

# Benzylic oligothioethers as ditopic ligands for Group 6 transition metal carbonyls

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The co-ordination preferences of a family of novel thioethers based on (alkylsulfanylmethyl)benzene were examined. The alkyl chain length and the number and position of the thioether substituents were varied. The ligands were synthesized by coupling the alkanethiol to the appropriate benzyl bromide or *via* the reaction of benzyl mercaptans with bromoethane;  $\text{Cs}_2\text{CO}_3$ -DMF was employed as the base-solvent mixture. The molecular structure of hexakis(propylsulfanylmethyl)benzene (**L3**) and 1,2,4,5-tetrakis(propylsulfanylmethyl)benzene (**L4**) were obtained at room temperature. Both have a crystallographic centre of symmetry. In **L3** the S-propyl substituents (“legs”) alternate “a(bove)” and “b(elow)” the plane of the benzene ring, whereas in **L4** the “legs” adopt an **abba** pattern. Several co-ordination modes of the ligands were observed. Bismetallated tetracarbonyl complexes where the ligand bridges two monometal Group 6 carbonyl fragments ( $\text{M}(\text{CO})_4$ ) were generated on reaction of  $[\text{W}(\text{CO})_4(\text{MeCN})_2]$  or  $[\text{Mo}(\text{CO})_3(\text{MeCN})_3]$  with the ligands **L1** and **L2**. The molecular structures of the resulting complexes  $[\{\text{Mo}(\text{CO})_4\}_2\text{L}]$  (**L** = **L1** or **L2** which are the pentyl analogues of **L3** and **L4** respectively) show that the conformations of the ligands change radically to accommodate the octahedral geometry about the metal centres. In all cases the metal atoms are chelated by “legs” positioned *ortho* to each other. Changing the stoichiometry of the reactions does not significantly influence the products.

## Introduction

Prior to the 1980s, relatively few thioether complexes had been prepared in comparison to those of phosphines, arsines and amines.<sup>1</sup> The development of cyclic thioethers<sup>2</sup> such as [9]aneS<sub>3</sub> and [12]aneS<sub>3</sub> redressed this imbalance, though subsequently it became clear that the macrocyclic effect of crown ethers was considerably less than for the analogous crown ethers. The recent resurgence in acyclic polythioether chemistry has resulted in reports of the synthesis of monometal complexes<sup>3</sup> and linear organometallic co-ordination polymers.<sup>4</sup>

In principle, thioether ligands possess unusual potential for structural control in inorganic chemistry. On the one hand divalent sulfur has a high affinity for a wide range of metallic elements. On the other it is easily manipulated by synthetic organic chemistry. Carbon-sulfur bonds are readily created through electrophilic attack on thiolates, without creation of the stereogenic centres which so complicate phosphine chemistry. Elaborate polysulfide ligands are readily conceived, and are realistic targets for synthesis.

Herein we report some initial results from a programme on the design, synthesis and study of extended non-macrocyclic polythioether ligands. The ligands studied, mainly **L1**–**L4** (see Chart 1), are still quite simple but are interesting in that their sulfur atoms are widely spaced and cannot co-ordinate simultaneously to a single metal atom. By design, they provide scope for an expanding multidimensional framework to support a variety of bridging metal atoms. The 1,3-bis(alkylsulfanylmethyl) substitution pattern present in **L2** and **L4** has previously appeared in orthopalladation reagents.<sup>4,5</sup> However, in the present work CH insertion is avoided and a different co-ordination pattern is observed. As far as we are aware, the hexa-(alkylsulfanylmethyl) pattern of **L1** and **L3** has no precedent in transition metal chemistry; previous work on similar systems concentrated on their host-guest properties<sup>6,7</sup> or their use as a support for polyoxygenated chains.<sup>8</sup> Related ligand geometries such as “star polysulfoxides”,<sup>9</sup> tripodal tri/hexathiols<sup>10</sup> and

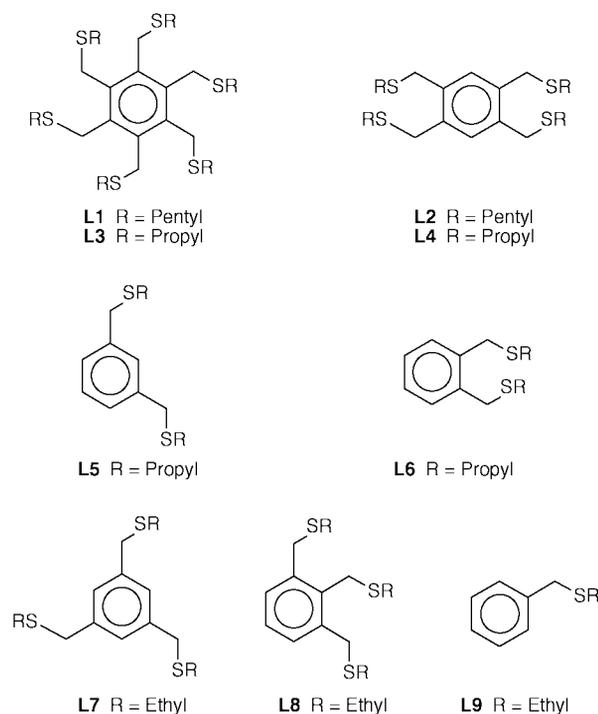


Chart 1

“coelenterands”<sup>11</sup> have recently been reported. The benzylic methylene groups in **L1** and **L3** allow the S-donor atoms to deviate from the planarity of the benzene ring, distinguishing these ligands from earlier hexakis aromatic thioether systems with direct S-Ar bonds.<sup>12,13</sup>

Thioethers have been treated with a large range of transition metal cations but zerovalent metal fragments are more unusual. In view of this, Group 6 transition metal carbonyls were used as a starting point to investigate the co-ordinating preferences

of these novel ligands. An advantage of preparing metal carbonyl complexes is that they have an additional spectroscopic handle. IR gives an indication of the number of carbonyl groups, geometry of the metal carbonyl fragment and the nature of the metal environment(s). Some examples of structurally characterised Group 6 metal thioether complexes include:  $[\text{Cr}(\text{CO})_4\text{L}]$  ( $\text{L} = \text{C}_6(\text{SMe})_6$ ,<sup>12</sup> or  $\text{RS}(\text{CH}_2)_n\text{SR}$ ,<sup>14</sup>  $n = 1$  or  $2$ ),  $[\{\text{Mo}(\text{CO})_4\}_2\text{L}]$  ( $\text{L} = 2,6,15,19\text{-tetrathia}[7.7]\text{paracyclophane}$ )<sup>15</sup> and  $[\text{Mo}(\text{CO})_3\text{L}]$  ( $\text{L} = [9]\text{janeS}_3$ ).<sup>16</sup>

## Results and discussion

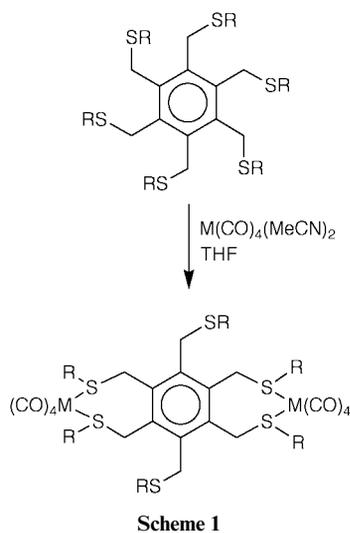
### (a) Synthesis

The ligands **L1–L6** were prepared *via* the coupling of each alkanethiol to the appropriate benzyl bromides or in the case of **L7**, **L8** and **L9** *via* the reaction of benzyl mercaptans with bromoethane. The base–solvent mixture employed was  $\text{Cs}_2\text{CO}_3$ –DMF as is also common for macrocyclisation reactions. This is in contrast to the literature preparations for analogous systems which use sodium alkoxides in ethanol and require reflux.<sup>5</sup>

The synthesis of Group 6 metal carbonyl complexes *via* reflux of the hexacarbonyl with the appropriate ligand is well documented. However more controlled reactions result from the use of intermediates with labile ligands, such as  $[\text{Mo}(\text{CO})_4(\text{MeCN})_2]$  or  $[\text{Cr}(\text{CO})_3(\text{C}_7\text{H}_8)]$ , where high temperatures are not required.<sup>17</sup> The literature procedures<sup>18</sup> for the generation of  $[\text{M}(\text{CO})_4(\text{MeCN})_2]$  were modified for  $\text{M} = \text{Cr}$  or  $\text{W}$  to include an initial photolysis step because the reported thermal reactions were found to be inefficient. As previously reported,<sup>19</sup> even lengthy reflux was found to give a significant amount of  $[\text{M}(\text{CO})_5]$  ( $\text{M} = \text{Cr}$ ) and unchanged  $[\text{M}(\text{CO})_6]$  ( $\text{M} = \text{W}$ ).

