

## Synthesis and alkyne coordination chemistry of thiacycloalkynes

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### Abstract

The reactions of 1,4-dichlorobut-2-yne with  $\text{HS}(\text{CH}_2)_n\text{SH}$  ( $n = 2-5$ ) or  $\text{HS}(\text{CH}_2\text{CH}_2\text{S})_n\text{H}$  ( $n = 2-3$ ) or  $\text{HSCH}_2\text{CH}(\text{OH})\text{CH}_2\text{SH}$  under high dilution conditions in industrial methylated spirits using KOH as the deprotonating agent produce thiacycloalkynes in remarkably high yields when the 1 : 1 product is a nine-, ten- or 11-membered ring. 1,5-dithiacyclonon-7-yne, 1,5-dithiacyclonon-7-yne-3-ol, 1,6-dithiacyclodec-8-yne, 1,7-dithiacycloundec-9-yne, 1,4,7-trithiacycloundec-9-yne and 1,7-dithia-4-oxa-cycloundec-9-yne are prepared in yields of 75%, 81%, 79%, 85%, 100% and 95% respectively. The X-ray crystal structures of 1,4-dithiacyclooct-6-yne and 1,6-dithiacyclodec-8-yne have been determined. Selective coordination of the alkyne functionality is demonstrated by the reaction of 1,4,7,10-tetrathiacyclotetradec-12-yne with  $[\text{Co}_2(\text{CO})_8]$  to afford a monoalkyne hexacarbonyldicobalt complex and by the reaction of 1,4,7-trithiacycloundec-9-yne with  $[\text{Mo}(\text{CO})_2(\text{S}_2\text{CNMe}_2)_2]$  to afford a bisalkynebis(dithiocarbamate)molybdenum complex. A base-catalysed rearrangement of 1,4,7-trithiacycloundec-9-yne affords 2-enyl-1,4,7-trithiacyclonon-2-ene which is an effective ligand for  $\text{Ag}^+$ .

**Keywords:** Alkynes; Thioethers; Macrocycles; Cobalt; Molybdenum; Thiacycloalkynes

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### 1. Introduction

The ability of polythioether macrocycles to coordinate metal ions and metal–ligand fragments has been extensively studied in recent years [1]. Interest has focused on 1,4,7-trithiacyclononane, which forms a remarkable range of stable complexes owing to its endo-dentate conformation, but several other thiacycloalkynes which are not preorganised for facial coordination, such as 2,5,8-trithia[9]-*o*-benzenophane (ttob) and 2,5,8-trithia[9]-*m*-benzenophane (tmb), display good ligating properties and useful selectivity [2]. We have studied the synthesis of hexacarbonyldicobalt-coordinated thiacycloalkynes which bond to  $\text{Ag}(\text{I})$  and  $\text{Cu}(\text{I})$  centres via the thioether groups [3], and recently have reported a route to 1,4,7-trithiacycloundec-9-yne via decomplexation from a hexacarbonyldicobalt fragment [4]. This is one of a growing number of thiacycloalkynes. Fig. 1 depicts some examples, ranging from the strained seven-membered ring (**1**) [5] to larger structures such as

(**7**), prepared as an intermediate in the synthesis of a DNA-cleaving bis(propargylic) sulphone crown ether [6].

A variety of synthetic methods have been employed in the preparation of thiacycloalkynes. The seven- and eight-membered rings **1** and **2** were prepared by generating the alkyne functionality in a preformed heterocycle. Compound **1** was prepared by oxidation of a 3,3,6,6-tetramethyl-1-thiacycloheptane-4,5-dione bis-hydrazone with  $\text{Ag}_2\text{O}$  [5], while **2** was produced by the selenadiazole method [7]. The larger rings were prepared by cyclisation of molecules containing alkyne functionalities. Compounds **3a–c** have been prepared by the reaction of 1,4-dibromobut-2-yne with the appropriate dithiol in  $\text{Cs}_2\text{CO}_3$ –DMF [8,9]. This methodology is effective for strained rings, especially 1,4,7-trithiacyclononane, but is not always optimal for larger rings [10]. Compound **3d** was prepared via the acid-catalysed reaction of  $[\text{Co}_2(\mu\text{-HOCH}_2\text{C}\equiv\text{CCH}_2\text{OH})(\text{CO})_6]$  with bis(2-mercaptoethyl)sulphide [3] followed by decomplexation of the hexacarbonyldicobalt unit with  $\text{Me}_3\text{NO}$  [4]. Compounds of type **4** are prepared by the reaction of 2,7-dimethyl-2,7-dichloroocta-3,5-diyne with the appropriate dithiols [11]. In the case of **4a** and **4b**, both the

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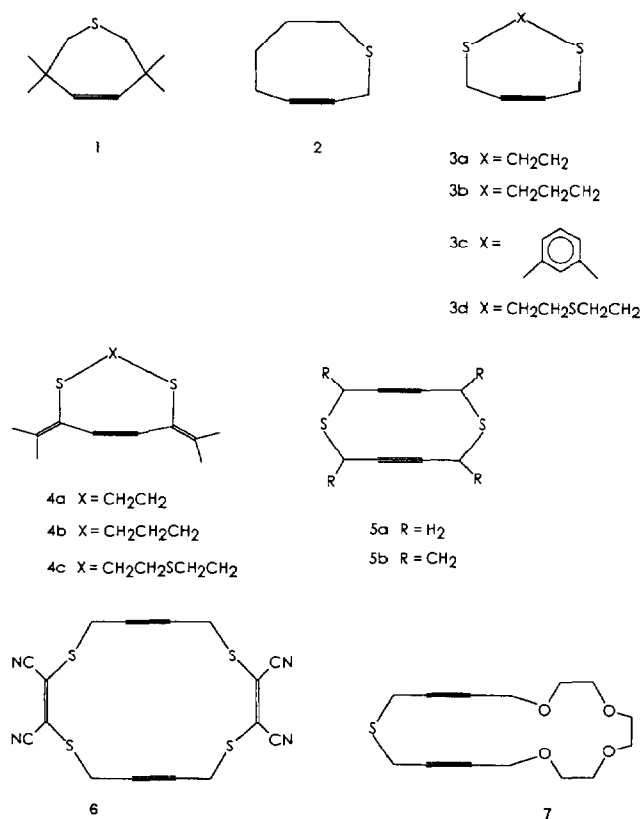


Fig. 1. Thiacycloalkynes.

