# Manganese(I) selenoether chemistry: synthesis, multinuclear NMR studies and the structures of [MnCl(CO)$_3$(MeSeCH$_2$CH$_2$SeMe)], [MnCl(CO)$_3$(MeSeCH$_2$CH$_2$CH$_2$SeMe)] and [MnBr(CO)$_3$\{C$_6$H$_4$(SeMe)$_2$-$o$\}]

**Julie Connolly, Maxwell K. Davies and Gillian Reid \***

*Department of Chemistry, University of Southampton, Highfield, Southampton, UK SO17 1BJ*

Reaction of [Mn(CO)$_5$X] (X = Cl, Br or I) with RSe(CH$_2$)$_n$SeR (R = Me or Ph, $n$ = 2; R = Me, $n$ = 3) or C$_6$H$_4$(SeMe)$_2$-$o$ in refluxing CHCl$_3$ yielded the neutral manganese(II) complexes [MnX(CO)$_3$\{RSe(CH$_2$)$_n$SeR\}] or [MnX(CO)$_3$\{C$_6$H$_4$(SeMe)$_2$-$o$\}] as yellow or orange solids. Infrared spectroscopic studies confirmed the *fac*-tricarbonyl arrangement. Proton, $^{13}$C-\{$^1$H\}, $^{77}$Se-\{$^1$H\} and $^{55}$Mn NMR spectroscopy has been used to probe the solution behaviour, and show that only those compounds involving PhSeCH$_2$CH$_2$SePh are undergoing rapid pyramidal inversion on the NMR timescale, with the individual NMR distinguishable invertomers observed for the other complexes (*meso*-1, *meso*-2 and DL) in varying ratios. X-Ray crystallographic analyses on three examples confirmed a *fac*-tricarbonyl arrangement, with the diselenoether ligand chelating: [MnCl(CO)$_3$(MeSeCH$_2$CH$_2$SeMe)] and [MnCl(CO)$_3$(MeSeCH$_2$CH$_2$CH$_2$SeMe)] adopt the DL arrangement, while [MnBr(CO)$_3$\{C$_6$H$_4$(SeMe)$_2$-$o$\}] is in the *meso*-2 form in the solid state. These are the first structure determinations on selenoether complexes of manganese(I) carbonyl halides. Most importantly, $^{55}$Mn NMR spectroscopic studies show that $\delta$($^{55}$Mn) is to low frequency of those of the corresponding thioether compounds, lying in the range $\delta$ −175 to −702, the lowest frequencies occurring for the iodo derivatives. The CO stretching frequencies and $^{55}$Mn NMR shifts show that, for a given X, the manganese(I) centre in [MnX(CO)$_3$(diselenoether)] is more shielded than in [MnX(CO)$_3$(dithioether)], possibly indicating increased σ donation in the former.

## Introduction

Recently we have been investigating the co-ordination chemistry of macrocyclic thio- and seleno-ethers with early transition metal centres, with particular interest in the hard (metal)–soft (ligand) interactions in these species. In the course of this work we have reported a range of complexes of hard chromium(III) and vanadium(III) ions, including [CrX$_2$([16]aneSe$_4$)]PF$_6$ (X = Cl or Br; [16]aneSe$_4$ = 1,5,9,13-tetraselenacyclohexadecane), *cis*-[CrX$_2$([14]aneS$_4$)]PF$_6$ ([14]aneS$_4$ = 1,4,8,11-tetrathiacyclotetradecane) and [VX$_3$([9]aneS$_3$)] (X = Cl, Br or I; [9]aneS$_3$ = 1,4,7-trithiacyclononane). EXAFS measurements and single crystal X-ray analyses have enabled us to establish the metal–thioether and –selenoether distances in these compounds.[1–3] More recently we have initiated a systematic investigation of manganese(I) carbonyl complexes incorporating Group 15 and 16 donor ligands. The lower electronegativity of Se over S leads one to anticipate that R$_2$Se might be a better ligand than R$_2$S to transition metal ions. However, experimental data to substantiate this are very limited. We proposed that $^{55}$Mn NMR and IR [$\nu$(CO)] data on a series of manganese(I) carbonyl halide adducts involving thioether and selenoether ligands might provide experimental evidence to support or refute this suggestion; $^{55}$Mn is 100% $I$ = 5/2 ($\varXi$ = 24.840 MHz) and possesses a moderately high quadrupole moment ($0.55 \times 10^{-28}$ m$^2$), thus for complexes with less than $O_h$ or $T_d$ symmetry a considerable electric field gradient is expected to result in substantial broadening of the resonances. However, $^{55}$Mn NMR studies have been conducted on several different classes of compound, including for example [Mn$_2$(CO)$_{10}$] and derivatives, [Mn(CO)$_5$X], [MnCp(CO)$_3$],

[Mn(CO)$_3$X(SbPh$_3$)$_2$] and [Mn(CO)$_4$X($\eta^1$-Ph$_2$SbCH$_2$SbPh$_2$)][4–9] and we have reported[10] the preparation and characterisation of [MnX(CO)$_3$(L–L)] [L–L = MeSCH$_2$CH$_2$SMe, MeSCH$_2$CH$_2$CH$_2$SMe, PhSCH$_2$CH$_2$SPh or C$_6$H$_4$(SMe)$_2$-$o$]. These species adopt *fac*-tricarbonyl arrangements with the dithioether chelating. The $^{55}$Mn NMR studies showed that where pyramidal inversion was slow on the NMR timescale the resonances for the individual invertomers were generally well resolved, giving $\delta$($^{55}$Mn) in the range +67 to −537. All of these species are significantly deshielded with respect to phosphine complexes such as [MnX(CO)$_3$(dppe)] (X = Cl, $\delta$ −1141; X = Br, −1254).[11]

In this paper we describe the first detailed preparations and spectroscopic characterisation, including $^1$H, $^{13}$C-\{$^1$H\}, $^{55}$Mn and $^{77}$Se-\{$^1$H\} NMR spectroscopy, of the manganese(I) diselenoether complexes [MnX(CO)$_3$(L–L)] [X = Cl, Br or I; L–L = MeSeCH$_2$CH$_2$SeMe, MeSeCH$_2$CH$_2$CH$_2$SeMe, PhSeCH$_2$CH$_2$SePh or C$_6$H$_4$(SMe)$_2$-$o$] and compare the results with those for related thioether compounds. The crystal structures of [MnCl(CO)$_3$(MeSeCH$_2$CH$_2$SeMe)], [MnCl(CO)$_3$(MeSeCH$_2$CH$_2$SeMe)] and [MnBr(CO)$_3$\{C$_6$H$_4$(SeMe)$_2$-$o$\}] are also described. Prior to this work there were very few known examples of selenoether complexes of Mn$^I$. The complex [MnBr(CO)$_3$(MeSeCH$_2$CH$_2$SeMe)] was first described by Abel and Hutson[12] some 30 years ago. We have resynthesized this in order to obtain multinuclear NMR data to allow comparisons with the other selenoether compounds and with the thioether analogue. The only other manganese(I) selenoether compounds reported are [Mn(NO)$_3$(Ph$_2$Se)$_2$][13] and the dinuclear [\{Mn(C$_5$H$_4$Me)(CO)$_2$\}$_2$(SeMe$_2$)] for which a crystal structure shows a bridging Me$_2$Se ligand.[14]

