



Synthesis, spectroscopic and structural characterisation of molybdenum, tungsten and manganese carbonyl complexes of tetrathio- and tetraseleno-ether ligands

William Levason*, Luke P. Ollivere, Gillian Reid, Nikolaos Tsoureas, Michael Webster

School of Chemistry, University of Southampton, Southampton SO17 1BJ, UK

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ABSTRACT

A range of complexes of the binucleating tetrathio- and tetraseleno-ether ligands, 1,2,4,5- $C_6H_2(CH_2E)Me_4$ ($E = S, L^3$ or Se, L^4) or $C(CH_2E)Me_4$ ($E = S, L^5$ or Se, L^6) and of bidentate analogues 1,2- $C_6H_2(CH_2E)Me_2$ ($E = S, L^1$ or $Se = L^2$) with molybdenum and tungsten carbonyls and manganese carbonyl chloride have been prepared, and characterised by IR and multinuclear NMR ($^1H, ^{13}C\{^1H\}, ^{77}Se, ^{55}Mn, ^{95}Mo$) spectroscopy and mass spectrometry. Crystal structures are reported for $[Mo(CO)_4(L^2)]$, $[Mo(CO)_4(L^3)]$, $[Mo(CO)_4(\mu-L^3)Mo(CO)_4]$, $[Mo(CO)_4(L^4)]$, $[Mn(CO)_3Cl(\mu-L^3)Mn(CO)_3Cl]$, $[Mo(CO)_4(\mu-L^5)Mo(CO)_4]$, $[Mn(CO)_3Cl(L^5)]$ and two forms (containing *meso* and *DL* diastereoisomers) of $[W(CO)_4(L^5)]$.

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1. Introduction

The removal of sulfur compounds, mainly thiophene derivatives, from natural gas and crude petroleum is one of the key chemical industrial processes. The process, hydrodesulfurisation, (HDS), involves hydrogen reduction of the sulfur compounds using molybdenum catalysts often with cobalt or nickel promoters, supported on alumina. Other catalysts containing tungsten and ruthenium, sometimes with a 3d metal promoter have been examined in attempts to achieve higher activity at lower temperatures [1–4]. One approach to preparing HDS catalysts is to prepare mono- or bi-metallic complexes with sulfur ligands, which can be absorbed or chemically tethered to an inert support and subsequently pyrolysed to yield the metallic components in a sulfur environment. Here we report the syntheses of some sulfur and selenium ligands based upon 1,2,4,5-tetrasubstituted aromatic or spirocyclic backbones, which are sterically incapable of coordinating as tetradentate monometallic chelates, but which can bridge two metal centres, and illustrate their chemistry by the preparation of mono- and di-nuclear complexes with molybdenum, tungsten and manganese carbonyl substrates. A small number of reports of similar ligands have appeared along with some metal halide complex chemistry [5]. Details of the metal carbonyl chemistry of polythio- and polyseleno-ethers are described in recent reviews [6].

2. Experimental

Infrared spectra were recorded as Nujol mulls between CsI plates over the range 4000–200 cm^{-1} or as chlorocarbon solutions in NaCl solution cells over the range 2200–1700 cm^{-1} , using Perkin–Elmer 983G or PE Spectrum100 instruments. 1H and $^{13}C\{^1H\}$ NMR spectra were recorded at ambient temperatures unless stated otherwise, using a Bruker AV300 spectrometer and referenced internally to the solvent resonance, and $^{13}C\{^1H\}$, $^{77}Se\{^1H\}$, ^{55}Mn and ^{95}Mo NMR spectra on a Bruker DPX400 spectrometer and are referenced to the solvent resonance, external neat $SeMe_2$, aqueous $KMnO_4$, aqueous Na_2MoO_4 at pH 11, respectively. Mass spectra were obtained using a VG Biotech platform. Microanalyses were undertaken by the University of Strathclyde microanalytical service or Medac Ltd. Solvents were dried prior to use and all preparations were undertaken using standard Schlenk techniques under a N_2 atmosphere. Metal carbonyls were obtained from Aldrich and used as received. $Mn(CO)_5Cl$ was made from $Mn_2(CO)_{10}$ and Cl_2/CCl_4 [7]. $o-C_6H_4(CH_2SMe)_2$ (L^1), $o-C_6H_4(CH_2SeMe)_2$ (L^2) and $C(CH_2SMe)_4$ (L^5) were made as described [8,9].

2.1. 1,2,4,5-Tetrakis(methylthiomethyl)benzene (L^3)

Liquid ammonia (150 mL) was condensed into a 500 mL three necked flask, equipped with condenser and pressure equalising addition funnel at $-78^\circ C$ using a dry-ice/acetone slush bath. Sodium (0.76 g, 33.2 mmol) was added and the blue solution stirred for 10 min under N_2 . Dimethyldisulfide (1.5 mL 17.3 mmol) was added slowly, which discharged the blue colour. The NH_3 was left

* Corresponding author. Fax: +44 023 80 593781.
E-mail address: wxl@soton.ac.uk (W. Levason).

to evaporate under a stream of N_2 , and the NaSMe dissolved in 100 mL of dry EtOH. 1,2,4,5-Tetrakis(bromomethyl)benzene (3.0 g, 6.7 mmol) was dissolved in warm degassed EtOH (250 mL), and added dropwise to the NaSMe solution. After half the solution was added the flask was heated to reflux and the addition completed. The mixture was refluxed overnight. The cooled reaction mixture was transferred to a separating funnel, and saturated aqueous $NaHCO_3$ (100 mL) added. The mixture was extracted with CH_2Cl_2 (3×200 mL) and the organic phase was collected, washed with 100 mL brine and dried over $MgSO_4$. Upon removal of most of the solvent, the product precipitated as a white solid which was collected by filtration, washed with hexane and dried under vacuum. A second crop of crystalline product was collected by combining the hexane washings with the CH_2Cl_2 mother-liquor and cooling at $-30^\circ C$. Overall yield: 1.85 g, 87%. Anal. Calc. for $C_{14}H_{22}S_4$: C, 52.78; H, 6.96. Found: C, 52.83; H, 6.79%. 1H NMR ($CDCl_3$): 2.05(s) 12[H] SMe, 3.81(s) 8[H] CH_2 , 7.13(s) 2[H] aromatic CH. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 15.6 SMe, 35.2 CH_2 , 133.0 CH 135.2 aromatic quaternary. CIMS: 319 [M] $^+$.

2.2. 1,2,4,5-Tetrakis(methylselenomethyl)benzene (L^4)

Freshly ground selenium powder (3.5 g, 44.4 mmol) was added to dry THF (25 mL) in a dry three necked round-bottomed flask under nitrogen. The solution was then frozen (77 K) with liquid nitrogen. MeLi solution (27.8 mL of 1.6 M solution in diethyl ether, 44.4 mmol) was then added via syringe and the mixture was left to thaw for 40 min, then stirred at room temperature for 2 h. 1,2,4,5-Tetrakis(bromomethyl)benzene (2.5 g, 5.6 mmol) was then added and the reaction mixture was refluxed for 1 h, cooled and hydrolysed with NaCl solution (25 mL). The organic layer was then separated and the aqueous layer was extracted with diethyl ether (3×20 mL). The combined extracts were dried over $MgSO_4$, filtered and the solvent removed under high vacuum to yield a yellow powder. Yield: 2.44 g, 86%. Anal. Calc. for $C_{14}H_{22}Se_4$: C, 33.22; H, 4.38. Found: C, 33.26, H, 4.17%. 1H NMR ($CDCl_3$): 1.96(s) 12[H] SeMe, 3.85(s) 8[H] CH_2 , 7.01(s) 2[H] CH. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 4.84 SeMe, 25.05 CH_2 , 132.8 CH 135.5 aromatic quaternary. $^{77}Se\{^1H\}$ NMR (CH_2Cl_2): 150.7. CIMS: 505 [M] $^+$. Crystals were grown by evaporation from CH_2Cl_2 solution.

2.3. 1,1,1,1-Tetrakis(methylthiomethyl)methane (L^5)

This was synthesized in a way similar to that described for L^3 above, starting from (5.0 g, 12.9 mmol) $C(CH_2Br)_4$, (1.42 g, 61.7 mmol) Na and (2.7 mL, 30.5 mmol) of Me_2S_2 . After removal of volatiles the yellow liquid was distilled to yield the product as a colourless liquid. Yield: 3.05 g, 92%. 1H NMR ($CDCl_3$): 2.12(s) 12[H] SMe, 2.81(s) 8[H] CH_2 . $^{13}C\{^1H\}$ NMR ($CDCl_3$): 17.5 SMe, 40.8 CH_2 , 44.9 quaternary C. CIMS: 257 [M] $^+$.

2.4. 1,1,1,1-Tetrakis(methylselenomethyl)methane (L^6)

Freshly ground selenium powder (2.8 g, 3.50 mmol) was added to dry THF (25 mL) and was stirred in a dry three necked round-bottomed flask under nitrogen. The solution was then frozen with liquid nitrogen. MeLi solution (21.9 mL of 1.6 M solution in diethyl ether, 35.0 mmol) was then added via syringe and left to thaw for 40 min, then stirred at room temperature for 2 h. Pentaerythrityl tetrabromide (3.0 g, 8.0 mmol) in THF (30 mL) was then added dropwise and the solution was stirred for 15 h before heating to $65^\circ C$ for 30 min. After cooling, the reaction mixture was hydrolysed with NaCl solution (25 mL). The organic layer was separated and the aqueous layer extracted via separation with diethyl ether (3×20 mL). The combined organic solutions were dried over

$MgSO_4$, filtered and the solvent removed under vacuum to yield pale yellow oil. Kugelrohr distillation ($110^\circ C$, 0.1 mmHg) removed volatiles, and the residue is pure L^6 . Yield: 1.91 g, 55%. 1H NMR ($CDCl_3$): 2.07(s) 12[H] SeMe, 2.86(s) 8[H] CH_2 . $^{13}C\{^1H\}$ NMR ($CDCl_3$): 6.27 SeMe, 35.2 CH_2 , 44.4 quaternary C. $^{77}Se\{^1H\}$ NMR (CH_2Cl_2): 24.5. CIMS: 445 [M] $^+$.

