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Synthesis, spectroscopic and structural studies on transition metal carbonyl complexes of cyclic di- and tetra-selenoether ligands

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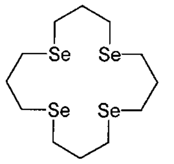
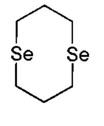
Reaction of [$M(CO)_4$(nbd)] (M = Cr or Mo, nbd = norbornadiene) or [$W(CO)_4$(TMPA)] (TMPA = *N*,*N*,*N′*,*N′*-tetramethyl-1,3-propanediamine) with [8]aneSe_2 (1,5-diselenacyclooctane) yielded the *cis*-disubstituted tetracarbonyl species [$M(CO)_4$([8]aneSe_2)] (M = Cr, Mo or W). The complexes [$M'X(CO)_5$] (M′ = Mn, X = Cl, Br or I; M′ = Re, X = Cl or Br) reacted similarly with [8]aneSe_2 to give *fac*-[$M'X(CO)_3$([8]aneSe_2)] in high yield. Infrared and multinuclear NMR spectroscopic studies confirmed these assignments and indicated a single species in solution; $\delta(^{55}Mn)$ lies in the same range as observed for other *fac*-[$MnX(CO)_3$(diselenoether)] complexes, while for all of the compounds $\delta(^{77}Se)$ is to low frequency of [8]aneSe_2 itself (δ 137). Crystal structures of [$W(CO)_4$([8]aneSe_2)], [$MnBr(CO)_3$([8]aneSe_2)] and [$ReBr(CO)_3$([8]aneSe_2)] show the cyclic diselenoether chelating and adopting a chair-boat conformation. The compounds [16]aneSe_4 (1,5,9,13-tetraselenacyclohexadecane) and L (1,6-diselena-3,4-benzocyclononane) reacted with the metal(II) species [{$MoBr_2(CO)_4$}$_2$] or [$MI_2(CO)_3(NCMe)_2$] in CH_2Cl_2 solution to give seven-co-ordinate [{$MoX_2(CO)_3$}$_2$([16]aneSe_4)], [$WI_2(CO)_3$([16]aneSe_4)], [$MoX_2(CO)_3$(L)] and [$WI_2(CO)_3$(L)], although these species decompose rapidly in co-ordinating solvents. Reaction of [16]aneSe_4 with two molar equivalents of [$M'Cl(CO)_5$] yielded the dinuclear complex [{$MnCl(CO)_3$}$_2$([16]aneSe_4)] (in which the tetraselenoether is thought to bind in a bidentate manner to each Mn) and the mononuclear complex [$ReCl(CO)_3$([16]aneSe_4)] (which is thought to involve bidentate ligation to [16]aneSe_4 with two free Se donors). The cationic species *fac*-[$Mn(CO)_3(\eta^3$-[16]aneSe_4)]CF_3SO_3 was generated by treatment of [$MnCl(CO)_5$] with $AgCF_3SO_3$ in Me_2CO followed by addition of [16]aneSe_4.

Introduction

Although the co-ordination chemistry of cyclic selenoether ligands has been studied in some detail over the past 10 years, this area is heavily dominated by complexes with metals from Groups 8–11 and there are no examples of low valent complexes involving Group 6 or 7 metal centres.[1–11] We have become interested in investigating the chemistry of Group 6 and 7 metal carbonyl species with cyclic selenoethers since the carbonyl ligands may offer a useful route into organometallic derivatives. A few years ago Yoshida and co-workers[12] showed that the tetrathia macrocyclic complex [$MoBr_2(Me_8$[16]aneS_4)] (Me_8-[16]aneS_4 = 3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetrathiacyclohexadecane) is reduced by Zn/Hg under a dinitrogen atmosphere to give the molybdenum(0) bis(dinitrogen) species *trans*-[$Mo(N_2)_2(Me_8$[16]aneS_4)], the first thioether complex to contain a dinitrogen ligand. Subsequently the electrochemistry and reactions of these species have been investigated in some detail.[13] In view of the ability of the tetrathia macrocycle to facilitate formation of a N_2 adduct, we were interested to determine whether the tetraselena macrocycle [16]aneSe_4 (1,5,9,13-tetraselenacyclohexadecane) would accommodate a molybdenum centre within the cavity and subsequently bind N_2 under appropriate conditions. With regard to Group 7 species, we have recently reported studies on manganese(I) carbonyl complexes involving bidentate selenoethers and shown that ^{55}Mn NMR spectroscopy can yield important information regarding the Mn–Se interaction.[14] In this paper we describe the results of our initial investigations on the preparation and characterisation of a range of complexes of Cr, Mo, W, Mn and Re involving [8]aneSe_2 (1,5-diselenacyclooctane), L (1,6-diselena-3,4-benzocyclononane) and [16]aneSe_4. Crystal structures of [$MnBr(CO)_3$([8]aneSe_2)], [$ReBr(CO)_3$([8]aneSe_2)] and [$W(CO)_4$([8]aneSe_2)] are also reported and these species are the first organometallic and early transition metal complexes incorporating cyclic selenoether ligands.


[16]aneSe_4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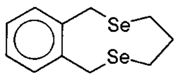

L

Results and discussion

The complexes [$Cr(CO)_4$(nbd)], [$Mo(CO)_4$(nbd)] (nbd = norbornadiene) and [$W(CO)_4$(TMPA)] (TMPA = *N*,*N*,*N′*,*N′*-tetramethyl-1,3-diaminopropane) react with one molar equivalent of [8]aneSe_2 in refluxing toluene to give the zerovalent complexes [$M(CO)_4$([8]aneSe_2)] in high yield. These reactions were monitored by solution IR spectroscopy which showed gradual disappearance of the CO bands associated with the tetracarbonyl precursor and the growth of new bands associated with the product (Table 1). The FAB or electrospray mass spectra of the complexes typically show peaks with the correct isotopic distributions for [$M(CO)_4$([8]aneSe_2)]$^+$. Further peaks due to fragmentation associated with loss of CO are also observed. Microanalyses and ^1H NMR spectroscopic studies are consistent with the [$M(CO)_4$([8]aneSe_2)] assignment.

The seven-co-ordinate molybdenum(II) species [{$MoBr_2(CO)_3$}$_2$([16]aneSe_4)], [{$MoI_2(CO)_3$}$_2$([16]aneSe_4)], [$MoBr_2(CO)_3$L] and [$MoI_2(CO)_3$L] are readily formed in high yield as brown solids by treatment of [16]aneSe_4 or L with [{$MoBr_2$-

Table 1 IR (CO region), ^{13}C-{^{1}H}, ^{77}Se-{^{1}H}, ^{55}Mn and ^{95}Mo NMR spectroscopic data