**Table 1** Infrared spectroscopic data (CO region) and FAB mass spectrometric data

| Compound | $\tilde{v}(CO)^a/cm^{-1}$ | $m/z^b$ |
|---|---|---|
| [MnCl(CO)₃(MeSeCH₂CH₂SeMe)] | 2034, 1959, 1917 | 392, [MnCl(CO)₃(L–L)]⁺; 357, [Mn(CO)₃(L–L)]⁺; 308, [MnCl(L–L)]⁺ |
| [MnBr(CO)₃(MeSeCH₂CH₂SeMe)] | 2031, 1955, 1917 | 436, [MnBr(CO)₃(L–L)]⁺; 357, [Mn(CO)₃(L–L)]⁺; 352, [MnBr(L–L)]⁺ |
| [MnI(CO)₃(MeSeCH₂CH₂SeMe)] | 2027, 1955, 1918 | 484, [MnI(CO)₃(L–L)]⁺; 400, [MnI(L–L)]⁺; 357, [Mn(CO)₃(L–L)]⁺ |
| [MnCl(CO)₃(MeSeCH₂CH₂CH₂SeMe)] | 2032, 1955, 1917 | 371, [Mn(CO)₃(L–L)]⁺; 322, [MnCl(L–L)]⁺ |
| [MnBr(CO)₃(MeSeCH₂CH₂CH₂SeMe)] | 2030, 1954, 1918 | 371, [Mn(CO)₃(L–L)]⁺; 366, [MnBr(L–L)]⁺ |
| [MnI(CO)₃(MeSeCH₂CH₂CH₂SeMe)] | 2025, 1951, 1918 | 414, [MnI(L–L)]⁺; 371, [Mn(CO)₃(L–L)]⁺ |
| [MnCl(CO)₃(PhSeCH₂CH₂SePh)] | 2034, 1956, 1925 | 481, [Mn(CO)₃(L–L)]⁺; 432, [MnCl(L–L)]⁺ |
| [MnBr(CO)₃(PhSeCH₂CH₂SePh)] | 2034, 1960, 1927 | 481, [Mn(CO)₃(L–L)]⁺; 476, [MnBr(L–L)]⁺ |
| [MnI(CO)₃(PhSeCH₂CH₂SePh)] | 2029, 1957, 1928 | 524, [MnI(L–L)]⁺; 481, [Mn(CO)₃(L–L)]⁺ |
| [MnCl(CO)₃{C₆H₄(SeMe)₂-o}] | 2037, 1964, 1924 | 405, [Mn(CO)₃(L–L)]⁺; 356, [MnCl(L–L)]⁺ |
| [MnBr(CO)₃{C₆H₄(SeMe)₂-o}] | 2035, 1963, 1924 | 484, [MnBr(CO)₃(L–L)]⁺; 405, [Mn(CO)₃(L–L)]⁺; 400, [MnBr(L–L)]⁺ |
| [MnI(CO)₃{C₆H₄(SeMe)₂-o}] | 2030, 1960, 1924 | 532, [MnI(CO)₃(L–L)]⁺; 448, [MnI(L–L)]⁺; 405, [Mn(CO)₃(L–L)]⁺ |

$^a$ Solutions in CHCl₃, all CO bands were strong. $^b$ Recorded using 3-nitrobenzyl alcohol matrix; major peaks only.

## Results and discussion

### Syntheses

Treatment of [MnX(CO)₅] (X = Cl, Br or I) with L–L [MeSeCH₂CH₂SeMe, MeSeCH₂CH₂CH₂SeMe, PhSeCH₂CH₂SePh or C₆H₄(SeMe)₂-o] in gently refluxing CHCl₃ affords the neutral species [MnX(CO)₃(L–L)] as yellow or orange solids. In all cases the reaction flasks were wrapped with foil to protect the manganese species from visible light. The isolated compounds are very soluble in chlorocarbons, but poorly soluble in hydrocarbons. The solids are reasonably stable, although solutions of the compounds decompose rapidly when exposed to oxygen and/or sunlight.

FAB Mass spectrometric data for these compounds are given in Table 1. Generally, peaks with the correct isotopic distributions consistent with [MnX(L–L)]⁺ and [Mn(CO)₃(L–L)]⁺ are observed, although the parent molecule and further peaks attributed to loss of X are also seen in a number of cases. Solution IR spectroscopic studies show three CO stretching vibrations, consistent with formation of *fac*-[MnX(CO)₃(L–L)]; v(CO) shifts to low frequency according to the series X = Cl > Br > I, although it is virtually insensitive to changes in the diselenoether ligand L. Importantly however, the values of v(CO) for these manganese selenoether compounds are consistently slightly to low frequency of those observed for [MnX(CO)₃(dithioether)], consistent with increased occupation of the CO π* orbitals in the former.[10]

### NMR Spectroscopy

We have recorded ¹H, ¹³C-{¹H}, ⁷⁷Se-{¹H} and ⁵⁵Mn NMR data for the compounds in this work. The combination of observable NMR nuclei, particularly ¹³C-{¹H}, ⁵⁵Mn and ⁷⁷Se-{¹H}, provides a very powerful way in which to monitor the species present in solution. Four isomers are possible for *fac*-[MnX(CO)₃(diselenoether)]; *meso*-1, *meso*-2 and a pair of NMR indistinguishable DL enantiomers, with interconversion occurring *via* pyramidal inversion at the co-ordinated selenoether donors. Abel *et al.*[15] have conducted detailed, quantitative NMR spectroscopic studies on a wide range of transition metal complexes with Group 16 donor ligands to probe inversion processes, and, the donor atom type, the nature of the interdonor linkage and the choice of transition metal have all been shown to be important parameters. In this work we are concerned with monitoring the trends in δ(⁵⁵Mn) and δ(⁷⁷Se) to probe the Se–Mn co-ordination rather than with the inversion barriers. Indeed Abel *et al.* have commented that the substantial quadrupole moment associated with ⁵⁵Mn is expected to lead to extensive broadening and hence these compounds are not suited to detailed dynamic ¹H NMR studies; we have shown that this is also true for [MnX(CO)₃(dithioether)], where broad resonances were observed at room temperature even for

compounds where inversion is slow on the NMR timescale; cooling the solutions sharpened the signals slightly.[10]
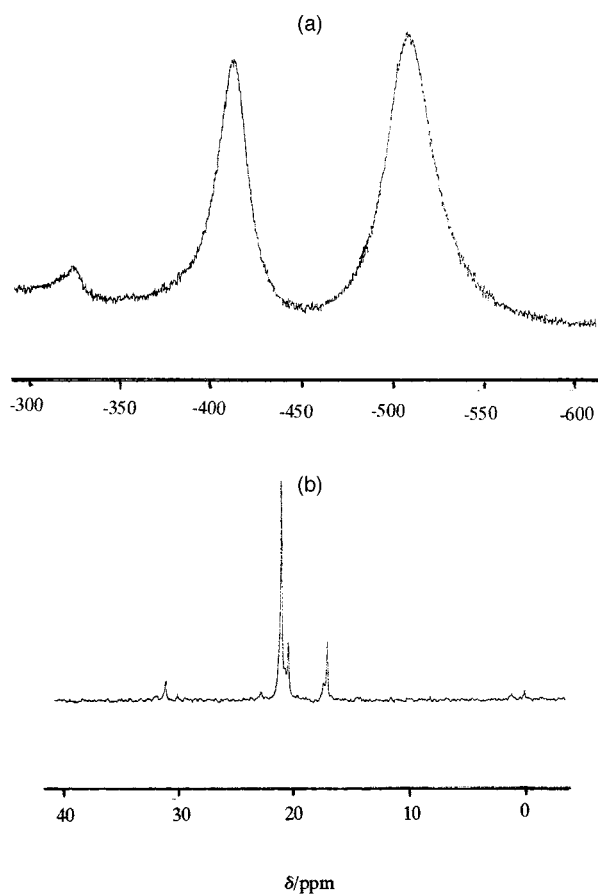


