

# Dithioether complexes of manganese carbonyl halides: synthesis, <sup>55</sup>Mn NMR spectroscopic, X-ray crystallographic and electrochemical studies

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Reaction of [Mn(CO)<sub>5</sub>X] (X = Cl, Br or I) with RS(CH<sub>2</sub>)<sub>n</sub>SR (R = Me or Ph, n = 2; R = Me, n = 3) or C<sub>6</sub>H<sub>4</sub>(SMe)<sub>2</sub>-o yielded the neutral manganese(i) complexes [MnX(CO)<sub>3</sub>{RS(CH<sub>2</sub>)<sub>n</sub>SR}] or [MnX(CO)<sub>3</sub>{C<sub>6</sub>H<sub>4</sub>(SMe)<sub>2</sub>-o}] as yellow or orange solids. These compounds have been characterised using IR, <sup>1</sup>H and <sup>13</sup>C-<sup>1</sup>H} NMR spectroscopy, FAB mass spectrometry and microanalyses. X-Ray crystallographic analyses on two examples confirmed a *fac*-tricarbonyl arrangement, with the dithioether ligand chelating. The complex [MnCl(CO)<sub>3</sub>-(MeSCH<sub>2</sub>CH<sub>2</sub>SMe)] adopts the *DL* arrangement, while [MnBr(CO)<sub>3</sub>(PhSCH<sub>2</sub>CH<sub>2</sub>SPh)] is in the *meso*-2 form in the solid state. Manganese-55 NMR spectroscopic studies show that δ(<sup>55</sup>Mn) lies in the range +67 to -567 for these compounds, and shifts to low frequency according to the series X = Cl → Br → I. For the compounds involving PhSCH<sub>2</sub>CH<sub>2</sub>SPh or MeSCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SMe pyramidal inversion is rapid on the NMR timescale at 300 K, giving a single broad <sup>55</sup>Mn NMR peak. The <sup>55</sup>Mn NMR spectra of the compounds involving MeSCH<sub>2</sub>CH<sub>2</sub>SMe and C<sub>6</sub>H<sub>4</sub>(SMe)<sub>2</sub>-o show three distinct resonances indicative of the three NMR distinguishable invertomers, *meso*-1, *meso*-2 and *DL*, the population of the *meso*-1 form decreasing with increasing halogen size. Reaction of [MnBr(CO)<sub>5</sub>] with 1 molar equivalent of MeSCH<sub>2</sub>SMe yielded the heterobridged dinuclear complex [Mn<sub>2</sub>(CO)<sub>6</sub>-(μ-Br)<sub>2</sub>(μ-MeSCH<sub>2</sub>SMe)]. The crystal structure revealed a pseudo-A-frame complex in which the two manganese(i) octahedra edge-share *via* two bromides with the dithioether bridging the Mn<sub>2</sub>Br<sub>2</sub> core, giving Mn...Mn 3.71 Å.

Thioether donors are usually regarded as relatively soft, and hence their co-ordination chemistry has largely been dominated by middle and late transition-metal systems. More recently, we and others have described complexes of hard chromium(III) and vanadium(III) centres involving macrocyclic thioether ligands, including *cis*-[CrX<sub>2</sub>([14]aneS<sub>4</sub>)]PF<sub>6</sub> ([14]aneS<sub>4</sub> = 1,4,8,11-tetra-thiacyclotetradecane), [MX<sub>3</sub>([9]aneS<sub>3</sub>)] ([9]aneS<sub>3</sub> = 1,4,7-trithiacyclononane) and [MX<sub>3</sub>([10]aneS<sub>3</sub>)] (M = Cr or V; X = Cl or Br; [10]aneS<sub>3</sub> = 1,4,7-trithiacyclodecane).<sup>1-3</sup> However, a survey of the literature revealed that there are very few examples of manganese complexes with Group 16 donor ligands. A small number of manganese(i) carbonyl compounds, including [MnBr(CO)<sub>3</sub>(MeSCH<sub>2</sub>CH<sub>2</sub>SMe)],<sup>4</sup> [MnBr(CO)<sub>3</sub>(PhSCH<sub>2</sub>CH<sub>2</sub>-SPh)]<sup>5</sup> and [MnBr(CO)<sub>3</sub>(MeSeCH<sub>2</sub>CH<sub>2</sub>SeMe)],<sup>6</sup> have been reported, however their characterisation was limited to IR and <sup>1</sup>H NMR spectroscopy and microanalyses. Also, Wiegardt and co-workers<sup>7</sup> reported the preparation and crystal structure of the cationic macrocyclic species *fac*-[Mn(CO)<sub>3</sub>([9]aneS<sub>3</sub>)]<sup>+</sup>. We have initiated a systematic investigation of manganese(i) carbonyl complexes incorporating Group 15 and 16 donor ligands, with particular interest in establishing trends in the carbonyl stretching frequencies (IR) and especially the <sup>55</sup>Mn chemical shift ranges. Manganese-55 (100%, *I* =  $\frac{5}{2}$ ,  $\Xi$  = 24.840 MHz) possesses a moderately high quadrupole moment (0.55 × 10<sup>-28</sup> m<sup>2</sup>), thus for complexes with less than *O<sub>h</sub>* or *T<sub>d</sub>* symmetry a considerable electric field gradient is expected to result in substantial broadening of the resonances.<sup>8</sup> On the other hand, <sup>55</sup>Mn is a highly sensitive nucleus, with *D<sub>p</sub>* = 0.175. Manganese-55 NMR studies have been undertaken previously for several classes of compound, including [Mn<sub>2</sub>(CO)<sub>10</sub>] and its derivatives,<sup>9</sup> [MnX(CO)<sub>5</sub>] (X = Cl, Br or I)<sup>10</sup> and *fac*-[Mn(CO)<sub>3</sub>-(MeCN)<sub>3</sub>]<sup>+</sup>.<sup>11</sup> However, no detailed synthetic or <sup>55</sup>Mn NMR studies have been reported for thio-, seleno- or telluro-ether complexes of manganese(i) carbonyls or carbonyl halides.

In this paper we describe the preparation and spectroscopic characterisation, including <sup>55</sup>Mn and <sup>13</sup>C-<sup>1</sup>H} NMR spectroscopy, of the mononuclear compounds [MnX(CO)<sub>3</sub>(L-L)] [X = Cl, Br or I; L-L = MeSCH<sub>2</sub>CH<sub>2</sub>SMe, MeSCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-SMe, PhSCH<sub>2</sub>CH<sub>2</sub>SPh or C<sub>6</sub>H<sub>4</sub>(SMe)<sub>2</sub>-o] and the dinuclear species [Mn<sub>2</sub>(CO)<sub>6</sub>(μ-Br)<sub>2</sub>(μ-MeSCH<sub>2</sub>SMe)]. The electrochemistry of the mononuclear species is also reported and the crystal structures of [MnBr(CO)<sub>3</sub>(PhSCH<sub>2</sub>CH<sub>2</sub>SPh)], [MnCl(CO)<sub>3</sub>(MeSCH<sub>2</sub>CH<sub>2</sub>SMe)] and [Mn<sub>2</sub>(CO)<sub>6</sub>(μ-Br)<sub>2</sub>(μ-MeSCH<sub>2</sub>-SMe)] described.