Compound	$\tilde{\nu}$(CO)^a/cm^{-1}	δ(^{13}C-{^{1}H})	δ(^{77}Se-{^{1}H})	δ(^{55}Mn)^b	δ(^{95}Mo)
$[Cr(CO)_4([8]aneSe_2)]$	2005, 1901, 1882, 1859	23.8, 21.6, 225.9, 220.6	134	—	—
$[Mo(CO)_4([8]aneSe_2)]$	2018, 1911, 1897, 1864	25.0, 23.9, 216.5, 210.2	119	—	−1424
$[W(CO)_4([8]aneSe_2)]$	2012, 1935, 1892, 1855	25.5, 25.0, 206.5, 204.7	84	—	—
$[MnCl(CO)_3([8]aneSe_2)]$	2035, 1961, 1907	22.6, 21.3, 19.9, 19.0, 216–221.5	79	−215 (1800)	—
$[MnBr(CO)_3([8]aneSe_2)]$	2033, 1959, 1910	22.5, 21.7, 21.2, 19.2, 217.0–223.0	70	−282 (1100)	—
$[MnI(CO)_3([8]aneSe_2)]$	2028, 1957, 1908	23.8, 22.0, 21.7, 19.5, 216.4–220.5	60	−448 (1800)	—
$[ReCl(CO)_3([8]aneSe_2)]$	2037, 1947, 1896	26.5, 22.7, 20.7, 19.6, 186.0–192.0	30	—	—
$[ReBr(CO)_3([8]aneSe_2)]$	2036, 1948, 1902	26.4, 22.9, 20.8, 20.6, 190.7, 188.5	19	—	—
$[\{MnCl(CO)_3\}_2([16]aneSe_4)]$	2033, 1956, 1913	29.5–32.3, 14.4–25.4, 215.5–222.0	See text	−210 (2100)	
$[ReCl(CO)_3([16]aneSe_4)]$	2034, 1941, 1901	n.o.	n.o.	—	—
$[Mn(CO)_3([16]aneSe_4)]CF_3SO_3$	2032, 1947	24.6, 32.3, 216–222	146.3 sh, 146.8^c	−499 (5000)	
$[\{MoBr_2(CO)_3\}_2([16]aneSe_4)]^d$	2033, 1959, 1927	n.o.	n.o.	—	n.o.
$[\{MoI_2(CO)_3\}_2([16]aneSe_4)]^d$	2018, 1947, 1883	n.o.	n.o.	—	n.o.
$[WI_2(CO)_3([16]aneSe_4)]^d$	2016, 1935, 1911	n.o.	n.o.	—	—
$[MoBr_2(CO)_3L]^d$	2039, 1981, 1913	n.o.	n.o.	—	n.o.
$[MoI_2(CO)_3L]^d$	2025, 1973, 1917	n.o.	n.o.	—	n.o.
$[WI_2(CO)_3L]^d$	2019, 1958, 1902	n.o.	n.o.	—	—

n.o. = Not obtained. ^{a} Spectra recorded in CHCl$_3$ solution. ^{b} $w_{\frac{1}{2}}$/Hz in parentheses. ^{c} At 200 K. ^{d} Spectra recorded as KBr discs.

$(CO)_4\}_2]$ or $[MoI_2(CO)_3(NCMe)_2]$ as appropriate in CH_2Cl_2 solution. Similarly, the orange tungsten(II) species $[WI_2(CO)_3([16]aneSe_4)]$ and $[WI_2(CO)_3L]$ are generated by treatment of $[WI_2(CO)_3(NCMe)_2]$ with one molar equivalent of [16]aneSe$_4$ or L, respectively, in CH_2Cl_2 solution. Compound L was used in these reactions rather than [8]aneSe$_2$ in an effort to improve the solubilities of the products. Microanalyses and conductivity measurements are consistent with the formulations given. The products are moderately air-sensitive powders and are very poorly soluble in chlorocarbons and hydrocarbons, and while they do dissolve in co-ordinating solvents such as MeCN, dmf or dmso this results in rapid decomposition *via* displacement of the selenoether ligand. This was confirmed by ^{1}H and ^{13}C-{^{1}H} NMR spectroscopic studies on the compounds in CD_3CN and d$_6$-dmso and precluded further NMR spectroscopic investigations on these species. Only $[WI_2(CO)_3([16]aneSe_4)]$ was sufficiently soluble in CD_2Cl_2 to enable a ^{1}H NMR spectrum to be obtained. This shows a set of broad multiplets in the methylene region associated with co-ordinated [16]aneSe$_4$. While it was not possible to obtain FAB mass spectrometry data due to the poor solubilities of these complexes in the 3-nitrobenzyl alcohol matrix, atmospheric pressure chemical ionisation (APCI) mass spectra were recorded from freshly prepared MeCN solutions. In each case the highest mass peaks were consistent with either [16]aneSe$_4$ or L as appropriate, again indicating very facile demetallation in this solvent. The IR spectra were recorded as pressed KBr discs, and each shows three CO stretching vibrations at frequencies comparable with those for the analogous seven-co-ordinate thioether macrocyclic derivatives, *e.g.* $[\{MoI_2(CO)_3\}_2([n]aneS_4)]$ ($n = 12$, 14 or 16) and $[\{WI_2(CO)_3\}_2([14]aneS_4)]$.[15] Thus, the dinuclear molybdenum(II) complexes of [16]aneSe$_4$ can be formulated as $[Mo_2X_4(CO)_6(\mu\text{-}[16]aneSe_4\text{-}Se,Se',Se'',Se''')]$ (X = Br or I). In contrast, the tungsten(II) complex of [16]aneSe$_4$ is mononuclear with two co-ordinated Se donors and the other two free. Reaction of $[WI_2(CO)_3(\eta^2\text{-}[16]aneSe_4)]$ with another molar equivalent of $[WI_2(CO)_3(NCMe)_2]$ does not permit formation of the dinuclear species, instead the reagents are recovered from the reaction mixture.

Table 2 Summary of the results of the conformational analysis of 1,6-diselena-3,4-benzocyclononane. The letter designations of the conformers correspond to those in Fig. 1^a

Conformer	Energy range/kJ	Number of times located
A	0.00–5.23	15
B	3.35–9.25	15
C	4.90–8.83	23
D	6.11–14.1	36
E	10.5–19.8	11
F	13.6–23.1	22
G	30.3–40.1	8

^{a} Four conformers were discarded as high energy forms of other structures.

In principle the seven-co-ordinate complexes of Mo^{II} and W^{II} involving L can adopt two structures; either monomeric with the diselenoether chelating, or polymeric with L bridging between metal centres. We have examined these possibilities by means of molecular mechanics calculations. The conformational behaviour of L in solution has been explored by multinuclear NMR,[16] and the ground state conformation in solution was deduced to be the same as that of the sulfur analogue.[17] In order to determine the co-ordination possiblities which are available to this compound as a ligand, we have carried out a complete conformational search using the molecular modelling program CHEM-X.[18] The standard forcefield for this program contains no parameters for selenium. However, the structures of a number of macrocyclic polyselenoethers have been determined by X-ray diffraction,[1,19] and these were used together with IR data for simple dialkyl selenoethers[20] to generate a minimum parameter set for this class of compound (see Experimental section). The parameter set was able to reproduce the published crystal structure conformations with good accuracy. The conformational search was carried out using established ring searching principles,[21] and the results are summarised in Table 2. The spread of energies for each conformer reflects the fact that different input geometries converge to slightly different versions of the same conformer, whilst the number of times each conformer was located gives an indication of the completeness of the search. The geometry of the global minimum was in excellent agreement with that of its sulfur analogue, as modelled by Rys *et al.*[16] on the basis of NMR data. Applying our results to the behaviour of L as a ligand, it is evident that although the ground state conformation **A** is predisposed towards bridging co-ordination, there are reasonably low energy alternatives which could chelate to a single metal (**C** and **D**, Fig. 1). Conformer **C** has an energy approximately 5 kJ mol^{-1} above the ground state and appears well suited for chelation to give a monomeric complex. Possible polymeric and monomeric complex structures were both successfully modelled by coupling conformers **A** and **C** respectively to *trans*- and *cis*-$[WI_2(CO)_3Se_2]$ cores produced from the crystal structures of $[WI_2(CO)_3(PEt_3)_2]$[22] and $[WI_2(CO)_3(\{4\text{-}MeC_6H_4SCH_2\}_2)]$[23] respectively (Scheme 1). Which structure is obtained in practice probably depends on kinetic effects; the low solubilities of the complexes of L in this work suggest that they may have the polymeric structure shown in Scheme 1a.

