Preparation of cyclic and acyclic thioethers via hexacarbonyldicobalt alkyne complexes

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Abstract

Demetallation of $[Co_2\{\mu\text{-}C_2(CH_2SCH_2CH_2)_2S\}(CO)_6]$ with trimethylamine *N*-oxide affords 1,4,7-trithiacycloundec-9-yne, while similar treatment of $[Co_2(CO)_6\{\mu\text{-}(CCH_2SCH_2CH_2SCH_2CH_2SCH_2C)_2\}Co_2(CO)_6]$ affords 1,4,7,12,15,18-hexathiacyclodocos-9,20-diyne. A single crystal X-ray diffraction study and ^{1}H NMR spectroscopy have confirmed that 1,4,7-trithiacycloundec-9-yne adopts an exodentate conformation in the solid and solution states. Trimethylamine *N*-oxide promoted Pauson-Khand reactions of $[Co_2(\mu\text{-}R^1C\equiv CCH_2SR^2)(CO)_6]$ ($R^1 = H$, $R^2 = Et$; $R^1 = Me$, $R^2 = Et$) or $[Co_2(\mu\text{-}RSCH_2C\equiv CCH_2SR)(CO)_6]$ ($R = Et$; $R\text{-}R = CH_2CH_2$, $CH_2CH_2CH_2$ or $CH_2CH_2SCH_2CH_2$) with norbornene or of $[Co_2(\mu\text{-}R^1C\equiv CCH_2SR^2)(CO)_6]$ ($R^1 = H$, $R^2 = Et$; $R^1 = Me$, $R^2 = Et$) with norbornadiene afford a range of cyclopentenone products, which have been characterised by NMR, IR and mass spectroscopy.

*Key words:* Cobalt; Alkyne; Macrocycle; Thioether; Pauson-Khand reaction; Cyclopentenone

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, but several other thiacrown ethers such as 2,5,8-trithia[9]-*o*-benzenophane (ttob) and 2,5,8-trithia[9]-*m*-benzenophane (ttmb) display good ligating properties and useful selectivity [2]. The low affinity of sulfur for alkali metal ions means that template effects observed in the synthesis of macrocyclic polyoxoethers cannot be employed with the same degree of success in the synthesis of polythia rings. Most synthetic methods involve high dilution techniques, and the use of Cs_2CO_3 as the thiol deprotonating agent has been observed greatly to improve the yields in some cases [3]. Alternatively 1,4,7-trithiacyclononane [4] and related ligands [5] have been prepared attached to tricarbonylmolybdenum fragments and then decomplexed. We recently described

the synthesis and co-ordination chemistry of hexacarbonyldicobalt complexed acyclic [6] and cyclic thiaalkynes [7,8] via the acid catalysed reaction of $[Co_2(\mu\text{-}HOCH_2C\equiv CCH_2OH)(CO)_6]$ with thiols and dithiols. Here we report methods of preparation of new thioether-containing compounds by decomplexing the hexacarbonyldicobalt unit or using the Pauson-Khand reaction.
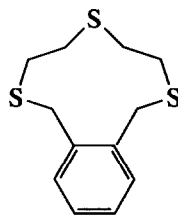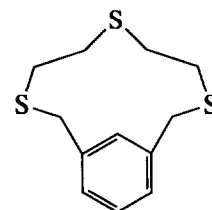
ttob   ttmb

2. Results and discussion

The hexacarbonyldicobalt unit is a well known protecting group for alkynes and one of the milder methods of deprotection involves treatment with trimeth-

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TABLE 1. Selected internuclear distances (Å), angles (°) and torsional angles for compound 1

