87.25(13)	Se(2)#2–Mn(2)–Se(2)	82.04(3)
C(33)–Mn(3)–C(34)	91.2(2)	C(33)–Mn(3)–C(31)	93.0(2)
C(34)–Mn(3)–C(31)	91.1(2)	C(33)–Mn(3)–C(32)	92.8(2)
C(34)–Mn(3)–C(32)	89.8(2)	C(31)–Mn(3)–C(32)	174.1(2)
C(33)–Mn(3)–Se(3)#3	92.62(12)	C(34)–Mn(3)–Se(3)#3	175.1(2)
C(31)–Mn(3)–Se(3)#3	85.51(12)	C(32)–Mn(3)–Se(3)#3	93.15(12)
C(33)–Mn(3)–Se(3)	173.93(13)	C(34)–Mn(3)–Se(3)	94.64(13)
C(31)–Mn(3)–Se(3)	88.63(13)	C(32)–Mn(3)–Se(3)	85.50(13)
Se(3)#3–Mn(3)–Se(3)	81.67(3)	C(43)–Mn(4)–C(44)	92.4(2)
C(43)–Mn(4)–C(41)	91.3(2)	C(44)–Mn(4)–C(41)	90.4(2)
C(43)–Mn(4)–C(42)	90.4(2)	C(44)–Mn(4)–C(42)	92.4(2)
C(41)–Mn(4)–C(42)	176.7(2)	C(43)–Mn(4)–Se(4)#4	93.88(14)
C(44)–Mn(4)–Se(4)#4	172.65(12)	C(41)–Mn(4)–Se(4)#4	85.63(13)
C(42)–Mn(4)–Se(4)#4	91.43(12)	C(43)–Mn(4)–Se(4)	174.69(13)
C(42)–Mn(4)–Se(4)	86.48(12)	Se(4)#4–Mn(4)–Se(4)	81.94(3)
C(15)–Se(1)–Mn(1)#1	106.13(13)	C(15)–Se(1)–Mn(1)	106.86(13)
Mn(1)#1–Se(1)–Mn(1)	98.02(3)	C(25)–Se(2)–Mn(2)#2	108.36(12)
C(25)–Se(2)–Mn(2)	103.77(12)	Mn(2)#2–Se(2)–Mn(2)	97.96(3)
C(35)–Se(3)–Mn(3)#3	106.85(12)	C(35)–Se(3)–Mn(3)	107.36(13)
Mn(3)#3–Se(3)–Mn(3)	98.33(3)	C(45)–Se(4)–Mn(4)#4	107.95(12)
C(45)–Se(4)–Mn(4)	107.49(12)	Mn(4)#4–Se(4)–Mn(4)	98.06(3)

Table 5 (continued)

O(11)–C(11)–Mn(1)	178.8(4)	O(12)–C(12)–Mn(1)	176.7(4)
O(13)–C(13)–Mn(1)	178.5(4)	O(14)–C(14)–Mn(1)	179.9(4)

Symmetry transformations used to generate equivalent atoms: #1, $-x + 1$, $-y + 1$, $-z + 1$; #2, $-x + 1$, $-y + 2$, $-z$; #3, $-ix + 1$, $-y + 1$, $-z$; #4, $-x + 2$, $-y$, $-z + 1$.

$(CO)_4(SeCF_3)]_2$ [8]. All CO groups bonded at manganese show comparable C–O bond lengths. The Mn–C bond lengths *trans* to selenium are consistently shorter (ca. 0.03–0.04 Å) than those *trans* to other carbonyls, reflecting the less pronounced *trans* influence of selenium donors.

The most striking feature common to all three structures is a planar Mn_2Se_2 core, which forms a parallelogram with Mn–Se bond lengths of 2.499(1), 2.493(1) Å (1), 2.482(1), 2.519(1) Å (2) and 2.483(1), 2.503(1) Å (4, average of four Mn–Se bond lengths per asymmetric unit, see below) respectively. These distances are considerably shorter than those found in $[Mn\{N(SiMe_3)_2\}$ $(Se-2,4,6-^iPr_3-C_6H_2)(THF)]_2$ (2.582(2), 2.645(2) Å) [4] or in the anion $[Mn(SePh)_4]^{2-}$ (2.555(2) to 2.581(2) Å) [9], but comparable with those observed in $[Mn(CO)_4(SeCF_3)]_2$ (2.505(6), 2.490(6) Å) [8]. The bond angles in the Mn_2Se_2 moiety at manganese are 82.55(1)° (1), 82.88(3)° (3) and 81.91(3)° (4, see above). At selenium the angles are 97.45(1)° (1), 97.12(3)° (3) and 98.09(3)° (4, see above) respectively. A similar arrangement was found in $[Mn(CO)_4(SeCF_3)]_2$ and in $[Mn\{N(SiMe_3)_2\}(Se-2,4,6-^iPr_3-C_6H_2)(THF)]_2$, where the steric requirements of the substituents at manganese are much larger. The asymmetric bridging in the latter compound was attributed to results of changes in the metal-chalcogen orbital overlap compared with the metal-ligand overlap with organic substituents; such