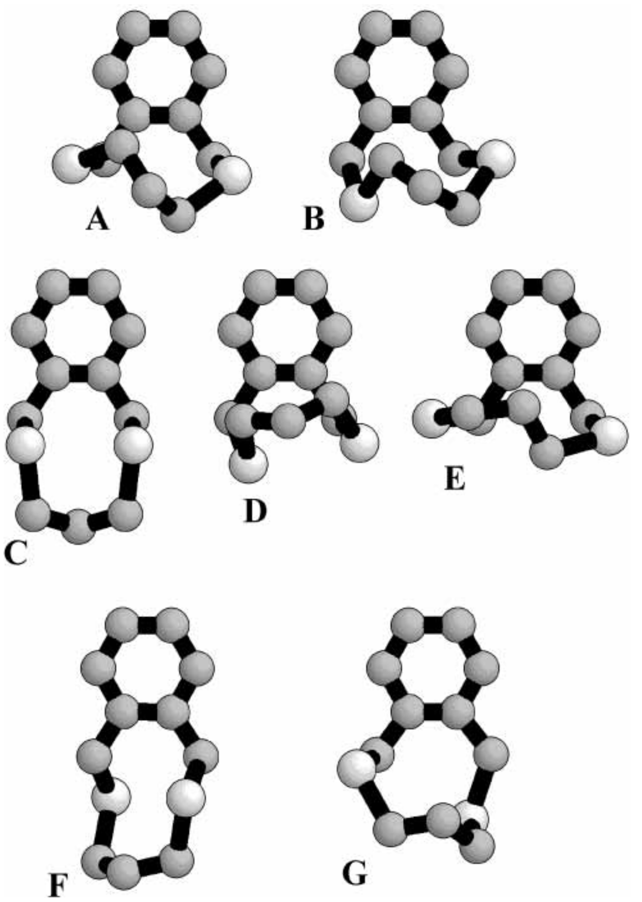
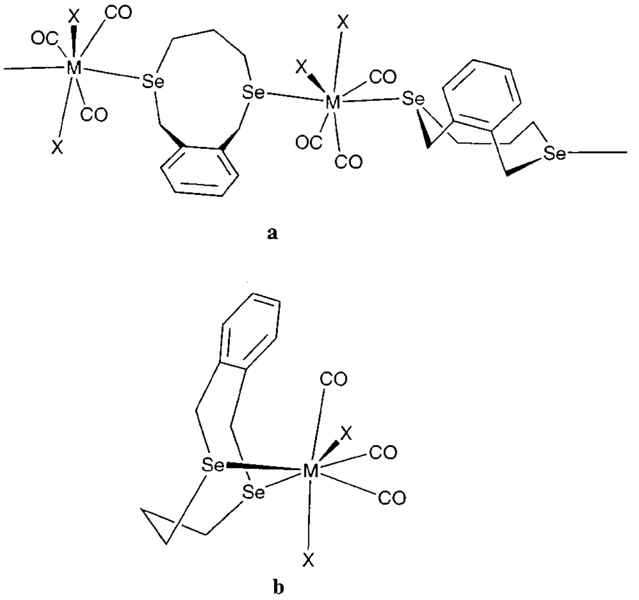


Fig. 1 Conformers of 1,6-diselena-3,4-benzocyclononane.



a

b

Scheme 1

The neutral *fac*-tricarbonyl species $[MnX(CO)_3([8]aneSe_2)]$ (X = Cl, Br or I) and $[ReX(CO)_3([8]aneSe_2)]$ (X = Cl or Br) are readily formed by reaction of $[MnX(CO)_5]$ or $[ReX(CO)_5]$ with $[8]aneSe_2$ in refluxing $CHCl_3$. The IR spectra of the products are consistent with C_s local symmetry (three CO stretching vibrations, 2a′ + a″), although this alone does not distinguish *mer* from *fac* geometries. However, the frequencies of the bands show very good agreement with those for *fac*-$[MnX(CO)_3(L–L)]$ (L–L = diselenoether ligand) the structures of which were confirmed by X-ray crystallography,[14] hence indicating a *fac* arrangement for the $[8]aneSe_2$ compounds. FAB Mass spectrometry typically shows peaks with the correct isotopic arrangement for $[MX(CO)_3([8]aneSe_2)]^+$ and $[M(CO)_3([8]aneSe_2)]^+$. Reaction of $[16]aneSe_4$ with two molar equivalents of $[MCl(CO)_5]$ in refluxing $CHCl_3$ affords the dinuclear 2:1 species $[\{MnCl(CO)_3\}_2([16]aneSe_4)]$ as an orange solid or the mononuclear species $[ReCl(CO)_3([16]aneSe_4)]$ as a cream solid. The IR spectra of these products are very similar to those of the complexes of Mn^I and Re^I of $[8]aneSe_2$, showing three strong $\nu(CO)$ bands at very similar frequencies. FAB Mass spectra do not show the parent ions, but do exhibit peaks attributed to $[M(CO)_3([16]aneSe_4)]^+$. The bright orange cationic maganese(I) species *fac*-$[Mn(CO)_3(\eta^3\text{-}[16]aneSe_4)]CF_3SO_3$ was generated by treatment of $[Mn(CO)_3(Me_2CO)_3]CF_3SO_3$ (formed *in situ* by treatment of $[MnCl(CO)_5]$ with $AgCF_3SO_3$ in refluxing acetone)[24] with one molar equivalent of $[16]aneSe_4$ in acetone solution. Solution IR spectroscopy on this highly soluble species shows two CO bands (2032, 1947 cm^{-1}), consistent with approximate C_{3v} symmetry at Mn^I (a_1 + e). The frequencies are comparable with those for *fac*-$[Mn(CO)_3\{MeC(CH_2SeMe)_3\}]^+$, the structure of which has been confirmed crystallographically (2039, 1962 cm^{-1}).[25] The electrospray mass spectrum shows an intense cluster of peaks consistent with $[Mn(CO)_3([16]aneSe_4)]^+$, as well as fragments at lower *m*/*z* values. Treatment of this complex with Me_3NO in CH_2Cl_2 at reflux leads to loss of the CO stretches associated with the *fac*-tricarbonyl species and the appearance of a new band at 1945 cm^{-1}. The electrospray mass spectrum of the product of this reaction shows no evidence for the tricarbonyl precursor, the highest intensity and highest mass peaks occurring at $m/z = 597$, consistent with $[Mn(CO)_2([16]aneSe_4)]^+$. These data suggest that the Me_3NO removes one of the CO ligands, allowing tetradentate co-ordination of $[16]aneSe_4$ possibly giving the *trans*-dicarbonyl species $[Mn(CO)_2([16]aneSe_4)]CF_3SO_3$. However, we have been unable to isolate a pure sample of this rather unstable compound to allow full characterisation.

$^{77}Se\text{-}\{^1H\}$ NMR studies were restricted to the complexes of Cr^0, Mo^0, W^0, Mn^I and Re^I with $[8]aneSe_2$, since those of Mo^{II} and W^{II} show very limited solubility. The data are presented in Table 1, together with ^{55}Mn and ^{95}Mo NMR data where appropriate. For the $[8]aneSe_2$ complexes we observe a progressive shift of $\delta(^{77}Se)$ to low frequency according to the series $Cr \longrightarrow Mo \longrightarrow W$, $Mn \longrightarrow Re$ and $Cl \longrightarrow Br \longrightarrow I$. In all cases $\delta(^{77}Se)$ is to low frequency of that for $[8]aneSe_2$ itself (δ 137). This contrasts with the situation for late transition metal halide derivatives of this ligand where high frequency shifts are observed.[7,10] Unlike the analogous complexes with acyclic diselenoethers which show invertomers, when $[8]aneSe_2$ acts as a bidentate ligand only one configuration is possible, hence one resonance is observed by $^{77}Se\text{-}\{^1H\}$ NMR spectroscopy.