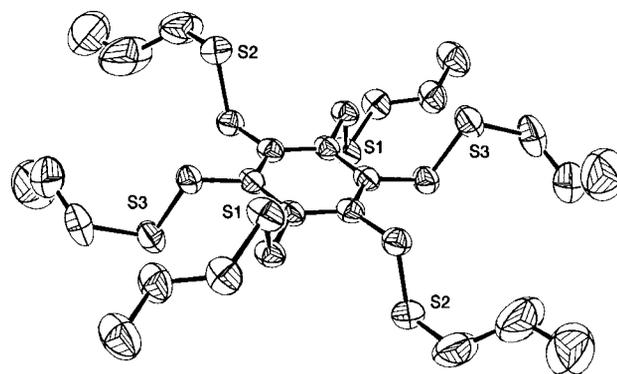
The clean preparation of  $\text{Cr}(\text{CO})_5$  complexes requires an alternative route in which the labile ligand is an olefin, here cyclooctene,<sup>20</sup> and the solvent is non-polar. The presence of co-ordinating solvents, such as MeCN or THF, compete with the thioether for metal complexation.

Bismetallated tetracarbonyl complexes were readily formed by stirring the acetonitrile intermediates  $[\text{M}(\text{CO})_4(\text{MeCN})_2]$  in the presence of the ligands **L1** and **L2** (shown for **L1** in Scheme 1). Even starting from the tricarboxyl acetonitrile deriv-

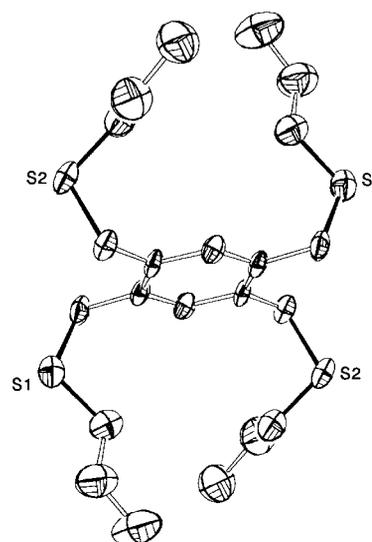


ative  $[\text{Mo}(\text{CO})_3(\text{MeCN})_3]$  the tetracarbonyl  $[\{\text{Mo}(\text{CO})_4\}_2\text{L}]$  ( $\text{L} = \text{L1}$  or **L2**) complexes were isolated. This is not without precedent and has been reported to result from the release of CO from the decomposition of some of the  $[\text{Mo}(\text{CO})_3(\text{MeCN})_3]$  intermediate.<sup>21</sup>

Changing the stoichiometry of the reactions does not significantly influence the products. Excess of metal reagent with **L1** does not give  $[\{\text{M}(\text{CO})_4\}_3\text{L1}]$  and excess of ligand does not give primarily  $[\text{M}(\text{CO})_4\text{L1}]$ . Only ligands with thioethers related



**Fig. 1** An ORTEX<sup>22</sup> drawing of the structure of **L3** (thermal ellipsoids have been drawn at 40% probability level, hydrogen atoms have been omitted for clarity).



**Fig. 2** An ORTEX drawing of the structure of **L4**. Details as in Fig. 1.

*ortho* to each other co-ordinate to give stable metal complexes. Reaction of the acetonitriles with ligands where the donors are *meta* e.g. **L5**, **L7** did not lead to stable complexes. This is attributed to the spatial positioning of the donors which are too far apart (4.6 Å by molecular modelling) to chelate to a *cis*-octahedral metal geometry. In the absence of a suitable chelate ring, the metal fragment is not stable to the reaction conditions, as seen from the reaction of  $[\text{Mo}(\text{CO})_3(\text{MeCN})_3]$  with two equivalents of **L9**, which also failed to yield stable complexes. Molybdenum complexes of the other ligands were successfully synthesized and isolated yielding  $[\{\text{M}(\text{CO})_4\}_2\text{L3}]$ ,  $[\{\text{M}(\text{CO})_4\}_2\text{L4}]$ ,  $[\text{Mo}(\text{CO})_4\text{L6}]$  and  $[\text{Mo}(\text{CO})_4\text{L8}]$ ;  $[\text{Cr}(\text{CO})_5\text{L9}]$  was synthesized by coupling  $[\text{Cr}(\text{CO})_5(\text{C}_8\text{H}_{14})]$  with **L9** in pentane.

### (b) Crystal structures

Data were collected on the propylsulfanyl ligands **L3** and **L4** (rather than the pentylsulfanyl **L1** and **L2**) as these were solids (not oils) at room temperature. Examination of the structure of **L3** shows that it has a crystallographic centre of symmetry. The S-propyl substituents alternate “a(bove)” and “b(elow)” the plane of the benzene ring in an **abab** pattern (as illustrated in Fig. 1). This is the expected conformation based on reported structures of other hexasubstituted benzenes<sup>5</sup> and has been attributed to the minimisation of steric interactions between neighbouring “legs”. The structure of **L4** (Fig. 2) also has a centre of symmetry. In this case it is because the legs adopt an **abba** pattern. Again this conformation minimises steric constraints.

Upon complexation to two  $\text{Mo}(\text{CO})_4$  fragments, the conformation of the ligands is radically changed to accommodate

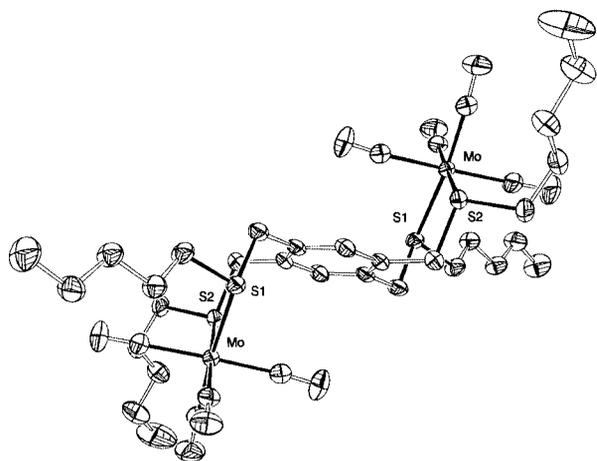


Fig. 3 An ORTEX drawing of the structure of  $[\{\text{Mo}(\text{CO})_4\}_2\text{L2}]$ . Details as in Fig. 1.

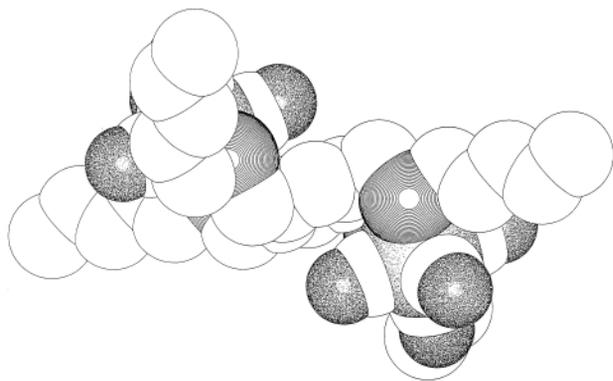


Fig. 4 Space-filling diagram of the structure of  $[\{\text{Mo}(\text{CO})_4\}_2\text{L2}]$  (hydrogen atoms have been omitted for clarity) illustrating the orientation of the carbonyl groups.

the octahedral geometry about the metal centre. In the simpler derivative,  $[\{\text{Mo}(\text{CO})_4\}_2\text{L2}]$  (Fig. 3) where **L2** is the pentyl analogue of **L4**, the “legs” are required to adopt an **aabb** conformation to chelate to the metal atoms. The metal bridges “legs” positioned *ortho* to each other exclusively. The two sides of the molecule, and hence the metal environments, are identical. The metal atoms are positioned above and below the plane of the benzene ring, as required by the centre of symmetry associated with  $P\bar{1}$ . A unique carbonyl ligand from each metal centre is positioned directly below the benzene ring at a distance of 3.6 Å. This may be due to some  $\pi$ – $\pi$  type interaction between the benzene ring and  $\pi$  cloud of the carbonyl ligand or simply a result of crystal packing. This carbonyl, C(16)–O(1), can be viewed upon looking through the centre of the benzene ring and has the parallel geometry required to maximise such an interaction (Fig. 4).