2.5. 1,1-Bis(methylselenomethyl)cyclopropane

Freshly ground selenium powder (5.0 g, 62.5 mmol) was added to dry THF (25 mL) and stirred in a dry three necked round-bottomed flask under nitrogen. The solution was then frozen with liquid nitrogen. MeLi solution (39.0 mL of 1.6 M solution in diethyl ether, 64.5 mmol) was then added via syringe to the selenium and left to thaw for 40 min, then stirred at room temperature for 2 h. Pentaerythrityl tetrabromide (3.0 g, 8.0 mmol) in THF (30 mL) was then added to the solution and refluxed for 1 h. The flask was allowed to cool and then hydrolysed with NaCl solution (25 mL). The product was then extracted via separation with diethyl ether (3×20 mL) dried over $MgSO_4$ filtered and the solvent and Me_2Se_2 removed under high vacuum to leave a pale yellow oil. Yield: 1.74 g, 87%. 1H NMR ($CDCl_3$): 0.61(s) 4[H] CH_2 cyclopropyl, 2.10(s) 8[H] SeMe, 2.82(s) 4[H] CH_2 . $^{13}C\{^1H\}$ NMR ($CDCl_3$): 5.3 C-cyclopropyl, 15.0 SeMe, 34.9 CH_2 . $^{77}Se\{^1H\}$ NMR (CH_2Cl_2): 58.6. GC-MS: 258 (RT. 5.2) [M] $^+$.

2.6. $[Mo(CO)_4(L^1)]$

$[Mo(CO)_4(nbd)]$ (nbd = norbornadiene), (0.085 g, 0.28 mmol) was dissolved in toluene (10 mL) and L^1 (0.055 g, 0.28 mmol) in toluene (5 mL) added. The mixture was stirred at $75^\circ C$ for 20 h, cooled, and the toluene removed in vacuo. The residue was dissolved in hot $CHCl_3$ (5 mL), filtered through Celite and *n*-pentane (5 mL) added. Refrigeration (-18°) for 3 days gave a yellow solid, which was filtered off, rinsed with *n*-pentane and dried in vacuo. Yield: 0.07 g, 62%. Anal. Calc. for $C_{14}H_{14}MoO_4S_2$: C, 41.38; H, 3.47. Found: C, 41.11; H, 3.89%. 1H NMR ($CDCl_3$): 2.56(s) 6[H] SMe, 3.84(s) 4[H] CH_2 , 7.1–7.3(m) 4[H] aromatic. $^{13}C\{^1H\}$ NMR ($CH_2Cl_2/CDCl_3$): 27.6 SMe, 40.7 CH_2 , 129.7, 132.4, 134.2 aromatic, 206.3, 215.7 CO. ^{95}Mo NMR (CH_2Cl_2): -1292 . APCI MS: found m/z 422; calc. $[M-Me]^+$ 423. IR (Nujol): $\nu(CO)$ 2020, 1904, 1878, 1833; (CH_2Cl_2): $\nu(CO)$ 2028, 1915, 1895, 1853 cm^{-1} .

2.7. $[W(CO)_4(L^1)]$

Was made similarly to the molybdenum complex using $[W(CO)_4(tmpa)]$ ($tmpa = Me_2N(CH_2)_3NMe_2$). Yield: 65%. Anal. Calc. for $C_{14}H_{14}O_4S_2W \cdot 1/3CHCl_3$: C, 32.66; H, 2.74. Found: C, 32.54; H, 2.28%. 1H NMR ($CDCl_3$): 2.76(s) 6[H] SMe, 3.99 (s) 4[H] CH_2 , 7.22–7.41(m) 4[H] aromatic. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 28.8 SMe, 41.9 CH_2 , 129.1, 132.1, 134.0 aromatic, 201.9 CO, $^1J_{WC} = 130$ Hz, 206.2 CO, $^1J_{WC} = 174$ Hz. APCI MS: found m/z 494, calc. $[M]^+$ 494. IR (CH_2Cl_2): $\nu(CO)$ 2022, 1904, 1888, 1849 cm^{-1} .

2.8. $[Mn(CO)_3Cl(L^1)]$

$[Mn(CO)_3Cl]$ (0.23 g, 1.0 mmol) was dissolved in CH_2Cl_2 (20 mL) and L^1 (0.2 g, 1.0 mmol) in toluene (20 mL) added. The mixture was stirred at $75^\circ C$ for 3 h, cooled, and the solvent removed in vacuo. The residue was dissolved in hot $CHCl_3$ (15 mL), cooled and the yellow solid filtered off, rinsed with $CHCl_3$ and dried in vacuo. Yield: 0.12 g, 32%. 1H NMR ($CDCl_3$): 2.23(s) 6[H] SMe, 4.20(s) 4[H] CH_2 , 7.5(m) 4[H] aromatic. $^{13}C\{^1H\}$ NMR ($CH_2Cl_2/CDCl_3$): 23.2 SMe, 35.1 CH_2 , 129.1, 131.8, 134.0 aromatic, 208.3(vbr) CO. ^{55}Mn NMR (CH_2Cl_2): +45. IR (Nujol): $\nu(CO)$ 2038, 1960 (vbr), 1910(sh) cm^{-1} .

2.9. $[Mo(CO)_4(L^2)]$

$[Mo(CO)_4(nbd)]$ (0.085 g, 0.28 mmol) was dissolved in toluene (10 mL) and L^2 (0.082 g, 0.28 mmol) in toluene (5 mL) added. The mixture was stirred at 75 °C for 24 h, cooled and the toluene removed in vacuo. The residue was dissolved in hot $CHCl_3$ (5 mL), filtered through Celite and *n*-pentane (5 mL) added, which gave a yellow solid, which was filtered off, rinsed with *n*-pentane and dried in vacuo. Yield: 0.061 g, 53%. Anal. Calc. for $C_{14}H_{14}MoO_4Se_2$: C, 33.62; H, 2.82. Found: C, 33.88; H, 2.90%. 1H NMR ($CDCl_3$): 2.93(s) 6[H] SeMe, 3.80(s) 4[H] CH_2 , 7.1–7.3(m) 4[H] aromatic. $^{13}C\{^1H\}$ NMR ($CH_2Cl_2/CDCl_3$): 16.8 SeMe, 31.3 CH_2 , 128.7, 131.6, 135.2 aromatic, 207.4, 215.5 CO. ^{95}Mo NMR (CH_2Cl_2): –1393. $^{77}Se\{^1H\}$ NMR (CH_2Cl_2): 157.6. APCI MS: found m/z 520, calc. $[M-Me]^+$ 519. IR (Nujol): $\nu(CO)$ 2015, 1913, 1879, 1834; (CH_2Cl_2): $\nu(CO)$ 2024, 1914, 1895, 1854 cm^{-1} . Crystals were grown by cooling a $CHCl_3$ solution in a freezer.

2.10. $[W(CO)_4(L^2)]$

Was made similarly to the molybdenum complex using $[W(CO)_4(tpma)]$. Yield: 53%. Anal. Calc. for $C_{14}H_{14}O_4Se_2W \cdot CHCl_3$: C, 25.47; H, 2.14. Found: C, 25.07; H, 2.40%. 1H NMR ($CDCl_3$): 2.56(s) 6[H] SeMe, 3.91(s) 4[H] CH_2 , 7.1–7.3(m) aromatic. $^{13}C\{^1H\}$ NMR ($CH_2Cl_2/CDCl_3$, 223 K): 17.9 SeMe, 30.6 CH_2 , 128.0, 131.0, 133.8 aromatic, 201.6, 205.6 CO. $^{77}Se\{^1H\}$ NMR (CH_2Cl_2): 115.8, 109.4 (223 K). APCI MS: found m/z 590, calc. $[M]^+$ 590. IR (CH_2Cl_2): $\nu(CO)$ 2018, 1904, 1886, 1850 cm^{-1} .

2.11. $[Mn(CO)_3Cl(L^2)]$

$[Mn(CO)_5Cl]$ (0.23 g, 1.3 mmol) was dissolved in $CHCl_3$ (50 mL) and L^2 (0.39 g, 1.3 mmol) in $CHCl_3$ (20 mL) added. The mixture was refluxed for 3 h, cooled, and the solvent removed in vacuo. The residue was washed in hot $CHCl_3$ (3×15 mL). The resulting orange solid, was filtered and then dried in vacuo. Yield: 0.19 g, 36%. Anal. Calc. for $C_{13}H_{14}ClMnO_3Se_2 \cdot 1/2CHCl_3$: C, 30.81; H, 2.78. Found: C, 30.66; H, 2.85%. 1H NMR ($CDCl_3$): 2.2–2.5(br) 6[H] SeMe, 3.5–4.1 (br) 4[H] CH_2 , 7.3–7.8(br) 4[H] aromatic. $^{13}C\{^1H\}$ NMR ($CH_2Cl_2/CDCl_3$): 14.8–15.9(br, overlapping) SeMe, 27.9–31.2 (br) CH_2 , 128.4, 129.9, 133.0, 135.2 aromatic, 217.0–220.5 (vbr) CO. $^{77}Se\{^1H\}$ NMR (CH_2Cl_2): 147.8, 124.1, 122.5, 120.5. ^{55}Mn NMR (CH_2Cl_2): –42(major), –77(minor), –113 (minor). IR (CH_2Cl_2): $\nu(CO)$ 2030, 1949, 1921 cm^{-1} .