Despite the moderately high quadrupole moment associated with ^{55}Mn (0.55×10^{-28} m^2), ^{55}Mn NMR spectroscopy is a valuable technique for characterising Mn-containing species. In addition to $\delta(^{55}Mn)$ being sensitive to factors such as the donor set and oxidation state, we have shown that for *fac*-$[MnX(CO)_3(L–L)]$ (L–L = dithio-, diseleno- or ditelluro-ether) the linewidths are typically <3000 Hz and hence individual invertomers are easily observed.[14,26] Since only one invertomer is possible for bidentate co-ordinated $[8]aneSe_2$, a single resonance is observed. The $\delta(^{55}Mn)$ values for these compounds show very good agreement with those for *fac*-$[MnX(CO)_3(diselenoether)]$ [diselenoether = $MeSe(CH_2)_nSeMe$ ($n = 2$ or 3), $PhSe(CH_2)_2SePh$ or *o*-$C_6H_4(SeMe)_2$],[14] and similarly show a shift to low frequency along the series $X = Cl \longrightarrow Br \longrightarrow I$. The ^{55}Mn NMR spectrum of the dinuclear $[\{MnCl(CO)_3\}_2([16]aneSe_4)]$ shows a single broad resonance at δ −210, indicative of the same donor set at the Mn as in the diselenoether species and hence bidentate co-ordination of the tetraselenoether macrocycle to each Mn^I. At 300 K the $^{77}Se\text{-}\{^1H\}$ NMR spectrum of this species shows a weak broad resonance at δ 152, and cooling this solution to 220 K gives rise to several resonances with

Table 3 Selected bond lengths (Å) and angles (°) of $[MnBr(CO)_3([8]aneSe_2)]$

Br(1)–Mn(1)	2.534(1)	Se(1)–Mn(1)	2.488(1)
Se(1)–C(1)	1.982(6)	Se(1)–C(6)	1.980(7)
Se(2)–Mn(1)	2.480(1)	Se(2)–C(3)	1.974(7)
Se(2)–C(4)	1.956(7)	Mn(1)–C(7)	1.805(7)
Mn(1)–C(8)	1.814(7)	Mn(1)–C(9)	1.788(7)
O(1)–C(7)	1.158(8)	O(2)–C(8)	1.134(8)
O(3)–C(9)	1.160(8)	C(1)–C(2)	1.517(10)
C(2)–C(3)	1.535(10)	C(4)–C(5)	1.535(10)
C(5)–C(6)	1.512(9)		
Mn(1)–Se(1)–C(1)	110.2(2)	Mn(1)–Se(1)–C(6)	108.1(2)
C(1)–Se(1)–C(6)	97.1(3)	Mn(1)–Se(2)–C(3)	108.7(2)
Mn(1)–Se(2)–C(4)	108.1(2)	C(3)–Se(2)–C(4)	97.5(3)
Br(1)–Mn(1)–Se(1)	88.47(4)	Br(1)–Mn(1)–Se(2)	92.41(4)
Br(1)–Mn(1)–C(7)	86.8(2)	Br(1)–Mn(1)–C(8)	86.6(2)
Br(1)–Mn(1)–C(9)	172.1(2)	Se(1)–Mn(1)–Se(2)	86.23(4)
Se(1)–Mn(1)–C(7)	175.1(2)	Se(1)–Mn(1)–C(8)	90.6(2)
Se(1)–Mn(1)–C(9)	97.8(2)	Se(2)–Mn(1)–C(7)	92.9(2)
Se(2)–Mn(1)–C(8)	176.7(2)	Se(2)–Mn(1)–C(9)	92.9(2)
C(7)–Mn(1)–C(8)	90.1(3)	C(7)–Mn(1)–C(9)	87.0(3)
C(8)–Mn(1)–C(9)	88.4(3)		

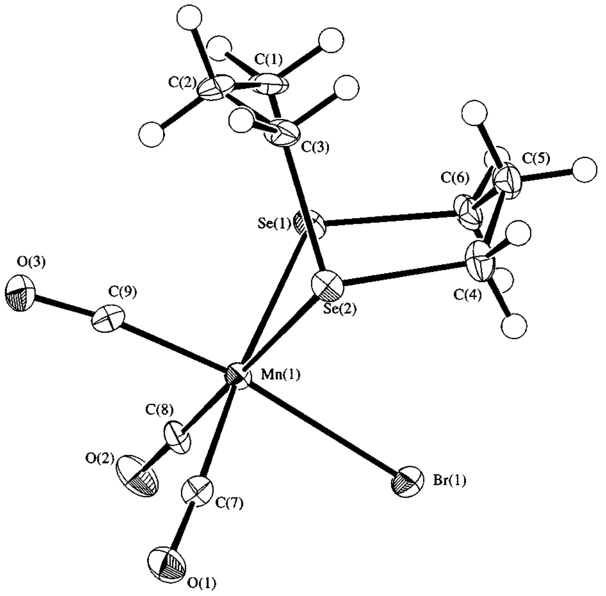


Fig. 2 View of the structure of $[MnBr(CO)_3([8]aneSe_2)]$ with numbering scheme adopted. Ellipsoids are drawn at 40% probability.

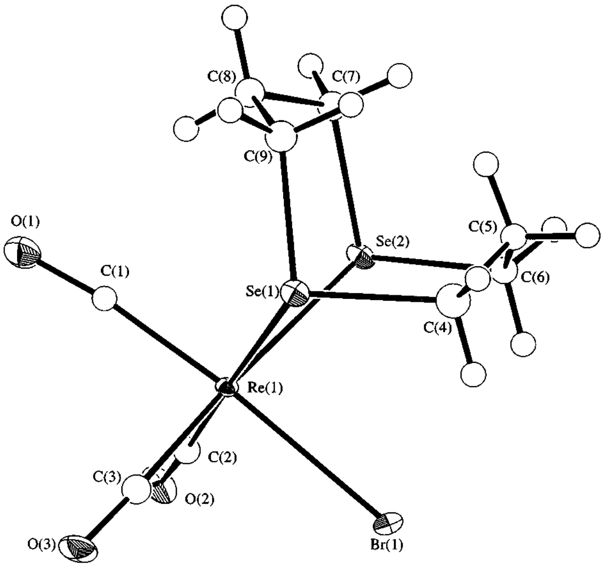


Fig. 3 View of the structure of $[ReBr(CO)_3([8]aneSe_2)]$. Details as in Fig. 2.

Table 4 Selected bond lengths (Å) and angles (°) of $[ReBr(CO)_3([8]aneSe_2)]$

Re(1)–Br(1)	2.633(2)	Re(1)–Se(1)	2.607(2)
Re(1)–Se(2)	2.611(2)	Re(1)–C(1)	1.88(2)
Re(1)–C(2)	1.92(2)	Re(1)–C(3)	1.92(2)
Se(1)–C(4)	1.97(2)	Se(1)–C(9)	1.98(2)
Se(2)–C(6)	2.00(2)	Se(2)–C(7)	1.99(2)
O(1)–C(1)	1.18(2)	O(2)–C(2)	1.16(2)
O(3)–C(3)	1.15(2)	C(4)–C(5)	1.50(3)
C(5)–C(6)	1.53(2)	C(7)–C(8)	1.53(2)
C(8)–C(9)	1.55(2)		
Br(1)–Re(1)–Se(1)	90.41(6)	Br(1)–Re(1)–Se(2)	86.72(6)
Br(1)–Re(1)–C(1)	175.7(5)	Br(1)–Re(1)–C(2)	88.4(5)
Br(1)–Re(1)–C(3)	89.4(5)	Se(1)–Re(1)–Se(2)	83.77(6)
Se(1)–Re(1)–C(1)	92.9(5)	Se(1)–Re(1)–C(2)	175.1(5)
Se(1)–Re(1)–C(3)	94.9(5)	Se(2)–Re(1)–C(1)	96.5(5)
Se(2)–Re(1)–C(2)	91.4(5)	Se(2)–Re(1)–C(3)	175.9(5)
C(1)–Re(1)–C(2)	88.6(7)	C(1)–Re(1)–C(3)	87.5(7)
C(2)–Re(1)–C(3)	89.9(7)	Re(1)–Se(1)–C(4)	108.1(6)
Re(1)–Se(1)–C(9)	107.7(5)	C(4)–Se(1)–C(9)	98.1(7)
Re(1)–Se(2)–C(6)	107.8(5)	Re(1)–Se(2)–C(7)	110.2(5)
C(6)–Se(2)–C(7)	97.1(7)		