## Results and Discussion

### Syntheses

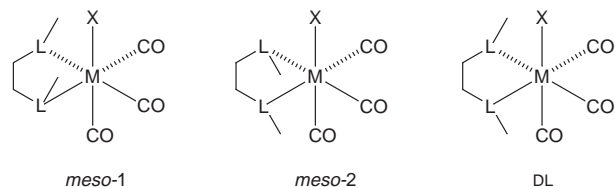
Treatment of [MnX(CO)<sub>5</sub>] (X = Cl, Br or I) with L-L [L-L = MeSCH<sub>2</sub>CH<sub>2</sub>SMe, MeSCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SMe, PhSCH<sub>2</sub>CH<sub>2</sub>SPh or C<sub>6</sub>H<sub>4</sub>(SMe)<sub>2</sub>-o] in CH<sub>2</sub>Cl<sub>2</sub> at room temperature (X = Cl), at reflux (X = Br) or in refluxing CHCl<sub>3</sub> solution (X = I) affords the neutral species [MnX(CO)<sub>3</sub>(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 dinuclear species [Mn<sub>2</sub>(CO)<sub>6</sub>(μ-Br)<sub>2</sub>(μ-MeSCH<sub>2</sub>SMe)] was prepared by treatment of [MnBr(CO)<sub>5</sub>] with 1 molar equivalent of MeSCH<sub>2</sub>SMe in refluxing CHCl<sub>3</sub>. The solid chloro and bromo compounds are stable for several weeks, although they were stored in foil-wrapped sample vials as a matter of course. The solid iodo species are less stable, darkening significantly over a few weeks, and all of the compounds appear to decompose readily in solution particularly when exposed to oxygen or visible light. The FAB mass spectrometric data for the mononuclear compounds are given in Table 1. The parent molecule is only observed in a few

**Table 1** Infrared (CO region),  $^{55}\text{Mn}$  NMR and FAB mass spectrometric data

Compound	$\tilde{\nu}(\text{CO})^a/\text{cm}^{-1}$	$\delta(^{55}\text{Mn})$ (w/Hz) <sup>b</sup>	<i>m/z</i> <sup>c</sup>
[MnCl(CO) <sub>3</sub> (MeSCH <sub>2</sub> CH <sub>2</sub> SMe)]	2038, 1960, 1921	-168 (1500), -228 (1520), -279 (2500)	261 [Mn(CO) <sub>3</sub> L] <sup>+</sup> ; 212 [MnCl(L)] <sup>+</sup>
[MnBr(CO) <sub>3</sub> (MeSCH <sub>2</sub> CH <sub>2</sub> SMe)]	2036, 1960, 1921	-229 (830), -305 (1510), -373 (2490)	261 [Mn(CO) <sub>3</sub> L] <sup>+</sup> ; 256 [MnBr(L)] <sup>+</sup>
[MnI(CO) <sub>3</sub> (MeSCH <sub>2</sub> CH <sub>2</sub> SMe)]	2033, 1962, 1923	-371 (700), -467 (1200), -553 (2000)	388 [MnI(CO) <sub>3</sub> L] <sup>+</sup> ; 304 [MnI(L)] <sup>+</sup> ; 261 [Mn(CO) <sub>3</sub> L] <sup>+</sup>
[MnCl(CO) <sub>3</sub> (MeSCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> SMe)]	2036, 1954, 1923	+67 (2700)	275 [Mn(CO) <sub>3</sub> L] <sup>+</sup> ; 226 [MnCl(L)] <sup>+</sup>
[MnBr(CO) <sub>3</sub> (MeSCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> SMe)]	2034, 1955, 1924	-133 (2370)	275 [Mn(CO) <sub>3</sub> L] <sup>+</sup> ; 272 [MnBr(L)] <sup>+</sup>
[MnI(CO) <sub>3</sub> (MeSCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> SMe)]	2031, 1957, 1927	-274 (4470)	402 [MnI(CO) <sub>3</sub> L] <sup>+</sup> ; 318 [MnI(L)] <sup>+</sup> ; 275 [Mn(CO) <sub>3</sub> L] <sup>+</sup>
[MnCl(CO) <sub>3</sub> (PhSCH <sub>2</sub> CH <sub>2</sub> SPh)]	2039, 1963, 1929	-55 (6500)	385 [Mn(CO) <sub>3</sub> L] <sup>+</sup> ; 336 [MnCl(L)] <sup>+</sup>
[MnBr(CO) <sub>3</sub> (PhSCH <sub>2</sub> CH <sub>2</sub> SPh)]	2036, 1962, 1930	-173 (6520)	385 [Mn(CO) <sub>3</sub> L] <sup>+</sup> ; 380 [MnBr(L)] <sup>+</sup>
[MnI(CO) <sub>3</sub> (PhSCH <sub>2</sub> CH <sub>2</sub> SPh)]	2033, 1961, 1931	-326 (5540)	512 [MnI(CO) <sub>3</sub> L] <sup>+</sup> ; 428 [MnI(L)] <sup>+</sup> ; 385 [Mn(CO) <sub>3</sub> L] <sup>+</sup>
[MnCl(CO) <sub>3</sub> {C <sub>6</sub> H <sub>4</sub> (SMe) <sub>2</sub> -o}]	2041, 1965, 1927	-137 (sh), -188 (4500), -289 (sh)	309 [Mn(CO) <sub>3</sub> L] <sup>+</sup> ; 260 [MnCl(L)] <sup>+</sup>
[MnBr(CO) <sub>3</sub> {C <sub>6</sub> H <sub>4</sub> (SMe) <sub>2</sub> -o}]	2039, 1965, 1927	-179 (2500), -249 (3200), -361 (5000)	390 [MnBr(CO) <sub>3</sub> L] <sup>+</sup> ; 309 [Mn(CO) <sub>3</sub> L] <sup>+</sup> ; 306 [MnBr(L)] <sup>+</sup>
[MnI(CO) <sub>3</sub> {C <sub>6</sub> H <sub>4</sub> (SMe) <sub>2</sub> -o}]	2035, 1963, 1928	-331 (minor), -432 (2550), -567 (4680)	512 [MnI(CO) <sub>3</sub> L] <sup>+</sup> ; 428 [MnI(L)] <sup>+</sup> ; 385 [Mn(CO) <sub>3</sub> L] <sup>+</sup>

<sup>a</sup> Solutions in CH<sub>2</sub>Cl<sub>2</sub> or CHCl<sub>3</sub>; all CO bands were strong. <sup>b</sup> Spectra recorded in CHCl<sub>3</sub>-CDCl<sub>3</sub> solution at 300 K, 89.27 MHz and referenced to external aqueous KMnO<sub>4</sub>. <sup>c</sup> Data recorded using 3-nitrobenzyl alcohol matrix; major peaks only, calculated values based upon <sup>35</sup>Cl and <sup>79</sup>Br.

instances, although in each case peaks consistent with [MnX(L-L)]<sup>+</sup> and [Mn(CO)<sub>3</sub>(L-L)]<sup>+</sup> are observed. Further peaks attributed to loss of X are also seen for some examples. Solution IR spectroscopic studies show the disappearance of the CO stretches associated with [MnX(CO)<sub>3</sub>] and the appearance of three strong CO bands, consistent with formation of *fac*-[MnX(CO)<sub>3</sub>(L-L)] in each case. For a given dithioether, the highest-frequency CO stretching vibration shifts to lower frequency upon going from Cl to Br to I, while the other two bands are virtually insensitive to changing the halogen X or the dithioether ligand L-L, and the values for these manganese compounds are also very similar to those observed for [ReX(CO)<sub>3</sub>(dithioether)] and [ReX(CO)<sub>3</sub>(diselenoether)].<sup>12-14</sup>



### NMR Spectroscopy

It is well known that co-ordination of a dithioether ligand to a metal centre leads to chirality at S,<sup>15,16</sup> and for *fac*-[MnX(CO)<sub>3</sub>(L-L)] several isomeric forms are possible; *meso*-1, where the S-bound terminal substituents are on the same side of the MnS<sub>2</sub>C<sub>2</sub> plane as X, *meso*-2, where the S-bound terminal substituents lie on the same side of the MnS<sub>2</sub>C<sub>2</sub> plane as the third CO ligand, and a pair of NMR-indistinguishable DL enantiomers in which the S-bound terminal substituents lie on opposite sides of the MnS<sub>2</sub>C<sub>2</sub> plane. Interconversion of these isomers can occur *via* pyramidal inversion at the co-ordinated thioether donor. Abel *et al.*<sup>12-14</sup> have described the preparations of the rhenium(i) complexes [ReX(CO)<sub>3</sub>(L-L)] [X = Cl, Br or I; L-L = MeE(CH<sub>2</sub>)<sub>n</sub>E Me or MeECH=CHE Me (E = S or Se, n = 2 or 3)], including the crystal structure of *fac*-[ReI(CO)<sub>3</sub>(MeSeCH<sub>2</sub>CH<sub>2</sub>SeMe)]. Detailed <sup>1</sup>H NMR studies were undertaken on them to establish the barriers to pyramidal inversion, and revealed that the energy barrier associated with inversion at selenium is higher than at sulfur, while changing the halogen has a negligible effect upon the overall energy barrier. The manganese(i) complexes described in detail below also show similar dynamic processes, and qualitatively, as might be expected, the inversion barriers are lower than in the rhenium(i) systems. (Detailed variable-temperature NMR studies were not undertaken since the <sup>55</sup>Mn quadrupolar broadening makes

these systems unsuitable for accurate measurements.<sup>16</sup>) We have recorded <sup>1</sup>H, <sup>13</sup>C-<sup>1</sup>H} and <sup>55</sup>Mn NMR spectra for each complex. At a particular temperature the appearance of the spectra will depend on the operating frequency of the observed nucleus and the separation (Hz) of the resonances for the individual invertomers at the low-temperature limit. Thus the coalescence temperature will be different for different nuclei.