2.12. $[Mo(CO)_4(L^3)]$

This complex was isolated as yellow crystals by diethyl ether extraction of the crude produce from the attempted synthesis of $[Mo(CO)_4(\mu-L^3)Mo(CO)_4]$ (see Section 2.13) and identified by the crystal structure. 1H NMR (CD_2Cl_2): 2.06(s) 6[H] SMe uncoord, 2.56(s) 6[H] SMe coord, 3.81(s) 4[H] CH_2 uncoord, 3.83(s) 4[H] CH_2 coord, 7.13(s) 2[H] aromatic. $^{13}C\{^1H\}$ NMR (CH_2Cl_2/CD_2Cl_2): 15.56 SMe uncoord, 27.15 SMe coord, 35.25 CH_2 uncoord, 40.46 CH_2 coord, 133.9, 134.9 135.2 aromatic, 206.4 and 215.6 CO. IR (CH_2Cl_2): $\nu(CO)$ 2036, 1927, 1884 cm^{-1} .

2.13. $[Mo(CO)_4(\mu-L^3)Mo(CO)_4]$

In an ampoule fitted with a Young's tap, $[Mo(CO)_4(nbd)]$ (0.10 g, 0.33 mmol) suspended in dry toluene (15 mL) was added slowly L^3 (0.106 g, 0.10 mmol) in CH_2Cl_2 (10 mL), the ampoule partially evacuated and placed in a thermostated oil bath at 100 °C for 3 h. Volatiles were removed under reduced pressure and the yellow-brown solid was extracted with dry Et_2O (3×30 mL) and filtered through Celite. The volume of the ether was reduced to 1/3 and

the solution was placed at –30 °C to give a crop of the 1:1 complex. The ether insoluble portion was taken up in THF, filtered and the solution was layered with hexane to produce crystals of the 2:1 compound identified by an X-ray crystal structure. Yields variable (see text). 1H NMR (CD_2Cl_2): 2.57(s) 12[H] SMe, 3.89(s) 8[H] CH_2 , 7.10(s) 2[H], aromatic. $^{13}C\{^1H\}$ NMR (CH_2Cl_2/CD_2Cl_2): 27.5 SMe, 40.7 CH_2 , 134.9, 137.6 aromatic, 206.4 and 215.6 CO. IR (Nujol): $\nu(CO)$ 2023, 1907, 1876, 1828 cm^{-1} .

2.14. $[Mn(CO)_3Cl(L^3)]$

L^3 (0.32 g, 1.0 mmol) and $[Mn(CO)_5Cl]$ (0.23 g, 1.0 mmol) were dissolved in CH_2Cl_2 (20 mL), the mixture was placed under partial vacuum and heated at 55 °C. After 2½ h at this temperature the ampoule was removed from the oil bath and the reaction mixture was left stirring overnight at room temperature. Volatiles were removed on a rotary evaporator and the yellow-brown oily residue was re-dissolved in CH_2Cl_2 (15 mL) and was filtered through Celite. The solvent from the bright yellow solution was then removed under vacuum and the residue was washed with *n*-pentane. It was then dissolved in a small amount of CH_2Cl_2 (2 mL) and *n*-pentane was added (20 mL) to precipitate a microcrystalline yellow solid, which was collected by filtration and dried under vacuum. Yield: 0.21 g, 43%. Anal. Calc. for $C_{17}H_{22}ClMnO_3S_4$: C, 41.42; H, 4.50. Found: C, 42.25; H, 4.66%. 1H NMR ($CDCl_3$): 1.96(s) 6[H] SMe uncoord, 2.33(s) 6[H] SMe coord, 3.71(s) 4[H] CH_2 uncoord, 4.73(m) 4[H] coord, 7.05(s) 2[H] aromatic. $^{13}C\{^1H\}$ NMR ($CH_2Cl_2/CDCl_3$): 15.7 SMe uncoord, 22.8 SMe coord, 34.1 CH_2 uncoord, 35.1 CH_2 coord, 134.5, 133.1, 138.0 aromatic, 217.6(vbr) CO. ^{55}Mn NMR (CH_2Cl_2): +68. IR (Nujol): $\nu(CO)$ 2027, 1941, 1906 cm^{-1} .

Layering a CH_2Cl_2 solution of $[Mn(CO)_3Cl(L^3)]$ with *n*-pentane produced crystals identified as $[Mn(CO)_3Cl(\mu-L^3)Mn(CO)_3Cl]$ whose structure is described below. Attempts to prepare the 2:1 complex directly gave a mixture of the 1:1 complex, ligand and $Mn_2(CO)_{10}$ (identified crystallographically).

2.15. $[Mo(CO)_4(L^4)]$

$[Mo(CO)_4(nbd)]$ (0.11 g, 0.4 mmol) was dissolved in toluene (10 mL) and L^4 (0.2 g, 0.4 mmol) in toluene (5 mL) added. The mixture was stirred at 75 °C for 8 h, cooled and stirred overnight, and the toluene was removed in vacuo. The residue was dissolved in hot $CHCl_3$ (5 mL), filtered through Celite and *n*-pentane (10 mL) added. The flask was placed in the freezer overnight which gave a yellow solid, and crystals formed on the side of the flask (used for the X-ray crystallography); the solid was filtered off, rinsed with *n*-pentane and dried in vacuo. Yield: 0.06 g, 21%. Anal. Calc. for $C_{18}H_{22}MoO_4Se_4$: C, 30.27; H, 3.11. Found: C, 30.31; H, 3.21%. 1H NMR ($CDCl_3$): 2.02(s) 6[H] SeMe uncoord, 2.46(s) 6[H] SeMe coord, 3.86(s) 4[H] CH_2 uncoord, 3.87(s) 4[H] CH_2 coord, 7.01(s) 2[H] aromatic. $^{13}C\{^1H\}$ NMR ($CH_2Cl_2/CDCl_3$): 6.6 SeMe uncoord, 17.4 SeMe coord, 19.1 CH_2 uncoord, 29.6 CH_2 coord, 133.5, 136.0, 137.9 aromatic, 211.4, 216.5 CO. $^{77}Se\{^1H\}$ NMR (CH_2Cl_2): 151.8 SeMe uncoord, 154.9 SeMe coord. ^{95}Mo NMR (CH_3CN): –1384. IR (CH_2Cl_2): $\nu(CO)$ 2024, 1917, 1895, 1856 cm^{-1} .

2.16. $[Mo(CO)_4(\mu-L^4)Mo(CO)_4]$

$[Mn(CO)_4(nbd)]$ (0.22 g, 0.78 mmol) was dissolved in toluene (20 mL) and L^4 (0.2 g, 0.4 mmol) in toluene (20 mL) added. The mixture was stirred at 110 °C for 3 h, cooled and stirred overnight, the solvent was removed in vacuo. The yellow solid was washed in CH_2Cl_2 (3×20 mL) and dried in vacuo. Yield: 45%. Anal. Calc. for $C_{22}H_{22}Mo_2O_8Se_4$: C, 28.66; H, 2.40. Found: C, 29.09; H, 2.20%. 1H NMR ($CDCl_3$): 2.39(s) 6[H] SeMe coord, 3.80(s) 4[H] CH_2 coord, 7.21(s) 2[H] aromatic. $^{13}C\{^1H\}$ NMR (MeCN): (v. poorly soluble)

14.7 SeMe, 24.8 CH₂ coord, 132.8, 136.3, 140.3 aromatic, 205.2, 217.7 CO. ⁷⁷Se{¹H} NMR (CH₂Cl₂): 151.9(s). ⁹⁵Mo NMR (MeCN): –1411. IR (CH₂Cl₂): ν(CO) 2025, 1914, 1893, 1829 cm⁻¹.

2.17. [Mo(CO)₄(L⁵)]

[Mo(CO)₄(nbd)] (0.10 g, 0.33 mmol) was placed in 20 mL Young's ampoule and dissolved in dry toluene (10 mL). A solution of L⁵ (2.1 mL of 40 mg/mL solution) in toluene are added slowly via syringe. The reaction mixture was placed under partial vacuum and heated overnight at 110 °C. Volatiles were removed in vacuo and the yellow solid was extracted in petroleum ether (60–80), and filtered through Celite. The solution was reduced to about 4 mL and cooled to –30 °C to produce a yellow precipitate which was isolated from the mother-liquor by filtration and dried under vacuum. A second crop was collected by reducing the volume of the mother-liquor and cooling at –30 °C. Overall yield: 0.10 g, 65%. Anal. Calc. for C₁₃H₂₀MoO₄S₄: C, 33.61; H, 4.34. Found: C, 33.10; H, 4.33%. ¹H NMR (CDCl₃): 2.19(s) 6[H] SMe uncoord, 2.51(s) 6[H] SMe coord, 2.74(s) 4[H] CH₂ uncoord, 2.85(s) 4[H] CH₂ coord. ¹³C{¹H} NMR (CH₂Cl₂/CDCl₃): 17.8 SMe uncoord, 27.6 SMe coord, 42.2 CH₂ uncoord., 43.8 C quaternary, 48.5 CH₂ coord., 206.4 and 217.0 CO. ⁹⁵Mo NMR (CH₂Cl₂): –1384. IR (Nujol): ν(CO) 2026, 1921, 1857 cm⁻¹.