Table 5 Selected bond lengths (Å) and angles (°) of $[W(CO)_4([8]aneSe_2)]$

W(1)–Se(1)	2.650(1)	W(1)–Se(1)	2.650(1)
W(1)–C(1)	2.08(2)	W(1)–C(2)	1.96(1)
W(1)–C(2)	1.96(1)	W(1)–C(3)	2.07(2)
Se(1)–C(4)	1.98(2)	Se(1)–C(7)	2.01(1)
O(1)–C(1)	1.13(2)	O(2)–C(2)	1.17(1)
O(3)–C(3)	1.12(2)	C(4)–C(5)	1.53(2)
C(6)–C(7)	1.49(2)	C(6)–C(7)	1.49(2)
Se(1)–W(1)–Se(1)	82.62(6)	Se(1)–W(1)–C(1)	95.9(4)
Se(1)–W(1)–C(2)	176.0(4)	Se(1)–W(1)–C(2)	93.9(4)
Se(1)–W(1)–C(3)	90.8(4)	Se(1)–W(1)–C(1)	95.9(4)
Se(1)–W(1)–C(2)	93.9(4)	Se(1)–W(1)–C(2)	176.0(4)
Se(1)–W(1)–C(3)	90.8(4)	C(1)–W(1)–C(2)	86.4(5)
C(1)–W(1)–C(2)	86.4(5)	C(1)–W(1)–C(3)	171.0(7)
C(2)–W(1)–C(2)	89.5(8)	C(2)–W(1)–C(3)	87.2(5)
C(2)–W(1)–C(3)	87.2(5)	W(1)–Se(1)–C(4)	105.3(4)
W(1)–Se(1)–C(7)	111.4(4)	C(4)–Se(1)–C(7)	98.4(6)

major peaks at δ 72.0, 119.6, 144.5 and 147.0. The complex $[ReCl(CO)_3([16]aneSe_4)]$ was not sufficiently soluble to enable $^{13}C\text{-}\{^1H\}$ and $^{77}Se\text{-}\{^1H\}$ NMR spectra to be obtained.

The ^{55}Mn NMR data were also recorded for the cationic manganese(I) complexes of $[16]aneSe_4$. Thus *fac*-$[Mn(CO)_3(\eta^3\text{-}[16]aneSe_4)]CF_3SO_3$ shows a single broad peak at δ −499. This compares with δ −721 (*syn*) and −672 (*anti*) for *fac*-$[Mn(CO)_3\{MeC(CH_2SeMe)_3\}]CF_3SO_3$ and δ −560 for *fac*-$[Mn(CO)_3\{MeSe(CH_2)_3Se(CH_2)_3SeMe\}]CF_3SO_3$.[25]

Single crystals of $[MnBr(CO)_3([8]aneSe_2)]$ and $[ReBr(CO)_3([8]aneSe_2)]$ were obtained by addition of hexane to solutions of the compounds in $CHCl_3$ and cooling to *ca.* −18 °C. The crystal structures show (Figs. 2 and 3, Tables 3 and 4) that these species are isostructural, each displaying a distorted octahedral arrangement at the metal centre comprising three mutually *fac* CO ligands, a bidentate $[8]aneSe_2$ and a Br^- ligand, Mn–Se 2.488(1), 2.480(1); Re–Se 2.607(2), 2.611(2) Å. The Se(1)–M–Se(2) angles are 86.23(4) and 83.77(6)° respectively for M = Mn and Re, and the co-ordinated diselenoether adopts a chair-boat conformation. The M–Se distances for these species compare well with those in other reported manganese(I) and rhenium(I) selenoether species, *e.g.* *fac*-$[MnCl(CO)_3\{MeSe(CH_2)_nSeMe\}]$ ($n = 2$ or 3)[14] and *fac*-$[ReI(CO)_3\{MeSe(CH_2)_3SeMe\}]$.[27] Crystals of $[W(CO)_4([8]aneSe_2)]$ were also obtained by cooling a $CHCl_3$–hexane solution of the compound to −18 °C. The crystal structure of this compound shows (Fig. 4, Table 5) the $[8]aneSe_2$ ligand occupying two mutually *cis* co-ordination sites with the CO ligands completing the distorted octahedral

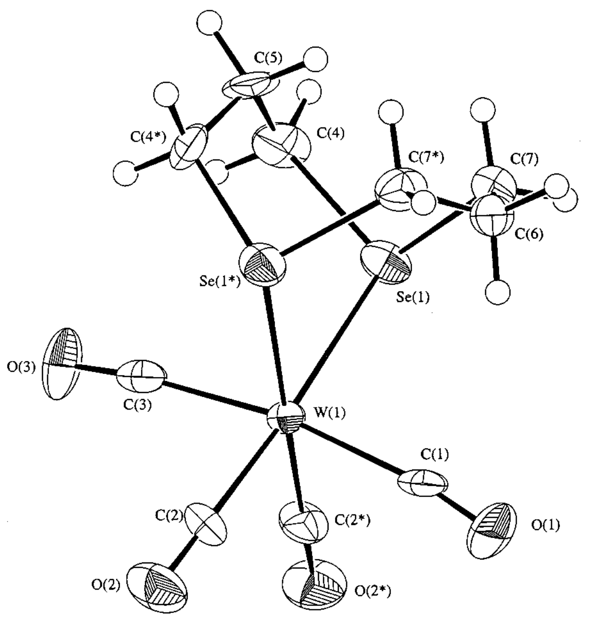


Fig. 4 View of the structure of [W(CO)$_4$([8]aneSe$_2$)]. Details as in Fig. 2.

geometry, W–Se(1) 2.650(1), W–C(1) 2.08(2), W–C(2) 1.96(1), W–C(3) 2.07(2) Å, thus the W–CO distance *trans* to Se is significantly shorter than those *trans* to CO. Similar trends have been observed for [Mo(CO)$_4$(PR$_3$)$_2$].[28]

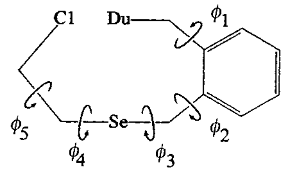
Experimental

Infrared spectra were measured as CsI or KBr discs using Perkin-Elmer 983 (200–4000 cm^{-1}) or Shimadzu FTIR-8300 (400–4000 cm^{-1}) spectrometers, or in solution using NaCl plates on a Perkin-Elmer 1600 FTIR spectrometer. Mass spectra were run by fast-atom bombardment (FAB) using 3-nitrobenzyl alcohol as matrix on a VG Analytical 70-250-Se normal geometry double focusing mass spectrometer or by electrospray or APCI (MeCN solution) using a Micromass Platform quadrupole mass analyser (*m*/*z* was calculated using ^{80}Se). The ^{1}H NMR spectra were recorded in CDCl$_3$ at 300 MHz unless otherwise stated using a Bruker AM300 spectrometer, ^{13}C-{^{1}H}, ^{55}Mn, ^{77}Se-{^{1}H} and ^{95}Mo NMR spectra using a Bruker AM360 spectrometer operating at 90.1, 89.27, 68.68 or 23.4 MHz respectively and referenced to Me$_4$Si, external saturated, aqueous K[MnO$_4$], external neat Me$_2$Se and external aqueous Na$_2$[MoO$_4$] respectively (δ 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 overcome the long relaxation times. Solution conductivities were obtained using *ca.* 10^{-3} M solutions and a Portland Electronic conductivity meter. Microanalyses were determined by the University of Strathclyde and the University of East Anglia microanalytical laboratories. The compounds [MnX(CO)$_5$] (X = Cl, Br or I),[29] [ReX(CO)$_5$] (X = Cl or Br),[30] [Mo(CO)$_4$(nbd)],[31] [W(CO)$_4$(TMPA)],[32] [{MoBr$_2$(CO)$_4$}$_2$],[33] [MI$_2$(CO)$_3$(NCMe)$_2$],[34] L,[10] [8]aneSe$_2$ and [16]aneSe$_4$[1] were prepared according to literature procedures and [Cr(CO)$_4$(nbd)] *via* a modified synthesis in refluxing xylene.[35]

Calculations

The molecular mechanics calculations were carried out using CHEM-X software.[18] The standard forcefield was supplemented with the following parameters to permit calculations on selenoethers: C–Se bond length $l_0 = 1.956$ Å, $k = 180$; C–Se-C $\theta_0 = 1.716$ rad, $k = 40$, cos $\theta = -0.144$, cos $k = 90$. All other selenium parameters were copied from the default set for sulfur.