The <sup>1</sup>H NMR spectra of the manganese compounds were recorded in CD<sub>2</sub>Cl<sub>2</sub> at 290 and 200 K. They typically show broad resonances associated with the ligand, although in some cases sharper resonances were observed at low temperature. The <sup>55</sup>Mn quadrupole is expected to lead to extensive broadening,<sup>16</sup> and lowering the temperature will affect the rate of quadrupolar relaxation irrespective of whether dynamic processes are occurring in solution.

The <sup>13</sup>C-<sup>1</sup>H} NMR spectra for [MnX(CO)<sub>3</sub>(L-L)] recorded at 300 K show that only those compounds involving MeSCH<sub>2</sub>CH<sub>2</sub>SMe are not undergoing rapid pyramidal inversion at this temperature. For these compounds the spectra show the presence of all three isomers, the other compounds showing broad resonances for the ligand carbon environments. In contrast to these <sup>13</sup>C-<sup>1</sup>H} NMR studies, <sup>55</sup>Mn NMR studies on [MnX(CO)<sub>3</sub>{C<sub>6</sub>H<sub>4</sub>(SMe)<sub>2</sub>-o}] (see below) show that these compounds are not inverting on the NMR timescale at 300 K. However, while the <sup>13</sup>C-<sup>1</sup>H} NMR spectrum of [MnBr(CO)<sub>3</sub>{C<sub>6</sub>H<sub>4</sub>(SMe)<sub>2</sub>-o}] at 300 K shows a single Me resonance, at 225 K two broad Me resonances are observed, indicating that inversion is slowing.

In all cases the CO resonances are broad, spanning several ppm. For those compounds not undergoing pyramidal inversion at 300 K two CO resonances are expected per isomer, and hence a total of six CO resonances are anticipated over a fairly small chemical shift range. These are then influenced by the manganese quadrupole which is directly bonded to the CO groups and results in overlapping broad resonances. This was confirmed from a <sup>13</sup>C-<sup>1</sup>H} spectrum of [MnBr(CO)<sub>3</sub>(MeSCH<sub>2</sub>CH<sub>2</sub>SMe)] recorded at 220 K which resulted in significant sharpening of the CO resonances (although not sufficiently such that those for the individual invertomers were resolved) giving two signals in the CO region (1:2 ratio) in addition to the CH<sub>2</sub> and CH<sub>3</sub> resonances associated with the individual NMR-distinguishable isomers. For the compounds undergoing pyramidal inversion at 300 K, the combination of the inversion processes and the effect of the manganese quadrupole probably also partially accounts for the broad CO signal.

The <sup>55</sup>Mn NMR data for [MnX(CO)<sub>3</sub>L] are presented in Table 1. At 300 K the compounds involving MeSCH<sub>2</sub>CH<sub>2</sub>SMe

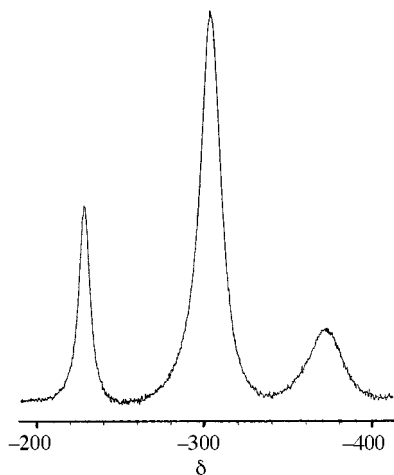


Fig. 1  $^{55}\text{Mn}$  (89.27 MHz, 300 K,  $\text{CDCl}_3$ ) NMR spectra of  $[\text{MnBr}(\text{CO})_3(\text{MeSCH}_2\text{CH}_2\text{SMe})]$  showing the presence of all three invertomers

and  $\text{C}_6\text{H}_4(\text{SMe})_2\text{-}o$  are not inverting on the NMR timescale, whereas for those involving  $\text{PhSCH}_2\text{CH}_2\text{SPh}$  or  $\text{MeSCH}_2\text{CH}_2\text{CH}_2\text{SMe}$  inversion is rapid. This trend in the energy barriers to inversion is consistent with that observed for other transition-metal complexes of these ligands.<sup>15,16</sup> Cooling a solution of  $[\text{MnBr}(\text{CO})_3(\text{MeSCH}_2\text{CH}_2\text{CH}_2\text{SMe})]$  from 300 to 185 K leads to the signal becoming much broader, but no splitting was observed, suggesting that inversion is still rapid on the NMR timescale at 185 K.

These manganese(I) compounds have  $C_s$  local symmetry, and hence we were surprised to find that, despite the large quadrupole moment associated with  $^{55}\text{Mn}$ , the linewidths at half-height were small enough (typically <5000 Hz) such that for the systems which were not inverting on the NMR timescale at room temperature [ $L = \text{MeSCH}_2\text{CH}_2\text{SMe}$  or  $\text{C}_6\text{H}_4(\text{SMe})_2\text{-}o$ ] resonances for the three NMR-distinguishable stereoisomers were resolved (Fig. 1). For  $[\text{MnX}(\text{CO})_3(L-L)]$  the linewidths are considerably smaller than for phosphine systems such as  $[\text{MnX}(\text{CO})_3(\text{PPh}_2)_2]$  or  $[\text{MnX}(\text{CO})_3(\text{PhHPCH}_2\text{CH}_2\text{PPh})]$  which give  $w_{1/2}$  ca. 10 000 Hz. Also, for the latter disubstituted phosphine species only a single broad resonance is seen by  $^{55}\text{Mn}$  NMR spectroscopy, despite the fact that the barrier to inversion at P is significantly higher, and hence the *meso*-1, *meso*-2 and *DL* stereoisomers are not expected to be inverting in solution.<sup>17</sup> The  $\delta(^{55}\text{Mn})$  value for these thioether compounds is substantially more positive than for  $[\text{MnX}(\text{CO})_5]$  ( $X = \text{Cl}$ ,  $\delta -1005$ ;  $\text{Br}$ ,  $-1160$ ;  $\text{I}$ ,  $-1485$ ),<sup>10</sup>  $[\text{Mn}_2(\text{CO})_{10}]$  ( $\delta -2227$ )<sup>9</sup> or  $[\text{Mn}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]$  ( $\delta -2225$ ), although to low frequency of *fac*- $[\text{Mn}(\text{CO})_3(\text{MeCN})_3]^+$  ( $\delta +490$ ).<sup>11</sup> Also, upon changing  $X$ ,  $\delta(^{55}\text{Mn})$  shifts approximately 100 ppm to low frequency according to the series  $\text{Cl} > \text{Br} > \text{I}$ , consistent with the trend observed for the parent manganese(I) pentacarbonyl halides.

Abel *et al.*<sup>12</sup> have shown that for rhenium(I) complexes with chelating dithio- or diseleno-ether ligands the relative populations of the invertomers were dependent upon  $X$ , with the *meso*-1 form less favoured for the larger halides. For  $[\text{MnX}(\text{CO})_3(\text{MeSCH}_2\text{CH}_2\text{SMe})]$  and  $[\text{MnX}(\text{CO})_3\{\text{C}_6\text{H}_4(\text{SMe})_2\text{-}o\}]$  we observe similar trends on the basis of  $^{13}\text{C}$ - $\{^1\text{H}\}$  and  $^{55}\text{Mn}$  NMR data, with the population of one isomer decreasing according to the series  $\text{Cl} > \text{Br} > \text{I}$ . The isomer most sensitive to  $X$  is the one which occurs at highest frequency by  $^{55}\text{Mn}$  NMR and is also assigned to the *meso*-1 form. The sensitivity to  $X$  presumably reflects the unfavourable steric interaction between the Me groups and the bulky halide ligand.