1 : 1 products illustrated and 2 : 2 products were isolated. 1,6-dithiacyclodeca-3,8-diyne (**5a**) can be prepared directly from 1,4-dichlorobut-2-yne and sodium sulphide [12] or by a higher yield multi-step synthesis [13]. Compound **5b** was prepared by the reaction of 2,7-dimethyl-2,7-dichloroocta-3,5-diyne with Na<sub>2</sub>S · Al<sub>2</sub>O<sub>3</sub> [14] and compound **6** was prepared by the reaction of disodiumdicyanoethylenethiolate with 1,4-dichlorobut-2-yne [15].

This paper reports improved syntheses and new compounds of type **3**, their alkyne coordination chemistry and a base-induced ring contraction of 1,4,7-trithiacycloundec-9-yne to afford a new nine-membered crown thioether ligand.

## 2. Results and discussion

We have previously demonstrated that **3d** can simultaneously coordinate to transition metals via its thioether and alkyne functionalities [3]. In order to facilitate further investigations of **3d** and related ligands we wished to develop a cheap, high yield synthetic route. A recent paper by Lockhart et al. [2] reported that 2,5,8-trithia[9]-*p*-benzenophane (ttbp) could be prepared in reasonable yield (41%) by reaction of bis(2-mercaptoethyl)sulphide and KOH with  $\alpha,\alpha'$ -dichloro-

*p*-xylene in methanol. The structure of ttbp is similar to **3d** in that both molecules contain linear units connected to an SCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>S bracket. Application of this methodology, which avoids the use of Cs<sub>2</sub>CO<sub>3</sub> and DMF, to the synthesis of **3d** works remarkably well. Addition of bis(2-mercaptoethyl)sulphide and 1,4-dichlorobut-2-yne to an industrial methylated spirits (IMS) solution of KOH under high dilution conditions (see Experimental) affords **3d** in practically quantitative yield. Routinely, yields in excess of 80% are obtained, and with care, yields as high as 100% of analytically pure material are obtained. Use of bis(2-mercaptoethyl)ether affords 1,7-dithia-4-oxa-cycloundec-9-yne in 95% yield and is a considerable improvement on the 35% yield obtained using Cs<sub>2</sub>CO<sub>3</sub>-DMF [8].

Using this approach to prepare the more strained ring **3a** was less successful than the Cs<sub>2</sub>CO<sub>3</sub>-DMF synthesis reported by Meier and Dai [8] (27%), and confirms that Cs<sub>2</sub>CO<sub>3</sub> is the better deprotonating agent for preparing strained cyclic thioethers. Slow addition of 1,2-ethanedithiol and 1,4-dichlorobut-2-yne to a large volume of KOH-IMS solution affords **3a** (3%) and 1,4,5,8-tetrathiacyclodec-10-yne (9%), as previously characterised by Meier and Dai [8], and also the 2:2 and 3:3 products 1,4,9,12-tetrathiacyclohexadec-6,14-diyne (**8**) and 1,4,9,12,17,20-hexathiacyclotetracos-6,14,22-triyne (**9**) both in 9% yield. The strained nature of **3a** was confirmed by a single crystal X-ray diffraction study. Selected structural parameters are listed in Table 1 and the molecular structure of **3a** is shown in Fig. 2. The bond lengths and angles are comparable with those determined for **3d**, with the exception of the angles at the sp-carbon atoms which are reduced from ca. 175° in **3d** to ca. 164° in **3a** [4]. Torsional angles are a sensitive measure of the strain in crown thioethers in which the SCCS units prefer anti placement of the C-C bonds [1]. The torsional angle S(1)-C(3)-C(4)-S(2) is 129.2°. The C<sub>2</sub> conformation of the molecule is similar to that adopted when it is coordinated via the alkyne bond to a Co<sub>2</sub>( $\mu$ -dppm)(CO)<sub>4</sub> unit [16]. The minimised energy of the crystallographic geometry, using the MM + force field in the HYPERCHEM (Release 3) package [17], is 11.57 kcal mol<sup>-1</sup> with an angle at the sp-carbon atoms of 161.5°. Using the same package, the minimised energy of the C<sub>3</sub> geometry of 1,4,7-trithiacyclononane is 18.56 kcal mol<sup>-1</sup>, indicating that 1,4,7-trithiacyclononane is substantially more strained [18]. For comparison, the crystallographic geometry of **3d** produced a minimised energy of 8.29 kcal mol<sup>-1</sup>. It has been observed previously that the strain in **3a** is also reflected by the chemical shift of the sp-carbon atoms which has a value of  $\delta$  90.9 [8]. This contrasts with **8** and **9** which have resonances at  $\delta$  79.2 and 79.1 respectively, in the normal region for unstrained cycloalkynes. Compounds **8** and **9** are practically indistinguishable by NMR spec-

Table 1  
Selected internuclear distances (Å), angles (deg) and torsional angles (deg) for 1,4-dithiacyclooct-6-yne (3a)

C(1)–C(2)	1.451(4)
C(1)–C(6)	1.191(3)
C(2)–S(1)	1.835(3)
C(3)–C(4)	1.542(4)
C(3)–S(1)	1.819(3)
C(4)–S(2)	1.820(2)
C(5)–C(6)	1.455(3)
C(5)–S(2)	1.837(3)
C(2)–C(1)–C(6)	163.9(2)
C(1)–C(2)–S(1)	107.9(2)
C(4)–C(3)–S(1)	116.3(2)
C(3)–C(4)–S(2)	115.9(2)
C(6)–C(5)–S(2)	108.4(2)
C(1)–C(6)–C(5)	164.0(2)
C(2)–S(1)–C(3)	101.0(1)
C(4)–S(2)–C(5)	101.4(1)
C(3)–S(1)–C(2)–C(1)	41.4
C(2)–S(1)–C(3)–C(4)	–91.0
C(5)–S(2)–C(4)–C(3)	–89.0
C(4)–S(2)–C(5)–C(6)	40.3
C(6)–C(1)–C(2)–S(1)	–29.3
C(2)–C(1)–C(6)–C(5)	21.8
S(1)–C(3)–C(4)–S(2)	129.2
S(2)–C(5)–C(6)–C(1)	–26.5

trospecty, but mass spectroscopy (Table 2) clearly established their 2 : 2 and 3 : 3 formulations.