The structure of  $[\{\text{Mo}(\text{CO})_4\}_2\text{L1}]$  (Fig. 5), where **L1** is the pentyl analogue of **L3**, is more complicated. Independent of reaction stoichiometry, only two out of a possible three  $\text{Mo}(\text{CO})_4$  fragments are co-ordinated. This is probably due to the steric constraints that would be imposed by complete complexation. The unco-ordinated legs play an important role in determining the conformation of the complex. Situated *para* relative to each other, they force the two metal centres to the same side of the benzene ring. The new arrangement of the legs is now **aabaab**. In contrast to  $[\{\text{Mo}(\text{CO})_4\}_2\text{L2}]$ , the two metal carbonyl fragments are not crystallographically related either by a centre of symmetry or a mirror plane. It is only possible for *one* metal centre, Mo(1), to direct a carbonyl ligand [C(24)–O(24)] under the benzene ring for steric reasons. The other tetracarbonyl fragment, Mo(2)(CO)<sub>4</sub>, “hangs” outside the “bowl” generated by the four co-ordinated legs (Fig. 6).

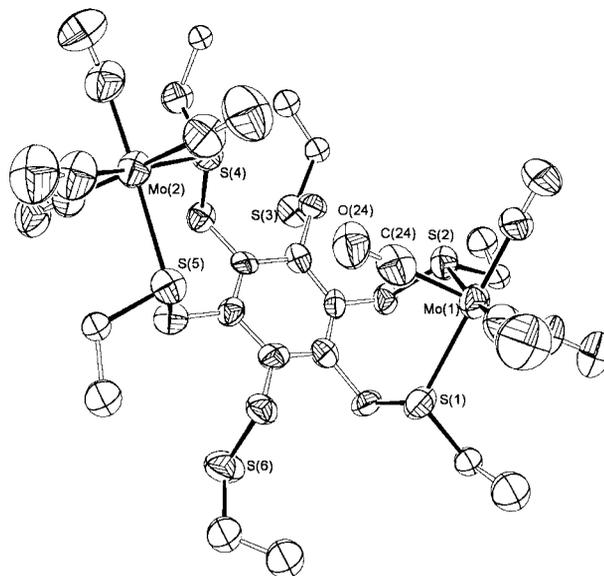


Fig. 5 An ORTEX drawing of the structure of  $[\{\text{Mo}(\text{CO})_4\}_2\text{L1}]$ . Details as in Fig. 1. The three terminal C atoms of each pentyl group have not been shown. The high disorder associated with these groups meant that their thermal ellipsoids obscured the metal benzene skeleton.

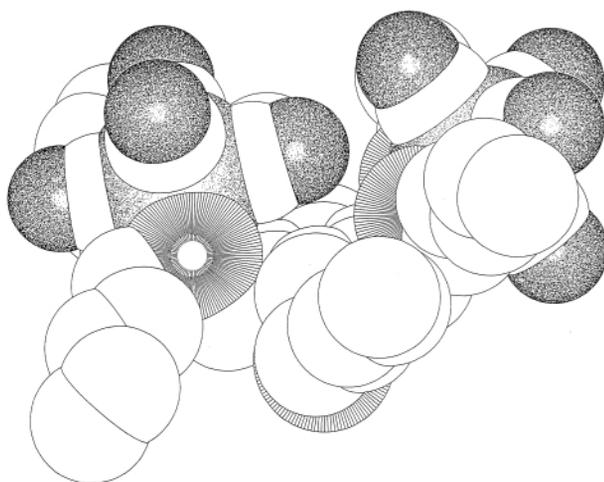


Fig. 6 Space-filling diagram of the structure of  $[\{\text{Mo}(\text{CO})_4\}_2\text{L1}]$  (hydrogen atoms have been omitted for clarity) illustrating the orientation of the carbonyl groups.

In both molybdenum structures the Mo–S distances are consistent with the literature (2.3–2.5 Å). The geometry about the S atoms is pyramidal with one remaining lone pair. Unfortunately due to poor crystal quality and the severe disorder of the pentyl groups which could not be satisfactorily modelled, the bond lengths and bond angles derived from the molecular structure of  $[\{\text{Mo}(\text{CO})_4\}_2\text{L1}]$  show large e.s.d. values and cannot reliably be discussed in any detail.

### NMR Spectra

For the “free” ligands it was noticed that <sup>1</sup>H NMR signals shift upfield with increasing distance from the benzene ring, *i.e.* along the alkyl chain. However in the <sup>13</sup>C NMR spectra this sequence is interrupted with the benzyl CH<sub>2</sub>S being further upfield than the SCH<sub>2</sub>R signals and in the pentyl derivatives the SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>R being further upfield than the SCH<sub>2</sub>CH<sub>2</sub>–CH<sub>2</sub>R. This phenomenon is a common feature of the <sup>13</sup>C NMR spectra of both the ligands and the complexes.

In the <sup>1</sup>H/<sup>13</sup>C NMR spectra of the complexes the downfield shifts (generally 0.5/10 ppm) of SCH<sub>2</sub>R with respect to the “free” ligand are most characteristic of complexation. In con-

**Table 1** Crystal data and refinement details for **L3**, **L4**, [ $\{\text{Mo}(\text{CO})_4\}_2\text{L1}$ ] and [ $\{\text{Mo}(\text{CO})_4\}_2\text{L2}$ ]

	<b>L3</b>	<b>L4</b>	[ $\{\text{Mo}(\text{CO})_4\}_2\text{L1}$ ]	[ $\{\text{Mo}(\text{CO})_4\}_2\text{L2}$ ]
Molecular formula	C <sub>30</sub> H <sub>54</sub> S <sub>6</sub>	C <sub>22</sub> H <sub>38</sub> S <sub>4</sub>	C <sub>50</sub> H <sub>78</sub> Mo <sub>2</sub> O <sub>8</sub> S <sub>6</sub>	C <sub>38</sub> H <sub>54</sub> Mo <sub>2</sub> O <sub>8</sub> S <sub>4</sub>
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 1̄	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 1̄
<i>a</i> /Å	9.6291(8)	5.127(2)	16.660(2)	7.783(2)
<i>b</i> /Å	16.0389(8)	9.294(2)	12.840(2)	11.458(1)
<i>c</i> /Å	11.5569(11)	13.945(4)	28.207(3)	13.551(2)
<i>a</i> /°		104.866(2)		72.341(9)
<i>β</i> /°	90.078(4)	94.880(3)	98.71(1)	77.92(1)
<i>γ</i> /°		100.868(2)		79.18(2)
<i>V</i> /Å <sup>3</sup>	1784.8(2)	624.5(3)	5965(2)	1115.9(3)
<i>Z</i>	2	1	2	1
$\mu(\text{Mo-K}\alpha)/\text{cm}^{-1}$	0.208	0.385	0.676	0.794
Total no. reflections	3029	1209	7588	2972
Independent reflections	2878	1147	7282	2725
<i>R</i> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0448	0.0580	0.1184	0.0269
<i>wR</i> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.1580	0.1449	0.2314	0.0548

trast the benzyl CH<sub>2</sub>S resonances do not shift as significantly in the <sup>1</sup>H NMR spectra on co-ordination and are less diagnostic.