### X-Ray crystallography

In order to confirm the stereochemistries at the metal centres and to establish bond length and angle distributions, single-crystal structure analyses were undertaken on  $[\text{MnBr}(\text{CO})_3\text{-}$

Table 2 Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for  $[\text{MnBr}(\text{CO})_3\text{-}(\text{PhSCH}_2\text{CH}_2\text{SPh})]$

Br–Mn	2.527(1)	S(1)–C(10)	1.74(2)
Mn–S(1)	2.362(2)	S(1*)–C(9*)	1.95(2)
Mn–C(1)	1.804(6)	O(1)–C(1)	1.145(6)
Mn–C(2)	1.791(7)	O(2)–C(2)	1.121(8)
S(1)–C(3)	1.788(6)	C(9*)–C(10)	1.47(2)
Br–Mn–S(1)	86.48(5)	Br–Mn–C(1)	88.1(2)
Br–Mn–C(2)	177.3(3)	S(1)–Mn–S(1*)	84.35(9)
S(1)–Mn–C(1)	92.1(2)	S(1)–Mn–C(2)	95.5(2)
C(1)–Mn–C(1*)	90.9(4)	C(1)–Mn–C(2)	90.0(2)
S(1*)–C(9*)–C(10)	113(1)	Mn–S(1)–C(3)	111.4(2)
Mn–S(1*)–C(9*)	96.3(6)	Mn–S(1)–C(10)	111.9(7)
C(3*)–S(1*)–C(9*)	99.9(7)	C(3)–S(1)–C(10)	110.0(9)
S(1)–C(10)–C(9*)	106(1)	Mn–C(1)–O(1)	179.2(5)
Mn–C(2)–O(2)	178.1(7)	S(1)–C(3)–C(4)	124.0(5)
S(1)–C(3)–C(8)	116.0(4)		

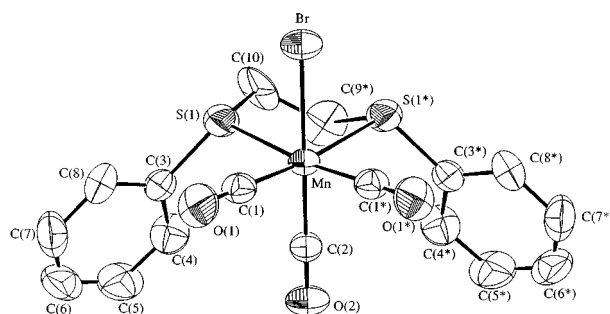


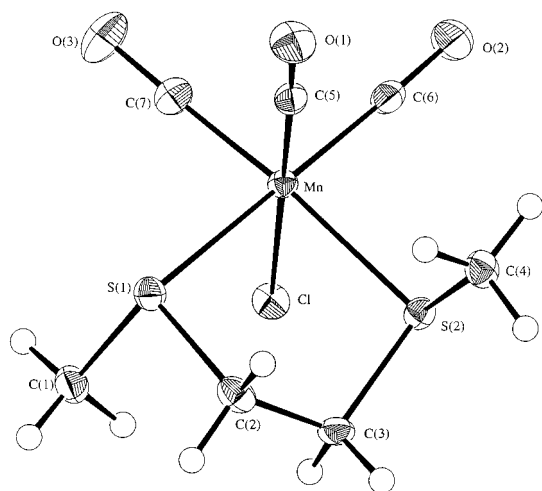
Fig. 2 View of the structure of  $[\text{MnBr}(\text{CO})_3(\text{PhSCH}_2\text{CH}_2\text{SPh})]$  with numbering scheme adopted. Ellipsoids are drawn at 40% probability, and atoms marked \* are related by a crystallographic mirror plane, H atoms are omitted for clarity

$(\text{PhSCH}_2\text{CH}_2\text{SPh})]$  and  $[\text{MnCl}(\text{CO})_3(\text{MeSCH}_2\text{CH}_2\text{SMe})]$ . Crystals of the complexes were obtained from vapour diffusion of light petroleum into a solution of the appropriate complex in  $\text{CH}_2\text{Cl}_2$ . The crystal structure of  $[\text{MnBr}(\text{CO})_3(\text{PhSCH}_2\text{CH}_2\text{SPh})]$  shows (Fig. 2, Table 2) the molecule having crystallographic *m* symmetry, with the dithioether disordered across this mirror plane. The Br, Mn and one CO ligand lie on the mirror plane, which bisects the two sulfur donors and the other two CO ligands. The manganese(I) centre is therefore co-ordinated to three mutually *fac* CO groups, one Br atom and to the two S-donors of a chelating  $\text{PhSCH}_2\text{CH}_2\text{SPh}$  ligand, giving a distorted octahedral geometry, Mn–Br 2.527(1), Mn–S(1) 2.362(2), Mn–C(1) 1.804(6), Mn–C(2) 1.791(7)  $\text{\AA}$ . The S(1)–Mn–S(1\*) angle is 84.35(9) $^\circ$ , and the ligand is in the *meso*-2 form with both Ph groups on the same side of the  $\text{MnS}_2\text{C}_2$  plane and directed towards the third CO ligand. The crystal structure of  $[\text{MnCl}(\text{CO})_3(\text{MeSCH}_2\text{CH}_2\text{SMe})]$  (Fig. 3, Table 3) also shows a distorted octahedral geometry at Mn, with a *fac* arrangement for the three CO ligands. In this case, however, the chelated dithioether adopts the *DL* arrangement, with one Me group on each side of the  $\text{MnS}_2\text{C}_2$  plane, Mn–S(1) 2.3698(9), Mn–S(2) 2.3633(9), Mn–Cl 2.3810(9), Mn–C(5) 1.796(3), Mn–C(6) 1.823(3), Mn–C(7) 1.798(3)  $\text{\AA}$ . The Mn–S bond lengths in this compound compare well with those in  $[\text{MnBr}(\text{CO})_3(\text{PhSCH}_2\text{CH}_2\text{SPh})]$  above, and are slightly longer than in  $[\text{Mn}(\text{CO})_3\text{-}(\text{[9]aneS}_3)]^+$  [2.321(3)–2.338(5)  $\text{\AA}$ ].<sup>7</sup>

We were also interested to establish the co-ordination mode adopted by  $\text{MeSCH}_2\text{SMe}$ , since if chelating, the single methylene linkage would lead to a highly strained four-membered chelate ring. Indeed the chelating mode has only been observed for this ligand in one example,  $[\text{SnCl}_4(\text{MeSCH}_2\text{SMe})]$ , which gave S–Sn–S 67.82(5) $^\circ$ .<sup>18</sup> We have previously shown that  $\text{MeE-CH}_2\text{EMe}$  ( $E = \text{S}$  or  $\text{Se}$ ) can bridge copper(I) or silver(I) centres

**Table 3** Selected bond lengths (Å) and angles (°) for [MnCl(CO)<sub>3</sub>(MeSCH<sub>2</sub>CH<sub>2</sub>SMe)]

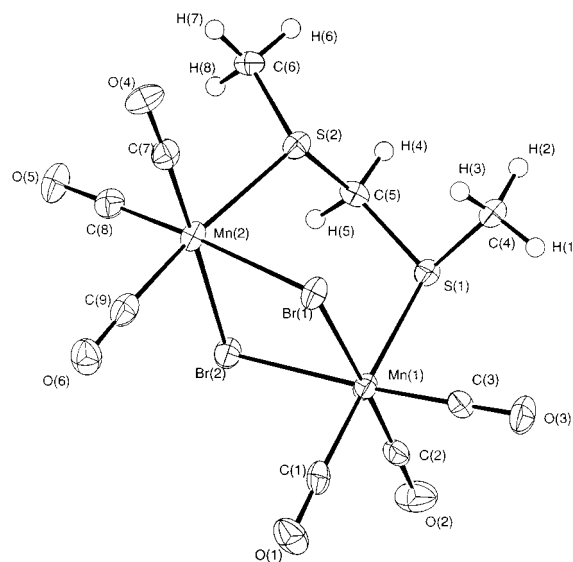
Mn–Cl	2.3810(9)	Mn–S(1)	2.3698(9)
Mn–S(2)	2.3633(9)	Mn–C(5)	1.796(3)
Mn–C(6)	1.823(3)	Mn–C(7)	1.798(3)
S(1)–C(1)	1.801(3)	S(1)–C(2)	1.819(3)
S(2)–C(3)	1.813(3)	S(2)–C(4)	1.801(3)
O(1)–C(5)	1.143(4)	O(2)–C(6)	1.138(4)
O(3)–C(7)	1.153(4)	C(2)–C(3)	1.517(4)
Cl–Mn–S(1)	92.05(3)	Cl–Mn–S(2)	83.23(3)
Cl–Mn–C(5)	178.44(10)	Cl–Mn–C(6)	90.8(1)
Cl–Mn–C(7)	90.9(1)	S(1)–Mn–S(2)	87.61(3)
S(1)–Mn–C(5)	86.62(10)	S(1)–Mn–C(6)	176.7(1)
S(1)–Mn–C(7)	90.8(1)	S(2)–Mn–C(5)	95.88(10)
S(2)–Mn–C(6)	91.16(10)	S(2)–Mn–C(7)	173.8(1)
C(5)–Mn–C(6)	90.5(1)	C(5)–Mn–C(7)	90.0(1)
C(6)–Mn–C(7)	90.8(1)	Mn–S(1)–C(1)	111.9(1)
Mn–S(1)–C(2)	103.2(1)	C(1)–S(1)–C(2)	100.9(1)
Mn–S(2)–C(3)	102.5(1)	Mn–S(2)–C(4)	109.9(1)
C(3)–S(2)–C(4)	100.4(1)	S(1)–C(2)–C(3)	112.3(2)
S(2)–C(3)–C(2)	112.1(2)	Mn–C(5)–O(1)	177.6(3)
Mn–C(6)–O(2)	177.9(3)	Mn–C(7)–O(3)	178.3(3)