2.18. [W(CO)₄(L⁵)]

This was prepared as for the molybdenum complex from [W(CO)₄(piperidine)₂] and L⁵ in toluene. Yield: 67%. Anal. Calc. for C₁₃H₂₀O₄S₄W: C, 28.27; H, 3.65. Found: C, 28.54; H, 3.79%. ¹H NMR (CDCl₃): 2.20(s) 6[H] SMe uncoord, 2.68(s) 6[H] SMe coord, 2.75(s) 4[H] CH₂ uncoord, 3.08(s) 4[H] CH₂ coord. ¹³C{¹H} NMR (CH₂Cl₂/CDCl₃): 17.8 SMe uncoord, 29.5 SMe coord, 42.2 CH₂ uncoord, 43.8 C quaternary, 48.9 CH₂ coord, 202.1 and 208.0 CO. IR (Nujol): ν(CO) 2010, 1900(sh), 1890, 1843 cm⁻¹. Crystals were grown from a CH₂Cl₂ solution layered with hexane and stored at –18 °C.

2.19. [(CO)₄Mo(μ-L⁵)Mo(CO)₄]

A Young's ampoule was charged with [Mo(CO)₄(nbd)] (0.080 g, 0.26 mmol) in dry toluene (5 mL) and a solution of L⁵ in toluene (0.9 mL, 0.14 mmol of a 40 mg/ml solution). The ampoule was placed under partial vacuum and the mixture left stirring overnight. Volatiles were removed in vacuo, and the yellow solid was washed with hot hexane to remove the 1:1 complex. The residue was taken up in CH₂Cl₂, filtered through Celite and volatiles were removed under vacuum. The solid was further washed with hexane and dried under vacuum. Yield: 0.03 g, 34%. Anal. Calc. for C₁₇H₂₀Mo₂O₈S₄: C, 30.36; H, 3.00. Found: C, 30.22; H, 3.09%. ¹H NMR (CDCl₃): 2.56(s) 12[H], SMe, 2.9(s) 8[H] CH₂. ¹³C{¹H} NMR (CH₂Cl₂/CDCl₃): 27.6 SMe, 42.2 C quaternary, 48.7 CH₂, 206.2 and 216.4 CO. IR (Nujol): ν(CO) 2024, 1919, 1860; (CH₂Cl₂): ν(CO) 2024, 1911, 1899, 1860 cm⁻¹. Crystals are grown by a layering a CH₂Cl₂ solution of the complex with hexane.

2.20. [Mn(CO)₃Cl(L⁵)]

This was prepared with a method analogous to the [W(CO)₄(L⁵)] complex starting from [Mn(CO)₅Cl] (0.08 g, 0.35 mmol), L⁵ (2.2 mL of a 40 mg/mL solution) in toluene. Yield: 0.10 g, 66%. Anal. Calc. for C₁₂H₂₀ClMnO₃S₄: C, 33.45; H, 4.68. Found: C, 33.13; H, 4.24%. ¹H NMR (CDCl₃): 2.16(s) 6[H] SMe uncoord, 2.48(s) 6[H] SMe coord, 2.67(s) 4[H] CH₂ uncoord, 3.12(s) 4[H] CH₂, coord. ¹³C{¹H} NMR (CH₂Cl₂/CDCl₃): 18.0 SMe uncoord, 22.9 SMe coord, 40.6 CH₂ uncoord, 41.2 CH₂ coord, 43.3 C quaternary, 207.6, 217.6 CO.

⁵⁵Mn NMR (CH₂Cl₂): –40 w_{1/2} 12000 Hz. IR (Nujol): ν(CO) 2027, 1941, 1909 cm⁻¹. Crystals were grown by cooling a hexane solution of the compound at –30 °C.

2.21. [Mo(CO)₄(L⁶)]

[Mo(CO)₄(nbd)] (0.14 g, 0.45 mmol) was dissolved in toluene (10 mL) and L⁴ (0.2 g, 0.45 mmol) in toluene (5 mL) added. The mixture was stirred at 75 °C for 3 h, cooled and stirred overnight, when the toluene was removed in vacuo. The residue was dissolved in hot CHCl₃ (5 mL), filtered through Celite and *n*-pentane (10 mL) added. The flask was placed in the freezer overnight which gave a dark yellow solid, which was filtered off, rinsed with *n*-pentane and dried in vacuo. Yield 0.14 g, 48%. Anal. Calc. for C₁₃H₂₀MoO₄Se₄: C, 23.93; H, 3.09. Found: C, 23.33; H, 3.09%. ¹H NMR (CDCl₃): 2.08(s) [6H] SeMe uncoord, 2.48(s) [6H] SeMe coord, 2.85(s) [4H] CH₂ uncoord, 2.89(s) [4H] CH₂ coord. ¹³C{¹H} NMR (CH₂Cl₂/CDCl₃): 6.2(s) MeSe uncoord, 25.3 MeSe coord, 41.0 CH₂ uncoord, 44.0 C quaternary, 47.6 CH₂ coord, 209.1, 215.1, CO. ⁹⁵Mo NMR (CH₂Cl₂): –1450. ⁷⁷Se{¹H} NMR (CH₂Cl₂): 16.0(s) MeSe coord, 23.1(s) MeSe uncoord. IR (Nujol): ν(CO) 2020, 1904, 1883, 1851 cm⁻¹.

2.22. X-ray crystallography experimental

Details of the crystallographic data collection and refinement are given in Table 1. The crystallisation details are provided under the section for each compound. Data collection used a Nonius Kappa CCD diffractometer fitted with monochromated Mo K α X-radiation ($\lambda = 0.71073$ Å), and with the crystals held at 120 K in a dinitrogen gas stream. Structure solution and refinement were straightforward [15–17] except as described below, and H atoms were introduced into the model in calculated positions using the default C–H distances. The compound [Mo(CO)₄(μ-L³)Mo(CO)₄] had two centrosymmetric molecules in the cell, the second of which showed disorder at S4. This was modelled as two sites (A and B (sofs: 0.63, 0.37)) and also the bonded C(H₃) was identified in the difference electron-density map (C18A/B). C16 and C18A are on opposite sides of the Mo₂/S₃/S₄A plane, whereas C16 and C18B are on the same side as the Mo₂/S₃/S₄B plane (i.e. *DL* and *meso* isomers). The compound [Mo(CO)₄(L⁴)] likewise shows disorder at the uncoordinated Se3, modelled as two sites (A/B) along with C12A/B. The compound [W(CO)₄(L⁵)] (*P*₂₁/*n* form) showed a large peak ca. 1 Å away from W1. This was added to the model as a fractional (refined) W1B atom which resulted in a large decrease in R1 and the identification of three potential (fractional) S atoms all about 1 Å away from S1, S2 and S3. The geometry of these sites gave bond lengths in good agreement with the major component, however the common refined sof for these atoms (0.11) was such as to make identification of O and C atoms unlikely, and this was the case. The major component is shown in Fig. 9a. Selected bond lengths and angles are given in Tables 2–10.

3. Results

3.1. Ligands

The approach described in the Introduction, required tetradentate ligands with architectures which would be incapable of tetradentate monometallic chelation, and hence two types were chosen (Fig. 1) based upon either a spirocyclic framework – C(CH₂E₂)₄ (E = S or Se) (L⁵, L⁶) or a tetrasubstituted aromatic backbone – 1,2,4,5-C₆H₂(CH₂E₂)₄ (L³, L⁴). We also report some compounds of *o*-C₆H₄(CH₂E₂)₂ (L¹, L²) [8] for comparison.