C(1)–C(2)	1.452(3)
C(1)–C(8)	1.191(3)
C(2)–S(1)	1.829(3)
C(3)–C(4)	1.519(3)
C(3)–S(1)	1.802(3)
C(4)–S(2)	1.824(3)
C(5)–C(6)	1.513(3)
C(5)–S(2)	1.807(3)
C(6)–S(3)	1.818(3)
C(7)–C(8)	1.460(4)
C(7)–S(3)	1.820(3)
C(2)–C(1)–C(8)	175.S(3)
C(1)–C(2)–S(1)	113.4(2)
C(4)–C(3)–S(1)	115.3(2)
C(3)–C(4)–S(2)	113.1(2)
C(6)–C(5)–S(2)	112.8(2)
C(5)–C(6)–S(3)	114.6(2)
C(8)–C(7)–S(3)	112.6(2)
C(1)–C(8)–C(7)	175.0(3)
C(2)–S(1)–C(3)	101.6(1)
C(4)–S(2)–C(5)	102.4(1)
C(6)–S(3)–C(7)	101.7(1)
C(3)–S(1)–C(2)–C(1)	38.6
C(2)–S(1)–C(3)–C(4)	61.7
C(5)–S(2)–C(4)–C(3)	67.3
C(4)–S(2)–C(5)–C(6)	67.9
C(7)–S(3)–C(6)–C(5)	59.1
C(6)–S(3)–C(7)–C(8)	43.2
C(8)–C(1)–C(2)–S(1)	−20.3
C(2)–C(1)–C(8)–C(7)	−26.9
S(1)–C(3)–C(4)–S(2)	−170.1
S(2)–C(5)–C(6)–S(3)	−168.2
S(3)–C(7)–C(8)–C(1)	−60.0

ylamine N-oxide [9]. Treatment of $[Co_2\{\mu\text{-}C_2(CH_2\text{-}SCH_2CH_2)_2S\}(CO)_6]$ with ten equivalents of Me_3NO at room temperature affords 1,4,7-trithiacycloundec-9-yne (1). The presence of the liberated acetylenic bond was confirmed by Raman spectroscopy, which detected

a strong absorption at 2227 cm^{-1}, and by ^{13}C NMR spectroscopy, a resonance at 79.6 ppm being, assigned to the acetylenic carbons. Compound 1 can also be prepared in good yield by a high dilution method [10]. The solid state structure of 1 was established by a single crystal X-ray diffraction study. Selected structural parameters are listed in Table 1 and the molecular structure is shown in Fig. 1. The bond lengths correspond closely to those in previously reported crown thioether structures and in the precursor $[Co_2\{\mu\text{-}C_2(CH_2SCH_2CH_2)_2S\}(CO)_6]$ [8]. The acetylenic bond [1.191(3) Å] is bent slightly (by ca. 5°) from linear. The eleven membered ring adopts an exodentate conformation with all three sulfur atoms pointing out of the ring and has a pseudo two fold rotation axis running through S(2) and the centre of the triple bond. Torsional angles in the $SCH_2CH_2SCH_2CH_2S$ bracket confirm that the carbon-carbon bonds adopt anti conformations while the carbon–sulfur linkages have gauche dispositions, as expected [1]. The non-bonded sulfur–sulfur distance (6.005 Å) is intermediate between that found in ttob (5.76 Å) and ttmb (6.84 Å) [11].
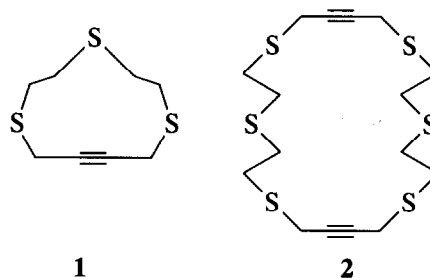

1   2

Information concerning the conformation of 1,4,7-trithiacycloundec-9-yne in solution was obtained from the ^{1}H NMR spectrum, which indicates that the molecule is fluxional, only one AA'BB' pattern being seen for the $SCH_2CH_2SCH_2CH_2S$ fragment. Simula-

TABLE 2. Analytical and physical data

| Compound	Appearance	Yield (%)	[a] ν(CO)(cm^{-1})	[b] Analysis (%)		[c] M
				C	H	
1	white solid	65	–	46.8(47.0)	6.2(5.9)	204
2	white solid	65	–	46.6(47.0)	6.3(5.9)	[d] 408
3	yellow oil	78	1696	70.3(70.2)	8.2(8.2)	222
4	yellow oil	36	1690	70.6(71.1)	8.6(8.5)	236
5	yellow-orange oil	22	1692	–	–	296
6	yellow-brown oil	65	1698	69.8(70.9)	7.3(7.3)	220
7	yellow-brown oil	69	1690	70.6(71.8)	8.5(7.8)	234
8	yellow oil	21	1688	–	–	266
9	dark yellow oil	11	1690	–	–	280
10	greenish yellow oil	2	1684	–	–	326

[a] Film on KBr disc. [b] Calculated values are given in parentheses. [c] Electron impact mass spectroscopy unless otherwise stated. [d] FAB mass spectroscopy.

tion and iterative fitting of the spectrum using LAO-COON PC [12] resulted in the values J 11.14(2), J' 5.13(2) and J_{gem} − 12.3(13) Hz. The vicinal coupling constants indicate an equilibrium containing predominantly *anti*-SCCS fragments [13].