*meso*-1    *meso*-2    **DL**
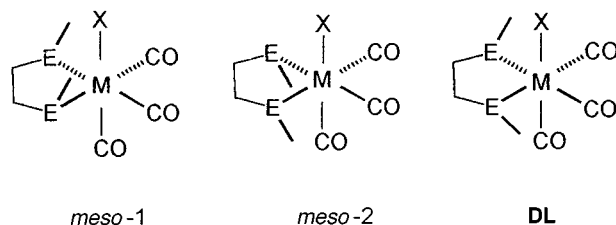
For the selenoether species ¹H NMR spectra were recorded at 300 K in CDCl₃ solution. These were not very informative since the broad ligand resonances made assignment of the isomers impossible. ¹³C-{¹H} NMR spectroscopy is rather more useful, providing evidence that pyramidal inversion is rapid on the NMR timescale at 300 K only for the compounds involving PhSeCH₂CH₂SePh. For these systems a single resonance is observed for the CH₂ groups and this is to high frequency of that for the 'free' ligand (δ 27.3). For the other compounds several resonances are observed for the CH₂ units and up to four for the Me groups (one for each of the *meso*-1 and *meso*-2 and two for the DL isomer), also to high frequency of the corresponding resonance of the 'free' ligand, confirming the presence of up to three NMR distinguishable invertomers. As for the dithioether species, the CO resonances are very broad even for the complexes where inversion is slow on the NMR timescale, due to rapid quadrupolar relaxation from the directly bonded ⁵⁵Mn nucleus and hence the individual CO resonances are not resolved.

The ⁷⁷Se-{¹H} and ⁵⁵Mn NMR data for [MnX(CO)₃(L–L)] are presented in Table 2. One ⁷⁷Se resonance is expected for each of the *meso* isomers and two for the DL isomer. The results from the ⁷⁷Se-{¹H} NMR studies are in accord with those from the ¹³C-{¹H} NMR studies. The rapidly inverting [MnX(CO)₃-(PhSeCH₂CH₂SePh)] species each show a single resonance approximately 100 ppm to high frequency of that of free PhSeCH₂CH₂SePh, confirming formation of a five-membered chelate ring.[16] Complexes involving the other diselenoether ligands each show the presence of either all three NMR distinguishable isomers (or two of the three); in cases where we only observe three δ(⁷⁷Se) resonances we conclude that either only two isomers are present in appreciable quantity (*meso*-2 and DL) or the resonances are coincidental. The co-ordination shifts [δ(complex) − δ('free' ligand)] for MeSeCH₂CH₂SeMe and C₆H₄(SeMe)₂-o are approximately 120 to 170 and 170 to 200 ppm respectively. These large shifts are consistent with the formation of a five-membered chelate ring, whereas δ(⁷⁷Se-{¹H}) for the complexes of MeSeCH₂CH₂CH₂SeMe, which involve a six-membered chelate ring, are close to those of the 'free' ligand.

| Compound | $\delta(^{55}\text{Mn})$ ($w_{1/2}$/Hz)[b] | $\delta(^{77}\text{Se-}\{^1\text{H}\})$[c] | Approximate ratio *meso*-1:*meso*-2:DL |
|---|---|---|---|
| [MnCl(CO)$_3$(MeSeCH$_2$CH$_2$SeMe)] | $-277$[d] (2000), $-342$ (2000), $-410$ (2900) | 256, 269, 282, 290 | 1:3:6 |
| [MnBr(CO)$_3$(MeSeCH$_2$CH$_2$SeMe)] | $-345$[d] (900), $-428$ (1500), $-506$ (2500) | 259 (*meso*-2); 281, 289 (DL) | 1:5:6 |
| [MnI(CO)$_3$(MeSeCH$_2$CH$_2$SeMe)] | $-500$[d] ($\approx$1340), $-607$ (1220), $-698$ (2170) | 283 (*meso*-2); 239, 276 (DL) | 1:5:10 |
| [MnCl(CO)$_3$(MeSeCH$_2$CH$_2$CH$_2$SeMe)] | $-175$ (2080), $-190$ (sh), $-219$ (sh) | 75, 80, 92, 118 | 1:2:4 |
| [MnBr(CO)$_3$(MeSeCH$_2$CH$_2$CH$_2$SeMe)] | $-257$ (2000), $-317$ (2000) | 62, 65, 81, 109 | 1:2:4 |
| [MnI(CO)$_3$(MeSeCH$_2$CH$_2$CH$_2$SeMe)] | $-402$[d] (sh), $-426$ (1550), $-499$ (1760) | 39, 66, 73, 92 | 1:2:7 |
| [MnCl(CO)$_3$(PhSeCH$_2$CH$_2$SePh)][e] | $-249$ (5200) | 445 | Inverting |
| [MnBr(CO)$_3$(PhSeCH$_2$CH$_2$SePh)][e] | $-346$ (4590) | 443 | Inverting |
| [MnI(CO)$_3$(PhSeCH$_2$CH$_2$SePh)][e] | $-537$ (3170) | 438 | Inverting |
| [MnCl(CO)$_3$\{C$_6$H$_4$(SeMe)$_2$-*o*\}] | $-247$[d] (2000), $-311$ (2600), $-394$ (4500) | 386, 400 (DL), 406 (*meso*-2) | 1:5:4 |
| [MnBr(CO)$_3$\{C$_6$H$_4$(SeMe)$_2$-*o*\}] | $-325$[d] (1070), $-414$ (1860), $-507$ (3000) | 375, 386 (DL), 400 (*meso*-2) | 1:10:5 |
| [MnI(CO)$_3$\{C$_6$H$_4$(SeMe)$_2$-*o*\}] | $-465$,[d] $-581$ (1500), $-702$ (3200) | 374, 388 (DL), 396 (*meso*-2) | 1:14:4 |

**Fig. 1** The $^{55}$Mn (89.27 MHz, CDCl$_3$) (a) and $^{13}$C-{$^1$H} (90.1 MHz, CDCl$_3$) NMR spectrum (b) of [MnBr(CO)$_3$\{C$_6$H$_4$(SeMe)$_2$-*o*\}] (methyl region only).