Table 1
Crystal data and structure refinement details.^a

Complex	L ³	L ⁴	[Mo(CO) ₄ (L ²)]	[Mo(CO) ₄ (L ³)]	[Mo(CO) ₄ (μ-L ³)Mo(CO) ₄]	[Mo(CO) ₄ (L ⁴)]	[Mn(CO) ₃ Cl(μ-L ³)Mn(CO) ₃ Cl]	[Mo(CO) ₄ (μ-L ⁵)Mo(CO) ₄]	[W(CO) ₄ (L ⁵)] <i>anti</i> Me (<i>DL</i>)	[W(CO) ₄ (L ⁵)] <i>syn</i> Me (<i>meso</i>) ^c	[Mn(CO) ₃ Cl(L ⁵)]
Formula	C ₁₄ H ₂₂ S ₄	C ₁₄ H ₂₂ Se ₄	C ₁₄ H ₁₄ MoO ₄ Se ₂	C ₁₈ H ₂₂ MoO ₄ S ₄	C ₂₂ H ₂₂ Mo ₂ O ₈ S ₄	C ₁₈ H ₂₂ MoO ₄ Se ₄	C ₂₀ H ₂₂ Cl ₂ Mn ₂ O ₆ S ₄	C ₁₇ H ₂₀ Mo ₂ O ₈ S ₄	C ₁₃ H ₂₀ O ₄ S ₄ W	C ₁₃ H ₂₀ O ₄ S ₄ W	C ₁₂ H ₂₀ ClMnO ₃ S ₄
<i>M</i>	318.56	506.16	500.11	526.54	734.52	714.14	667.40	672.45	552.38	552.38	430.91
Crystal system	Monoclinic	Triclinic	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P2</i> ₁ / <i>c</i> (#14)	<i>P</i> $\bar{1}$ (#2)	<i>Pbcn</i> (#60)	<i>P2</i> ₁ / <i>n</i> (#14)	<i>P</i> $\bar{1}$ (#2)	<i>P2</i> ₁ / <i>n</i> (#14)	<i>P2</i> ₁ / <i>c</i> (#14)	<i>P2</i> ₁ / <i>c</i> (#14)	<i>Cc</i> (#9)	<i>P2</i> ₁ / <i>n</i> (#14)	<i>P2</i> ₁ / <i>c</i> (#14)
<i>a</i> (Å)	9.6553(10)	9.172(3)	27.939(6)	9.5685(15)	10.020(4)	9.7804(10)	12.772(2)	14.607(2)	10.783(2)	10.5626(10)	11.205(3)
<i>b</i> (Å)	20.575(3)	9.618(4)	7.9549(10)	13.647(2)	10.040(4)	13.602(3)	14.996(2)	10.0424(15)	21.010(5)	12.9810(15)	18.940(4)
<i>c</i> (Å)	9.2189(15)	11.742(6)	14.676(3)	17.069(3)	14.683(6)	17.285(3)	14.065(2)	18.333(3)	8.7967(15)	14.0075(15)	8.8494(15)
α (°)	90	107.83(2)	90	90	74.107(15)	90	90	90	90	90	90
β (°)	113.249(7)	91.12(3)	90	98.572(8)	76.174(15)	98.852(10)	96.880(10)	111.735(5)	106.853(10)	95.518(10)	91.266(6)
γ (°)	90	116.92(2)	90	90	88.089(15)	90	90	90	90	90	90
<i>U</i> (Å ³)	1682.7(4)	863.9(7)	3261.7(10)	2203.9(6)	1378.8(10)	2272.2(7)	2674.4(7)	2498.1(7)	1907.2(7)	1911.7(4)	1877.6(7)
<i>Z</i>	4	2	8	4	2	4	4	4	4	4	4
(Mo μ K α) (mm ⁻¹)	0.547	8.477	5.278	0.994	1.255	7.005	1.490	1.376	6.506	6.491	1.294
<i>F</i> (0 0 0)	680	484	1920	1072	732	1360	1352	1336	1072	1072	888
Total no. of reflections	22 435	9140	21 685	41 954	24 815	23 510	31 146	30 458	8583	22 551	31 174
Unique reflections	3122	3647	3719	5074	6326	5186	6126	5714	3923	4376	4309
[<i>R</i> _{int}]	0.048	0.086	0.066	0.040	0.053	0.057	0.109	0.044	0.057	0.030	0.026
No. of parameters	168	167	192	248	349	266	311	284	204	225	194
<i>R</i> ₁ ^b [<i>I</i> ₀ > 2 σ (<i>I</i> ₀)]	0.075	0.059	0.038	0.027	0.053	0.054	0.055	0.029	0.035	0.029	0.022
<i>R</i> ₁ (all data)	0.106	0.114	0.056	0.037	0.083	0.085	0.092	0.046	0.040	0.032	0.028
<i>wR</i> ₂ ^b [<i>I</i> ₀ > 2 σ (<i>I</i> ₀)]	0.224	0.099	0.082	0.064	0.113	0.090	0.088	0.060	0.080	0.064	0.049
<i>wR</i> ₂ (all data)	0.247	0.117	0.090	0.068	0.123	0.102	0.099	0.065	0.084	0.066	0.051

^a Common items: temperature = 120 K; wavelength (Mo K α) = 0.71073 Å; θ (max) = 27.5°.

^b $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$.

^c Ignoring disorder in the formula, *M* value and *F*(0 0 0).

Table 2
Selected bond lengths (Å) and angles (°) for L³ and L⁴.

L ³			
S1–C7	1.815(4)	S2–C9	1.811(5)
S1–C8	1.801(4)	S2–C10	1.787(7)
S3–C11	1.833(5)	S4–C13	1.815(4)
S3–C12	1.770(8)	S4–C14	1.786(4)
C7–S1–C8	100.4(2)	C9–S2–C10	99.9(3)
C11–S3–C12	102.7(3)	C13–S4–C14	101.2(2)
L ⁴			
Se1–C4	1.971(9)	Se2–C6	1.974(8)
Se1–C5	1.940(8)	Se2–C7	1.947(9)
C4–Se1–C5	99.0(4)	C6–Se2–C7	97.5(4)
C1–C4–Se1	115.4(5)	C2–C6–Se2	112.6(6)

Table 3
Selected bond lengths (Å) and angles (°) for [Mo(CO)₄(L²)].

Mo1–Se1	2.6670(6)	Mo1–Se2	2.6799(7)
Mo1–C1	2.045(5)	Mo1–C3	1.963(4)
Mo1–C2	1.963(5)	Mo1–C4	2.053(5)
C1–Mo1–C2	87.54(18)	C2–Mo1–C4	87.28(18)
C1–Mo1–C3	86.96(18)	C3–Mo1–C4	90.44(18)
C2–Mo1–C3	88.98(17)	Se1–Mo1–Se2	96.059(17)
C6–Se1–C5	97.1(2)	C13–Se2–C14	96.74(18)
C1–Mo1–Se1	93.80(13)	C4–Mo1–Se1	91.17(12)
C1–Mo1–Se2	93.36(12)	C4–Mo1–Se2	88.99(12)

Table 4
Selected bond lengths (Å) and angles (°) for [Mo(CO)₄(L³)].

Mo1–S1	2.5955(7)	Mo1–S2	2.5731(7)
Mo1–C15	1.957(2)	Mo1–C17	2.057(2)
Mo1–C16	1.954(2)	Mo1–C18	2.044(2)
C15–Mo1–C16	85.15(9)	C16–Mo1–C17	87.91(9)
C15–Mo1–C17	90.98(9)	C16–Mo1–C18	83.03(9)
C15–Mo1–C18	86.49(10)	S1–Mo1–S2	91.89(2)
C7–S1–C8	99.63(11)	C9–S2–C10	99.43(10)
C17–Mo1–S1	93.28(6)	C18–Mo1–S1	95.59(7)
C17–Mo1–S2	93.56(6)	C18–Mo1–S2	88.71(7)

Table 5
Selected bond lengths (Å) and angles (°) for [Mo(CO)₄(μ-L³)Mo(CO)₄].

Mo1–S1	2.5647(16)	Mo1–S2	2.5939(17)
Mo1–C8	1.962(7)	Mo1–C10	2.015(6)
Mo1–C9	1.942(7)	Mo1–C11	2.066(6)
C8–Mo1–C9	85.4(3)	C9–Mo1–C10	86.7(3)
C8–Mo1–C10	88.4(3)	C9–Mo1–C11	88.0(3)
C8–Mo1–C11	87.9(3)	S1–Mo1–S2	95.31(5)
C4–S1–C5	97.9(3)	C6–S2–C7	99.9(3)
C10–Mo1–S1	92.95(19)	C11–Mo1–S1	90.22(15)
C10–Mo1–S2	93.40(17)	C11–Mo1–S2	91.62(16)

Table 6
Selected bond lengths (Å) and angles (°) for [Mo(CO)₄(L⁴)].

Mo1–Se1	2.6715(9)	Mo1–Se2	2.6871(10)
Mo1–C15	1.962(7)	Mo1–C17	2.040(7)
Mo1–C16	1.962(7)	Mo1–C18	2.053(7)
C15–Mo1–C16	86.1(3)	C16–Mo1–C17	87.2(3)
C15–Mo1–C17	82.6(3)	C16–Mo1–C18	90.2(3)
C15–Mo1–C18	88.2(3)	Se1–Mo1–Se2	90.72(3)
C7–Se1–C8	96.6(3)	C9–Se2–C10	96.7(3)
C17–Mo1–Se1	88.1(2)	C18–Mo1–Se1	94.4(2)
C17–Mo1–Se2	95.6(2)	C18–Mo1–Se2	93.4(2)

Table 7
Selected bond lengths (Å) and angles (°) for [Mn(CO)₃Cl(μ-L³)Mn(CO)₃Cl].

Mn1–S1	2.3908(11)	Mn2–S3	2.3709(11)
Mn1–S2	2.4005(11)	Mn2–S4	2.3675(11)
Mn1–C11	2.3781(11)	Mn2–C12	2.3892(11)
Mn1–C15	1.811(4)	Mn2–C18	1.810(4)
Mn1–C16	1.804(4)	Mn2–C19	1.812(4)
Mn1–C17	1.806(4)	Mn2–C20	1.795(4)
S1–Mn1–S2	92.69(3)	S3–Mn2–S4	103.61(4)
C11–Mn1–S1	89.09(4)	C12–Mn2–S3	82.51(4)
C11–Mn1–S2	90.37(4)	C12–Mn2–S4	81.51(4)
C15–Mn1–C11	85.75(12)	C18–Mn2–C12	95.11(12)
C16–Mn1–C11	93.13(12)	C19–Mn2–C12	95.25(12)
C–Mn1–C (ca. 90°)	87.1(2)–93.6(2)	C–Mn2–C (ca. 90°)	87.0(2)–93.2(2)

Table 8
Selected bond lengths (Å) and angles (°) for [Mo(CO)₄(μ-L⁵)Mo(CO)₄].