effects can also be seen in the Group 12 chalcogenolato complexes $[M(EAr')_2]_2$ (M = Zn and Cd; Ar' = 2,4,6-$^tBu_3-C_6H_2$) [10]. However, in complex 1 the bridging is symmetric and complex 4 shows some deviation from equal Mn–Se bond lengths, whereas in complex 2 the difference in the Mn–Se bond lengths is almost 0.04 Å. The observed symmetric bridging in $[Mn(CO)_4(SeCF_3)]_2$ and $[Mn(CO)_4(SeCH_2Ph)]_2$ suggests that electronic effects alone cannot be responsible for asymmetry of the selenolato bridges in the complexes discussed above.

3. Experimental details

All syntheses were carried out in dried solvents using conventional Schlenk techniques. NMR spectra were recorded on a Bruker AC 200 spectrometer (^1H at 200.1, ^{13}C at 50.3 and ^{77}Se at 38.2 MHz). Tetramethyl-silane (^1H, ^{13}C) and $SeMe_2$ (^{77}Se) were used as external references. Mass spectra (EI) were obtained on a Finnigan MAT 8430 instrument. Elemental analyses were performed locally. IR spectra were recorded on a Biorad FTS 165 spectrometer.

$Mn_2(CO)_{10}$ and $Mn(CO)_5Br$ were prepared according to established literature methods [11,12]. The following chemicals were purchased from Aldrich: $PhCH_2Cl$, $PhC(O)Cl$, $PhCO_2Cl$, $MeCO_2Cl$ and 1M THF solutions of $Li[BEt_3H]$ and $Na[BEt_3H]$.

3.1. Synthesis of $[Mn(CO)_4(SeR)]_2$ (general procedure) 1–4

THF solutions containing 2 mmol $Na[Mn(CO)_5]$ were prepared from $Mn_2(CO)_{10}$ or $Mn(CO)_5Br$ by reaction with excess $Na[BEt_3H]$ according to the literature method [6]. 1 cm^3 ^tBuOH was added to destroy the excess $Na[BEt_3H]$. After a further 15 min of stirring, the solvent was removed in vacuo to eliminate BEt_3. 158 mg grey selenium (2 mmol) and 20 cm^3 of THF were then added to the residue. Immediate CO gas evolution occurred and the resulting solutions turned deep red–brown. After 20 min stirring, 1 cm^3 of the organochloride (excess) was added. The solutions turned deep red immediately. After stirring overnight, the reaction mixture was filtered over Celite, evaporated to dryness and the remaining residue was extracted with ethyl acetate. Crystallization with light-petroleum af-
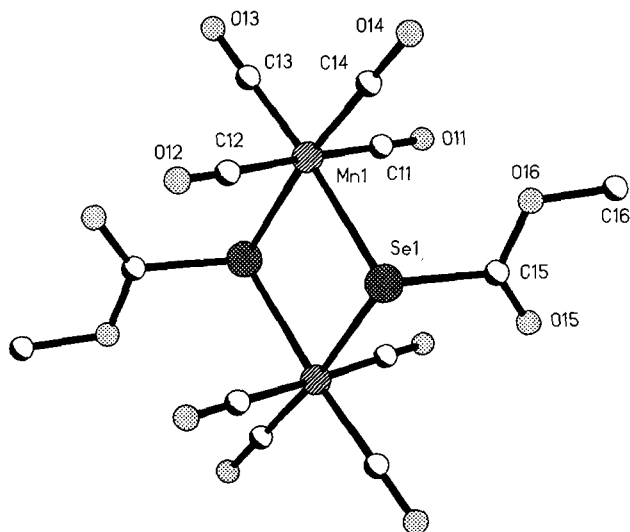

Fig. 3. One of the four independent molecules of 4 in the unit cell; radii are arbitrary; H-atoms omitted for clarity.