Slow addition of 1,3-propanedithiol and 1,4-dichlorobut-2-yne to a large volume of KOH–IMS affords **3b** in 75% yield and the 2:2 product 1,5,10,14-tetrathia-cyclooctadec-7,16-diyne (**10**) in 5% yield. The yield of **3b** is remarkably high considering its sp-carbon shift of  $\delta$  86.5, which indicates considerable strain in the nine-membered ring, and also in the light of the more modest

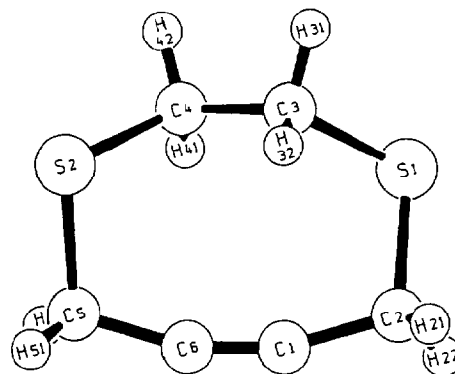


Fig. 2. The molecular structure of (3a) showing the atom labelling system.

yield of 33% obtained using  $\text{Cs}_2\text{CO}_3$ –DMF [8]. A similar procedure using 1,3-dimercaptopropan-2-ol afforded 1,5-dithiacyclonon-7-yne-3-ol (**11**), a nine-membered ring with a pendant hydroxyl group also in excellent yield (81%). Again an sp-carbon shift of  $\delta$  86.2 confirms that a strained nine-membered ring has been formed.

Increasing the ring size by the use of 1,4-butanedithiol or 1,5-pentanedithiol affords predominantly the 1:1 products 1,6-dithiacyclodec-8-yne (**12**) in 79% or 1,7-dithiacycloundec-9-yne (**14**) in 85% yield and small amounts of the 2:2 products 1,6,11,16-tetrathia-cycloeicos-8,18-diyne (**13**) in 6% or 1,7,12,18-tetrathia-cyclodocos-9,20-diyne (**15**) in 4% yield. The sp-carbon shift of **12** ( $\delta$  80.3) suggests that it is relatively unstrained and is only 1.1 ppm larger than the corresponding shift for **13**.

The solid-state structure of **12** was established by a single crystal X-ray diffraction study. Selected structural parameters are listed in Table 3 and the molecular

Table 2  
Analytical<sup>a</sup> and physical data

Compound	Appearance	Yield (%)	Analysis (%)		$M^b$
			C	H	
<b>8</b>	white solid	9	49.3 (50.0)	6.0 (5.6)	289(+H) <sup>d</sup>
<b>9</b>	white solid	9	49.6 (50.0)	5.7 (5.6)	433(+H) <sup>d</sup>
<b>10</b>	white solid	5	51.7 (53.1)	6.1 (6.4)	317(+H) <sup>c</sup>
<b>11</b>	yellow solid	81	47.9 (48.2)	5.7 (5.8)	174
<b>12</b>	white solid	79	55.8 (55.8)	7.0 (7.0)	172
<b>13</b>	white solid	6	54.7 (55.8)	6.9 (7.0)	345(+H) <sup>c</sup>
<b>14</b>	yellow solid	85	58.2 (58.0)	8.4 (7.6)	186
<b>15</b>	white solid	4	—	—	372 <sup>c</sup>
<b>16</b>	white solid	44	45.3 (45.4)	6.3 (6.1)	265(+H) <sup>c</sup>
<b>17</b>	red solid	45	35.9 (36.9)	2.9 (3.6)	551(+H) <sup>c</sup>
<b>18</b> <sup>c</sup>	orange solid	40	34.9 (35.5)	4.7 (4.9)	—
<b>19</b>	yellow solid	12	46.4 (47.0)	5.9 (5.9)	204

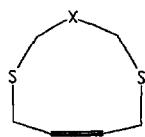
<sup>a</sup> Calculated values are given in parentheses.

<sup>b</sup> Electron impact mass spectroscopy unless otherwise stated.

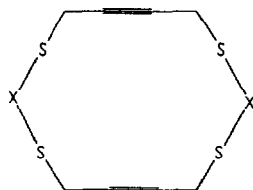
<sup>c</sup> FAB mass spectroscopy.

<sup>d</sup> Chemical ionization.

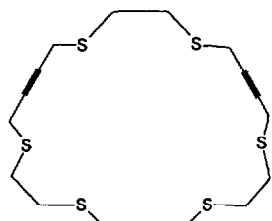
<sup>e</sup> Nitrogen analysis 3.3 (3.8).



- 11 X = CH(OH)  
 12 X = CH<sub>2</sub>CH<sub>2</sub>  
 14 X = CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>  
 16 X = CH<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>SCH<sub>2</sub>



- 8 X = CH<sub>2</sub>CH<sub>2</sub>  
 10 X = CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>  
 13 X = CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>  
 15 X = CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>



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structure of **12** is shown in Fig. 3. The molecule adopts a  $C_2$  conformation and angles at the sp-carbon atoms are ca.  $168.3^\circ$ . The MM + minimised energy of the crystallographic geometry is  $7.48 \text{ kcal mol}^{-1}$  with sp-carbon angles of  $169.7^\circ$ .