Mo1–S1	2.5650(7)	Mo2–S3	2.5613(7)
Mo1–S2	2.5572(7)	Mo2–S4	2.5641(7)
Mo1–C1	1.972(3)	Mo2–C5	1.980(3)
Mo1–C2	1.971(3)	Mo2–C6	1.965(3)
Mo1–C3	2.073(3)	Mo2–C7	2.062(3)
Mo1–C4	2.014(3)	Mo2–C8	2.011(3)
S1–Mo1–S2	84.26(2)	S3–Mo2–S4	84.21(2)
C10–S1–C14	98.06(11)	C12–S3–C16	97.85(11)
C11–S2–C15	96.04(11)	C13–S4–C17	96.14(11)
C–Mo1–C (ca. 90°)	86.0(1)–90.3(1)	C–Mo2–C (ca. 90°)	87.7(1)–91.6(1)
S–Mo1–C (ca. 90°)	90.7(1)–93.5(1)	S–Mo2–C (ca. 90°)	87.4(1)–95.0(1)

Table 9
Selected bond lengths (Å) and angles (°) for the two conformers of [W(CO)₄(L⁵)].

<i>(a) DL containing form</i>			
W1–S1	2.543(2)	W1–S2	2.554(2)
W1–C10	1.963(8)	W1–C12	2.035(9)
W1–C11	1.946(10)	W1–C13	2.034(8)
S1–W1–S2	83.88(6)	C10–W1–C13	89.3(3)
C10–W1–C11	91.6(4)	C11–W1–C12	89.3(4)
C10–W1–C12	87.7(3)	C11–W1–C13	86.1(4)
C12–W1–S1	93.8(2)	C13–W1–S1	89.4(2)
C12–W1–S2	89.2(2)	C13–W1–S2	95.6(2)
C2–S1–C6	98.7(4)	C3–S2–C7	98.7(4)
C4–S3–C8	98.3(5)	C5–S4–C9	98.4(5)
<i>(b) meso containing form</i>			
W1–S1	2.5394(12)	W1–S2	2.5367(11)
W1–C10	1.961(5)	W1–C12	2.036(4)
W1–C11	1.980(5)	W1–C13	2.037(5)
S1–W1–S2	86.75(4)	C10–W1–C13	88.2(2)
C10–W1–C11	89.8(2)	C11–W1–C12	89.4(2)
C10–W1–C12	90.6(2)	C11–W1–C13	87.4(2)
C12–W1–S1	89.57(14)	C13–W1–S1	91.74(14)
C12–W1–S2	90.16(13)	C13–W1–S2	93.05(13)
C2–S1–C6	97.2(2)	C3–S2–C7	98.5(2)

Table 10
Selected bond lengths (Å) and angles (°) for [Mn(CO)₃Cl(L⁵)].

Mn1–S1	2.3763(5)	Mn1–S2	2.3823(6)
Mn1–C1	1.7946(15)	Mn1–C3	1.8117(15)
Mn1–C2	1.8153(15)	Mn1–C11	2.3789(6)
S1–Mn1–S2	85.506(17)	S1–Mn1–C11	91.724(16)
S2–Mn1–C11	89.775(13)	C1–Mn1–C3	91.54(7)
C1–Mn1–C2	92.47(6)	C2–Mn1–C3	87.67(6)
C5–S1–C9	98.18(7)	C6–S2–C10	97.57(7)
C–Mn1–S (ca. 90°)	86.74(5)–93.93(5)		

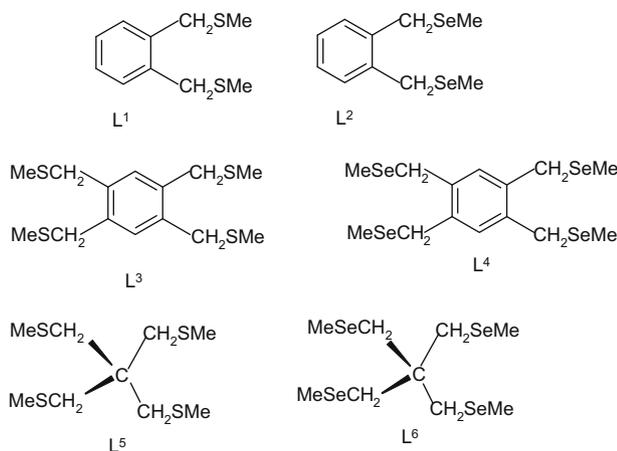


Fig. 1. Key to the ligands used.

L⁵ was made in good yield by the reaction of NaSeMe with C(CH₂Br)₄ in refluxing ethanol [9]. The reaction of LiSeMe with C(CH₂Br)₄ in THF was reported [10] to give L⁶ in poor yield (~10%). In attempts to optimise the yield we examined this reaction under a variety of conditions and reactant ratios. We found that reaction of LiSeMe with C(CH₂Br)₄ in a 4.5:1 molar ratio in hot THF stirred for 15 h gave a fair yield (~55%) of L⁶. Increasing the LiSeMe with C(CH₂Br)₄ molar ratio to 8:1 in refluxing THF produced the cyclopropane derivative $\overline{\text{CH}_2\text{CH}_2\text{C}(\text{CH}_2\text{SeMe})_2}$ in ~90% yield, and under a variety of other conditions mixtures of the two are produced. The corresponding reaction of LiTeMe with C(CH₂Br)₄ in THF affords only the cyclopropyltelluroether, $\overline{\text{CH}_2\text{CH}_2\text{C}(\text{CH}_2\text{TeMe})_2}$ [11].

The reaction of excess NaSeMe in ethanol or LiSeMe in THF with 1,2,4,5-C₆H₂(CH₂Br)₄ gave excellent yields (>85%) of the 1,2,4,5-C₆H₂(CH₂ESeMe)₄, which are air-stable crystalline solids. The spectroscopic properties (Sections 2.1 and 2.2) are unexceptional. The structures of both ligands were determined (Figs. 2 and 3, Table 2). The 1,2,4,5-C₆H₂(CH₂SMe)₄ has similar dimensions to those of *o*-C₆H₄(CH₂ESeMe)₂ [8] with the sulfur atoms directed outwards presumably minimising lone pair repulsions. The tetraselenoether although not isomorphous, has a very similar molecular structure, and in both cases the CH₂ESeMe groups on adjacent ring carbon atoms are on opposite sides of the ring.

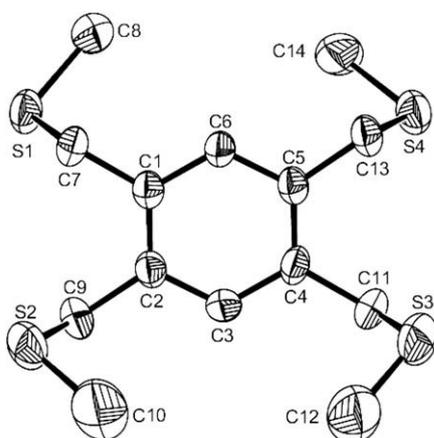


Fig. 2. Structure of C₆H₂(CH₂SMe)₄ (L³) showing the numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

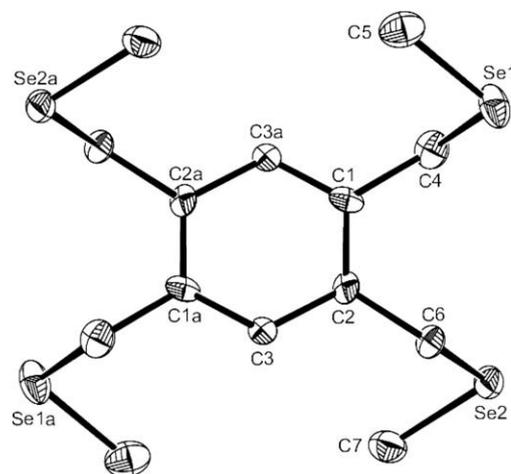


Fig. 3. Structure of C₆H₂(CH₂SeMe)₄ (L⁴) showing the numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. Symmetry operation: $a = 1 - x, 2 - y, -z$.

3.2. Complexes of L¹ and L²

The tetradentates L³ and L⁴ produce seven-membered rings on chelation, and for comparison purposes, complexes of the two bidentate xylyl backbone ligands, *o*-C₆H₄(CH₂ESeMe)₂ (L¹ and L²) were prepared. The spirocyclic L⁵ and L⁶ produce six-membered rings and comparisons here are provided by complexes of MeE(CH₂)₃ESeMe [12,13]. The complexes [Mo(CO)₄(L¹)], [W(CO)₄(L¹)], [Mo(CO)₄(L²)] and [W(CO)₄(L²)] were produced in high yields by reaction of the appropriate ligands with [Mo(CO)₄(nbd)] or [W(CO)₄(tmpa)], respectively. They are air-stable yellow crystalline solids with spectroscopic properties (Section 2) consistent with *cis*-tetracarbonyls [12–14]. The only point of note is the absence of ⁷⁷Se resonances in the spectrum of [W(CO)₄(L²)] at ambient temperatures, whereas two resonances are observed at 233 K, which reflects the rate of pyramidal inversion at E; as usual inversion is a lower energy process in the molybdenum system and a single (averaged) resonance is present at ambient temperatures¹. The structure of [Mo(CO)₄(L²)] (Fig. 4 and Table 2) confirms the geometry and shows the ligand present as the *meso*-1 diastereoisomer, with the Me groups and the xylyl backbone on the same side of the MoSe₂C₂ plane. The Se–Mo–Se angle is 96.06(2)°, reflecting the seven-membered ring, and as usual the Mo–C_{trans}C are considerably longer than Mo–C_{trans}Se [12]. The [Mn(CO)₃Cl(L)] (L = L¹ or L²) were made from the appropriate ligand and [Mn(CO)₅Cl]. They have relatively poor solubilities in halocarbon solvents, but have similar properties to those of other group 16 donor examples [13]. As is always observed in complexes of this type, the ¹H NMR resonances are significantly broadened by the quadrupolar manganese nucleus, as are the ¹³C carbonyl resonances, although ⁵⁵Mn NMR resonances themselves are relatively sharp. Unlike five-membered chelate ring dithioether analogues, where the ⁵⁵Mn NMR spectra show separate resonances for the various invertomers [13], in the [Mn(CO)₃Cl(L¹)] with a seven-membered ring, fast inversion results in a single ⁵⁵Mn resonance. For [Mn(CO)₃Cl(L²)] inversion is a higher energy process and three broad overlapping

¹ When neutral bidentate group 16 donor ligands chelate to a metal centre, *meso* and *DL* diastereoisomers are generated. These interconvert (pyramidal inversion) at varying rates depending upon the donor atom, the chelate ring size and the metal ion involved. Fast inversion on the appropriate NMR timescales results in simple (averaged) NMR spectra, whilst slower inverting systems may show resonances for the individual isomers. These processes have been investigated in detail elsewhere (Ref. [12] and references therein) and were not investigated in the present work, although they do influence the NMR spectra observed.