**Fig. 3** View of the structure of [MnCl(CO)<sub>3</sub>(MeSCH<sub>2</sub>CH<sub>2</sub>SMe)] with numbering scheme adopted. Ellipsoids are drawn at 40% probability

to yield infinite three-dimensional arrays which incorporate large channels.<sup>19</sup> Examples where these ligands bind in an  $\eta^1$  mode are also known.<sup>20</sup> The crystal structure of [Mn<sub>2</sub>(CO)<sub>6</sub>( $\mu$ -Br)<sub>2</sub>( $\mu$ -MeSCH<sub>2</sub>SMe)] shows (Fig. 4, Table 4) the dithiapentane ligand bridging the two manganese(I) centres of a Mn<sub>2</sub>Br<sub>2</sub> core, yielding a pseudo-A-frame structure. Thus, each manganese(I) centre is approximately octahedral, with a *fac*-(CO)<sub>3</sub> arrangement, one thioether donor from a bridging ligand and two bridging Br<sup>−</sup> ligands, Mn(1)–Br(1) 2.555(2), Mn(1)–Br(2) 2.513(2), Mn(2)–Br(1) 2.547(2), Mn(2)–Br(2) 2.529(2), Mn(1)–S(1) 2.377(3), Mn(2)–S(2) 2.372(3) Å. The Mn–S distances in this dimer are very similar to those seen in the mononuclear species described above. The Mn–Br distances are similar in the mono- and di-nuclear complexes, despite the fact that in [MnBr(CO)<sub>3</sub>(PhSCH<sub>2</sub>CH<sub>2</sub>SPh)] the Br is terminal and in the dimer the bromides are bridging. The angle between the two MnBr<sub>2</sub> planes is 163.4°. The angles around the Mn lie in the ranges 83.53(8)–96.8(3) and 170.6(3)–178.3(3)°, indicating a slightly distorted octahedral geometry for each of the edge-bridged octahedra. The S(1)–C(5)–S(2) angle is 114.9(5)°, suggesting that the bite angle of the dithioether is well suited to this bonding mode. This is the first time that this type of bridging has been observed for a methylene-linked Group 16 ligand. Several examples of other ligands bridging an Mn<sub>2</sub>X<sub>2</sub> core in this fashion have been structurally characterised, including PhTeTePh, PhSeSePh, Ph<sub>2</sub>PPPh<sub>2</sub> and Ph<sub>2</sub>AsAsPh<sub>2</sub>. For the

**Table 4** Selected bond lengths (Å) and angles (°) for [Mn<sub>2</sub>(CO)<sub>6</sub>( $\mu$ -Br)<sub>2</sub>( $\mu$ -MeSCH<sub>2</sub>SMe)]

Br(1)–Mn(1)	2.555(2)	Br(1)–Mn(2)	2.547(2)
Br(2)–Mn(1)	2.513(2)	Br(2)–Mn(2)	2.529(2)
Mn(1)–S(1)	2.377(3)	Mn(1)–C(1)	1.822(10)
Mn(1)–C(2)	1.80(1)	Mn(1)–C(3)	1.795(10)
Mn(2)–S(2)	2.372(3)	Mn(2)–C(7)	1.78(1)
Mn(2)–C(8)	1.794(10)	Mn(2)–C(9)	1.84(1)
S(1)–C(4)	1.81(1)	S(1)–C(5)	1.809(9)
S(2)–C(5)	1.804(10)	S(2)–C(6)	1.801(9)
O(1)–C(1)	1.14(1)	O(2)–C(2)	1.16(1)
O(3)–C(3)	1.16(1)	O(4)–C(7)	1.16(1)
O(5)–C(8)	1.16(1)	O(6)–C(9)	1.13(1)
Mn(1)–Br(1)–Mn(2)	93.20(5)	Mn(1)–Br(2)–Mn(2)	94.66(6)
Br(1)–Mn(1)–Br(2)	84.86(5)	Br(1)–Mn(1)–S(1)	92.65(8)
Br(1)–Mn(1)–C(1)	90.4(3)	Br(1)–Mn(1)–C(2)	177.8(3)
Br(1)–Mn(1)–C(3)	90.4(3)	Br(2)–Mn(1)–S(1)	89.72(7)
Br(2)–Mn(1)–C(1)	90.1(3)	Br(2)–Mn(1)–C(2)	93.0(3)
Br(2)–Mn(1)–C(3)	175.2(3)	S(1)–Mn(1)–C(1)	176.9(3)
S(1)–Mn(1)–C(2)	88.1(3)	S(1)–Mn(1)–C(3)	89.9(3)
C(1)–Mn(1)–C(2)	88.9(4)	C(1)–Mn(1)–C(3)	90.5(4)
C(2)–Mn(1)–C(3)	91.7(4)	Br(1)–Mn(2)–Br(2)	84.68(5)
Br(1)–Mn(2)–S(2)	83.53(8)	Br(1)–Mn(2)–C(7)	96.8(3)
Br(1)–Mn(2)–C(8)	174.6(3)	Br(1)–Mn(2)–C(9)	87.5(3)
Br(2)–Mn(2)–S(2)	93.67(8)	Br(2)–Mn(2)–C(7)	178.3(3)
Br(2)–Mn(2)–C(8)	90.0(3)	Br(2)–Mn(2)–C(9)	88.2(3)
S(2)–Mn(2)–C(7)	87.4(3)	S(2)–Mn(2)–C(8)	96.7(3)
S(2)–Mn(2)–C(9)	170.6(3)	C(7)–Mn(2)–C(8)	88.6(4)
C(7)–Mn(2)–C(9)	91.0(4)	C(8)–Mn(2)–C(9)	92.5(4)
S(1)–C(5)–S(2)	114.9(5)		

**Fig. 4** View of the structure of [Mn<sub>2</sub>(CO)<sub>6</sub>( $\mu$ -Br)<sub>2</sub>( $\mu$ -MeSCH<sub>2</sub>SMe)] with numbering scheme adopted. Ellipsoids are drawn at 40% probability

bromo-bridged examples<sup>21</sup> the Mn⋯Mn distances compare well with the 3.71 Å observed in this work, as does that in the parent [Mn<sub>2</sub>Br<sub>2</sub>(CO)<sub>8</sub>], Mn⋯Mn 3.74 Å.<sup>22</sup>

The IR spectrum of solid [Mn<sub>2</sub>(CO)<sub>6</sub>( $\mu$ -Br)<sub>2</sub>( $\mu$ -MeSCH<sub>2</sub>SMe)] shows CO stretching vibrations at 2098, 2033, 1945 and 1914 cm<sup>−1</sup>. The <sup>55</sup>Mn NMR spectrum of this dinuclear compound shows a single broad resonance at  $\delta$  −647 ( $\nu_2 = 4750$  Hz). This is to low frequency of the chemical shift range shown in Table 1 for [MnBr(CO)<sub>3</sub>(L–L)], and is consistent with introduction of a second Br<sup>−</sup> ligand at Mn<sup>I</sup>, yielding a Br<sub>2</sub>C<sub>3</sub>S donor set, and hence increased electron density (increased shielding) at the Mn<sup>I</sup>.