Reaction of 3,6-dithiaoctane-1,8-dithiol, KOH and 1,4-dichlorobut-2-yne in IMS under high dilution conditions affords 1,4,7,10-tetrathiacyclotetradec-12-yne (**16**). Reaction of **16** with  $[\text{Co}_2(\text{CO})_8]$  affords compound **17**, which is analogous to a number of previously prepared dicobalt complexed thiacycloalkynes [16]. This particular compound could not be prepared by the acid-catalysed reaction of  $[\text{Co}_2(\mu\text{-HOCH}_2\text{C}\equiv\text{CCH}_2\text{OH})(\text{CO})_6]$  with 3,6-dithiaoctane-1,8-dithiol owing to C–S bond cleavage [3].

The synthesis of **17** demonstrates the preference for the hexacarbonyldicobalt moiety for the alkyne functionality. Treatment of two equivalents of **3d** with  $[\text{Mo}(\text{CO})_2(\text{S}_2\text{CNMe}_2)_2]$  affords **18** in which the alkynes are again coordinated in preference to the thioether groups. Compound **18** was characterised by comparison with a number of other  $[\text{Mo}(\text{alkyne})_2(\text{dtc})_2]$  derivatives

Table 3

Selected internuclear distances (Å), angles (deg) and torsional angles (deg) for 1,6-dithiacyclodec-8-yne (**12**)

C(1)–C(2)	1.453(5)
C(1)–C(8)	1.174(5)
C(2)–S(1)	1.823(3)
C(3)–C(4)	1.522(5)
C(3)–S(1)	1.815(4)
C(4)–C(5)	1.483(5)
C(5)–C(6)	1.532(5)
C(6)–S(2)	1.818(4)
C(7)–C(8)	1.471(6)
C(7)–S(2)	1.808(4)
C(2)–C(1)–C(8)	167.9(4)
C(1)–C(2)–S(1)	112.3(2)
C(4)–C(3)–S(1)	117.2(3)
C(3)–C(4)–C(5)	116.9(3)
C(4)–C(5)–C(6)	117.4(3)
C(5)–C(6)–S(2)	116.7(2)
C(8)–C(7)–S(2)	112.6(3)
C(1)–C(8)–C(7)	168.7(5)
C(2)–S(1)–C(3)	102.4(2)
C(6)–S(2)–C(7)	102.5(2)
C(3)–S(1)–C(2)–C(1)	72.4
C(2)–S(1)–C(3)–C(4)	–59.4
C(7)–S(2)–C(6)–C(5)	–58.9
C(6)–S(2)–C(7)–C(8)	75.0
C(8)–C(1)–C(2)–S(1)	11.7
C(2)–C(1)–C(8)–C(7)	–78.7
S(1)–C(3)–C(4)–C(5)	–55.0
C(3)–C(4)–C(5)–C(6)	175.1
C(4)–C(5)–C(6)–S(2)	–53.5
S(2)–C(7)–C(8)–C(1)	–1.8

[19]. In particular, the alkyne resonances at  $\delta$  181.4 and 178.5 are characteristic of three-electron donor alkynes.

The base-catalysed rearrangement of 2,7-dithiaoct-4-yne to 1,2-bis(methylthio)-1,3-butadiene has been reported by Garst and Arrhenius [20]. Treatment of **3d** with  $\text{KO}^t\text{Bu}$  affords **19**. The electron impact mass spectrum shows the molecular ion at  $m/z$ , 204 confirm-

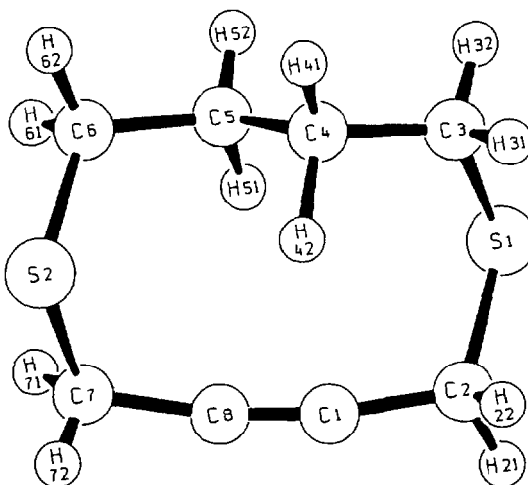
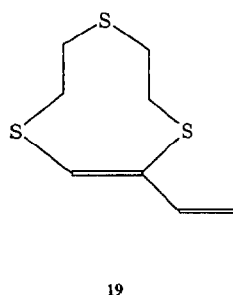
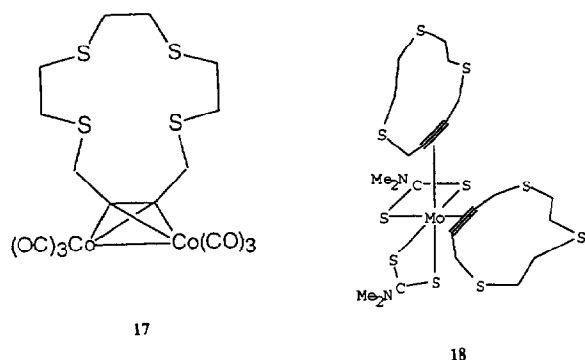


Fig. 3. The molecular structure of (**12**) showing the atom labelling system.



ing **19** is an isomer of **3d**. The presence of the butadiene unit was confirmed by the characteristic  $^1\text{H}$  and  $^{13}\text{C}$  resonances (see Table 4). The modest yield of 12% compared with 85% for bis(methylthio)-1,3-butadiene [20] is possibly a reflection of the strain in the nine-membered ring. Molecular-mechanics and dynamics calculations suggest that the lowest energy conforma-

tion of 1,4,7-trithiacyclonon-2-ene is exodentate with a minimised energy of 18.15 kcal mol $^{-1}$ , while the lowest energy endodentate conformation has a minimised energy of 23.04 kcal mol $^{-1}$ . A similar nine-membered, trithiabenzocrown-3, has been prepared previously by C–S bond cleavage at a ruthenium centre [21]. This ligand is facially coordinated to a Ru(CO)Br $_2$  fragment and adopts an endodentate conformation. Preliminary investigations suggest that **19** will exhibit interesting coordination chemistry. For example, when **19** was treated with equimolar quantities of AgBF $_4$  and PPh $_3$  in the anticipation of preparing [Ag(**19**)(PPh $_3$ )][BF $_4$ ], the fast atom bombardment (FAB) mass spectrum of the product mixture showed isotope envelopes at  $m/z$  631 and 517 corresponding to [Ag(PPh $_3$ ) $_2$ ] $^+$  and [Ag(**19**) $_2$ ] $^+$ .