At room temperature, unexpectedly complex coupling and broadening of the benzyl signals in <sup>1</sup>H NMR spectra of the *hexakis* complexes [ $\{\text{Mo}(\text{CO})_4\}_2\text{L1/3}$ ] (but not the “free” ligands) is observed. This type of effect has been reported for *uncomplexed* hexasubstituted (polyether)(sulfanylmethyl)benzenes and was attributed to steric overcrowding.<sup>6</sup> As samples are warmed (35 °C) the benzyl regions sharpen to give two singlets integrating for the “co-ordinated” protons (H<sup>\*</sup>, for numbering scheme see diagram in Experimental section) and unco-ordinated (H) protons. On cooling (−50 °C), the benzyl region, although sharper, is a complex set of multiplets and spreads over a larger frequency range. In addition, the triplet corresponding to “co-ordinated” H<sup>2\*</sup> and H<sup>2</sup> splits. No significant temperature dependency is observed in <sup>13</sup>C NMR spectra.

## Conclusion

The co-ordination of a series of (alkylsulfanylmethyl)benzene ligands to Group 6 metal carbonyl fragments has been illustrated. The ligands are readily synthesized and bischelate to octahedral metal centres. The benzyl CH<sub>2</sub> introduces a degree of flexibility allowing the ligands to rearrange so as to minimise steric interactions both in the free and co-ordinated forms. Co-ordination is exclusively *via* the *ortho* substituents on the ligand. Chelation dominates so that only bischelated complexes are isolated. The syntheses are ligand-directed in that irrespective of the reaction stoichiometry two metal centres are bischelated. This work has established that the number of metal centres co-ordinated can be controlled by the number and position of the thioether substituents on the benzene ring. Modification of the ligand design should permit the synthesis of preorganised ligands that will act as templates for the generation of metal clusters. Work is ongoing but we have already shown the versatile nature of thioethers as ligands in transition metal chemistry.

## Experimental

### General

All syntheses involving transition metal compounds were carried out under an argon atmosphere using standard Schlenk techniques. Dry, oxygen-free solvents were used for reactions but not for chromatographic separations, which were undertaken in air. Acetonitrile, CH<sub>2</sub>Cl<sub>2</sub> and DMF were distilled from CaH<sub>2</sub>, THF and hexane from sodium–benzophenone; CHCl<sub>3</sub>-*d* was vacuum distilled from molecular sieves. The IR spectra were recorded on a Perkin-Elmer Paragon 2000 spectrophotometer, mass spectra on a Micromass AutospecQ mass

spectrometer operating in a FAB<sup>+</sup> mode and NMR spectra on Bruker MSL 300 and DPX 400 spectrometers operating at 300.13 and 400.13 MHz for <sup>1</sup>H and 75.47 and 100.61 MHz for <sup>13</sup>C respectively. All NMR spectra were recorded in CHCl<sub>3</sub>-*d* and referenced relative to SiMe<sub>4</sub>. Hexakis(bromomethyl)benzene,<sup>5</sup> 1,3,5-tris(sulfanylmethyl)benzene,<sup>23</sup> 1,2,3-tris(sulfanylmethyl)benzene,<sup>23</sup> [Mo(CO)<sub>3</sub>(MeCN)<sub>3</sub>]<sup>18</sup> and [Cr(CO)<sub>5</sub>(C<sub>8</sub>H<sub>14</sub>)]<sup>20</sup> were made following published methods. Unless otherwise stated reagents were used as purchased and without further purification.

### Crystallography

Data were collected on an Enraf-Nonius CAD-4 diffractometer (Mo-K $\alpha$ ,  $\lambda$  = 0.71073 Å radiation, graphite monochromator,  $\omega$ –2 $\theta$  scan mode) at 20 °C. The crystal data and experimental parameters are summarised in Table 1. The final cell parameters were determined using the Celdim routine. It was not found necessary to apply decay or absorption corrections.

The structures were solved by automatic direct methods using SHELXS 86<sup>24</sup> and refined by full-matrix least-squares analysis on *F*<sup>2</sup> with SHELXL 93.<sup>25</sup> Apart from the structure of [ $\{\text{Mo}(\text{CO})_4\}_2\text{L1}$ ], all the non-hydrogen atoms were refined anisotropically. The hydrogen atoms which could not be located from subsequent Fourier difference maps were added in calculated positions, “riding” on the parent C atom. Poor crystal quality in the case of [ $\{\text{Mo}(\text{CO})_4\}_2\text{L1}$ ] meant that some of the outlying C atoms of the alkyl chains could not be satisfactorily located and required fixing. However the important structural features, such as those of the phenyl backbone and the local environments about both metal centres, were well refined. Diagrams of the structures were drawn using ORTEX<sup>22</sup> and SCHAKAL.<sup>26</sup>

CCDC reference number 186/1742.

### Synthesis of the ligands

**Hexakis(pentylsulfanylmethyl)benzene L1.** Pentanethiol (0.50 g, 0.43 mL, 4.6 mmol) was added to a suspension of hexakis(bromomethyl)benzene (0.50 g, 0.77 mmol) and caesium carbonate (0.77 g, 2.4 mmol) in DMF (5 mL). The reaction was allowed to proceed for 12 h at room temperature then HCl (0.1 M, 25 mL) was added and extracted into diethyl ether (2 × 25 mL). The combined diethyl ether layers were dried over MgSO<sub>4</sub> and the solvent was removed by a rotary evaporator. The final traces of DMF were removed from the oily residue by flash chromatography on silica (eluent hexane–ethyl acetate 10:1). The pure product was recovered as a colourless oil that was soluble in most organic solvents (0.54 g, 93%) (Found: C, 65.0; H, 9.9. C<sub>7</sub>H<sub>13</sub>S requires C, 65.1; H, 10.0%). All analyses were performed by the analytical service at University College Dublin.  $\delta_{\text{H}}$ (300 MHz) 4.04 (12 H, s, aryl CH<sub>2</sub>S), 2.63 (12 H, t,

$J(\text{HH})$  7.6,  $\text{CH}_2\text{SCH}_2$ , 1.68 (12 H, qn,  $J(\text{HH})$  7.2,  $\text{SCH}_2\text{CH}_2$ ), 1.36 (24 H, m,  $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$ ) and 0.91 (18 H, t,  $J(\text{HH})$  7 Hz, Me).  $\delta_{\text{C}}$ (300 MHz) 31.0 (aryl  $\text{CH}_2\text{S}$ ), 33.7 ( $\text{CH}_2\text{SCH}_2$ ), 29.5 ( $\text{SCH}_2\text{CH}_2$ ), 31.1 ( $\text{SCH}_2\text{CH}_2\text{CH}_2$ ), 22.3 ( $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$ ), 14.0 (Me) and 135.8 (aryl).

Compounds **L2–L6** were synthesized *via* a similar procedure. Their yields (based on 0.5 g starting bromide) and spectroscopic data are reported below. The oils or oily solids **L2**, **L4–L9** were submitted for elemental analysis but solvent inclusion meant that the results were not adequate for publication. In some cases elemental analyses were successfully obtained for complexes generated from the ligands ( $\{\text{Mo}(\text{CO})_4\}_2\text{L3}$ ,  $[\text{Mo}(\text{CO})_4\text{L8}]$  and  $[\text{Cr}(\text{CO})_5\text{L9}]$ ).

**1,2,4,5-Tetrakis(pentylsulfanylmethyl)benzene L2.** Yield 0.52 g (96%).  $\delta_{\text{H}}$  (300 MHz) 3.83 (8 H, s, aryl  $\text{CH}_2\text{S}$ ), 2.46 (8 H, t,  $J(\text{HH})$  7.3,  $\text{CH}_2\text{SCH}_2$ ), 1.57 (8 H, m,  $\text{SCH}_2\text{CH}_2$ ), 1.32 (16 H, m,  $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$ ), 0.89 (12 H, t,  $J(\text{HH})$  7 Hz, Me) and 7.12 (2 H, s,  $\text{CH}_{\text{aryl}}$ ).  $\delta_{\text{C}}$  31.1 (aryl  $\text{CH}_2\text{S}$ ), 33.2 ( $\text{CH}_2\text{SCH}_2$ ), 29.1 ( $\text{SCH}_2\text{CH}_2$ ), 32.0 ( $\text{SCH}_2\text{CH}_2\text{CH}_2$ ), 22.3 ( $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$ ), 14.0 (Me), 135.3 ( $\text{C}_{\text{quat/aryl}}$ ) and 132.6 ( $\text{CH}_{\text{aryl}}$ ).