### Electrochemistry

Bond *et al.*<sup>23</sup> have reported detailed studies on the electro-

chemistry of phosphine complexes of manganese(i) carbonyl halides. Many of these compounds, including *mer*-[MnBr(CO)<sub>3</sub>L'<sub>2</sub>] [L' = PPh<sub>3</sub>, P(C<sub>6</sub>H<sub>4</sub>Me-*p*)<sub>3</sub> or P(C<sub>6</sub>H<sub>4</sub>Me-*m*)<sub>3</sub>], show reversible Mn<sup>I</sup>-Mn<sup>II</sup> redox couples, while others such as [MnX(CO)<sub>3</sub>(Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)] show redox-induced *fac* → *mer* isomerisation processes. We were interested to ascertain whether the thioether ligands would also stabilise Mn<sup>II</sup>, and if so to compare the redox potentials with those for the phosphine compounds. Cyclic voltammetry measurements were therefore conducted on a range of the manganese(i) thioether compounds in CH<sub>2</sub>Cl<sub>2</sub> (0.1 mol dm<sup>-3</sup> NBu<sup>n</sup><sub>4</sub>BF<sub>4</sub> supporting electrolyte) at a double platinum electrode. At room temperature the cyclic voltammograms of [MnCl(CO)<sub>3</sub>{C<sub>6</sub>H<sub>4</sub>(SMe)<sub>2</sub>-*o*}], [MnCl(CO)<sub>3</sub>(MeSCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SMe)], [MnCl(CO)<sub>3</sub>(MeSCH<sub>2</sub>CH<sub>2</sub>-SMe)] and [MnCl(CO)<sub>3</sub>(PhSCH<sub>2</sub>CH<sub>2</sub>SPh)] recorded at 200 mV s<sup>-1</sup> each show an irreversible oxidation at around +1.0 V *vs.* ferrocene-ferrocenium, and a reduction product wave associated with this at *ca.* +0.2 V. Upon cooling at 0 °C the oxidation becomes slightly more reversible. These results are consistent with the behaviour observed by Bond *et al.*<sup>23</sup> for *fac*-[MnX(CO)<sub>3</sub>(dppm)] (X = Cl or Br), which shows an irreversible oxidation to Mn<sup>II</sup>, which rapidly undergoes *fac* → *mer* isomerisation, the product wave corresponding to the reduction of *mer*-[MnX(CO)<sub>3</sub>(dppm)]<sup>+</sup>. Further detailed electrochemical studies are underway to establish whether similar processes occur for the thioether compounds reported here.

## Experimental

Infrared spectra were measured as CsI discs using a Perkin-Elmer 983 spectrometer over the range 200–4000 cm<sup>-1</sup>, 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, <sup>1</sup>H, <sup>13</sup>C-<sup>1</sup>H and <sup>55</sup>Mn NMR spectra using a Bruker AM360 spectrometer operating at 360.0, 90.55 or 89.27 MHz respectively and referenced to SiMe<sub>4</sub> and external saturated, aqueous KMnO<sub>4</sub> respectively (δ 0). The compound [Cr(acac)<sub>3</sub>] was added to the NMR solutions prior to recording <sup>13</sup>C-<sup>1</sup>H spectra and a pulse delay of 2 s was employed to take account of the long relaxation times. Cyclic voltammetry measurements used an EG&G Princeton Applied Research model 362 scanning potentiostat with 0.1 mol dm<sup>-3</sup> NBu<sup>n</sup><sub>4</sub>BF<sub>4</sub> supporting electrolyte, using a double platinum electrode as working and auxiliary electrode and a standard calomel reference electrode. All potentials are quoted *versus* ferrocene-ferrocenium. The compounds MeSCH<sub>2</sub>CH<sub>2</sub>SMe, MeSCH<sub>2</sub>-CH<sub>2</sub>CH<sub>2</sub>SMe, PhSCH<sub>2</sub>CH<sub>2</sub>SPh, C<sub>6</sub>H<sub>4</sub>(SMe)<sub>2</sub>-*o*<sup>24</sup> and [MnX(CO)<sub>3</sub>] (X = Cl, Br or I)<sup>25</sup> were prepared according to literature procedures.

## Preparations

All of the compounds were synthesized by the same general procedure, with slight modifications for X = Cl, Br or I. Only one of each of these preparations is therefore described in detail below.

**[MnCl(CO)<sub>3</sub>(MeSCH<sub>2</sub>CH<sub>2</sub>SMe)].** To a degassed solution of [MnCl(CO)<sub>3</sub>] (0.081 g, 0.35 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 cm<sup>3</sup>) was added MeSCH<sub>2</sub>CH<sub>2</sub>SMe (0.043 g, 0.35 mmol). The resulting mixture was stirred at room temperature for 48 h, and the solution IR spectrum monitored until the reaction had gone to completion. The solvent volume was reduced to *ca.* 2 cm<sup>3</sup> *in vacuo* to give a yellow solution. Addition of ice-cold light petroleum (b.p. 40–60 °C, 10 cm<sup>3</sup>) gave a yellow precipitate. This solid was filtered off and then recrystallised from CH<sub>2</sub>Cl<sub>2</sub>-light petroleum (yield 0.026 g, 25%) (Found: C, 28.0; H, 3.1. C<sub>7</sub>H<sub>10</sub>ClMnO<sub>3</sub>S<sub>2</sub> requires C, 28.3; H, 3.4%). <sup>1</sup>H NMR (360

MHz, CD<sub>2</sub>Cl<sub>2</sub>, 290 K): δ 3.04, 2.83, 2.80 (CH<sub>2</sub>), 2.46, 2.41, 2.33 (Me). <sup>13</sup>C-<sup>1</sup>H NMR (300 K, CD<sub>2</sub>Cl<sub>2</sub>): δ 223.1–216.7 (CO), 36.1, 35.5 (sh) (CH<sub>2</sub>), 22.9 (sh), 22.2, 16.9 (Me).

**[MnCl(CO)<sub>3</sub>(MeSCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SMe)].** Method as for [MnCl(CO)<sub>3</sub>(MeSCH<sub>2</sub>CH<sub>2</sub>SMe)] above, but using [MnCl(CO)<sub>3</sub>] (0.105 g, 0.46 mmol) and MeSCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SMe (0.062 g, 0.46 mmol), giving a yellow precipitate (yield 0.050 g, 35%) (Found: C, 30.4; H, 4.0. C<sub>8</sub>H<sub>12</sub>ClMnO<sub>3</sub>S<sub>2</sub> requires C, 30.9; H, 3.9%). <sup>1</sup>H NMR (360 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 290 K): δ 3.14, 2.60 (CH<sub>2</sub>S), 2.41 (Me) and 2.15 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C-<sup>1</sup>H NMR (300 K, CDCl<sub>3</sub>): δ 223.0–216.9 (CO), 31.2 (CH<sub>2</sub>S), 23.7 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>) and 22.5 (Me).

**[MnCl(CO)<sub>3</sub>(PhSCH<sub>2</sub>CH<sub>2</sub>SPh)].** Method as for [MnCl(CO)<sub>3</sub>(MeSCH<sub>2</sub>CH<sub>2</sub>SMe)] above, but using [MnCl(CO)<sub>3</sub>] (0.100 g, 0.43 mmol) and PhSCH<sub>2</sub>CH<sub>2</sub>SPh (0.107 g, 0.43 mmol), giving a yellow precipitate (yield 0.101 g, 55%) (Found: C, 45.1; H, 3.1. C<sub>17</sub>H<sub>14</sub>ClMnO<sub>3</sub>S<sub>2</sub>·0.5CH<sub>2</sub>Cl<sub>2</sub> requires C, 45.4; H, 3.2%). <sup>1</sup>H NMR (360 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 290 K): δ 7.70–7.20 (Ph), 3.68–3.25 (CH<sub>2</sub>). <sup>13</sup>C-<sup>1</sup>H NMR (300 K, CDCl<sub>3</sub>): δ 221.7–218.0 (CO), 132.9–129.9 (Ph) and 36.1 (CH<sub>2</sub>).

**[MnCl(CO)<sub>3</sub>{C<sub>6</sub>H<sub>4</sub>(SMe)<sub>2</sub>-*o*}].** Method as for [MnCl(CO)<sub>3</sub>(MeSCH<sub>2</sub>CH<sub>2</sub>SMe)] above, but using [MnCl(CO)<sub>3</sub>] (0.074 g, 0.32 mmol) and C<sub>6</sub>H<sub>4</sub>(SMe)<sub>2</sub>-*o* (0.055 g, 0.32 mmol), giving a yellow precipitate (yield 0.043 g, 38%) (Found: C, 38.2; H, 3.0. C<sub>11</sub>H<sub>10</sub>ClMnO<sub>3</sub>S<sub>2</sub> requires C, 38.3; H, 2.9%). <sup>1</sup>H NMR (360 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 290 K): δ 7.75, 7.50 (*o*-C<sub>6</sub>H<sub>4</sub>) and 2.76 (Me). <sup>13</sup>C-<sup>1</sup>H NMR (300 K, CDCl<sub>3</sub>): δ 221.0–217.5 (CO), 137.9, 132.8, 130.8 (*o*-C<sub>6</sub>H<sub>4</sub>) and 18.9 (Me).