### 3. Experimental

All reactions were carried out under an atmosphere of nitrogen using standard Schlenk tube and vacuum line techniques, and all solvents were freshly distilled under a nitrogen atmosphere and over appropriate drying agents, except IMS which was used as-received. Light petroleum (boiling point 40–60°C) and dichloromethane were distilled over calcium hydride and tetrahydrofuran was distilled over potassium. 3,6-dithiaoctane-1,8-dithiol [22] and [Mo(CO) $_2$ (S $_2$ CNMe $_2$ ) $_2$ ] [23] were prepared by literature methods. FAB and chemical ionisation spectra were recorded by the EP-SRC mass spectrometry service at the University of Swansea with a VG ZAB-E instrument. FAB spectra were recorded from a matrix sample with NOBA. Molecular-mechanics calculations were carried out using HYPERCHEM (Release 3) [17]. Structures were minimised with conjugate gradients (Polak–Ribiere algo-

Table 4  
 $^1\text{H}$  and  $^{13}\text{C}$  NMR data<sup>a</sup>

Compound	$^1\text{H}$ ( $\delta$ )	$^{13}\text{C}$ -{ $^1\text{H}$ } ( $\delta$ )
<b>8</b>	3.38 (s, 8H, CCH $_2$ ), 2.97 (s, 8 H, SCH $_2$ )	79.2 (C $_2$ ), 30.4 (SCH $_2$ ), 19.3 (CCH $_2$ )
<b>9</b>	3.38 (s, 12 H, CCH $_2$ ), 2.97 (s, 12 H, SCH $_2$ )	79.1 (C $_2$ ), 30.3 (SCH $_2$ ), 19.3 (CCH $_2$ )
<b>10</b>	3.32 (s, 8 H, CCH $_2$ ), 2.84 (t, 8 H, SCH $_2$ , $J(\text{HH})$ 7), 2.01 (qnt, 4H, CH $_2$ , $J(\text{HH})$ 7)	79.1 (C $_2$ ), 30.8 (CH $_2$ ), 28.7 (SCH $_2$ ), 20.0 (CCH $_2$ )
<b>11</b>	4.03–3.91 (m, 1 H, CH), 3.40–3.04 (m, 8 H, CCH $_2$ and SCH $_2$ ), 2.68 (s br, 1 H, OH)	86.2 (C $_2$ ), 72.4 (CH), 33.9 (SCH $_2$ ), 20.6 (CCH $_2$ )
<b>12</b>	3.34 (s, 4 H, CCH $_2$ ), 2.82–2.70 (m, 4 H, SCH $_2$ ), 1.96–1.84 (m, 4 H, CH $_2$ )	80.3 (C $_2$ ), 30.4 (CH $_2$ ), 27.8 (SCH $_2$ ), 21.2 (CCH $_2$ )
<b>13</b>	3.31 (s, 8 H, CCH $_2$ ), 2.79–2.68 (m, 8 H, SCH $_2$ ), 1.84–1.74 (m, 8 H, CH $_2$ )	79.2 (C $_2$ ), 31.0 (CH $_2$ ), 28.7 (SCH $_2$ ), 19.7 (CCH $_2$ )
<b>14</b>	3.22 (s, 4 H, CCH $_2$ ), 2.78 (t, 4 H, SCH $_2$ , $J(\text{HH})$ 6), 1.91–1.71 (m, 6 H, CH $_2$ )	80.9 (C $_2$ ), 31.9, 22.5 (CH $_2$ ), 27.6 (SCH $_2$ ), 20.7 (CCH $_2$ )
<b>15</b>	3.30 (s, 8 H, CCH $_2$ ), 2.76–2.63 (m, 8 H, SCH $_2$ ), 1.82–1.47 (m, 12 H, CH $_2$ )	79.0 (C $_2$ ), 31.4, 22.6 (CH $_2$ ), 28.7 (SCH $_2$ ), 19.8 (CCH $_2$ )
<b>16</b>	3.39 (s, 4 H, CCH $_2$ ), 2.98–2.75 (m, 12 H, SCH $_2$ )	78.7 (C $_2$ ), 31.5, 30.7, 30.5 (SCH $_2$ ), 19.4 (CCH $_2$ )
<b>18</b>	4.60–4.30 (m, 8 H, CCH $_2$ ), 3.48 (s, 6 H, CH $_3$ ), 3.18 (s, 6 H, CH $_3$ ), 2.96–2.27 (m, 16 H, CH $_2$ )	207.9 (S $_2$ CNMe $_2$ ), 181.4, 178.5 (C $_2$ ), 39.6, 39.3, 33.9, 32.4, 32.3, 29.63, 29.59 (CH $_2$ and CH $_3$ )
<b>19</b>	6.67 (s, 1 H, CH), 6.41 (dd, 1 H, $J(\text{HH})$ 10 and 17), 5.60 (dd, 1 H, $J(\text{HH})$ 1 and 17), 5.10 (dd, 1 H, $J(\text{HH})$ 1 and 10), 3.02–2.66 (m, 8 H, CH $_2$ ) <sup>b</sup>	138.9 (CH), 136.6, 129.3 (=CH $_2$ ), 114.4 (CH), 34.0, 33.1, 32.4, 32.0 (SCH $_2$ ) <sup>b</sup>

<sup>a</sup> Chemical shifts  $\delta$  (ppm), coupling constants (Hz). Measured in CDCl $_3$  unless otherwise stated.