**Hexakis(propylsulfanylmethyl)benzene L3.** Yield 0.44 g (95%) (Found: C, 59.6; H, 8.9.  $\text{C}_5\text{H}_9\text{S}$  requires C, 59.4; H, 8.7%).  $\delta_{\text{H}}$ (300 MHz) 4.04 (12 H, s, aryl  $\text{CH}_2\text{S}$ ), 2.62 (12 H, t,  $J(\text{HH})$  7.0,  $\text{CH}_2\text{SCH}_2$ ), 1.73 (m, 12 H,  $\text{SCH}_2\text{CH}_2$ ) and 1.04 (t, 18 H,  $J = 7.2$  Hz, Me).  $\delta_{\text{C}}$  30.9 (aryl  $\text{CH}_2\text{S}$ ), 35.8 ( $\text{CH}_2\text{SCH}_2$ ), 22.9 ( $\text{SCH}_2\text{CH}_2$ ), 13.5 (Me) and 135.8 (aryl).

**1,2,4,5-Tetrakis(propylsulfanylmethyl)benzene L4.** Yield 0.43 g (91%).  $\delta_{\text{H}}$ (300 MHz) 3.83 (8 H, s, aryl  $\text{CH}_2\text{S}$ ), 2.44 (8 H, t,  $J(\text{HH})$  7.2,  $\text{CH}_2\text{SCH}_2$ ), 1.61 (8 H, m,  $\text{SCH}_2\text{CH}_2$ ), 0.96 (16 H, t,  $J(\text{HH})$  7.5 Hz, Me) and 7.11 (2 H, s,  $\text{CH}_{\text{aryl}}$ ).  $\delta_{\text{C}}$  31.4 (aryl  $\text{CH}_2\text{S}$ ), 36.5 ( $\text{CH}_2\text{SCH}_2$ ), 22.7 ( $\text{SCH}_2\text{CH}_2$ ), 13.5 (Me), 135.3 ( $\text{C}_{\text{quat/aryl}}$ ) and 132.7 ( $\text{CH}_{\text{aryl}}$ ).

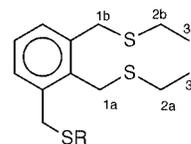
**1,3-Bis(propylsulfanylmethyl)benzene L5.** Yield 0.47 g (98%).  $\delta_{\text{H}}$ (400 MHz) 3.71 (4 H, s, aryl  $\text{CH}_2\text{S}$ ), 2.42 (4 H, t,  $J(\text{HH})$  7.0,  $\text{CH}_2\text{SCH}_2$ ), 1.61 (4 H, m,  $\text{SCH}_2\text{CH}_2$ ), 0.98 (6 H, t,  $J(\text{HH})$  7.2 Hz, Me) and 7.20 (4 H, m,  $\text{CH}_{\text{aryl}}$ ).  $\delta_{\text{C}}$  33.0 (aryl  $\text{CH}_2\text{S}$ ), 35.5 ( $\text{CH}_2\text{SCH}_2$ ), 22.1 ( $\text{SCH}_2\text{CH}_2$ ), 13.0 (Me), 138.4 ( $\text{C}_{\text{quat/aryl}}$ ), 128.8, 128.0 and 126.9 ( $\text{CH}_{\text{aryl}}$ ).

**1,2-Bis(propylsulfanylmethyl)benzene L6.** Yield 0.47 g (98%).  $\delta_{\text{H}}$ (300 MHz) 3.91 (4 H, s, aryl  $\text{CH}_2\text{S}$ ), 2.48 (4 H, t,  $J(\text{HH})$  7.0,  $\text{CH}_2\text{SCH}_2$ ), 1.63 (4 H, m,  $\text{SCH}_2\text{CH}_2$ ), 0.99 (6 H, t,  $J(\text{HH})$  7.2 Hz, Me), 7.21 and 7.20 (4 H, m, m,  $\text{CH}_{\text{aryl}}$ ).  $\delta_{\text{C}}$  33.2 (aryl  $\text{CH}_2\text{S}$ ), 33.7 ( $\text{CH}_2\text{SCH}_2$ ), 22.3 ( $\text{SCH}_2\text{CH}_2$ ), 13.0 (Me), 136.2 ( $\text{C}_{\text{quat/aryl}}$ ), 130.0 and 126.7 ( $\text{CH}_{\text{aryl}}$ ).

**1,3,5-Tris(ethylsulfanylmethyl)benzene L7.** Bromoethane (1.6 mL, 15 mmol) was added to a suspension of 1,3,5-tris(sulfanylmethyl)benzene (1 g, 4.6 mmol) and caesium carbonate (1.12 g, 3.4 mmol) in DMF (5 mL). The reaction was allowed to proceed for 12 h at room temperature, then HCl (0.1 M, 25 mL) was added and extracted into diethyl ether (2 × 25 mL). The combined diethyl ether layers were dried over  $\text{MgSO}_4$  and the solvent was removed by a rotary evaporator. The final traces of DMF were removed from the oily residue by flash chromatography on silica (eluent hexane–ethyl acetate 10:1). The pure product was recovered as a colourless oil (1.20 g, 86%).  $\delta_{\text{H}}$ (300 MHz) 3.68 (6 H, s, aryl  $\text{CH}_2\text{S}$ ), 2.43 (8 H, q,  $J(\text{HH})$  7.2,  $\text{CH}_2\text{SCH}_2$ ), 1.22 (9 H, t,  $J(\text{HH})$  7.5 Hz, Me) and 7.14 (3 H, s,  $\text{CH}_{\text{aryl}}$ ).  $\delta_{\text{C}}$  33.1 (aryl  $\text{CH}_2\text{S}$ ), 22.0 ( $\text{CH}_2\text{SCH}_2$ ), 12.9 (Me), 134.7 ( $\text{C}_{\text{quat/aryl}}$ ) and 128.1 ( $\text{CH}_{\text{aryl}}$ ).

**1,2,3-Tris(ethylsulfanylmethyl)benzene L8.** By a similar procedure to that for **L7** (1.35 g, 97%).  $\delta_{\text{H}}$ (400 MHz) 4.10 (2 H, s,  $\text{H}^{\text{1a}}$ ), 3.19 (4 H, s,  $\text{H}^{\text{1b}}$ ), 2.67 (2 H, q,  $J(\text{HH})$  7.4,  $\text{H}^{\text{2a}}$ ), 2.54 (4 H, q,  $J(\text{HH})$  7.5,  $\text{H}^{\text{2b}}$ ), 1.38 (3 H, t,  $J(\text{HH})$  7.4,  $\text{H}^{\text{3a}}$ ), 1.29 (6 H, t,

$J(\text{HH})$  7.5 Hz,  $\text{H}^{\text{3b}}$ ) and 7.17 (3 H, m,  $\text{CH}_{\text{aryl}}$ ).  $\delta_{\text{C}}$  33.2 ( $\text{C}^{\text{2a}}$ ), 28.6 ( $\text{C}^{\text{1a}}$ ), 27.0 ( $\text{C}^{\text{1b}}$ ), 25.7 ( $\text{C}^{\text{2b}}$ ), 14.4 ( $\text{C}^{\text{3b}}$ ), 14.1 ( $\text{C}^{\text{3a}}$ ), 129.0, 126.5 ( $\text{CH}_{\text{aryl}}$ ) and 133.0 ( $\text{C}_{\text{quat/aryl}}$ ).