**[MnBr(CO)<sub>3</sub>(MeSCH<sub>2</sub>CH<sub>2</sub>SMe)].** To a degassed solution of [MnBr(CO)<sub>3</sub>] (0.180 g, 0.45 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 cm<sup>3</sup>) was added MeSCH<sub>2</sub>CH<sub>2</sub>SMe (0.085 g, 0.45 mmol). The resulting mixture was gently warmed to reflux for *ca.* 6 h, and the solution IR spectrum monitored until the reaction had gone to completion. The solvent volume was reduced to *ca.* 2 cm<sup>3</sup> *in vacuo* to give an orange solution. Addition of light petroleum (10 cm<sup>3</sup>) gave an orange precipitate which was filtered off and recrystallised from CH<sub>2</sub>Cl<sub>2</sub>-light petroleum (yield 0.090 g, 40%) (Found: C, 24.5; H, 3.2. C<sub>7</sub>H<sub>10</sub>BrMnO<sub>3</sub>S<sub>2</sub> requires C, 24.7; H, 2.9%). <sup>1</sup>H NMR (360 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 290 K): δ 3.12, 2.85, 2.75 (CH<sub>2</sub>), 2.46, 2.44 (Me). <sup>13</sup>C-<sup>1</sup>H NMR (300 K, CDCl<sub>3</sub>): δ 224.6–214.0 (CO), 36.3, 36.0, 35.7 (CH<sub>2</sub>), 23.3 (Me, *meso*-2), 22.8, 18.6 (Me, *DL*), 18.8 (Me, *meso*-1).

**[MnBr(CO)<sub>3</sub>(MeSCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SMe)].** Method as for [MnBr(CO)<sub>3</sub>(MeSCH<sub>2</sub>CH<sub>2</sub>SMe)] above, but using [MnBr(CO)<sub>3</sub>] (0.059 g, 0.21 mmol) and MeSCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SMe (0.029 g, 0.21 mmol), giving an orange precipitate (yield 0.025 g, 33%) (Found: C, 26.7; H, 3.5. C<sub>8</sub>H<sub>12</sub>BrMnO<sub>3</sub>S<sub>2</sub> requires C, 27.0; H, 3.4%). <sup>1</sup>H NMR (360 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 290 K): δ 3.22, 2.67 (SCH<sub>2</sub>), 2.44 (Me) and 2.21 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C-<sup>1</sup>H NMR (300 K, CDCl<sub>3</sub>): δ 220.9–217.4 (CO), 31.9 (CH<sub>2</sub>S), 23.7 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>) and 23.0 (Me).

**[MnBr(CO)<sub>3</sub>(PhSCH<sub>2</sub>CH<sub>2</sub>SPh)].** Method as for [MnBr(CO)<sub>3</sub>(MeSCH<sub>2</sub>CH<sub>2</sub>SMe)] above, but using [MnBr(CO)<sub>3</sub>] (0.060 g, 0.22 mmol) and PhSCH<sub>2</sub>CH<sub>2</sub>SPh (0.054 g, 0.22 mmol), giving a yellow precipitate (yield 0.081 g, 80%) (Found: C, 44.1; H, 3.3. C<sub>17</sub>H<sub>14</sub>BrMnO<sub>3</sub>S<sub>2</sub> requires C, 43.9; H, 3.0%). <sup>1</sup>H NMR (360 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 290 K): δ 7.85–7.18 (Ph), 3.75–3.30 (CH<sub>2</sub>). <sup>13</sup>C-<sup>1</sup>H NMR (300 K, CDCl<sub>3</sub>): δ 222.1–219.4 (CO), 133.5–127.9 (Ph) and 36.2 (CH<sub>2</sub>).

**[MnBr(CO)<sub>3</sub>{C<sub>6</sub>H<sub>4</sub>(SMe)<sub>2</sub>-*o*}].** Method as for [MnBr(CO)<sub>3</sub>(MeSCH<sub>2</sub>CH<sub>2</sub>SMe)] above, but using [MnBr(CO)<sub>3</sub>] (0.100 g, 0.36 mmol) and C<sub>6</sub>H<sub>4</sub>(SMe)<sub>2</sub>-*o* (0.062 g, 0.36 mmol), giving an orange precipitate (yield 0.076 g, 54%) (Found: C, 33.9; H, 2.7. C<sub>11</sub>H<sub>10</sub>BrMnO<sub>3</sub>S<sub>2</sub> requires C, 33.9; H, 2.6%). <sup>1</sup>H NMR (360 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K): δ 7.78, 7.55 (*o*-C<sub>6</sub>H<sub>4</sub>) and 2.81 (Me). <sup>13</sup>C-

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

	[MnBr(CO) <sub>3</sub> (PhSCH <sub>2</sub> CH <sub>2</sub> SPh)]	[MnCl(CO) <sub>3</sub> (MeSCH <sub>2</sub> CH <sub>2</sub> SMe)]	[Mn <sub>2</sub> (CO) <sub>6</sub> (μ-Br) <sub>2</sub> (μ-MeSCH <sub>2</sub> SMe)]
Formula	C <sub>17</sub> H <sub>14</sub> BrMnO <sub>3</sub> S <sub>2</sub>	C <sub>7</sub> H <sub>10</sub> ClMnO <sub>3</sub> S <sub>2</sub>	C <sub>9</sub> H <sub>8</sub> Br <sub>2</sub> Mn <sub>2</sub> O <sub>6</sub> S <sub>2</sub>
<i>M</i>	465.26	826.46	545.96
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	<i>Pnma</i>	<i>Pbca</i>	<i>P2<sub>1</sub>/n</i>
<i>a</i> /Å	8.1102(2)	12.239(4)	9.151(7)
<i>b</i> /Å	17.2184(4)	18.982(5)	18.45(1)
<i>c</i> /Å	13.2002(2)	9.982(6)	9.747(8)
β/°			93.71(6)
<i>U</i> /Å <sup>3</sup>	1843.34(6)	2297(1)	1642(1)
<i>Z</i>	4	8	4
μ(Mo-Kα)/cm <sup>-1</sup>	31.28	17.21	66.88
Unique observed reflections	1553	2336	3002
<i>R</i> <sub>int</sub> (based on <i>F</i> <sup>2</sup> )	0.039	—	0.064
Observed reflections [ <i>I</i> <sub>o</sub> > 2σ( <i>I</i> <sub>o</sub> )]	1071	1930	2217
<i>R</i>	0.043	0.032	0.053
<i>R</i> '	0.047	0.045	0.070

$$R = \frac{\sum(|F_{o,i}| - |F_{c,i}|)}{\sum|F_{o,i}|}, R' = \frac{[\sum w_i(|F_{o,i}| - |F_{c,i}|)^2 / \sum w_i|F_{o,i}|^2]^{1/2}}$$

{<sup>1</sup>H} NMR (300 K, CDCl<sub>3</sub>): δ 222.8–216.9 (CO), 137.9, 133.0, 132.8, 131.0 (*o*-C<sub>6</sub>H<sub>4</sub>), 19.0, 18.2 (sh, Me).

**[MnI(CO)<sub>3</sub>(MeSCH<sub>2</sub>CH<sub>2</sub>SMe)].** To a degassed solution of [MnI(CO)<sub>3</sub>] (0.082 g, 0.25 mmol) in CHCl<sub>3</sub> (15 cm<sup>3</sup>) was added MeSCH<sub>2</sub>CH<sub>2</sub>SMe (0.031 g, 0.25 mmol). The resulting mixture was gently refluxed for 18 h, and the solution IR spectrum monitored until the reaction had gone to completion. The solvent volume was reduced to *ca.* 2 cm<sup>3</sup> *in vacuo* to give an orange-red solution. Addition of light petroleum (10 cm<sup>3</sup>) gave an orange precipitate which was filtered off and recrystallised from CH<sub>2</sub>Cl<sub>2</sub>–light petroleum (yield 0.036 g, 36%) (Found: C, 22.1; H, 2.6. C<sub>7</sub>H<sub>10</sub>IMnO<sub>3</sub>S<sub>2</sub> requires C, 21.7; H, 2.6%). <sup>1</sup>H NMR (360 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 290 K): δ 2.95, 2.70 (CH<sub>2</sub>), 2.35, 2.23 (sh, Me). <sup>13</sup>C-<sup>1</sup>H} NMR (300 K, CDCl<sub>3</sub>): δ 224.9–216.2 (CO), 37.2 (CH<sub>2</sub>), 25.1, 24.5 (sh), 22.2 (Me).