Table 6
Crystal data for 1, 2 and 4

Compound	1	2	4
Formula	$C_{22}H_{14}Mn_2O_8Se_2$	$C_{22}H_{10}Mn_2O_{10}Se_2$	$C_{12}H_6Mn_2O_{12}Se_2$
Crystal size (mm³)	0.5 × 0.4 × 0.4	0.55 × 0.12 × 0.1	0.8 × 0.2 × 0.15
M	674.13	702.1	609.97
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Cell constants			
a (Å)	6.4337(8)	6.5956(10)	6.480(2)
b (Å)	9.4811(10)	8.8902(14)	17.721(4)
c (Å)	10.4500(12)	11.022(2)	17.959(4)
α (°)	84.397(8)	92.907(14)	67.93(2)
β (°)	84.566(8)	103.013(14)	83.71(2)
γ (°)	72.430(8)	106.298(8)	89.58(2)
U (Å³)	603.4(1)	599.9(2)	1898.2(8)
Z	1	1	4
D_C (g cm⁻³)	1.855	1.944	2.134
μ (mm⁻¹)	4.107	4.142	5.224
max., min. transmissions	0.97, 0.43	0.92, 0.83	0.99, 0.73
$F(000)$	328	340	1168
No. data measured	4038	3548	12903
$2\Theta_{max}$ (°)	55	50	55
No. unique data	2782	2098	8735
No. parameters	155	163	509
$wR(F^2)$ (all reflections)	0.0525	0.0791	0.0826
$R(F)$, $F > 4\sigma(F)$	0.0209	0.0328	0.0371
Weighting parameters			
a	0.0352	0.0361	0.0277
b	0	0	0.8514
GOF	1.0	1.05	1.07
Max. $\Delta\rho$ (e Å⁻³)	0.5	0.6	0.7

forded orange to red solids. The products can be purified by recrystallization from dichloromethane/light-petroleum at −20°C.

For analytical and NMR data see Tables 1 and 2.

3.2. Crystallography

Crystals of $[Mn(CO)_4(SeCH_2Ph)]_2$ (1), $[Mn(CO)_4\{SeC(O)Ph\}]_2$ (2) and $[Mn(CO)_4(SeCO_2Me)]_2$ (4) were mounted on glass fibres in inert oil and transferred to

Table 7
Atomic coordinates (×10⁴) for compound 1

	x	y	z
Se	3501.8(3)	53.4(2)	3793.2(2)
Mn	4009.1(4)	2076.5(2)	4970.1(3)
O(1)	7973(2)	2199(2)	3273(2)
O(2)	90(2)	1876(2)	6680(2)
O(3)	4739(3)	4253(2)	6586(2)
O(4)	1070(3)	4465(2)	3374(2)
C(1)	6464(3)	2138(2)	3912(2)
C(2)	1593(3)	1921(2)	6035(2)
C(3)	4449(3)	3407(2)	5972(2)
C(4)	2226(3)	3528(2)	3963(2)
C(5)	4970(3)	75(2)	2036(2)
C(11)	3679(3)	1285(2)	1139(2)
C(12)	1722(4)	1224(3)	729(2)
C(13)	623(4)	2312(3)	−174(2)
C(14)	1473(5)	3440(3)	−661(2)
C(15)	3372(6)	3518(2)	−236(2)
C(16)	4489(4)	2445(2)	667(2)

Table 8
Atomic coordinates (×10⁴) for compound 2

	x	y	z
Mn	4055.0(10)	2790.4(7)	−312.7(5)
Se	3970.8(7)	4876.7(5)	1242.1(4)
C(1)	1399(8)	2947(5)	−1203(4)
C(2)	6840(8)	2704(5)	485(4)
C(3)	3920(7)	1316(6)	−1550(4)
C(4)	2757(7)	1320(5)	580(4)
C(10)	6135(8)	4853(6)	2818(4)
C(11)	6413(8)	6100(5)	3837(4)
C(12)	4753(9)	6719(6)	3968(4)
C(13)	5153(11)	7883(7)	4944(5)
C(14)	7142(12)	8425(7)	5778(5)
C(15)	8795(11)	7794(7)	5675(5)
C(16)	8440(9)	6632(7)	4705(5)
O(1)	−223(6)	3019(4)	−1782(3)
O(2)	8509(6)	2558(4)	873(3)
O(3)	3793(6)	353(4)	−2325(3)
O(4)	1940(5)	409(4)	1138(3)
O(10)	7101(6)	3892(4)	2884(3)

the cold gas stream of the diffractometer (**1, 2** Siemens R3, −100°C; **4** Stoe Stadi4, −130°C; both equipped with a Siemens LT-2 low temperature attachment). Mo Kα radiation ($\lambda = 0.71073$ Å, graphite monochroma-