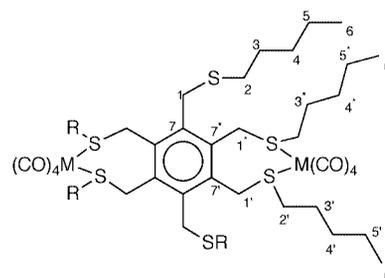


**Ethylsulfanylmethylbenzene L9.** This was prepared as for **L8** starting from phenylmethanethiol (0.5 g, 4 mmol), bromoethane (0.44 g, 4 mmol) and caesium carbonate (1.3 g, 4 mmol). The pure product was recovered as a colourless oil that was soluble in most organic solvents (0.48 g, 78%).  $\delta_{\text{H}}$ (400 MHz) 3.75 (2 H, s, aryl  $\text{CH}_2\text{S}$ ), 2.48 (2 H, q,  $J(\text{HH})$  5,  $\text{CH}_2\text{SCH}_2$ ), 1.25 (3 H, t,  $J(\text{HH})$  7.5 Hz, Me) and 7.30 (5 H, m,  $\text{CH}_{\text{aryl}}$ ).  $\delta_{\text{C}}$  33.5 (aryl  $\text{CH}_2\text{S}$ ), 24.8 ( $\text{CH}_2\text{SCH}_2$ ), 14.0 (Me), 138.2 ( $\text{C}_{\text{quat/aryl}}$ ), 128.4, 128.0 and 126.4 ( $\text{CH}_{\text{aryl}}$ ).

### Synthesis of complexes

Suitable elemental analyses could not be obtained for all the metal complexes. This was due to difficulties in separating the pure product from unchanged ligand: prolonged or repeated column chromatography results in the degradation of the product to metal residues that stick to the silica and “free” ligand which travels at the same rate as the product. In these cases mass spectra were obtained.

**$\mu$ -Hexakis(pentylsulfanylmethyl)benzenebis(tetracarbonylmolybdenum)  $[\{\text{Mo}(\text{CO})_4\}_2\text{L1}]$ .** A solution of hexakis(pentylsulfanylmethyl)benzene (0.25 g, 0.32 mmol) in THF (20 mL) was added dropwise to a solution of  $[\text{Mo}(\text{CO})_3(\text{MeCN})_3]$  (0.30 g, 0.99 mmol) in THF (20 mL) at 0 °C. The resulting solution gradually became brown and was allowed to stir for 12 h at room temperature. Evaporation of the solvent under reduced pressure gave a brown oil. Purification using column chromatography on silica (first eluent hexane–ethyl acetate 10:1, second hexane– $\text{CH}_2\text{Cl}_2$  1:1) yielded a yellow solid which after washing (hexane, 2 × 20 mL) was crystallised from hexane– $\text{CH}_2\text{Cl}_2$  at –20 °C. Recrystallisation gave yellow crystals suitable for single crystal X-ray analysis (0.23 g, 60%) (Found: C, 50.4; H, 6.2.  $\text{C}_{25}\text{H}_{39}\text{MoO}_4\text{S}_3$  requires C, 50.4; H, 6.6%).  $\tilde{\nu}/\text{cm}^{-1}(\text{CO})$  (KBr disk) 2026w, 1949w, 1917s, 1890s and 1845m.  $\delta_{\text{H}}$ (300 MHz) 4.4–3.8 (12 H, br m,  $\text{H}^{\text{1}}$ ,  $\text{H}^{\text{1*}}$ ), 2.99 (8 H, br t,  $\text{H}^{\text{2*}}$ ), 2.64 (4 H, t,  $J(\text{HH})$  7.2,  $\text{H}^{\text{2}}$ ), 1.86 (8 H, m,  $\text{H}^{\text{3}}$ ), 1.70 (4 H, m,  $\text{H}^{\text{3}}$ ), 1.44 (24 H, m,  $\text{H}^{\text{4}}$ ,  $\text{H}^{\text{4*}}$ ,  $\text{H}^{\text{5}}$ ,  $\text{H}^{\text{5*}}$ ) and 0.96 (18 H, t,  $J(\text{HH})$  6.0 Hz,  $\text{H}^{\text{6}}$ ,  $\text{H}^{\text{6*}}$ ).  $\delta_{\text{C}}$  36.3, 36.0 ( $\text{C}^{\text{1}}$ ,  $\text{C}^{\text{1*}}$ ), 44.2, 44.1 ( $\text{C}^{\text{2}}$ ,  $\text{C}^{\text{2*}}$ ), 33.7 ( $\text{C}^{\text{2}}$ ), 31.1 ( $\text{C}^{\text{4}}$ ), 30.8, 30.7 ( $\text{C}^{\text{1}}$ ,  $\text{C}^{\text{4*}}$ ,  $\text{C}^{\text{4}}$ ), 29.4 ( $\text{C}^{\text{3}}$ ), 28.4, 28.2 ( $\text{C}^{\text{3}}$ ,  $\text{C}^{\text{3*}}$ ), 22.28, 22.33 ( $\text{C}^{\text{5*}}$ ,  $\text{C}^{\text{5}}$ ,  $\text{C}^{\text{5}}$ ), 13.9 ( $\text{C}^{\text{6*}}$ ,  $\text{C}^{\text{6}}$ ,  $\text{C}^{\text{6}}$ ), 138.3 ( $\text{C}^{\text{7}}$ ), 135.4, 134.0 ( $\text{C}^{\text{7}}$ ,  $\text{C}^{\text{7*}}$ ), 214.8, 215.1 (CO).



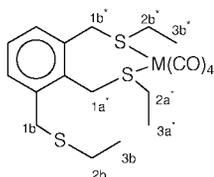
The complexes  $\{\{\text{Mo}(\text{CO})_4\}_2\text{L3}\}$ ,  $\{\{\text{Mo}(\text{CO})_4\}_2\text{L2}\}$ ,  $[\text{Mo}(\text{CO})_4\text{L6}]$  and  $[\text{Mo}(\text{CO})_4\text{L8}]$  were made by a similar procedure. Yields (based on 0.99 mmol  $[\text{Mo}(\text{CO})_3(\text{MeCN})_3]$ ) and spectral details are reported below.

**$\mu$ -Hexakis(propylsulfanylmethyl)benzene-bis(tetracarbonylmolybdenum) [ $\{\text{Mo}(\text{CO})_4\}_2\text{L3}$ ].** Yield 0.18 g (55%) (Found: C, 47.3; H, 7.8.  $\text{C}_{19}\text{H}_{27}\text{MoO}_4\text{S}_2$  requires C, 47.6; H, 8.2%).  $\tilde{\nu}/\text{cm}^{-1}(\text{CO})$  ( $\text{CH}_2\text{Cl}_2$ -hexane 1:1) 2026m, 1921s, 1901s and 1861s.  $\delta_{\text{H}}(300 \text{ MHz})$  4.4–3.8 (12 H, br m,  $\text{H}^1, \text{H}^{1*}$ ), 2.99 (8 H, br t,  $\text{H}^{2*}$ ), 2.64 (4 H, t,  $J(\text{HH})$  7.2,  $\text{H}^2$ ), 1.88 (8 H, m,  $\text{H}^{3*}$ ), 1.72 (4 H, m,  $\text{H}^3$ ), 1.13 (18 H, td,  $J(\text{HH})$  6.0, 1.8,  $\text{H}^{4*}$ ) and 1.06 (4 H, t,  $J(\text{HH})$  6.0 Hz,  $\text{H}^4$ ).  $\delta_{\text{C}}$  36.0, 35.7 ( $\text{C}^1, \text{C}^{1*}$ ), 46.3, 46.2 ( $\text{C}^2, \text{C}^{2*}$ ), 35.7 ( $\text{C}^2$ ), 30.7 ( $\text{C}^1$ ), 22.9 ( $\text{C}^3$ ), 22.03, 21.97 ( $\text{C}^3, \text{C}^{3*}$ ), 13.4, 13.3 ( $\text{C}^4, \text{C}^{4*}, \text{C}^4$ ), 138.3 ( $\text{C}_{\text{quat}}$ ), 135.5 and 134.0 ( $\text{CH}_{\text{aryl}}$ ).