<sup>b</sup> Recorded in CD $_2$ Cl $_2$ .

rithm) using the MM + force field until the gradients were less than  $0.01 \text{ kcal mol}^{-1} \text{ \AA}^{-1}$ .

### 3.1. Syntheses of 1,4,7-trithiacycloundec-9-yne (**3d**), 1,7-dithia-4-oxa-cycloundec-9-yne, 1,5-dithiacyclonon-7-yne-3-ol (**11**) and 1,4,7,10-tetrathiacyclotetradec-12-yne (**16**)

A solution of bis(2-mercaptoethyl)sulphide ( $0.78 \text{ cm}^3$ ,  $6.00 \text{ mmol}$ ) and 1,4-dichlorobut-2-yne ( $0.59 \text{ cm}^3$ ,  $6.00 \text{ mmol}$ ) in IMS ( $500 \text{ cm}^3$ )–THF ( $50 \text{ cm}^3$ ) was added dropwise to a vigorously stirred solution of KOH ( $0.67 \text{ g}$ ,  $12.00 \text{ mmol}$ ) in IMS ( $1000 \text{ cm}^3$ ). After the addition was complete, stirring was continued for a further 5 h, after which time the KCl formed was removed by filtration and the resulting solution evaporated to dryness. The yellowish residue was extracted with dichloromethane ( $100 \text{ cm}^3$ ) and then the solvent was removed in vacuo and the product purified by recrystallisation from  $\text{CH}_2\text{Cl}_2$ –light petroleum at  $-25^\circ\text{C}$  to afford **3d** as a pale yellow solid ( $1.22 \text{ g}$ ,  $99.7\%$ ). 1,7-dithia-4-oxa-cycloundec-9-yne ( $95\%$ ) and 1,4,7,10-tetrathiacyclotetradec-12-yne (**16**) were prepared on a  $6.0 \text{ mmol}$  scale using the same procedure. 1,5-dithiacyclonon-7-yne-3-ol (**11**) was also prepared by the same procedure, except that a light-petroleum– $\text{CH}_2\text{Cl}_2$  (1 : 1) mixture was used for extraction.

### 3.2. Reaction of 1,2-ethanedithiol with 1,4-dichlorobut-2-yne

The reaction was performed on a  $6.0 \text{ mmol}$  scale following the procedure described for compound **3d**. After removal of the KCl and the reaction solvent the solid residue was first extracted in dichloromethane ( $100 \text{ cm}^3$ ) and the solvent was removed in vacuo and then extracted with light petroleum ( $100 \text{ cm}^3$ ) and the solvent removed in vacuo. The residue was dissolved in the minimum volume of dichloromethane and then light petroleum ( $50 \text{ cm}^3$ ) was added. Compound **8** precipitated as a white solid ( $0.08 \text{ g}$ ,  $9\%$ ) at  $-25^\circ\text{C}$  overnight; the supernatant was removed by a cannula to another Schlenk tube. Removal of the solvent in vacuo and sublimation at ca.  $1 \text{ mm Hg}$  and  $60$ – $70^\circ\text{C}$  afforded **3a** as a white solid ( $0.03 \text{ g}$ ,  $3\%$ ) leaving 1,4,5,8-tetrathiacyclodec-10-yne unsublimed as a yellow oil ( $0.12 \text{ g}$ ,  $8\%$ ). Compound **9** was extracted into a mixture of light petroleum and  $\text{CH}_2\text{Cl}_2$  (9 : 1) from the residue of the light petroleum extraction, and removal of the solvent in vacuo afforded **9** as a white solid ( $0.08 \text{ g}$ ,  $9\%$ ).

### 3.3. Synthesis of 1,5-dithiacyclonon-7-yne (**3b**) and 1,5,10,14-tetrathiacyclooctadec-7,16-diyne (**10**)

The reaction was performed on a  $6.0 \text{ mmol}$  scale following the procedure described for compound **3d**.

Compound **3b** was extracted in light petroleum and the solvent removed in vacuo to afford **3b** as a yellow oil ( $0.71 \text{ g}$ ,  $75\%$ ). From the residue, compound **10** was extracted into a mixture of light petroleum and  $\text{CH}_2\text{Cl}_2$  (9 : 1) and removal of the solvent in vacuo afforded **10** as a white solid ( $0.05 \text{ g}$ ,  $5\%$ ).

### 3.4. Synthesis of 1,6-dithiacyclodec-8-yne (**12**) and 1,6,11,16-tetrathiacycloicos-8,18-diyne (**13**) and 1,7-dithiacycloundec-9-yne (**14**) and 1,7,12,18-tetrathiacyclodocos-9,20-diyne (**15**)

The reaction was performed on a  $6.0 \text{ mmol}$  scale following the procedure described for compound **3d**. Compound **12** was extracted into light petroleum ( $120 \text{ cm}^3$ ) and removal of the solvent in vacuo afforded **12** as a yellow solid ( $0.82 \text{ g}$ ,  $79\%$ ). Compound **13** was extracted in a mixture of light petroleum and  $\text{CH}_2\text{Cl}_2$  (9 : 1) and removal of the solvent in vacuo afforded **13** as a white solid ( $0.06 \text{ g}$ ,  $6\%$ ). 1,7-dithiacycloundec-9-yne (**14**) and 1,7,12,18-tetrathiacyclodocos-9,20-diyne (**15**) were prepared using the same procedure.

### 3.5. Synthesis of (**17**)

A solution of 1,4,7,10-tetrathiacyclotetradec-12-yne ( $0.100 \text{ g}$ ,  $0.38 \text{ mmol}$ ) and  $[\text{Co}_2(\text{CO})_8]$  ( $0.129 \text{ g}$ ,  $0.38 \text{ mmol}$ ) in  $\text{CH}_2\text{Cl}_2$  was stirred for 2 h. After removal of the solvent in vacuo the residue was chromatographed on a silica gel column ( $7 \times 3 \text{ cm}$ ) eluting with a  $\text{CH}_2\text{Cl}_2$ –light petroleum mixture (1 : 4). Removal of the solvent in vacuo from the red band afforded (**17**) ( $0.094 \text{ g}$ ,  $45\%$ ).