Table 9
Atomic coordinates ($\times 10^4$) for compound **4**

	x	y	z
Mn(1)	4125.8(9)	6034.7(3)	4940.0(3)
Mn(2)	6163.8(9)	10601.7(3)	−1069.4(3)
Mn(3)	5677.1(9)	5626.9(3)	588.9(3)
Mn(4)	9412.3(9)	−543.7(3)	4321.4(3)
Se(1)	7372.9(6)	5368.0(2)	4653.7(3)
Se(2)	7227.0(6)	9576.0(2)	217.0(2)
Se(3)	2559.3(6)	4977.5(2)	337.0(2)
Se(4)	7726.6(6)	411.7(2)	4914.3(2)
C(11)	3411(6)	6235(3)	3917(3)
C(12)	4920(7)	5812(3)	5960(3)
C(13)	1674(7)	6421(2)	5206(2)
C(14)	5431(7)	7032(2)	4566(2)
C(15)	8032(7)	5778(3)	3482(3)
C(16)	8776(8)	6971(3)	2329(3)
O(11)	2951(6)	6367(2)	3295(2)
O(12)	5469(6)	5707(3)	6568(2)
O(13)	116(5)	6667(2)	5357(2)
O(14)	6254(6)	7658(2)	4331(2)
O(15)	8367(7)	5364(2)	3102(2)
O(16)	8148(5)	6580(2)	3196(2)
C(21)	5161(7)	9768(3)	−1338(2)
C(22)	7130(6)	11406(3)	−746(2)
C(23)	5219(7)	11370(3)	−1948(2)
C(24)	8667(7)	10600(3)	−1639(2)
C(25)	7677(6)	8601(2)	−25(2)
C(26)	9577(8)	8147(3)	−971(3)
O(21)	4554(5)	9259(2)	−1500(2)
O(22)	7789(5)	11902(2)	−573(2)
O(23)	4677(6)	11849(2)	−2512(2)
O(24)	10214(5)	10606(2)	−2007(2)
O(25)	6932(5)	7941(2)	371(2)
O(26)	9017(5)	8799(2)	−689(2)
C(31)	6113(6)	4650(3)	1402(2)
C(32)	5013(6)	6561(3)	−258(2)
C(33)	8084(6)	6093(2)	674(2)
C(34)	4248(6)	5989(3)	1311(3)
C(35)	1587(6)	4076(3)	1339(2)
C(36)	668(8)	3760(3)	2732(2)
O(31)	6339(6)	4042(2)	1901(2)
O(32)	4514(5)	7126(2)	−751(2)
O(33)	9578(5)	6385(2)	738(2)
O(34)	3420(6)	6223(2)	1763(2)
O(35)	1159(6)	3411(2)	1389(2)
O(36)	1388(5)	4349(2)	1932(2)
C(41)	10773(7)	313(3)	3459(2)
C(42)	8113(6)	−1383(2)	5228(2)
C(43)	10730(6)	−1282(3)	3980(2)
C(44)	7249(6)	−504(2)	3737(2)
C(45)	7528(6)	1454(2)	4030(2)
C(46)	6426(8)	2050(3)	2730(3)
O(41)	11609(6)	831(2)	2926(2)
O(42)	7318(5)	−1890(2)	5781(2)
O(43)	11537(5)	−1741(2)	3752(2)
O(44)	5927(5)	470(2)	3361(3)
O(45)	7907(6)	2099(2)	4051(2)
O(46)	6798(5)	1324(2)	3419(2)

tor) was used to collect the intensity data with the ω-scan (Siemens) or the ω/Θ-scan (Stoe) technique. Cell constants were refined from setting angles of 61 (**1**, 2Θ range 15–24°) and 62 (**2**, 2Θ range 11–23°) or from $\pm\omega$ angles of 56 reflections (**4**, 2Θ range 20–23°). Absorption corrections were based on ψ-scans. The crystallographic program system used was SHELXL 93 [13]. The structures were solved by direct methods and refined by a full-matrix least-squares procedure on F^2. All non H-atoms were refined anisotropically; hydrogen atoms were included using a riding model or as rigid methyl groups. Weighting schemes were of the form $w^{-1} = [\sigma^2(F_o)^2 + (aP)^2 + bP]$ with $P = (F_o^2 + 2F_c^2)/3$.

Special features of refinement. For compound **1**, an extinction correction of the form $F_{corr.} = F/[1 + 0.001\,xF^2\lambda^3/\sin 2\Theta]^{0.25}$ was made, with a refined extinction coefficient x of 0.022(2).

A summary of crystal data is presented in Table 6; fractional atomic coordinates are given in Tables 7–9. Further details of the crystal structure determinations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD-401692 (**1**), 401693 (**2**), 401694 (**4**), the names of the authors, and the journal citation.

Acknowledgements

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