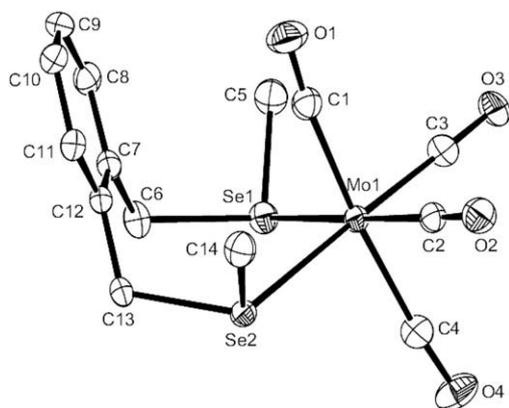


Fig. 4. Structure of $[\text{Mo}(\text{CO})_4(\text{L}^2)]$ showing the numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

^{55}Mn resonances of disparate intensities, were observed at ambient temperatures, and these correlate with several broad overlapping features in the $^{77}\text{Se}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ spectra, showing a system approaching fast inversion at 295 K on the various energy scales.

3.3. Complexes of L^3 and L^4

The reaction of $[\text{Mo}(\text{CO})_4(\text{nbdl})]$ with L^3 in a 1:1 molar ratio in toluene/ CH_2Cl_2 gave a yellow-brown solid which was shown by ^1H NMR spectroscopy to be a mixture of $[\text{Mo}(\text{CO})_4(\text{L}^3)]$ and $[\text{Mo}(\text{CO})_4(\mu\text{-L}^3)\text{Mo}(\text{CO})_4]$, the relative amounts varying from preparation to preparation. Extraction of the crude product with diethyl ether and crystallisation produced yellow $[\text{Mo}(\text{CO})_4(\text{L}^3)]$, whilst recrystallisation of the ether insoluble residue from THF afforded $[\text{Mo}(\text{CO})_4(\mu\text{-L}^3)\text{Mo}(\text{CO})_4]$. The spectroscopic data, especially the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR easily distinguish the two complexes, although samples of either usually show small amounts of the other complex and sometimes traces of free L^3 , suggesting that rearrangement occurs quite readily. The structures of both complexes were determined. The structure of $[\text{Mo}(\text{CO})_4(\text{L}^3)]$ (Fig. 5 and Table 4) shows the $\text{Mo}(\text{CO})_4$ residue κ^2 coordinated to L^3 with the coordinated dithioether group as the *meso*-1 isomer, with the $\angle\text{S1-Mo-S2} = 91.89(2)^\circ$, and the pattern of Mo–C(O) bond lengths similar to those in $[\text{Mo}(\text{CO})_4(\text{L}^2)]$ (above). The structure of $[\text{Mo}(\text{CO})_4(\mu\text{-L}^3)\text{Mo}(\text{CO})_4]$ (Fig. 6 and Table 5) shows L^3 $\kappa^2\kappa'^2$ coordinated to two $\text{Mo}(\text{CO})_4$ residues which adopt an *anti*-arrangement with respect to the plane of the aromatic backbone. The molecule is centrosymmetric with *DL* conformations for the coordinated

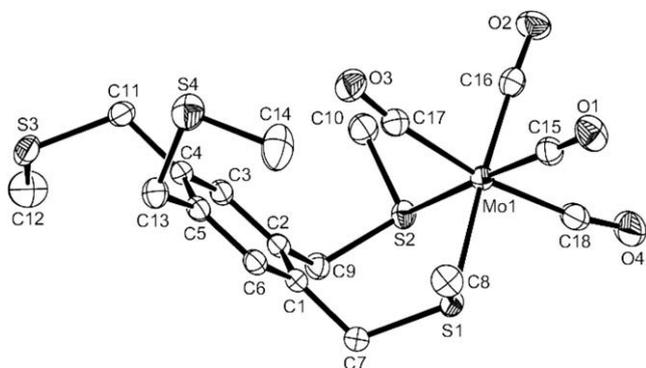


Fig. 5. Structure of $[\text{Mo}(\text{CO})_4(\text{L}^3)]$ showing the numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

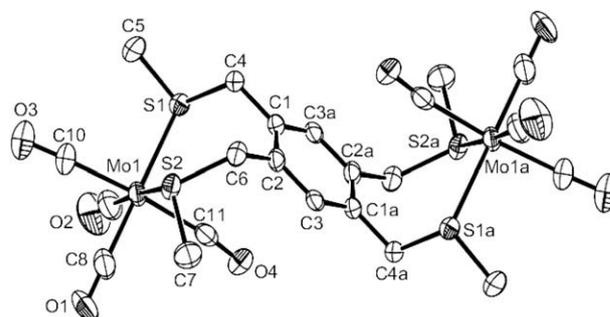


Fig. 6. Structure of the centrosymmetric Mo1 centred molecule $[\text{Mo}(\text{CO})_4(\mu\text{-L}^3)\text{Mo}(\text{CO})_4]$ showing the numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. Symmetry operation: $a = -x, -y, 1 - z$. There is a second molecule in the asymmetric unit (Mo2 centred) with a similar structure but showing some disorder at one SME group.

dithioether units. The only notable structural difference is the slightly wider ($\sim 3^\circ$) S1-Mo-S2 angle of $95.31(5)^\circ$ for the *DL* form compared with that in the *meso* form in $[\text{Mo}(\text{CO})_4(\text{L}^3)]$. There is no significant communication between the metal centres in the dinuclear complex as would be expected given the saturated carbon links in the ligand, and hence the spectroscopy reflects the fingerprints of the octahedral metal centres, closely following that of the model compounds and $[\text{Mo}(\text{CO})_4(\text{L}^3)]$ (Section 3.2). The tendency to rearrange and modest solubility of $[\text{Mo}(\text{CO})_4(\text{L}^3)]$ makes it a rather poor synthon for bimetallics. We were unable to obtain pure samples of the corresponding tungsten complexes which are even less soluble but seem to be prone to similar rearrangement.

In contrast to the complexes with L^3 , both $[\text{Mo}(\text{CO})_4(\text{L}^4)]$ and $[\text{Mo}(\text{CO})_4(\mu\text{-L}^4)\text{Mo}(\text{CO})_4]$ can be prepared directly under appropriate conditions (Sections 2.16 and 2.17). The structure of the former was determined (Fig. 7 and Table 6) and like the L^3 analogue, contains the *meso*-1 isomer of the ligand. The dimensions are unexceptional and the M–C(O) and C–O distances are not significantly different from those in $[\text{Mo}(\text{CO})_4(\text{L}^3)]$ showing that the electronic effects of S and Se donors are similar. The dinuclear $[\text{Mo}(\text{CO})_4(\mu\text{-L}^4)\text{Mo}(\text{CO})_4]$ was poorly soluble in chlorocarbons which hindered solution spectroscopic studies.

The reaction of $[\text{Mn}(\text{CO})_5\text{Cl}]$ with L^3 in either a 1:1 or 2:1 molar ratio in hot CH_2Cl_2 gave yellow crystals of $[\text{Mn}(\text{CO})_3\text{Cl}(\text{L}^3)]$, the reaction using the higher $\text{Mn}:\text{L}^3$ ratio also caused some decompo-

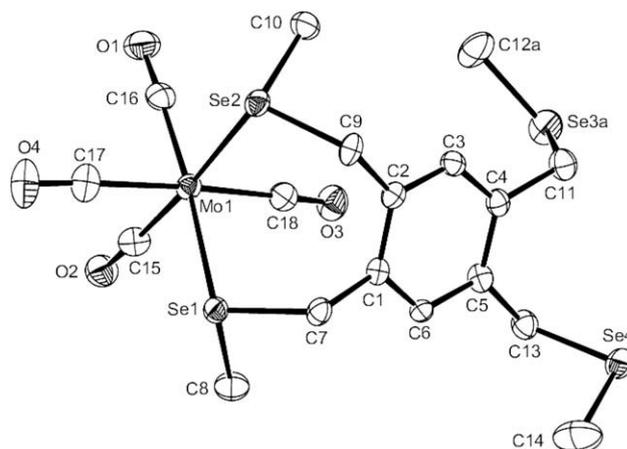


Fig. 7. Structure of $[\text{Mo}(\text{CO})_4(\text{L}^4)]$ showing the numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. There is disorder at Se3 and C12 modelled as two sites (A and B) with only the major A component shown.