**$\mu$ -1,2,4,5-Tetrakis(pentylsulfanylmethyl)benzene-bis(tetracarbonylmolybdenum) [ $\{\text{Mo}(\text{CO})_4\}_2\text{L2}$ ].** Yield 0.15 g (50%).  $\tilde{\nu}/\text{cm}^{-1}(\text{CO})$  ( $\text{CH}_2\text{Cl}_2$ -hexane 1:1) 2026m, 1918s, 1900 (sh) and 1864m.  $\delta_{\text{H}}(400 \text{ MHz})$  3.83 (8 H, s,  $\text{H}^{1*}$ ), 2.87 (8 H, t,  $J(\text{HH})$  7.5,  $\text{H}^{2*}$ ), 1.82 (8H, m,  $\text{H}^{3*}$ ), 1.44 (16 H, m,  $\text{H}^{4*}, \text{H}^{5*}$ ), 0.96 (12 H, t,  $J(\text{HH})$  7.0 Hz,  $\text{H}^{6*}$ ) and 1.44 (2 H, s,  $\text{CH}_{\text{aryl}}$ ).  $\delta_{\text{C}}$  37.0 ( $\text{C}^{1*}$ ), 42.9 ( $\text{C}^{2*}$ ), 28.1 ( $\text{C}^{3*}$ ), 30.6 ( $\text{C}^{4*}$ ), 22.3 ( $\text{C}^{5*}$ ), 14.0 ( $\text{C}^{6*}$ ), 133.8 ( $\text{C}_{\text{quat/aryl}}$ ), 135.0 ( $\text{CH}_{\text{aryl}}$ ), 215.2 and 205.9 (CO).  $m/z$  958 ( $\text{M}^+$ ) and 902 ( $\text{M}^+ - 2\text{CO}$ ).

**[1,2-Bis(propylsulfanylmethyl)benzene]tetracarbonylmolybdenum [ $\text{Mo}(\text{CO})_4\text{L6}$ ].** Yield 0.34 g (80%).  $\tilde{\nu}/\text{cm}^{-1}(\text{CO})$  ( $\text{CH}_2\text{Cl}_2$ -hexane 1:1) 2028m, 1920s, 1900s and 1860m.  $\delta_{\text{H}}(400 \text{ MHz})$  3.87 (4 H, s,  $\text{H}^{1*}$ ), 2.88 (4 H, t,  $J(\text{HH})$  7.5,  $\text{H}^{2*}$ ), 1.88 (4 H, m,  $\text{H}^{3*}$ ), 1.44 (6 H, m,  $J(\text{HH})$  7.3 Hz,  $\text{H}^4$ ), 7.36 and 7.22 (4 H, m,  $\text{CH}_{\text{aryl}}$ ).  $\delta_{\text{C}}$  37.0 ( $\text{C}^{1*}$ ), 44.4 ( $\text{C}^{2*}$ ), 21.8 ( $\text{C}^{3*}$ ), 13.1 ( $\text{C}^{4*}$ ), 133.8 ( $\text{C}_{\text{quat/aryl}}$ ), 130.9, 128.2 ( $\text{CH}_{\text{aryl}}$ ), 215.2 and 205.5 (CO).  $m/z$  462 ( $\text{M}^+$ ) and 434 ( $\text{M} - \text{CO}$ ).

**Tetracarbonyl[1,2,3-tris(ethylsulfanylmethyl)benzene]molybdenum [ $\text{Mo}(\text{CO})_4\text{L8}$ ].** Yield 0.28 g (80%) (Found: C, 44.3; H, 4.4.  $\text{C}_{19}\text{H}_{24}\text{MoO}_4\text{S}_3$  requires C, 44.8; H, 4.7%).  $\tilde{\nu}/\text{cm}^{-1}(\text{CO})$  ( $\text{CH}_2\text{Cl}_2$ -hexane 1:1) 2026m, 1921s, 1901s and 1861s.  $\delta_{\text{H}}(400 \text{ MHz})$  4.19 (2 H, s,  $\text{H}^{1a*}$ ), 3.93, 3.91 (2 H, 2 H, s, s,  $\text{H}^{1b*}, \text{H}^{1b}$ ), 3.02 (2 H, q,  $J(\text{HH})$  7.5,  $\text{H}^{2a*}$ ), 2.91 (2 H, q,  $J(\text{HH})$  7.5,  $\text{H}^{2b*}$ ), 2.53 (2 H, q,  $J(\text{HH})$  7.5,  $\text{H}^{2b}$ ), 1.52 (6 H, m,  $\text{H}^{3a*}, \text{H}^{3b*}$ ), 1.29 (3 H, t,  $J(\text{HH})$  7.5,  $\text{H}^{3b}$ ), 7.26 (2 H, d,  $J(\text{HH})$  7.6,  $\text{CH}_{\text{aryl}}^{(46)}$ ) and 7.11 (1 H, t,  $J(\text{HH})$  7.6 Hz,  $\text{CH}_{\text{aryl}}^{(5)}$ ).  $\delta_{\text{C}}$  37.4 ( $\text{C}^{2a*}$ ), 36.8 ( $\text{C}^{1b*}$ ), 35.9 ( $\text{C}^{2b*}$ ), 34.0 ( $\text{C}^{1a*}$ ), 33.2 ( $\text{C}^{1b}$ ), 25.7 ( $\text{C}^{2b}$ ), 14.0 ( $\text{C}^{3b}$ ), 13.4, 13.3 ( $\text{C}^{3a*}, \text{C}^{3b*}$ ), 138.0, 135.3, 132.1 ( $\text{C}_{\text{quat/aryl}}$ ), 130.7, 129.8, 127.9 ( $\text{CH}_{\text{aryl}}$ ), 215.0 and 205.5 (CO).



**Bis(acetonitrile)tetracarbonylchromium(0).** A suspension of  $[\text{Cr}(\text{CO})_6]$  (0.60 g, 2.7 mmol) in acetonitrile (80 mL) was photolysed for 3 h. The resulting yellow solution was brought to reflux for 12 h, yielding, by IR analysis, predominantly the tetracarbonyl product.  $\tilde{\nu}/\text{cm}^{-1}(\text{CO})$  ( $\text{CH}_2\text{Cl}_2$ -hexane 1:1) 2017w, 1941w, 1906vs, 1988 (sh), 1841s and 1795m.

**$\mu$ -Hexakis(pentylsulfanylmethyl)benzene-bis(tetracarbonylchromium) [ $\{\text{Cr}(\text{CO})_4\}_2\text{L1}$ ].** A solution of hexakis(pentylsulfanylmethyl)benzene (0.18 g, 0.23 mmol) in THF (20 mL) was added dropwise to a solution of  $[\text{Cr}(\text{CO})_4(\text{MeCN})_2]$  (0.68 mmol) in MeCN (20 mL) at 0 °C. The resulting yellow/orange solution gradually darkened and was allowed to stir for 12 h at room temperature. Evaporation of the solvent under reduced pressure gave a green/brown oil. Purification using column chromatography on silica (hexane- $\text{CH}_2\text{Cl}_2$  1:1) yielded a yellow solid which was crystallised from hexane (0.18 g, 72%).  $\tilde{\nu}/\text{cm}^{-1}(\text{CO})$  (hexane) 2020w, 1918w, 1898s and 1880s.  $\delta_{\text{H}}(300 \text{ MHz})$  4.3–3.7 (12 H, br m,  $\text{H}^1, \text{H}^{1*}$ ), 2.95 (8 H, br t,  $\text{H}^{2*}$ ), 2.64

(4 H, br t,  $J(\text{HH})$  7.2,  $\text{H}^2$ ), 1.86 (8 H, m,  $\text{H}^3$ ), 1.70 (4 H, m,  $\text{H}^3$ ), 1.44 (24 H, m,  $\text{H}^4, \text{H}^{4*}, \text{H}^5, \text{H}^{5*}$ ) and 0.94 (18H, t,  $J(\text{HH})$  6.0 Hz,  $\text{H}^6, \text{H}^{6*}$ ).  $\delta_{\text{C}}$  35.22, 35.20 ( $\text{C}^1, \text{C}^{1*}$ ), 43.7, 43.6 ( $\text{C}^2, \text{C}^{2*}$ ), 33.6 ( $\text{C}^2$ ), 31.1 ( $\text{C}^4$ ), 30.9, 30.7 ( $\text{C}^1, \text{C}^{4*}, \text{C}^4$ ), 29.4 ( $\text{C}^3$ ), 28.4, 28.2 ( $\text{C}^3, \text{C}^{3*}$ ), 22.29, 22.23 ( $\text{C}^{5*}, \text{C}^5, \text{C}^5$ ), 13.97 ( $\text{C}^{6*}, \text{C}^6$ ), 13.90 ( $\text{C}^6$ ), 137.9 ( $\text{C}^7$ ), 135.2, 133.6 ( $\text{C}^7, \text{C}^{7*}$ ), 224.3 and 224.5 (CO). Preliminary crystallographic data were obtained on a suitable crystal. The data were solved so as to confirm the metal and sulfur arrangement. This was found to be isostructural with the completely refined molybdenum analogue. The data were of insufficient quality for further refinement: monoclinic, space group,  $P2_1/c$ ;  $Z = 2$ ;  $a = 16.555(3)$ ,  $b = 12.710(2)$ ,  $c = 28.456(6)$  Å;  $\beta = 100.525(2)^\circ$ ;  $V = 5887(2)$  Å<sup>3</sup>.