The $^{55}$Mn NMR studies also confirm that at 300 K only the complexes involving PhSeCH$_2$CH$_2$SePh are undergoing rapid pyramidal inversion on the NMR timescale, showing only a single broad resonance. For the other compounds up to three distinct resonances attributable to the presence of up to three NMR distinguishable stereoisomers were observed (Fig. 1). The linewidths (<3000 Hz) are very similar to those for the thioether analogues reported previously, and again considerably smaller than for phosphine systems such as [MnX(CO)$_3$(PPh$_2$H)$_2$] ($w_{1/2}$ *ca.* 10 000 Hz).[11] For the thioether species, $^{55}$Mn NMR studies showed that for the compounds involving MeSCH$_2$CH$_2$SMe and C$_6$H$_4$(SMe)$_2$-*o* pyramidal inversion is slow on the $^{55}$Mn NMR timescale at 300 K, whereas for MeSCH$_2$CH$_2$CH$_2$SMe or PhSCH$_2$CH$_2$SPh inversion is rapid at this temperature. Thus, the energy barrier to inversion is higher for the manganese(I) selenoether complexes than for the corresponding thioethers. This is consistent with the trends observed in other transition metal complexes of these ligands.[16] As for the thioether complexes we observe a shift in $\delta(^{55}\text{Mn})$ to low frequency upon changing X from Cl to Br to I. Of greatest significance, however, is the observation that $\delta(^{55}\text{Mn})$ for the diselenoether compounds occurs to low frequency (more shielded) of the thioether compounds by *ca.* 100 ppm. This is consistent with the trend in $\nu(\text{CO})$ discussed above, *i.e.* $\nu(\text{CO})$ for the selenoether compounds is to low frequency of $\nu(\text{CO})$ for the thioethers. These results indicate that there is more electron density associated with the manganese(I) centre in the selenoether compounds (greater occupation of the CO $\pi^*$ orbitals). This can arise in three ways: greater $\pi$ donation from the selenoether donor, poorer $\pi$ acceptance by the selenoether donor, or increased $\sigma$ donation by the selenoether donor. Since there is little or no evidence for $\pi$ bonding from thio- or seleno-ether donors to metal centres, it is highly likely that these results indicate an increase in L$\rightarrow$Mn$^{\text{I}}$ $\sigma$ donation from thio- to selenoether. This would also support the work of Hoffmann and co-workers[17] who predicted theoretically that R$_2$E$\rightarrow$M $\sigma$ donation (E = S, Se or Te) would increase in the order S < Se $\ll$ Te.

Abel and co-workers[18–20] have described the preparations of the rhenium(I) complexes [ReX(CO)$_3$(L–L)] [X = Cl, Br or I; L–L = MeE(CH$_2$)$_n$EMe or MeECH=CHEMe (E = S or Se, $n$ = 2 or 3)], including the crystal structure of *fac*-[ReI(CO)$_3$(MeSeCH$_2$CH$_2$SeMe)]. Detailed $^1$H NMR studies revealed that the energy barrier associated with inversion at selenium is higher than at sulfur, and that changing the halogen has a negligible effect upon the overall energy barrier. The results from our work on manganese(I) compounds are consistent with these observations. Also, the relative populations of the invertomers in solution vary with the particular system although the *meso*-2 and DL forms are always dominant, and population of the *meso*-1 form decreases with increasing halide size (due to unfavourable Me$\cdots$X or Ph$\cdots$X interactions).

## X-Ray crystallography

A search of the Cambridge Crystallographic Database revealed that there are no structurally characterised examples of selenoether complexes of manganese(I) carbonyl halides, although the structure of the dinuclear species [\{Mn(C$_5$H$_4$Me)(CO)$_2$\}$_2$(SeMe$_2$)] is known.[14] In order to identify the isomeric arrangement in the solid state and to compare the Mn–Se bond lengths with those in the Me$_2$Se-bridged dimer [\{Mn(C$_5$H$_4$Me)(CO)$_2$\}$_2$(SeMe$_2$)] and with $d$(Mn–S) in the thioether analogues, we have conducted single crystal X-ray analyses on [MnCl(CO)$_3$(MeSeCH$_2$CH$_2$SeMe)], [MnCl(CO)$_3$(MeSeCH$_2$CH$_2$CH$_2$-
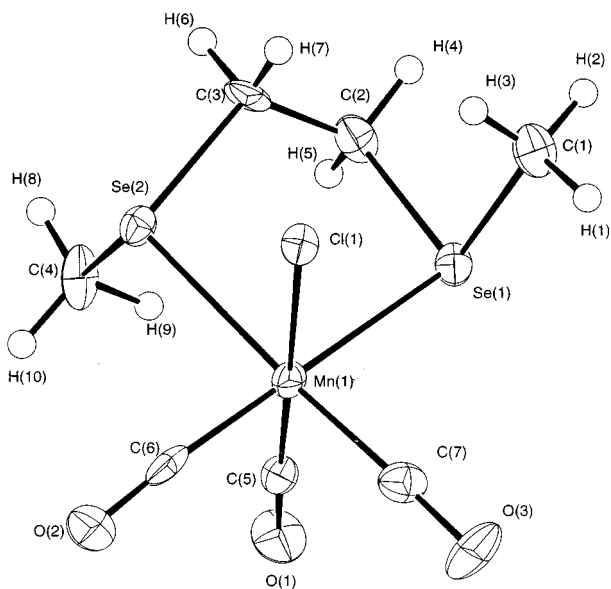
**Fig. 2** View of the structure of $[MnCl(CO)_3(MeSeCH_2CH_2SeMe)]$ with numbering scheme adopted. Ellipsoids are drawn at 40% probability.
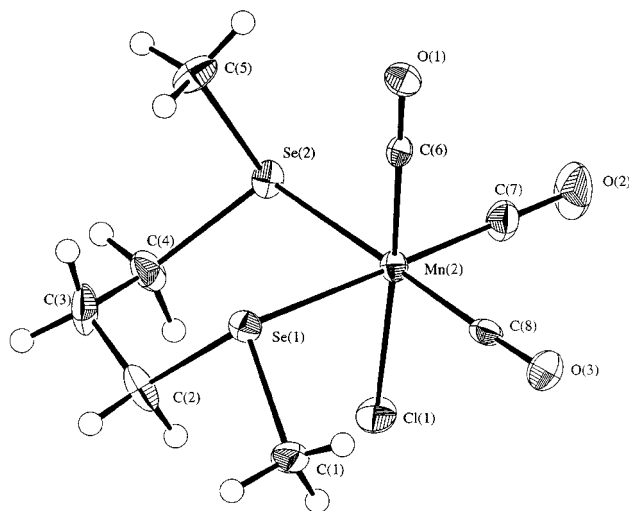


**Fig. 3** View of the structure of $[MnCl(CO)_3(MeSeCH_2CH_2CH_2\text{-}SeMe)]$ with numbering scheme adopted. Ellipsoids are drawn at 40% probability.