### 3.6. Synthesis of (**18**)

To a solution of  $[\text{Mo}(\text{CO})_2(\text{S}_2\text{CNMe}_2)_2]$  ( $1.90 \text{ g}$ ,  $4.84 \text{ mmol}$ ) in toluene ( $20 \text{ cm}^3$ ) was added 1,4,7-trithiacycloundec-9-yne ( $2.04 \text{ g}$ ,  $10.0 \text{ mmol}$ ) and the mixture refluxed for 1 h. After removal of the solvent in vacuo the residue was chromatographed on a silica gel column ( $15 \times 3 \text{ cm}$ ) eluting with a  $\text{CH}_2\text{Cl}_2$ –THF mixture (5 : 1). Removal of the solvent in vacuo from the orange band afforded (**17**) ( $0.96 \text{ g}$ ,  $40\%$ ).

### 3.7. Synthesis of (**19**)

**3d** ( $1.02 \text{ g}$ ,  $5 \text{ mmol}$ ) was added to a solution of  $\text{KO}^t\text{Bu}$  ( $0.06 \text{ g}$ ,  $0.5 \text{ mmol}$ ) in DMSO ( $30 \text{ cm}^3$ ). The mixture was kept below  $30^\circ\text{C}$  using a waterbath and stirred for 18 h. Water ( $30 \text{ cm}^3$ ) was then added to the brown solution and the product extracted into toluene ( $3 \times 30 \text{ cm}^3$ ). The combined toluene extracts were washed with water ( $3 \times 40 \text{ cm}^3$ ) and dried with  $\text{MgSO}_4$ . The toluene was removed using a rotary evaporator and the residue recrystallised at  $-10^\circ\text{C}$  by dissolving in

$\text{CH}_2\text{Cl}_2$  ( $5 \text{ cm}^3$ ) followed by addition of light petroleum ( $100 \text{ cm}^3$ ) to afford **19** (0.12 g, 12%).

### 3.8. Crystal structure determinations

Crystals of 1,4-dithiacyclooct-6-yne (**3a**) were obtained from  $\text{CH}_2\text{Cl}_2$ -light petroleum as colourless prisms with crystal dimensions ca.  $0.30 \times 0.25 \times 0.25 \text{ mm}^3$ . Data were collected using an Enraf-Nonius FAST area detector diffractometer (293 K, Mo K $\alpha$  X-radiation, graphite monochromator,  $\bar{\lambda} = 0.071069 \text{ \AA}$ ) by the SERC X-ray crystallographic service using procedures described elsewhere [24]. Of the 2338 data collected ( $2\theta \leq 50^\circ$ ), 989 unique data had  $F \geq 5\sigma(F)$ , and only these were used for the structure refinement. The data were corrected for Lorentz and polarisation effects.

*Crystal data:*  $\text{C}_6\text{H}_8\text{S}_2$ ,  $M = 144.3$ , monoclinic, space group  $P2_1/a$ ,  $a = 7.4870(10)$ ,  $b = 11.9584(7)$ ,  $c = 8.4663(13) \text{ \AA}$ ,  $\beta = 114.001(8)^\circ$ ,  $U = 692.47 \text{ \AA}^3$ ,  $Z = 4$ ,  $D_c = 1.38 \text{ g cm}^{-3}$ ,  $F(000) = 304.0$ ,  $\mu = (\text{Mo K}\alpha) = 0.63 \text{ mm}^{-1}$ .

The structure was solved by direct methods and successive difference Fourier syntheses were used to locate all the atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters, while the hydrogen atoms were refined with isotropic thermal parameters. A weighting scheme of the form  $w^{-1} = [\sigma^2(F) + 0.0005 |F|^2]$  gave a satisfactory analysis of variance. Refinement by full matrix least squares using a Digital Vax 8800 computer with the SHELX76 system of programs led to  $R = 0.033$  ( $R_w = 0.036$ ) [25]. A final difference Fourier map calculation showed no peaks of chemical significance. Scattering factors with corrections for anomalous dispersion were taken from Ref. [26]. Atomic co-ordinates are listed in Table 5.

Crystals of 1,6-dithiacyclodec-8-yne (**12**) were obtained from  $\text{CH}_2\text{Cl}_2$ -light petroleum as colourless prisms with crystal dimensions ca.  $0.30 \times 0.25 \times 0.25 \text{ mm}^3$ . Data were collected using an Enraf-Nonius FAST area detector diffractometer (293 K, Mo K $\alpha$  X-radiation, graphite monochromator,  $\bar{\lambda} = 0.071069 \text{ \AA}$ ) by the SERC X-ray crystallographic service using procedures described elsewhere [24]. Of the 6209 data collected

Table 5

Atomic coordinates for 1,4-dithiacyclooct-6-yne (**3a**) with e.s.d.s in parentheses

Atom	x	y	z
S(1)	0.0762(1)	0.3905(1)	0.8563(1)
S(2)	0.3106(1)	0.6844(1)	0.7143(1)
C(1)	0.3091(4)	0.3924(2)	0.6877(3)
C(2)	0.1663(4)	0.3198(2)	0.7107(4)
C(3)	0.0508(4)	0.5332(2)	0.7758(3)
C(4)	0.2304(4)	0.6098(2)	0.8613(3)
C(5)	0.4815(4)	0.5833(2)	0.6885(4)
C(6)	0.3988(4)	0.4718(2)	0.6756(3)

Table 6

Atomic coordinates for 1,6-dithiacyclodec-8-yne (**12**) with e.s.d.s in parentheses

Atom	x	y	z
S(1)	0.4595(1)	0.0130(1)	0.1530(1)
S(2)	0.0565(1)	-0.0031(1)	-0.1391(1)
C(1)	0.3422(3)	-0.1871(7)	-0.0413(3)
C(2)	0.4345(3)	-0.2434(6)	0.0560(3)
C(3)	0.3455(3)	-0.0239(8)	0.1947(3)
C(4)	0.2305(3)	0.0007(6)	0.1104(3)
C(5)	0.2052(3)	0.2402(6)	0.0470(4)
C(6)	0.0930(3)	0.2582(6)	-0.0439(4)
C(7)	0.1655(3)	0.0073(9)	-0.1880(3)
C(8)	0.2691(3)	-0.0979(9)	-0.1124(3)

( $2\theta \leq 50^\circ$ ), 1201 unique data had  $F \geq 5\sigma(F)$ , and only these were used for the structure refinement. The data were corrected for Lorentz and polarisation effects.