**[MnI(CO)<sub>3</sub>(MeSCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SMe)].** Method as for [MnI(CO)<sub>3</sub>(MeSCH<sub>2</sub>CH<sub>2</sub>SMe)] above, but using [MnI(CO)<sub>3</sub>] (0.120 g, 0.37 mmol) and MeSCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SMe (0.051 g, 0.37 mmol), giving an orange precipitate (yield 0.070 g, 53%) (Found: C, 24.0; H, 3.0. C<sub>8</sub>H<sub>12</sub>IMnO<sub>3</sub>S<sub>2</sub> requires C, 23.9; H, 3.0%). <sup>1</sup>H NMR (360 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 290 K): δ 3.22, 2.82 (SCH<sub>2</sub>), 2.47 (Me) and 2.17 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C-<sup>1</sup>H} NMR (300 K, CDCl<sub>3</sub>): δ 226.5–217.3 (CO), 33.7 (CH<sub>2</sub>S), 27.1 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>) and 24.4 (CH<sub>3</sub>).

**[MnI(CO)<sub>3</sub>(PhSCH<sub>2</sub>CH<sub>2</sub>SPh)].** Method as for [MnI(CO)<sub>3</sub>(MeSCH<sub>2</sub>CH<sub>2</sub>SMe)] above, but using [MnI(CO)<sub>3</sub>] (0.081 g, 0.25 mmol) and PhSCH<sub>2</sub>CH<sub>2</sub>SPh (0.062 g, 0.25 mmol), giving an orange precipitate (yield 0.099 g, 77%) (Found: C, 40.5; H, 2.8. C<sub>17</sub>H<sub>14</sub>IMnO<sub>3</sub>S<sub>2</sub> requires C, 40.0; H, 2.7%). <sup>1</sup>H NMR (360 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 290 K): δ 7.66–7.28 (Ph), 3.62–3.29 (CH<sub>2</sub>). <sup>13</sup>C-<sup>1</sup>H} NMR (300 K, CDCl<sub>3</sub>): δ 223.8–220.7 (CO), 134.5–129.2 (Ph) and 36.8 (CH<sub>2</sub>).

**[MnI(CO)<sub>3</sub>{C<sub>6</sub>H<sub>4</sub>(SMe)<sub>2</sub>-*o*}].** Method as for [MnI(CO)<sub>3</sub>(MeSCH<sub>2</sub>CH<sub>2</sub>SMe)] above, but using [MnI(CO)<sub>3</sub>] (0.078 g, 0.24 mmol) and C<sub>6</sub>H<sub>4</sub>(SMe)<sub>2</sub>-*o* (0.041 g, 0.24 mmol), giving an orange precipitate (yield 0.089 g, 84%) (Found: C, 29.6; H, 2.5. C<sub>11</sub>H<sub>10</sub>IMnO<sub>3</sub>S<sub>2</sub> requires C, 30.3; H, 2.3%). <sup>1</sup>H NMR (360 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 290 K): δ 7.80, 7.50 (*o*-C<sub>6</sub>H<sub>4</sub>) and 2.72 (Me). <sup>13</sup>C-<sup>1</sup>H} NMR (300 K, CDCl<sub>3</sub>): δ 224.0–217.6 (CO), 140.7–127.3 (*o*-C<sub>6</sub>H<sub>4</sub>) and 20.0 (Me).

**[Mn<sub>2</sub>(CO)<sub>6</sub>(μ-Br)<sub>2</sub>(μ-MeSCH<sub>2</sub>SMe)].** Method as for [MnBr(CO)<sub>3</sub>(MeSCH<sub>2</sub>CH<sub>2</sub>SMe)] above, but using [MnBr(CO)<sub>3</sub>] (0.163 g, 0.59 mmol), MeSCH<sub>2</sub>SMe (0.064 g, 0.59 mmol) and refluxing in CHCl<sub>3</sub> (30 cm<sup>3</sup>) for 28 h giving an orange solid (0.030 g, 9%) (Found: C, 20.3; H, 1.6. C<sub>9</sub>H<sub>8</sub>Br<sub>2</sub>Mn<sub>2</sub>O<sub>6</sub>S<sub>2</sub>

requires C, 19.8; H, 1.5%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 300 K): δ 3.70 (CH<sub>2</sub>) and 2.45 (Me).

### X-Ray crystallography

Details of the crystallographic data collection and refinement parameters are given in Table 5 for the structures. The crystals were grown by vapour diffusion to light petroleum onto solutions of the complexes in CH<sub>2</sub>Cl<sub>2</sub>. For [MnBr(CO)<sub>3</sub>(PhSCH<sub>2</sub>CH<sub>2</sub>SPh)] data collection using a Siemens SMART diffractometer, for [MnCl(CO)<sub>3</sub>(MeSCH<sub>2</sub>CH<sub>2</sub>SMe)] and [Mn<sub>2</sub>(CO)<sub>6</sub>(μ-Br)<sub>2</sub>(μ-MeSCH<sub>2</sub>SMe)] a Rigaku AFC7S four-circle diffractometer operating at 150 K, using graphite-monochromated Mo-Kα X-radiation (λ = 0.710 73 Å). No significant crystal decay or movement was observed.

**[MnBr(CO)<sub>3</sub>(PhSCH<sub>2</sub>CH<sub>2</sub>SPh)].** The systematic absences indicated the space group to be either *Pnma* or *Pna2<sub>1</sub>*, and the data suggested a centric space group. The structure was solved in *Pnma* by heavy-atom Patterson methods<sup>26</sup> and developed by iterative cycles of full-matrix least-squares refinement and Fourier-difference syntheses which located one half [MnBr(CO)<sub>3</sub>(PhSCH<sub>2</sub>CH<sub>2</sub>SPh)] molecule with Mn, Br, C(2) and O(2) lying on the mirror plane (*x*, 0.25, *z*).<sup>27</sup> This arrangement involved the mirror plane bisecting the dithioether ligand (through the midpoint of the dimethylene linkage), and was not chemically sensible since this would lead to the dimethylene units being eclipsed. At this point an attempt was made to refine the structure in the acentric space group *Pna2<sub>1</sub>*, however although this removed the mirror symmetry and hence the problem of eclipsed CH<sub>2</sub> groups, the bond lengths and angles were not sensible and the Ph groups were severely distorted and non-planar. Therefore, it was assumed that the molecule has crystallised in the centric space group *Pnma*, with the dithioether disordered across the mirror plane. The disorder was modelled successfully through identification of two alternative, 50% occupied sites for the methylene groups, C(9) and C(10), with C(9) linked to C(10\*) and C(10) linked across the mirror plane to C(9\*), breaking the mirror symmetry. A similar disorder problem was identified and successfully modelled previously for [Pt([12]aneS<sub>4</sub>)]<sub>2</sub>[PF<sub>6</sub>]<sub>2</sub> ([12]aneS<sub>4</sub> = 1,4,7,10-tetrathia-cyclododecane).<sup>28</sup> All non-H atoms were refined anisotropically while H atoms were placed in fixed, calculated positions with *d*(C–H) = 0.96 Å [the H atoms associated with C(9) and C(10) were not located in the difference map and therefore were omitted from the final structure-factor calculation]. The weighting scheme *w*<sup>-1</sup> = σ<sup>2</sup>(*F*) gave satisfactory agreement analyses.

**[MnCl(CO)<sub>3</sub>(MeSCH<sub>2</sub>CH<sub>2</sub>SMe)] and [Mn<sub>2</sub>(CO)<sub>6</sub>(μ-Br)<sub>2</sub>(μ-MeSCH<sub>2</sub>SMe)].** The structures were solved by heavy-atom

Patterson methods<sup>26</sup> and developed by iterative cycles of full-matrix least-squares refinement and Fourier-difference syntheses which located all non-H atoms for one complete molecule on a general position.<sup>27</sup> All non-H atoms were refined anisotropically while H atoms were placed in fixed, calculated positions with  $d(\text{C-H}) = 0.96 \text{ \AA}$ . The weighting scheme  $w^{-1} = \sigma^2(F)$  gave satisfactory agreement analyses.

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