SeMe)] and $[MnBr(CO)_3\{C_6H_4(SeMe)_2\text{-}o\}]$. Crystals of the complexes were obtained from vapour diffusion of light petroleum into a solution of the appropriate complex in $CH_2Cl_2$. The crystal structures of $[MnCl(CO)_3(MeSeCH_2CH_2\text{-}SeMe)]$ (Fig. 2, Table 3) and $[MnCl(CO)_3(MeSeCH_2CH_2CH_2\text{-}SeMe)]$ (Fig. 3, Table 4) both show a distorted octahedral geometry at Mn, with a *fac* arrangement for the three CO ligands and the chelating diselenoether adopting the DL arrangement, with one Me group on each side of the $MnSe_2C_2$ plane: $[MnCl(CO)_3(MeSeCH_2CH_2SeMe)]$, Mn–Se(1) 2.481(3), Mn–Se(2) 2.467(3), Mn–Cl(1) 2.406(4), Mn–C(5) 1.79(2), Mn–C(6) 1.79(2), Mn–C(7) 1.80(2) Å; $[MnCl(CO)_3(MeSeCH_2\text{-}CH_2CH_2SeMe)]$, Mn–Se(1) 2.474(2), Mn–Se(2) 2.482(2), Mn–Cl(1) 2.379(3), Mn–C(6) 1.792(9), Mn–C(7) 1.805(10), Mn–C(8) 1.810(9) Å. The Se–Mn–Se angles involved in the chelate rings are 88.79(8) and 89.29(5)° respectively. The DL isomer was also identified in the crystal structure of $[MnCl(CO)_3\text{-}(MeSCH_2CH_2SMe)_2]$, suggesting that this might be the preferred solid state arrangement for $[Mn(CO)_3X\{MeE\text{-}(CH_2)_nEMe\}]$, E = S or Se, and indeed this is the dominant isomer in solution at room temperature for these species. The

**Table 3** Selected bond lengths (Å) and angles (°) for $[MnCl(CO)_3(MeSeCH_2CH_2SeMe)]$

| | | | |
|---|---|---|---|
| Se(1)–Mn(1) | 2.481(3) | Se(1)–C(1) | 1.96(1) |
| Se(1)–C(2) | 1.98(2) | Se(2)–Mn(1) | 2.467(3) |
| Se(2)–C(3) | 1.95(1) | Se(2)–C(4) | 1.96(1) |
| Mn(1)–Cl(1) | 2.406(4) | Mn(1)–C(5) | 1.79(2) |
| Mn(1)–C(6) | 1.79(2) | Mn(1)–C(7) | 1.80(2) |
| O(1)–C(5) | 1.16(2) | O(2)–C(6) | 1.18(2) |
| O(3)–C(7) | 1.15(2) | C(2)–C(3) | 1.47(2) |
| | | | |
| Mn(1)–Se(1)–C(1) | 109.0(5) | Mn(1)–Se(1)–C(2) | 101.6(4) |
| C(1)–Se(1)–C(2) | 96.6(7) | Mn(1)–Se(2)–C(3) | 101.2(4) |
| Mn(1)–Se(2)–C(4) | 107.9(5) | C(3)–Se(2)–C(4) | 96.3(7) |
| Se(1)–Mn(1)–Se(2) | 88.79(8) | Se(1)–Mn(1)–Cl(1) | 92.2(1) |
| Se(1)–Mn(1)–C(5) | 86.4(5) | Se(1)–Mn(1)–C(6) | 176.6(5) |
| Se(1)–Mn(1)–C(7) | 90.2(5) | Se(2)–Mn(1)–Cl(1) | 82.7(1) |
| Se(2)–Mn(1)–C(5) | 95.2(4) | Se(2)–Mn(1)–C(6) | 90.1(4) |
| Se(2)–Mn(1)–C(7) | 175.1(5) | Cl(1)–Mn(1)–C(5) | 177.5(5) |
| Cl(1)–Mn(1)–C(6) | 90.8(5) | Cl(1)–Mn(1)–C(7) | 92.6(5) |
| C(5)–Mn(1)–C(6) | 90.4(6) | C(5)–Mn(1)–C(7) | 89.5(6) |
| C(6)–Mn(1)–C(7) | 91.1(7) | | |

**Table 4** Selected bond lengths (Å) and angles (°) for $[MnCl(CO)_3(MeSeCH_2CH_2CH_2SeMe)]$

| | | | |
|---|---|---|---|
| Se(1)–Mn(2) | 2.474(2) | Se(1)–C(1) | 1.939(10) |
| Se(1)–C(2) | 1.96(1) | Se(2)–Mn(2) | 2.482(2) |
| Se(2)–C(4) | 1.961(10) | Se(2)–C(5) | 1.94(1) |
| Mn(2)–Cl(1) | 2.379(3) | Mn(2)–C(6) | 1.792(9) |
| Mn(2)–C(7) | 1.805(10) | Mn(2)–C(8) | 1.810(9) |
| O(1)–C(6) | 1.14(1) | O(2)–C(7) | 1.16(1) |
| O(3)–C(8) | 1.14(1) | C(3)–C(4) | 1.53(2) |
| C(2)–C(3) | 1.50(2) | | |
| | | | |
| Mn(2)–Se(1)–C(1) | 105.4(3) | Mn(2)–Se(1)–C(2) | 107.4(3) |
| C(1)–Se(1)–C(2) | 95.5(5) | Mn(2)–Se(2)–C(4) | 110.1(3) |
| Mn(2)–Se(2)–C(5) | 107.3(3) | C(4)–Se(2)–C(5) | 97.9(5) |
| Se(1)–Mn(2)–Se(2) | 89.29(5) | Se(1)–Mn(2)–Cl(1) | 90.65(8) |
| Se(1)–Mn(2)–C(6) | 88.0(3) | Se(1)–Mn(2)–C(7) | 179.2(3) |
| Se(1)–Mn(2)–C(8) | 90.5(3) | Se(2)–Mn(2)–Cl(1) | 86.56(8) |
| Se(2)–Mn(2)–C(6) | 89.9(3) | Se(2)–Mn(2)–C(7) | 90.2(3) |
| Se(2)–Mn(2)–C(8) | 178.8(3) | Cl(1)–Mn(2)–C(6) | 176.2(3) |
| Cl(1)–Mn(2)–C(7) | 89.8(4) | Cl(1)–Mn(2)–C(8) | 92.3(3) |
| C(6)–Mn(2)–C(7) | 91.4(5) | C(6)–Mn(2)–C(8) | 91.3(4) |
| C(7)–Mn(2)–C(8) | 90.0(4) | | |

crystals of $[MnBr(CO)_3\{C_6H_4(SeMe)_2\text{-}o\}]$† were of poorer quality and hence the data less reliable, therefore detailed comparisons of the geometric parameters requires caution. However, the molecular arrangement (Fig. 4) is very similar to the structures described above, with three mutually *fac* CO ligands, a chelating diselenoether and a Br ligand completing the distorted octahedron. In this case the co-ordinated diselenoether adopts the *meso*-2 form with both Me groups directed to the opposite side of the $MnSe_2C_2$ plane from the Br ligand, Mn–Se(1) 2.454(6), Mn–Se(2) 2.468(6), Mn–Br(1) 2.562(6), Mn–C(9) 1.79(4), Mn–C(10) 1.82(3), Mn–C(11) 1.82(3) Å. This is also the isomer which dominates in solution at room temperature. The Se–Mn–Se angle in the chelate ring is 88.3(2)°. As expected on the basis of the radii of Se *vs.* S, the Mn–Se bond lengths in these compounds are approximately 0.10–0.15 Å