sition and significant amounts of $\text{Mn}_2(\text{CO})_{10}$ (identified crystallographically) were formed. The spectroscopic data on $[\text{Mn}(\text{CO})_3\text{Cl}(\text{L}^3)]$ mirrors that of $[\text{Mn}(\text{CO})_3\text{Cl}(\text{L}^1)]$. Curiously in view of the failure to synthesise it directly, a CH_2Cl_2 solution of $[\text{Mn}(\text{CO})_3\text{Cl}(\text{L}^3)]$ layered with pentane, produced a few crystals which were identified as the dinuclear $[\text{Mn}(\text{CO})_3\text{Cl}(\mu\text{-L}^3)\text{Mn}(\text{CO})_3\text{Cl}]$, which presumably result from rearrangement in solution and deposit preferentially due to low solubility. The structure (Fig. 8 and Table 7) shows the tetrathioether in a quite different conformation to that in the dimolybdenum complex above; the Mn residues are coordinated *syn* with respect to the aromatic backbone, and whilst one $\text{Mn}(\text{CO})_3\text{Cl}$ group is bound to a dithioether unit in the *DL* form, the second is bound to a *meso*-1 dithioether group. In both groups the chlorine is directed away towards the less hindered faces of the molecule. Comparison of the bond lengths and angles shows little differences in Mn–Cl or

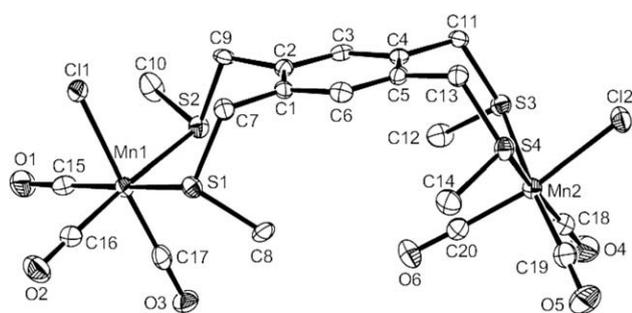


Fig. 8. Structure of $[\text{Mn}(\text{CO})_3\text{Cl}(\mu\text{-L}^3)\text{Mn}(\text{CO})_3\text{Cl}]$ showing the numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

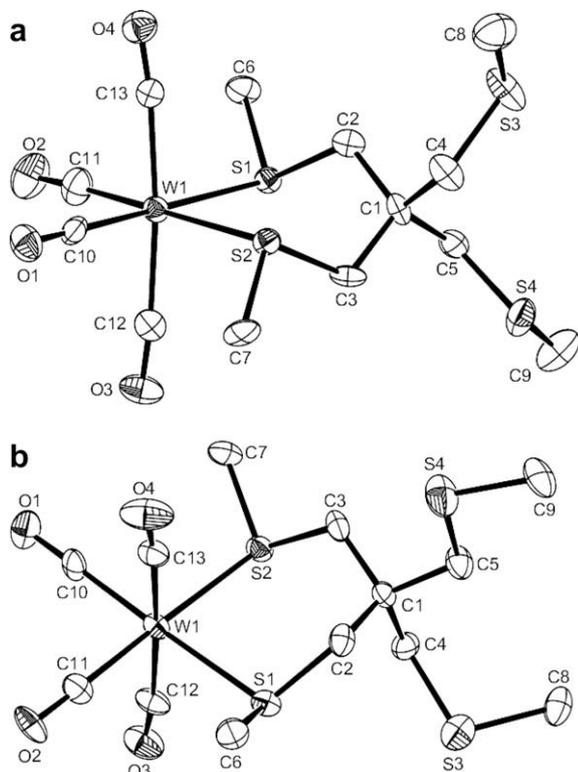


Fig. 9. Structure of two conformational isomers of $[\text{W}(\text{CO})_4(\text{L}^5)]$ showing the numbering schemes adopted. Ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. (a) C atoms C6 and C7 are *anti* with respect to the WS_2 plane. (b) C atoms C6 and C7 are *syn* with respect to the WS_2 plane.

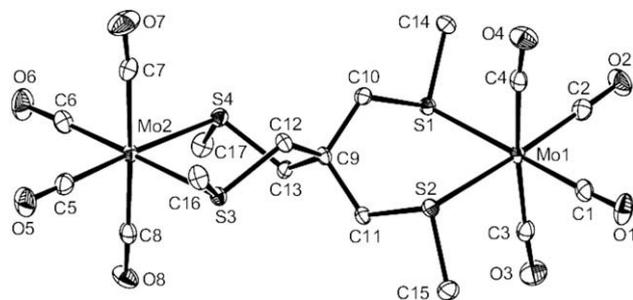


Fig. 10. Structure of $[\text{Mo}(\text{CO})_4(\mu\text{-L}^5)\text{Mo}(\text{CO})_4]$ showing the numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

Mn–C(O) distances, but the Mn–S distances within the *DL* coordinated unit are slightly longer ($\sim 0.02 \text{ \AA}$) than in the *meso*, while the $\angle \text{S–Mn–S}$ is quite different ($92.7(1)^\circ$ for the *DL* versus $103.6(1)^\circ$ for the *meso*).

3.4. Complexes of L^5 and L^6

The complexes of these two ligands are generally more soluble in non-polar solvents than those of L^3 and L^4 . For the spirocyclic thioether L^5 , the complexes $[\text{Mo}(\text{CO})_4(\text{L}^5)]$, $[\text{W}(\text{CO})_4(\text{L}^5)]$, $[(\text{CO})_4\text{Mo}(\mu\text{-L}^5)\text{Mo}(\text{CO})_4]$ and $[\text{Mn}(\text{CO})_3\text{Cl}(\text{L}^5)]$ were isolated and fully characterised, their spectroscopic properties being much as expected. Crystal structures were obtained for two forms of $[\text{W}(\text{CO})_4(\text{L}^5)]$, the dinuclear $[(\text{CO})_4\text{Mo}(\mu\text{-L}^5)\text{Mo}(\text{CO})_4]$ and for $[\text{Mn}(\text{CO})_3\text{Cl}(\text{L}^5)]$ which reveal some interesting structural features. Yellow crystals of $[\text{W}(\text{CO})_4(\text{L}^5)]$ obtained from CH_2Cl_2 /hexane were found to contain the *DL* invertomer of the κ^2 coordinated ligand (Fig. 9a and Table 8) whilst a second set of crystals obtained from the same solvent mixture showed some small amount of disorder but contained the corresponding κ^2 coordinated *meso* invertomer (Fig. 9b and Table 8). Although the W–C and W–S distances are not significantly different and the axial carbonyl groups ($\text{C13–W1–C12} \sim 175^\circ$) are bent away from the dithioether, the notable difference is in the S1–W1–S2 chelate angle which is some 3° wider in the *meso* form, a similar trend but smaller than in the dinuclear manganese complex of L^3 . The dinuclear $[(\text{CO})_4\text{Mo}(\mu\text{-L}^5)\text{Mo}(\text{CO})_4]$ (Fig. 10 and Table 9) has both chelating S_2 units in the *DL* forms and the two Mo environments are very similar. In contrast, the $[\text{Mn}(\text{CO})_3\text{Cl}(\text{L}^5)]$ (Fig. 11 and Table 10) contains a *meso*-1 form of κ^2 coordinated ligand with both SME groups on the same side of the MnC_2S_2 plane as the chloride ligand. The

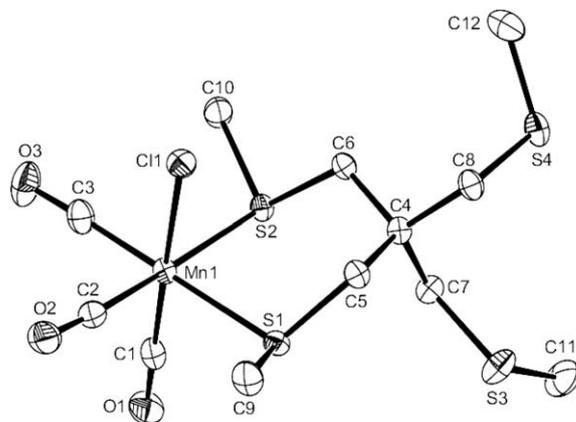


Fig. 11. Structure of $[\text{Mn}(\text{CO})_3\text{Cl}(\text{L}^5)]$ showing the numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

[Mo(CO)₄(L⁶)] was also isolated and is little different to the thioether analogue.

4. Conclusions

Several series of monometallic and homo-bimetallic carbonyl complexes of tetrathio- and tetraseleno-ether ligands have been prepared and characterised. The X-ray structural data reveals some interesting comparisons, particularly in those cases where structures of units containing *meso* and *DL* forms of the same ligand have been determined. Overall the spirocyclic ligand complexes appear the best candidates for attempting to prepare heterobimetallics, since the complexes have better solubility than those based upon 1,2,4,5-C₆H₂ linkages. The poor solubility of some of the latter may contribute to the disproportionation observed in some cases, with the equilibria driven by crystallisation of poorly soluble forms. Work in underway to incorporate 3d or 4d metal halide units along with the κ² coordinated metal carbonyl units from the present work into heterobimetallics.

Acknowledgement

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Appendix A. Supplementary material

CCDC 722298, 722299, 722300, 722301, 722302, 722303, 722304, 722305, 722306, 722307 and 722308 contains the supplementary crystallographic data for [L³], [L⁴], [Mo(CO)₄(L²)], [Mo(CO)₄(L³)], [Mo₂(CO)₈(L³)], [Mo(CO)₄(L⁴)], [Mn₂(CO)₆Cl₂(L³)], [W(CO)₄(L⁵)], [W(CO)₄(L⁵)], [Mo₂(CO)₈(L⁵)], [Mn(CO)₃Cl(L⁵)]. These

data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2009.03.041](https://doi.org/10.1016/j.jorganchem.2009.03.041).

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