*Crystal data:*  $\text{C}_8\text{H}_{12}\text{S}_2$ ,  $M = 172.3$ , monoclinic, space group  $P2_1/n$ ,  $a = 13.2066(13)$ ,  $b = 5.1944(23)$ ,  $c = 13.7544(69) \text{ \AA}$ ,  $\beta = 112.550(31)^\circ$ ,  $U = 871.42 \text{ \AA}^3$ ,  $Z = 4$ ,  $D_c = 1.31 \text{ g cm}^{-3}$ ,  $F(000) = 368.0$ ,  $\mu = (\text{Mo K}\alpha) = 0.51 \text{ mm}^{-1}$ .

The structure was solved by direct methods and successive difference Fourier syntheses were used to locate all the atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters, while the hydrogen atoms were refined with isotropic thermal parameters. A weighting scheme of the form  $w^{-1} = [\sigma^2(F) + 0.0005 |F|^2]$  gave a satisfactory analysis of variance. Refinement by full matrix least squares using a Digital Vax 8800 computer with the SHELX76 system of programs led to  $R = 0.050$  ( $R_w = 0.056$ ) [25]. A final difference Fourier map calculation showed no peaks of chemical significance. Scattering factors with corrections for anomalous dispersion were taken from Ref. [26]. Atomic co-ordinates are listed in Table 6. Full listings of bond distances and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Structure factors are available from the authors.

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### References

- [1] S.R. Cooper and S.C. Rawle, *Struct. Bonding (Berlin)*, 72 (1990) 1; A.J. Blake and M. Schröder, *Adv. Inorg. Chem.*, 35 (1990) 1.

- [2] See for example J.C. Lockhart, D.P. Mousley, M.N.S. Hill, N.P. Tomkinson, F. Teixidor, M.P. Almajano, L. Escriche, J.F. Casabo, R. Sillanpää and R. Kivekäs, *J. Chem. Soc. Dalton Trans.*, (1992) 2889; B. de Groot, H.A. Jenkins and S.J. Loeb, *Inorg. Chem.*, 31 (1992) 203.
- [3] F. Demirhan, A. Gelling, S. İrişli, J.C. Jeffery, S.N. Salek, O.S. Şentürk and M.J. Went, *J. Chem. Soc. Dalton Trans.*, (1994) 2765.
- [4] G.F. Mohmand, K. Thiele and M.J. Went, *J. Organomet. Chem.*, 471 (1994) 241.
- [5] A. Krebs and H. Kimling, *Tetrahedron Lett.*, (1970) 761.
- [6] S.M. Kerwin, *Tetrahedron Lett.*, 35 (1995) 1023.
- [7] E. Stavridou, H. Schuhmacher and H. Meier, *Liebigs Ann. Chem.*, (1989) 435.
- [8] H. Meier and Y. Dai, *Tetrahedron Lett.*, 33 (1993) 5277.
- [9] Y. Dai, H. Kolshorn and H. Meier, *Chem. Ber.*, 127 (1994) 1533.
- [10] J.J.H. Edema, J. Buter, F.S. Schoonbeek, R.M. Kellogg, F. van Bolhuis and A.L. Spek, *Inorg. Chem.*, 33 (1994) 2448.
- [11] R. Gleiter, H. Röckel and B. Nuber, *Tetrahedron Lett.*, 36 (1995) 1835.
- [12] G. Elington, I.A. Lardy, R.A. Raphael and G.A. Sim, *J. Chem. Soc.*, (1964) 1154.
- [13] R. Gleiter and S. Rittinger, *Tetrahedron Lett.*, 29 (1988) 4529.
- [14] R. Gleiter, H. Röckel, H. Irgartinger and T. Oeser, *Angew. Chem. Int. Ed. Engl.*, 33 (1994) 1270.
- [15] G. Märkl and R. Vybiral, *Tetrahedron Lett.*, 30 (1989) 2903.
- [16] A. Gelling, G.F. Mohmand, J.C. Jeffery and M.J. Went, *J. Chem. Soc. Dalton Trans.*, (1993) 1857.
- [17] J.L. Pazun, *J. Chem. Inf. Comput. Sci.*, 33 (1993) 931.
- [18] R.J. Smith, S.N. Salek, M.J. Went, P.J. Blower and N.J. Barnard, *J. Chem. Soc. Dalton Trans.*, (1994) 3165.
- [19] R.S. Herrick and J.L. Templeton, *Organometallics*, 1 (1982) 842.
- [20] M.E. Garst and P. Arrhenius, *Synth. Commun.*, 11 (1981) 481.
- [21] D. Sellmann, F. Knoch and C. Wronna, *Angew. Chem. Int. Ed. Engl.*, 27 (1988) 691.
- [22] R.E. Wolf, J.A.R. Hartman, J.M.E. Storey, M.B. Foxman and S.R. Cooper, *J. Am. Chem. Soc.*, 109 (1987) 4328.
- [23] S.J.N. Burgmayer and J.L. Templeton, *Inorg. Chem.*, 24 (1985) 2224.
- [24] A.A. Danopoulos, G. Wilkinson, B. Hussain-Bates and M.B. Hursthouse, *J. Chem. Soc. Dalton Trans.*, (1991) 1855.
- [25] G.M. Sheldrick, *SHELX76 System of Computing Programs*, UK, 1976.
- [26] *International Tables for X-ray Crystallography*, Vol. 4, Kynoch Press, Birmingham, 1974.