---

† Crystal data: $M$ 482.96, orthorhombic, space group $Pna2_1$, $a = 21.34(2)$, $b = 9.50(2)$, $c = 7.08(1)$ Å, $V = 1448(6)$ Å$^3$, $Z = 4$, $D_c = 2.214$ g cm$^3$, $\mu$(Mo-K$\alpha$), 86.97 cm$^{-1}$. 1513 unique observed reflections, 1148 with $I_o > 2\sigma(I_o)$, $R = 0.084$, $R' = 0.105$. The structure was solved in $Pna2_1$ (since the data indicated an acentric space group) by direct methods[21] and developed by iterative cycles of full-matrix least-squares refinement and difference Fourier syntheses (an attempt to solve the structure in $Pnma$ yielded no solution).[22] The Mn, Br, Se and O atoms were refined anisotropically while H atoms were placed in fixed, calculated positions with $d$(C–H) = 0.96 Å. The weighting scheme $w^{-1} = \sigma^2(F)$ gave satisfactory agreement analyses and the Flack parameter indicated that the hand chosen was the correct enantiomorph.
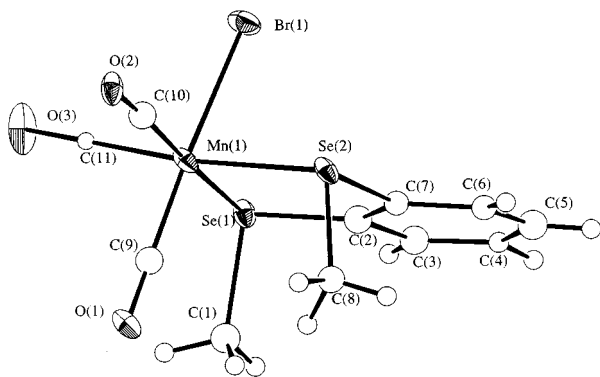
**Fig. 4** View of the structure of [MnBr(CO)$_3${C$_6$H$_4$(SeMe)$_2$-*o*}] with the numbering scheme adopted. Ellipsoids are drawn at 40% probability. Mn–Se(1) 2.454(6), Mn–Se(2) 2.468(6), Mn–Br(1) 2.562(6), Mn–C(9) 1.79(4), Mn–C(10) 1.82(3), Mn–C(11) 1.82(3) Å.

longer than $d$(Mn–S) in the corresponding thioether compounds. However, the increased σ bonding in the selenoethers compared to the thioethers deduced from the spectroscopic studies would be expected to have a very small effect on the M–S and M–Se distances, and is therefore not expected to be detected by X-ray crystallography. The Mn–Se bond lengths in the selenoether compounds reported here are longer than those observed in the SeMe$_2$ bridged species [{Mn(C$_5$H$_4$Me)(CO)$_2$}$_2$-(SeMe$_2$)] [2.375(1), 2.378(1) Å].[14] This may be attributed to the repulsive effect of the second Se-based lone pair in the mononuclear species, whereas in the bridged dimer there is no such repulsion.

## Experimental

Infrared spectra were measured as CsI discs using a Perkin-Elmer 983 spectrometer over the range 200–4000 cm$^{-1}$, or in solution using NaCl plates on a Perkin-Elmer 1600 FTIR spectrometer, mass spectra by fast-atom bombardment (FAB) using 3-nitrobenzyl alcohol as matrix on a VG Analytical 70-250-SE normal geometry double focusing mass spectrometer, $^1$H NMR spectra in CDCl$_3$ at 300 MHz unless otherwise stated, using a Bruker AM300 spectrometer, $^{13}$C-{$^1$H}, $^{55}$Mn and $^{77}$Se-{$^1$H} NMR spectra using a Bruker AM360 spectrometer operating at 90.1, 89.27 or 68.68 MHz respectively and referenced to Me$_4$Si, external saturated, aqueous K[MnO$_4$] and external neat Me$_2$Se respectively ($\delta$ 0); [Cr(acac)$_3$] was added to the NMR solutions prior to recording $^{13}$C-{$^1$H} and $^{77}$Se-{$^1$H} spectra and a pulse delay of 2 s was employed for the $^{13}$C-{$^1$H} spectra to take account of the long relaxation times. The compounds [MnX(CO)$_5$] (X = Cl, Br or I), MeSeCH$_2$CH$_2$-SeMe, MeSeCH$_2$CH$_2$CH$_2$SeMe, PhSeCH$_2$CH$_2$SePh and C$_6$H$_4$-(SeMe)$_2$-*o* were prepared according to literature procedures.[23,24]

### Preparations

All of the compounds were synthesized by the same general procedure, hence only one is described in detail below.

**[MnCl(CO)$_3$(MeSeCH$_2$CH$_2$SeMe)].** To a degassed solution of [MnCl(CO)$_5$] (0.070 g, 0.30 mmol) in CHCl$_3$ (30 ml), MeSeCH$_2$CH$_2$SeMe (0.066 g, 0.305 mmol) was added. The resulting mixture was gently refluxed for 24 h, and the solution IR spectrum monitored until the reaction had gone to completion. The solvent volume was reduced *in vacuo* to *ca.* 2 ml to give a yellow solution. Addition of light petroleum (bp 40–60 °C) at 0 °C afforded a yellow solid which was filtered off, washed with light petroleum and dried *in vacuo*. The compound was recrystallised from CHCl$_3$–light petroleum (yield 0.087 g, 73%) (Found: C, 21.3; H, 2.7. Calc. for C$_7$H$_{10}$ClMnO$_3$Se$_2$: C, 21.5; H, 2.6%). $^1$H NMR spectrum: $\delta$ 3.28, 3.04, 2.75 (CH$_2$), 2.30, 2.12, 2.02 (sh) (Me). $^{13}$C-{$^1$H} NMR spectrum: $\delta$ 222.5–

218.4 (CO), 29.6, 29.4, 29.0 (CH$_2$), 12.6 (Me, *meso*-1), 11.9 and 8.9 (Me, DL).

**[MnCl(CO)$_3$(MeSeCH$_2$CH$_2$CH$_2$SeMe)].** [MnCl(CO)$_5$] (0.100 g, 0.43 mmol) and MeSeCH$_2$CH$_2$CH$_2$SeMe (0.100 g, 0.43 mmol), giving a yellow precipitate (yield 0.111 g, 63%) (Found: C, 23.4; H, 3.3. Calc. for C$_8$H$_{12}$ClMnO$_3$Se$_2$: C, 23.7; H, 3.0%). $^1$H NMR spectrum: $\delta$ 3.25, 3.10, 2.78, 2.65 (SeCH$_2$), 2.40, 2.18 (Me) and 1.98 (CH$_2$C*H*$_2$CH$_2$). $^{13}$C-{$^1$H} NMR spectrum: $\delta$ 223.1–216.7 (CO), 26.9, 26.8, 25.3, 25.0, 24.5 (CH$_2$), 13.4, 12.6, 11.2, 10.7 (Me).

**[MnCl(CO)$_3$(PhSeCH$_2$CH$_2$SePh)].** [MnCl(CO)$_5$] (0.047 g, 0.21 mmol) and PhSeCH$_2$CH$_2$SePh (0.070 g, 0.21 mmol), giving a yellow precipitate (yield 0.078 g, 75%) (Found: C, 39.4; H, 2.8. Calc. for C$_{17}$H$_{14}$ClMnO$_3$Se$_2$: C, 39.7; H, 2.7%). $^1$H NMR spectrum: $\delta$ 7.25–7.70 (Ph), 3.25–3.78 (CH$_2$). $^{13}$C-{$^1$H} NMR spectrum: $\delta$ 223.2–219.6 (CO), 130.8 (sh), 130.4, 129.9 (Ph) and 30.7 (CH$_2$).