The conformational analysis of L was carried out as follows. The molecule was first constructed in an arbitrary conformation and energy minimised. The structure was then modified to the ring-opened form shown in Scheme 2, where Du is a dummy



Scheme 2

atom. The angles φ_1 and φ_2–φ_5 were varied systematically over 180° in 37 steps and 360° in 48 steps respectively, giving a total of 196411392 input conformations. These were filtered by skipping those exhibiting Corey–Pauling–Koltun (CPK) contacts, and by use of the following acceptance criteria; Cl···Du 1.93–1.98 Å, Cl···Du–C 95.5–101.1°, C–Cl···Du 108.5–110.5°. This gave 134 accepted conformations. Each of these was then reconstructed to the original compound, energy minimised, and compared to those already processed. Enantiomeric forms were treated as one conformer. This gave a final set of seven conformers (Table 2).

Syntheses

All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques and one representative synthesis of each type is presented in detail.

[Cr(CO)$_4$([8]aneSe$_2$)]. To a solution of [Cr(CO)$_4$(nbd)] (0.077 g, 0.30 mmol) in chloroform (10 cm^3) a solution of [8]aneSe$_2$ (0.073 g, 0.30 mmol) in chloroform (2 cm^3) was added. This dark yellow reaction mixture was refluxed overnight. Solution IR confirmed that the reaction had gone to completion, by the disappearance of bands associated with starting material. The resulting solution was filtered (Celite) and solvent volume reduced *in vacuo* to *ca.* 4 cm^3 before precipitating the product by the addition of cold hexane (8 cm^3). The bright yellow solid was isolated by filtration and dried under vacuum. Yield 0.072 g, 59% (Found: C, 29.2; H, 2.5. Calc. for C$_{10}$H$_{12}$CrO$_4$Se$_2$: C, 29.6; H, 3.0%). APCI mass spectrum (MeCN): found *m*/*z* = 379, 323; calculated for [Cr(CO)$_3$([8]aneSe$_2$)]$^+$ *m*/*z* = 380, [Cr(CO)([8]aneSe$_2$)]$^+$ *m*/*z* = 324. ^{1}H NMR spectrum (CDCl$_3$): δ 2.55–2.90 (br, m, SeCH$_2$, 8 H) and 2.05 (br, CH$_2$C*H*$_2$CH$_2$, 4 H).

[Mo(CO)$_4$([8]aneSe$_2$)]. Yield 74% (Found: C, 27.0; H, 2.9. Calc. for C$_{10}$H$_{12}$MoO$_4$Se$_2$: C, 26.7; H, 2.7%). APCI mass spectrum (MeCN): found *m*/*z* = 244; calculated for ([8]aneSe$_2$)$^+$ *m*/*z* = 244. ^{1}H NMR spectrum (CDCl$_3$): δ 2.80–2.95 (br, m, SeCH$_2$, 8 H) and 2.28 (m, CH$_2$C*H*$_2$CH$_2$, 4 H).

[W(CO)$_4$([8]aneSe$_2$)]. Yield 53% (Found: C, 22.0; H, 2.2. Calc. for C$_{10}$H$_{12}$O$_4$Se$_2$W: C, 22.3; H, 2.2%). FAB mass spectrum: found *m*/*z* = 538; calculated for [^{184}W(CO)$_4$([8]aneSe$_2$)]$^+$ *m*/*z* = 540. ^{1}H NMR spectrum (CDCl$_3$): δ 2.75–2.90 (m, SeCH$_2$, 8 H) and 2.15–2.35 (m, CH$_2$C*H*$_2$CH$_2$, 4 H).

[MnCl(CO)$_3$([8]aneSe$_2$)]. To a solution of [MnCl(CO)$_5$] (0.069 g, 0.30 mmol) in chloroform (10 cm^3) a solution of [8]aneSe$_2$ (0.073 g, 0.30 mmol) in chloroform (2 cm^3) was added *via* syringe. The reaction mixture was refluxed and monitored by solution IR until there was an absence of bands associated with starting material (*ca.* 4 h). The resulting orange solution was filtered (Celite) and the solvent volume reduced *in vacuo* to *ca.* 4 cm^3 before inducing precipitation of the product by the addition of cold hexane (8 cm^3). The orange solid was isolated by filtration and dried under vacuum. Yield 0.072 g, 58% (Found: C, 25.3; H, 3.0. Calc. for C$_9$H$_{12}$ClMnO$_3$Se$_2$: C, 25.9; H, 2.9%). FAB mass spectrum: found $m/z = 418$, 383, 334; calculated for $[Mn^{35}Cl(CO)_3([8]aneSe_2)]^+$ $m/z = 418$; $[Mn(CO)_3([8]aneSe_2)]^+$ $m/z = 383$, $[Mn^{35}Cl([8]aneSe_2)]^+$ $m/z = 334$. ^{1}H NMR spectrum ($CDCl_3$): δ 2.1–4.0 (br, m, CH_2).

$[MnBr(CO)_3([8]aneSe_2)]$. Orange crystals of product were obtained from a solvent mixture of chloroform and hexane at −18 °C. Yield 55% (Found: C, 23.5; H, 2.5. Calc. for $C_9H_{12}BrMnO_3Se_2$: C, 23.4; H, 2.6%). FAB mass spectrum: found $m/z = 462$, 378; calculated for $[Mn^{79}Br(CO)_3([8]aneSe_2)]^+$ $m/z = 462$; $[MnBr([8]aneSe_2)]^+$ $m/z = 378$. ^{1}H NMR spectrum ($CDCl_3$): δ 1.8–4.1 (br, m, CH_2).

$[MnI(CO)_3([8]aneSe_2)]$. Yield 51% (Found: C, 21.5; H, 2.5. Calc. for $C_9H_{12}IMnO_3Se_2$: C, 21.3, H, 2.4%). ^{1}H NMR spectrum ($CDCl_3$): δ 1.8–4.1 (br, m, CH_2).

$[ReCl(CO)_3([8]aneSe_2)]$. To a solution of $[ReCl(CO)_5]$ (0.090 g, 0.25 mmol) in chloroform (10 cm^3) a solution of $[8]aneSe_2$ (0.061 g, 0.25 mmol) in chloroform (2 cm^3) was added *via* a syringe. This light yellow reaction mixture was refluxed overnight. Solution IR confirmed that the reaction had gone to completion, by the disappearance of bands associated with starting material. The resulting solution was filtered (Celite) and solvent volume reduced *in vacuo* to *ca.* 4 cm^3 before inducing precipitation of the product by the addition of cold hexane (8 cm^3). The pale cream solid was isolated by filtration, dried under vacuum and retained for analysis. Yield 0.076 g, 54% (Found: C, 18.9; H, 2.4. Calc. for $C_9H_{12}ClO_3ReSe_2$: C, 19.7; H, 2.2%). FAB mass spectrum: found $m/z = 548$, 513; calculated for $[^{187}Re^{35}Cl(CO)_3([8]aneSe_2)]^+$ $m/z = 550$; $[Re(CO)_3([8]aneSe_2)]^+$ $m/z = 515$. ^{1}H NMR spectrum ($CDCl_3$): δ 3.9, 1.9–3.1 (m, CH_2).