Treatment of $[Co_2(CO)_6\{\mu\text{-}(CCH_2SCH_2CH_2SCH_2\text{-}CH_2SCH_2C)_2\}Co_2(CO)_6]$ with Me_3NO affords 1,4,7, 12,15,18-hexathiacyclodocos-9,20-diyne (2) in a similar manner to 1. The dimeric nature of 2 was confirmed by observation of the molecular ion in the fast atom bombardment (FAB) mass spectrum (see Table 2).

An alternative way to release the cyclothiaalkynes is to utilise the Pauson-Khand reaction [14]. When we started this research it was not known whether sulfide

substituents in the propargylic positions would interfere with the cyclisation process. The only reported studies for this type of substituent were for intramolecular reactions of 1,6-enynes bearing sulfur or oxygen in the homo- or bishomo-propargylic positions, which show an acceleration in rate due to the formation of cyclic intermediates via coordination of the heteroatom to a cobalt centre [15]. This is less likely to occur with the sulfur in the propargylic position, and a procedure was chosen which could be expected to tolerate the sulfide functionality. Use of Me_3NO as a promoter has been shown to allow propargyl alcohol to undergo the Pauson-Khand reaction [16], and the alkenes norbornene and norbornadiene were chosen as they un-
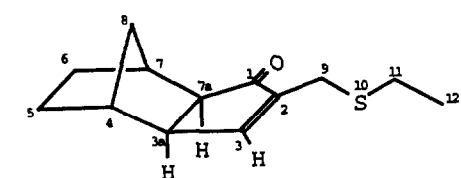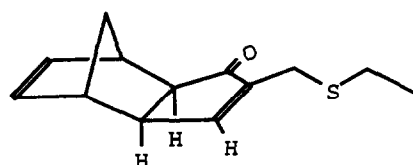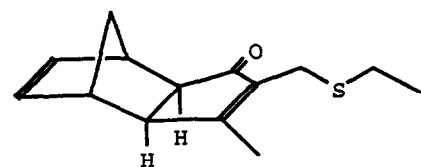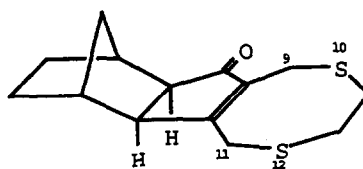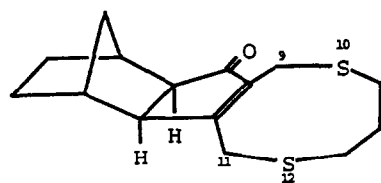

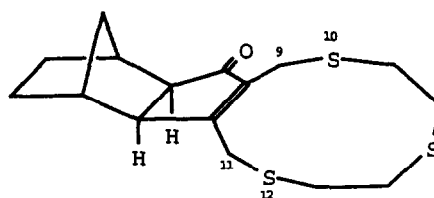3
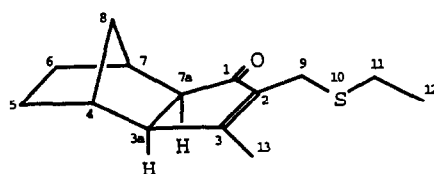
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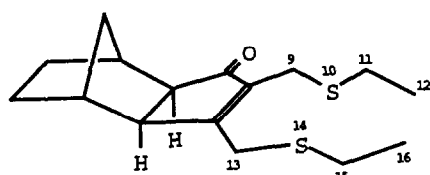
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TABLE 3. ^{1}H-NMR data for the acyclic thioether cyclopentenones [a]

	3-H	3a-H	4-H	5,6-H exo	5,6-H endo	7-H	7a-H	8-H	9-H	11-H	12-H	13-H	15-H	16-H
3	7.31–7.29m	2.64–2.62m	2.24–2.20m	1.33–1.21m	1.69–1.58m	2.42 d,br	2.24–2.20m	0.98m	3.28s	2.51q	1.25t			
4		b	2.28d	1.36–1.23m	1.73–1.55m	2.41s	2.19d	0.96s	3.28s	2.52 m,3H	1.29t	2.11s		
5 [c]		2.82d	2.26d,br	1.35–1.15m	1.66–1.60m (5-H) 1.55–1.49m (6-H)	2.37 d,br	2.17d	0.91s	3.29, 3.20 AB	2.48q	1.21t	3.73, 3.28 AB	2.47q	1.20t
				5-H	6-H									
6	7.36s	2.76s	2.94s	6.23–6.20 app.t	6.31–6.28 app.t	2.71s	2.33d	1.40 d,1H [d]	3.27s	2.52q	1.26 t,4H			
7		2.63d	2.94s	6.24–6.21m	6.29–6.26m	2.78s	2.31d	1.40–1.36 m,1H 1.20–1.17 m,1H	3.28s	2.54q	1.27t	2.12s		