**[MnCl(CO)$_3${C$_6$H$_4$(SeMe)$_2$-*o*}].** [MnCl(CO)$_5$] (0.024 g, 0.100 mmol) and C$_6$H$_4$(SeMe)$_2$-*o* (0.027 g, 0.100 mmol), giving a yellow precipitate (yield 0.031 g, 68%) (Found: C, 27.1; H, 2.3. Calc. for C$_{11}$H$_{10}$ClMnO$_3$Se$_2$·CH$_2$Cl$_2$: C, 27.5; H, 2.7%). $^1$H NMR spectrum: $\delta$ 7.80, 7.45 (*o*-C$_6$H$_4$), 2.70, 2.55, 2.40 (Me). $^{13}$C-{$^1$H} NMR spectrum: $\delta$ 221.7–218.8 (CO), 134.6, 133.5, 131.1, 130.5 (*o*-C$_6$H$_4$), 20.0 (Me, *meso*-2), 19.5, 15.1 (Me, DL) and 14.2 (Me, *meso*-1).

**[MnBr(CO)$_3$(MeSeCH$_2$CH$_2$SeMe)].** [MnBr(CO)$_5$] (0.085 g, 0.31 mmol) and MeSeCH$_2$CH$_2$SeMe (0.067 g, 0.31 mmol) giving an orange precipitate (yield 0.117 g, 87%) (Found: C, 19.8; H, 2.5. Calc. for C$_7$H$_{10}$BrMnO$_3$Se$_2$: C, 19.3; H, 2.3%). $^1$H NMR spectrum: $\delta$ 3.36, 3.23 (sh), 3.10, 2.82 (CH$_2$), 2.37 (sh), 2.35, 2.23 (Me). $^{13}$C-{$^1$H} NMR spectrum: $\delta$ 124.3–116.5 (CO), 29.6, 29.3 (CH$_2$), 15.5, 13.4, 12.9 and 10.3 (Me).

**[MnBr(CO)$_3$(MeSeCH$_2$CH$_2$CH$_2$SeMe)].** [MnBr(CO)$_5$] (0.011 g, 0.40 mmol) and MeSeCH$_2$CH$_2$CH$_2$SeMe (0.092 g, 0.40 mmol), giving an orange precipitate (yield 0.079 g, 44%) (Found: C, 21.6; H, 2.9. Calc. for C$_8$H$_{12}$BrMnO$_3$Se$_2$: C, 21.4; H, 2.7%). $^1$H NMR spectrum: $\delta$ 3.42, 3.20 (sh), 2.75, 2.62 (sh) (SeCH$_2$), 2.28 (Me) and 1.98 (CH$_2$CH$_2$CH$_2$). $^{13}$C-{$^1$H} NMR spectrum: $\delta$ 223.0–216.0 (CO), 27.3, 27.2 (sh), 25.6, 24.5 (CH$_2$), 14.2, 13.2, 12.4, 11.5 (Me).

**[MnBr(CO)$_3$(PhSeCH$_2$CH$_2$SePh)].** [MnBr(CO)$_5$] (0.072 g, 0.26 mmol) and PhSeCH$_2$CH$_2$SePh (0.089 g, 0.26 mmol), giving a yellow precipitate (yield 0.109 g, 74%) (Found: C, 35.9; H, 2.3. Calc. for C$_{17}$H$_{14}$BrMnO$_3$Se$_2$: C, 36.5; H, 2.5%). $^1$H NMR spectrum: $\delta$ 7.75–7.18 (Ph), 3.75–3.30 (CH$_2$). $^{13}$C-{$^1$H} NMR spectrum: $\delta$ 224.5–220.1 (CO), 130.0, 129.5 (Ph) and 30.9 (CH$_2$).

**[MnBr(CO)$_3${C$_6$H$_4$(SeMe)$_2$-*o*}].** [MnBr(CO)$_5$] (0.085 g, 0.31 mmol) and C$_6$H$_4$(SeMe)$_2$-*o* (0.082 g, 0.31 mmol), giving an orange precipitate (yield 0.095 g, 64%) (Found: C, 27.2; H, 2.0. Calc. for C$_{11}$H$_{10}$BrMnO$_3$Se$_2$: C, 27.3; H, 2.1%). $^1$H NMR spectrum: $\delta$ 7.85, 7.54 (*o*-C$_6$H$_4$), 2.81 (sh), 2.62 (Me). $^{13}$C-{$^1$H} NMR spectrum: $\delta$ 222.9–218.6 (CO), 134.9, 133.7, 131.1, 130.4 (*o*-C$_6$H$_4$), 31.0 (Me, *meso*-1), 21.0 (Me, *meso*-2), 20.4 and 17.1 (Me, DL).

**[MnI(CO)$_3$(MeSeCH$_2$CH$_2$SeMe)].** [MnI(CO)$_5$] (0.119 g, 0.37 mmol) and MeSeCH$_2$CH$_2$SeMe (0.080 g, 0.37 mmol) giving an orange precipitate (yield 0.108 g, 61%) (Found: C, 17.7; H, 1.9. Calc. for C$_7$H$_{10}$IMnO$_3$Se$_2$: C, 17.4; H, 2.1%). $^1$H NMR spectrum: $\delta$ 3.45, 3.12, 2.88 (CH$_2$), 2.50, 2.31, 2.22, 2.05 (Me). $^{13}$C-{$^1$H} NMR spectrum: $\delta$ 225.0–220.5 (CO), 30.5, 30.1 (CH$_2$), 15.4 (Me, *meso*-2), 15.3, 1.3 (Me, DL).

**Table 5** Crystallographic data collection and refinement parameters

| | [MnCl(CO)$_3$(MeSe-CH$_2$CH$_2$SeMe)] | [MnCl(CO)$_3$(MeSe-CH$_2$CH$_2$CH$_2$SeMe)] |
|---|---|---|
| Formula | C$_7$H$_{10}$ClMnO$_3$Se$_2$ | C$_8$H$_{12}$ClMnO$_3$Se$_2$ |
| $M$ | 390.47 | 404.49 |
| Space group | $Pbca$ | $P2_12_12_1$ |
| Crystal symmetry | Orthorhombic | Orthorhombic |
| $a$/Å | 12.283(4) | 11.342(5) |
| $b$/Å | 19.293(5) | 12.223(7) |
| $c$/Å | 10.154(4) | 9.464(6) |
| $V$/Å$^3$ | 2406(1) | 1311(1) |
| $Z$ | 8 | 4 |
| $D_c$/g cm$^{-3}$ | 2.155 | 2.048 |
| $\mu$(Mo-K$\alpha$)/cm$^{-1}$ | 72.51 | 66.53 |
| Unique observed reflections | 2430 | 1360 |
| Observed reflections with [$I_o > 2\sigma(I_o)$] | 1206 | 1157 |
| No. parameters | 127 | 136 |
| $R$ | 0.058 | 0.036 |
| $R'$ | 0.064 | 0.046 |

**[MnI(CO)$_3$(MeSeCH$_2$CH$_2$CH$_2$SeMe)].** [MnI(CO)$_5$] (0.124 g, 0.38 mmol) and MeSeCH$_2$CH$_2$CH$_2$SeMe (0.087 g, 0.38 mmol), giving an orange precipitate (yield 0.126 g, 66%) (Found: C, 19.5; H, 2.6. Calc. for C$_8$H$_{12}$IMnO$_3$Se$_2$: C, 19.4; H, 2.4%). $^1$H NMR spectrum: $\delta$ 3.30, 2.85 (SeCH$_2$), 2.70, 2.40 (Me) and 2.00 (CH$_2$C$H_2$CH$_2$). $^{13}$C-{$^1$H} NMR spectrum: $\delta$ 226.7–217.5 (CO), 27.8, 27.5, 27.2, 26.3, 24.6, 24.3 (CH$_2$), 15.7, 14.5, 13.9, 12.2 (Me).