$[ReBr(CO)_3([8]aneSe_2)]$. Colourless crystals of product were obtained from a solvent mixture of chloroform and hexane at −18 °C. Yield 54% (Found: C, 18.3; H, 1.9. Calc. for $C_9H_{12}BrO_3ReSe_2$: C, 18.2; H, 2.0%). FAB mass spectrum: found $m/z = 594$, 566, 538, 513; calculated for $[^{187}Re^{79}Br(CO)_3([8]aneSe_2)]^+$ $m/z = 594$; $[^{187}Re^{79}Br(CO)_2([8]aneSe_2)]^+$ $m/z = 566$; $[^{187}Re^{79}Br(CO)([8]aneSe_2)]^+$ $m/z = 538$, $[Re(CO)_3([8]aneSe_2)]^+$ $m/z = 515$. ^{1}H NMR spectrum ($CDCl_3$): δ 4.05, 2.0–3.1 (m, CH_2).

$[\{MnCl(CO)_3\}_2([16]aneSe_4)]$. To a solution of $[MnCl(CO)_5]$ (0.096 g, 0.41 mmol) in chloroform (20 cm^3) a solution of $[16]aneSe_4$ (0.100 g, 0.21 mmol) in chloroform (3 cm^3) was added. This orange mixture was refluxed overnight. Solution IR showed an absence of bands associated with starting material. The orange solution was filtered before reducing the solvent volume *in vacuo* to *ca.* 7 cm^3 and inducing precipitation by the addition of cold hexane (10 cm^3). This gave a bright orange solid which was isolated by filtration, recrystallised from CH_2Cl_2 and dried under vacuum. Yield 0.066 g, 49% (Found: C, 24.6; H, 3.2. Calc. for $C_{18}H_{24}Cl_2Mn_2O_6Se_4{\cdot}CH_2Cl_2$: C, 24.8; H, 2.8%). Electrospray mass spectrum (MeCN): found $m/z = 622$, 594; calculated for $[Mn(CO)_3([16]aneSe_4)]^+$ $m/z = 627$; $[Mn(CO)_2([16]aneSe_4)]^+$ $m/z = 599$. ^{1}H NMR spectrum ($CDCl_3$): δ 0.9–3.7 (br, m, CH_2).

$[ReCl(CO)_3([16]aneSe_4)]$. The method employed was essentially the same as above, except $[ReCl(CO)_5]$ (0.149 g 0.41 mmol) was used. A poorly soluble, pale cream solid was produced, which was isolated by filtration and dried under vacuum. Yield 0.106 g, 47% (Found: C, 22.1; H, 2.5. Calc. for $C_{15}H_{24}ClO_3ReSe_4$: C, 22.8; H, 3.0%). Electrospray mass spectrum (MeCN): found $m/z = 756$; calculated for $[^{187}Re(CO)_3([16]aneSe_4)]^+$ $m/z = 759$. ^{1}H NMR spectrum ($CDCl_3$): δ 4.0, 2.0–3.0 (m, CH_2).

$[Mn(CO)_3([16]aneSe_4)]CF_3SO_3$. To a solution of $[MnBr(CO)_5]$ (0.103 g, 0.38 mmol) in acetone, $AgCF_3SO_3$ (0.096 g, 0.38 mmol) was added. This mixture was refluxed in darkness for 3 h. The reaction was allowed to cool to room temperature before removing the precipitated AgBr by filtration (Celite). The conversion was assumed to be 80%. To the resulting light orange solution $[16]aneSe_4$ (0.147 g, 0.30 mmol) was added and the mixture stirred at room temperature overnight. The bright orange product was precipitated by the addition of cold hexanes, recrystallised from CH_2Cl_2–EtOH, isolated by filtration and vacuum dried. Yield 0.150 g, 52% (Found: C, 24.3; H, 2.8. Calc. for $C_{16}H_{24}F_3MnO_6SSe_4$: C, 24.9; H, 3.1%). Electrospray mass spectrum (MeCN): found $m/z = 625$, 595, 541; calculated for $[Mn(CO)_3([16]aneSe_4)]^+$ $m/z = 627$; $[Mn(CO)_2([16]aneSe_4)]^+$ $m/z = 599$; $[Mn([16]aneSe_4)]^+$ $m/z = 543$. ^{1}H NMR spectrum ($CDCl_3$): δ 2.1–3.6 (br, m, CH_2).

$[\{MoBr_2(CO)_3\}_2([16]aneSe_4)]$. Dichloromethane (20 cm^3) was added to a solid mixture of $[\{MoBr_2(CO)_4\}_2]$ (0.190 g, 0.26 mmol) and $[16]aneSe_4$ (0.130 g, 0.27 mmol). The mixture was stirred at room temperature for 1.5 h and then filtered. The resulting pale brown solid was washed with CH_2Cl_2 and dried *in vacuo*. Yield 0.27 g, 82% (Found: C, 18.0; H, 2.0. Calc. for $C_{18}H_{24}Br_4Mo_2O_6Se_4{\cdot}CH_2Cl_2$: C, 18.3; H, 2.1%). Λ_M/S cm^2 mol^{-1}: 39 (dmf). APCI mass spectrum (MeCN): found $m/z = 487$; calculated for $([16]aneSe_4)^+$ $m/z = 488$.

$[\{MoI_2(CO)_3\}_2([16]aneSe_4)]$. Yield 46%. (Found: C, 16.2; H, 1.9. Calc. for $C_9H_{12}I_2MoO_3Se_2$: C, 16.0; H, 1.8%). Λ_M/S cm^2 mol^{-1}: 74 (dmf). APCI mass spectrum (MeCN): found $m/z = 487$; calculated for $([16]aneSe_4)^+$ $m/z = 488$.

$[WI_2(CO)_3([16]aneSe_4)]$. Yield 97% (Found: C, 18.0; H, 2.3. Calc. for $C_{15}H_{24}I_2O_3Se_4W$: C, 17.9; H, 2.4%). Λ_M/S cm^2 mol^{-1}: 21 (dmf). ^{1}H NMR spectrum (CD_2Cl_2): δ 3.5–1.8 (br, m). APCI mass spectrum (MeCN): found $m/z = 489$; calculated for $([16]aneSe_4)^+$ $m/z = 488$.

$[MoBr_2(CO)_3L]$. Yield 82% (Found: C, 25.1; H, 2.0. Calc. for $C_{14}H_{14}Br_2MoO_3Se_2{\cdot}0.5CH_2Cl_2$: C, 25.4; H, 2.2%). Λ_M/S cm^2 mol^{-1}: 8 (dmf). APCI mass spectrum (MeCN): found $m/z = 306$; calculated for $[L]^+$ $m/z = 306$.

$[MoI_2(CO)_3L]$. Yield 85% (Found: C, 22.8; H, 1.8. Calc. for $C_{14}H_{14}I_2MoO_3Se_2$: C, 22.8; H, 1.9%). Λ_M/S cm^2 mol^{-1}: 11 (dmf). APCI mass spectrum (MeCN): found $m/z = 304$; calculated for $[L]^+$ $m/z = 306$.

$[WI_2(CO)_3L]$. Yield 90% (Found: C, 20.4; H, 1.6. Calc. for $C_{14}H_{14}I_2O_3Se_2W$: C, 20.4; H, 1.7%). Λ_M/S cm^2 mol^{-1}: 19 (dmf). APCI mass spectrum (MeCN): found $m/z = 304$; calculated for $[L]^+$ $m/z = 306$.