**Bis(acetonitrile)tetracarbonyltungsten(0).** A suspension of  $[\text{W}(\text{CO})_6]$  (0.60 g, 1.7 mmol) in acetonitrile (80 mL) was photolysed for 3 h. The resulting yellow solution was brought to reflux for 24 h, yielding, by IR analysis, predominantly the tetracarbonyl product.  $\tilde{\nu}/\text{cm}^{-1}(\text{CO})$  ( $\text{CH}_2\text{Cl}_2$ ) 2019w, 1976m, 1936s, 1937s, 1884 (sh) and 1839m.

**$\mu$ -Hexakis(pentylsulfanylmethyl)benzene-bis(tetracarbonyltungsten) [ $\{\text{W}(\text{CO})_4\}_2\text{L1}$ ].** A solution of hexakis(pentylsulfanylmethyl)benzene (0.11 g, 0.14 mmol) in THF (20 mL) was added dropwise to a solution of  $[\text{W}(\text{CO})_4(\text{MeCN})_2]$  (0.43 mmol) in MeCN (20 mL) at 0 °C. The resulting yellow/orange solution gradually darkened and was allowed to stir for 12 h at room temperature. Evaporation of the solvent under reduced pressure gave a green/brown oil. Purification using column chromatography on silica (hexane- $\text{CH}_2\text{Cl}_2$  1:1) followed by washing in hexane ( $2 \times 20$  mL) yielded a yellow solid (0.12 g, 63%).  $\tilde{\nu}/\text{cm}^{-1}(\text{CO})$  (KBr disk) 2026w, 1949w, 1917s, 1890s and 1845 (m).  $\delta_{\text{H}}(300 \text{ MHz})$  4.6–4.0 (12 H, br m,  $\text{H}^1, \text{H}^{1*}$ ), 3.14 (8 H, t,  $\text{H}^{2*}$ ), 2.66 (4 H, t,  $J(\text{HH})$  7.2,  $\text{H}^2$ ), 1.87 (8 H, m,  $\text{H}^3$ ), 1.72 (4 H, m,  $\text{H}^3$ ), 1.45 (24 H, m,  $\text{H}^4, \text{H}^{4*}, \text{H}^5, \text{H}^{5*}$ ) and 0.99 (18 H, m,  $J(\text{HH})$  6.0 Hz,  $\text{H}^6, \text{H}^{6*}$ ).  $\delta_{\text{C}}$  37.0 ( $\text{C}^1, \text{C}^{1*}$ ), 45.51, 45.45 ( $\text{C}^2, \text{C}^{2*}$ ), 33.3 ( $\text{C}^2$ ), 30.6 ( $\text{C}^4$ ), 30.3, 30.2 ( $\text{C}^1, \text{C}^{4*}, \text{C}^4$ ), 28.9 ( $\text{C}^3$ ), 28.1, 28.0 ( $\text{C}^3, \text{C}^{3*}$ ), 21.84, 21.79 ( $\text{C}^{5*}, \text{C}^5, \text{C}^5$ ), 13.5, 13.4 ( $\text{C}^{6*}, \text{C}^6, \text{C}^6$ ), 138.3 ( $\text{C}^7$ ), 135.4, 134.0 ( $\text{C}^7, \text{C}^{7*}$ ), 204.9 and 204.7 (CO).  $m/z$  1367 ( $\text{M}^+$ ) and 1071 ( $\text{M} - \text{W}(\text{CO})_4$ ).

**$\mu$ -Hexakis(propylsulfanylmethyl)benzene-bis(tetracarbonyltungsten) [ $\{\text{W}(\text{CO})_4\}_2\text{L3}$ ].** This was prepared as for  $[\{\text{W}(\text{CO})_4\}_2\text{L1}]$  starting from hexakis(propylsulfanylmethyl)benzene (85 mg, 0.14 mmol) and  $[\text{W}(\text{CO})_4(\text{MeCN})_2]$  (0.43 mmol) (0.14 g, 84%).  $\tilde{\nu}/\text{cm}^{-1}(\text{CO})$  ( $\text{CH}_2\text{Cl}_2$ -hexane 1:1) 2020m, 1939m, 1910s, 1921s, 1896s and 1865m.  $\delta_{\text{H}}(300 \text{ MHz})$  4.6–3.7 (12 H, br m,  $\text{H}^1, \text{H}^{1*}$ ), 3.11 (8 H, br t,  $\text{H}^{2*}$ ), 2.64 (4 H, t,  $J(\text{HH})$  7.2,  $\text{H}^2$ ), 1.87 (8 H, m,  $\text{H}^{3*}$ ), 1.73 (4 H, m,  $\text{H}^3$ ), 1.16 (18 H, td,  $J(\text{HH})$  6.0, 1.8,  $\text{H}^{4*}$ ) and 1.06 (8 H, t,  $J(\text{HH})$  6.0 Hz,  $\text{H}^4$ ).  $\delta_{\text{C}}$  37.3 ( $\text{C}^1, \text{C}^{1*}$ ), 49.0, 47.8 ( $\text{C}^2, \text{C}^{2*}$ ), 35.7 ( $\text{C}^2$ ), 30.7 ( $\text{C}^1$ ), 22.8 ( $\text{C}^3$ ), 22.15, 22.22 ( $\text{C}^3, \text{C}^{3*}$ ), 13.5, 13.2 ( $\text{C}^4, \text{C}^{4*}, \text{C}^4$ ), 138.5 ( $\text{C}_{\text{quat}}$ ), 135.5, 134.0 ( $\text{CH}_{\text{aryl}}$ ), 205.4 and 205.2 (CO).  $m/z$  1198 ( $\text{M}^+$ ) and 902 ( $\text{M} - \text{W}(\text{CO})_4$ ).

**Pentacarbonyl(ethylsulfanylmethylbenzene)chromium [ $\text{Cr}(\text{CO})_5\text{L9}$ ].** A solution of ethylsulfanylmethylbenzene (50 mg, 0.33 mmol) in pentane (20 mL) was added dropwise to  $[\text{Cr}(\text{CO})_5(\text{C}_8\text{H}_{14})]$  (100 g, 0.33 mmol) at -60 °C. The solution was allowed to warm to room temperature and purified by column chromatography on silica (first eluent hexane, second hexane- $\text{CH}_2\text{Cl}_2$  1:1). The pure product was recovered as an oily solid, soluble in common organic solvents (90 mg, 80%) (Found: C, 48.6; H, 3.4.  $\text{C}_{30}\text{H}_{54}\text{CrO}_5\text{S}_6$  requires C, 48.8; H, 3.5%).  $\tilde{\nu}/\text{cm}^{-1}(\text{CO})$  ( $\text{CH}_2\text{Cl}_2$ -hexane 1:1) 2068w, 1943s and 1935 (sh).  $\delta_{\text{H}}(400 \text{ MHz})$  3.83 (2 H, s, aryl  $\text{CH}_2\text{S}$ ), 2.60 (2 H, q,  $J(\text{HH})$  7.5,  $\text{CH}_2\text{SCH}_2$ ), 1.30 (3 H, t,  $J(\text{HH})$  7.5 Hz, Me) and 7.35 (5 H, m,  $\text{CH}_{\text{aryl}}$ ).  $\delta_{\text{C}}$  45.0 (aryl  $\text{CH}_2\text{S}$ ), 32.7 ( $\text{CH}_2\text{SCH}_2$ ), 12.0 (Me), 134.5 ( $\text{C}_{\text{quat/aryl}}$ ), 128.8, 128.5, 127.9 ( $\text{CH}_{\text{aryl}}$ ), 220.6 and 214.5 (CO).

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