**[MnI(CO)$_3$(PhSeCH$_2$CH$_2$SePh)].** [MnI(CO)$_5$] (0.063 g, 0.20 mmol) and PhSeCH$_2$CH$_2$SePh (0.067 g, 0.20 mmol), giving an orange precipitate (yield 0.096 g, 81%) (Found: C, 33.3; H, 2.4. Calc. for C$_{17}$H$_{14}$IMnO$_3$Se$_2$: C, 33.7; H, 2.3%). $^1$H NMR spectrum: $\delta$ 7.55–7.25 (Ph), 3.80–3.40 (CH$_2$). $^{13}$C-{$^1$H} NMR spectrum: $\delta$ 226.0–220.2 (CO), 131.1, 130.3, 129.8 (Ph) and 31.3 (CH$_2$).

**[MnI(CO)$_3${C$_6$H$_4$(SeMe)$_2$-$o$}].** [MnI(CO)$_5$] (0.032 g, 0.098 mmol) and C$_6$H$_4$(SeMe)$_2$-$o$ (0.026 g, 0.098 mmol), giving an orange precipitate (yield 0.043 g, 82%) (Found: C, 21.6; H, 1.9. Calc. for C$_{11}$H$_{10}$IMnO$_3$Se$_2$·CHCl$_3$: C, 22.1; H, 1.7%). $^1$H NMR spectrum: $\delta$ 7.90, 7.55 ($o$-C$_6$H$_4$), 2.95, 2.60, 2.48 (sh), 2.35 (Me). $^{13}$C-{$^1$H} NMR spectrum: $\delta$ 223.8–219.6 (CO), 134.8, 134.1, 131.0 ($o$-C$_6$H$_4$), 22.7 (Me, $meso$-2), 21.9, 20.7, 14.3 (Me, $meso$-1 and DL).

### Crystal structures of [MnCl(CO)$_3$(MeSeCH$_2$CH$_2$SeMe)] and [MnCl(CO)$_3$(MeSeCH$_2$CH$_2$CH$_2$SeMe)]

Details of the crystallographic data collection and refinement parameters are given in Table 5. The crystals were grown by vapour diffusion of light petroleum into solutions of the complexes in CH$_2$Cl$_2$. Data collection used a Rigaku AFC7S four-circle diffractometer operating at 150 K, with graphite-monochromated Mo-K$\alpha$ X-radiation ($\lambda$ = 0.71073 Å). No significant crystal decay or movement was observed. The structures were solved by heavy atom Patterson methods [25] and developed by iterative cycles of full-matrix least-squares refinement and Fourier-difference syntheses which located one complete molecule in the asymmetric unit.[22] All non-H atoms were refined anisotropically while H atoms were placed in fixed, calculated positions with $d$(C–H) = 0.96 Å. The weighting scheme $w^{-1} = \sigma^2(F)$ gave satisfactory agreement analyses and the Flack parameter indicated that the correct enantiomorph of [MnCl(CO)$_3$(MeSeCH$_2$CH$_2$CH$_2$SeMe)] was refined.

CCDC reference number 186/1187.

### References

1 N. R. Champness, S. R. Jacob, G. Reid and C. S. Frampton, *Inorg. Chem.*, 1995, **34**, 396; N. R. Champness, S. J. A. Pope and G. Reid, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 1639; W. Levason, G. Reid and S. M. Smith, *Polyhedron*, 1997, **16**, 5253.
2 M. C. Durrant, S. Davies, D. L. Hughes, C. Le Floc'h, R. L. Richards, J. R. Sanders, N. R. Champness, S. J. A. Pope and G. Reid, *Inorg. Chim. Acta*, 1996, **251**, 13.
3 S. Davies, M. C. Durrant, D. L. Hughes, C. LeFloc'h, S. J. A. Pope, G. Reid, R. L. Richards and J. R. Sanders, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 2191.
4 D. Rehder, *Multinuclear NMR*, ed. J. Mason, Plenum, New York, 1987, ch. 19.
5 A. Kekeci and D. Rehder, *Z. Naturforsch.*, *Teil B*, 1981, **36**, 20.
6 F. Calderazzo, E. A. C. Lucken and D. F. Williams, *J. Chem. Soc. A*, 1967, 154.
7 D. Rehder, H.-C. Bechtold, A. Kekeci, H. Schmidt and M. Z. Siewing, *Z. Naturforsch.*, *Teil B*, 1982, **37**, 631.
8 N. J. Holmes, W. Levason and M. Webster, *J. Organomet. Chem.*, 1998, **568**, 213.
9 A. M. Hill, W. Levason, M. Webster and I. Albers, *Organometallics*, 1997, 16, 5641.
10 J. Connolly, G. W. Goodban, G. Reid and A. M. Z. Slawin, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 2125.
11 S. J. A. Pope and G. Reid, unpublished work.
12 E. W. Abel and G. V. Hutson, *J. Inorg. Nucl. Chem.*, 1969, **31**, 3333.
13 D. Rehder, K. Ihmels, D. Wenke and P. Oltmanns, *Inorg. Chim. Acta*, 1985, **100**, L13.
14 A. Belforte, F. Calderazzo, D. Vitali and P. F. Zanazzi, *Gazz. Chim. Ital.*, 1985, **115**, 125.
15 E. W. Abel, S. K. Bhargava and K. G. Orrell, *Prog. Inorg. Chem.*, 1984, **33**, 1.
16 E. G. Hope and W. Levason, *Coord. Chem. Rev.*, 1993, **122**, 109.
17 H. Schumann, A. M. Arif, A. L. Rheingold, C. Janiak, R. Hoffmann and N. Kuhn, *Inorg. Chem.*, 1991, **30**, 1618.
18 E. W. Abel, S. K. Bhargava, M. M. Bhatti, K. Kite, M. A. Mazid, K. G. Orrell, V. Sik, B. L. Williams, M. B. Hursthouse and K. M. A. Malik, *J. Chem. Soc.*, *Dalton Trans.*, 1982, 2065.
19 E. W. Abel, M. M. Bhatti, K. G. Orrell and V. Sik, *J. Organomet. Chem.*, 1981, **208**, 195.
20 E. W. Abel, S. K. Bhargava, M. M. Bhatti, M. A. Mazid, K. G. Orrell, V. Sik, M. B. Hursthouse and K. M. A. Malik, *J. Organomet. Chem.*, 1983, **250**, 373.
21 SHELXS 86, Program for crystal structure solution, G. M. Sheldrick, *Acta Crystallogr.*, *Sect. A*, 1990, **46**, 467.
22 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1995.
23 K. J. Reimer and A. Shaver, *Inorg. Synth.*, 1979, **19**, 159.
24 D. J. Gulliver, E. G. Hope, W. Levason, S. G. Murray, D. M. Potter and G. L. Marshall, *J. Chem. Soc.*, *Perkin Trans. 2*, 1984, 429.
25 PATTY, The DIRDIF Program System, P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, Technical Report of the Crystallography Laboratory, University of Nijmegen, 1992.

*Paper 8/06881J*