Crystal structures of $[MnBr(CO)_3([8]aneSe_2)]$, $[ReBr(CO)_3([8]aneSe_2)]$ and $[W(CO)_4([8]aneSe_2)]$

Details of the crystallographic data collection and refinement parameters are given in Table 6. Data collection used a Rigaku AFC7S four-circle diffractometer operating at 150 K and graphite-monochromated Mo-Kα X-radiation ($\lambda = 0.71073$ Å). No significant crystal decay or movement was observed. The data were corrected for absorption using ψ-scans. The structures were solved by heavy atom methods[36] and developed by iterative cycles of full-matrix least-squares refinement and Fourier-difference syntheses.[37] For $[MnBr(CO)_3([8]aneSe_2)]$ and $[W(CO)_4([8]aneSe_2)]$ all non-H atoms were refined anisotropically, while for $[ReBr(CO)_3([8]aneSe_2)]$ the dominance of the rhenium scattering prevented refinement of the C-atom anisotropic displacement parameters. The H atoms were placed in fixed, calculated positions with d(C–H) = 0.96 Å. The Flack

Table 6 Crystallographic data collection and refinement parameters

	[MnBr(CO)$_3$([8]aneSe$_2$)]	[ReBr(CO)$_3$([8]aneSe$_2$)]	[W(CO)$_4$([8]aneSe$_2$)]
Formula	$C_9H_{12}BrMnO_3Se_2$	$C_9H_{12}BrO_3ReSe_2$	$C_{10}H_{12}O_4Se_2W$
M	480.95	592.22	537.97
Space group	$P2_12_12_1$	$P2_12_12_1$	$Pnma$
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
a/Å	12.274(1)	12.302(2)	12.861(2)
b/Å	12.684(1)	12.726(1)	9.978(1)
c/Å	8.611(1)	8.656(2)	10.715(2)
U/Å^3	1340.6(2)	1355.1(4)	1375.0(3)
Z	4	4	4
D_c/g cm^{-3}	2.284	2.903	2.599
μ(Mo-Kα)/cm^{-1}	92.66	173.21	137.05
Maximum and minimum transmission factors	1.000, 0.887	1.000, 0.641	1.000, 0.328
Unique obs. reflections	1392	1409	1421
Obs. reflections with [$I_o > 2\sigma(I_o)$]	1231	1215	956
No parameters	145	100	88
R	0.021	0.032	0.035
R'	0.022	0.043	0.040

parameter indicated the correct enantiomorph for the manganese and rhenium structures.[38] The weighting scheme $w^{-1} = \sigma^2(F)$ gave satisfactory agreement analyses.

CCDC reference number 186/1341.

See http://www.rsc.org/suppdata/dt/1999/1077/ for crystallographic files in .cif format.

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References

1 R. J. Batchelor, F. W. B. Einstein, I. D. Gay, J.-H. Gu, B. D. Johnston and B. M. Pinto, *J. Am. Chem. Soc.*, 1989, **111**, 6852.
2 R. J. Batchelor, F. W. B. Einstein, I. D. Gay, J.-H. Gu, B. M. Pinto and X.-M. Zhou, *Inorg. Chem.*, 1996, **35**, 3667.
3 R. J. Batchelor, F. W. B. Einstein, I. D. Gay, J.-H. Gu, B. M. Pinto and X.-M. Zhou, *J. Am. Chem. Soc.*, 1990, **112**, 3706.
4 R. J. Batchelor, F. W. B. Einstein, I. D. Gay, J.-H. Gu, B. M. Pinto and X.-M. Zhou, *J. Organomet. Chem.*, 1991, **411**, 147.
5 W. Levason, J. J. Quirk and G. Reid, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 3713; P. F. Kelly, W. Levason, G. Reid and D. J. Williams, *J. Chem. Soc.*, *Chem. Commun.*, 1993, 1716.
6 N. R. Champness, P. F. Kelly, W. Levason, G. Reid, A. M. Z. Slawin and D. J. Williams, *Inorg. Chem.*, 1995, **34**, 651; C. S. Frampton, W. Levason, J. J. Quirk and G. Reid, *Inorg. Chem.*, 1994, **33**, 3120.
7 N. R. Champness, J. J. Quirk, W. Levason, G. Reid and C. S. Frampton, *Polyhedron*, 1995, **14**, 2753.
8 W. Levason, G. Reid and S. M. Smith, *Polyhedron*, 1997, **16**, 4253.
9 W. Levason, J. J. Quirk, G. Reid and S. M. Smith, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 3719.
10 D. G. Booth, W. Levason, J. J. Quirk, G. Reid and S. M. Smith, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 3493.
11 M. K. Davies, W. Levason and G. Reid, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 2185.
12 T. Yoshida, T. Adachi, T. Ueda, M. Watanabe, M. Kaminaka and T. Higuchi, *Angew. Chem.*, *Int. Ed. Engl.*, 1987, **26**, 1171; T. Yoshida, T. Adachi, M. Kaminaka and T. Ueda, *J. Am. Chem. Soc.*, 1988, **110**, 4872; T. Adachi, N. Sasaki, T. Ueda, M. Kaminaka and T. Yoshida, *J. Chem. Soc.*, *Chem. Commun.*, 1989, 1320.
13 T. Adachi, M. C. Durrant, D. L. Hughes, C. J. Pickett, R. L. Richards, J. Talarmin and T. Yoshida, *J. Chem. Soc.*, *Chem. Commun.*, 1992, 1464.
14 J. Connolly, M. K. Davies and G. Reid, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 3833.
15 P. K. Baker, M. C. Durrant, S. D. Davies, D. L. Hughes and R. L. Richards, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 509.
16 B. Rys, H. Duddeck and M. Hiegemann, *J. Heterocycl. Chem.*, 1992, **29**, 967.
17 B. Rys, H. Duddeck and M. Hiegemann, *Tetrahedron*, 1991, **47**, 1417.
18 CHEM-X, Chemical Design Ltd., Oxon, July 1996 version.
19 R. D. Adams and K. T. McBride, *Chem. Commun.*, 1997, 525; G. W. Bushnell and R. H. Mitchell, *Can. J. Chem.*, 1982, **60**, 362; T. Okajima, Z. H. Wang and Y. Fukazawa, *Tetrahedron Lett.*, 1989, **30**, 1551; M. Iwaoka, H. Komatsu and S. Tomoda, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 1825.
20 K. Ohno, H. Matsuura and H. Murata, *J. Mol. Struct.*, 1980, **66**, 45; J. R. Alkins and P. J. Hendra, *Spectrochim. Acta*, 1966, **22**, 2075.
21 W. C. Still and I. Galynker, *Tetrahedron*, 1981, **37**, 3981; Y. Fukazawa, S. Usui and Y. Uchio, *Tetrahedron Lett.*, 1986, **27**, 1825.
22 P. K. Baker, A. I. Clark, M. M. Meehan, E. E. Parker, A. E. Underhill, M. G. B. Drew, M. C. Durrant and R. L. Richards, *Transition Met. Chem.*, 1998, **23**, 155.
23 P. K. Baker, S. D. Harris, M. C. Durrant, D. L. Hughes and R. L. Richards, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 1401.
24 R. Uson, V. Riera, J. Gimeno, M. Laguna and M. P. Gamasa, *J. Chem. Soc.*, *Dalton Trans.*, 1979, 996.
25 J. Connolly, W. Levason, S. D. Orchard, S. J. A. Pope and G. Reid, unpublished work.
26 J. Connolly, G. W. Goodban, G. Reid and A. M. Z. Slawin, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 2225; W. Levason, S. D. Orchard and G. Reid, *Organometallics*, in the press.
27 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.
28 F. A. Cotton, D. J. Darensbourg, S. Klein and B. W. S. Kilthammer, *Inorg. Chem.*, 1982, **21**, 2661.
29 K. J. Reimer and A. Shaver, *Inorg. Synth.*, 1979, **19**, 159.
30 S. P. Schmidt, W. C. Trogler and F. Basolo, *Inorg. Synth.*, 1990, **28**, 160.
31 J. J. Eisch and R. B. King, *Organomet. Synth.*, 1965, **1**, 123.
32 G. R. Dobson and G. C. Faber, *Inorg. Chim. Acta*, 1987, **4**, 87.
33 J. A. Broomhead, J. Budge and W. Grumley, *Inorg. Synth.*, 1990, **28**, 145.
34 P. K. Baker, S. G. Fraser and E. M. Keys, *J. Organomet. Chem.*, 1986, **309**, 319.
35 H. Werner and R. Prinz, *Chem. Ber.*, 1967, **100**, 265.
36 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.
37 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1995.
38 H. D. Flack, *Acta Crystallogr.*, *Sect. A*, 1983, **39**, 876.

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