[a] Chemical shifts (δ) in ppm. Measured at 270 MHz in CDCl$_3$ unless otherwise stated. [b] Signal appeared under 11-H signal at 2.52 (m, 3H). [c] Measured at 500 MHz. [d] Signal for other proton appeared under 12-H signal

TABLE 4. ^{13}C-NMR data for the acyclic thioether cyclopentenones[a]

	1	2	3	3a	4	5	6	7	7a	8	9	11	12	13	15	16
3	208.9	145.8	160.1	48.1	38.2	29.1	28.4	39.0	53.8	31.1	24.6	26.0	14.4			
4	208.9	140.9	173.0	52.8	37.4	29.1	28.6	38.8	53.5	31.3	22.8	26.4	14.6	16.0		
5 [b]	209.2	142.0	171.4	49.6	37.5	29.0	28.5	39.0	53.4	31.4	22.6	26.5 [c]	14.5	29.6	26.8 [c]	14.5
6	208.3	147.1	160.3	47.7	43.8	137.1	138.5	43.1	52.7	41.3	25.1	26.3	14.4			
7	207.7	142.0	173.0	52.2	43.5	137.7	138.0	42.3	52.3	41.1	22.9	26.6	14.6	16.0		

[a] Hydrogen-1 decoupled, chemical shifts (δ) in ppm. Measured at 67.8 MHz in CDCl$_3$ unless otherwise stated. [b] Measured at 125.6 MHz. [c] Interchangeable values.
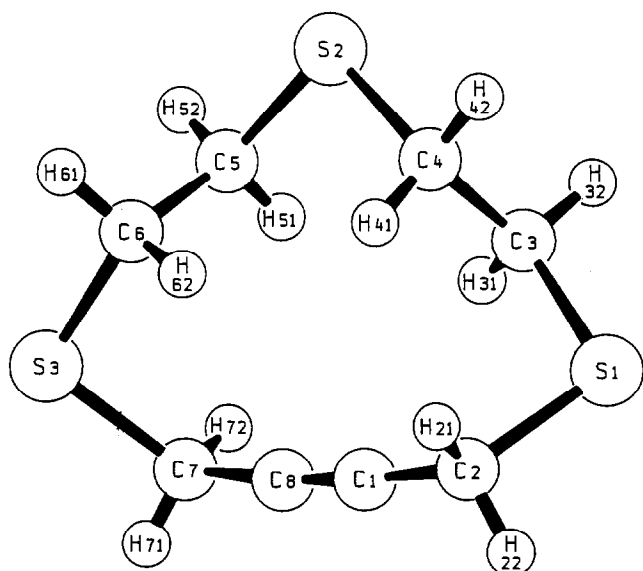
Fig. 1. The molecular structure of 1 showing the atom labelling system.

dergo the Pauson-Khand reaction easily [17]. While this paper was in preparation, Krafft et al. reported the accelerated intramolecular reaction of a 1,6-enyne complex bearing a sulfide in the propargylic position, and suggested that the acceleration is due to polarisation of the alkyne rather than to sulfur coordination [18].

Treatment of solutions of $[Co_2(\mu$-$R^1C\equiv CCH_2SR^2)$-$(CO)_6]$ $(R^1 = H,$ $R^2 = Et;$ $R^1 = Me,$ $R^2 = Et)$ or $[Co_2(\mu$-$RSCH_2C\equiv CCH_2SR)(CO)_6]$ $(R = Et;$ R–$R =$ $CH_2CH_2,$ $CH_2CH_2CH_2$ or $CH_2CH_2SCH_2CH_2)$ and norbornene or of $[Co_2(\mu$-$R^1C\equiv CCH_2SR^2)(CO)_6]$ $(R^1 = H,$ $R^2 = Et;$ $R^1 = Me,$ $R^2 = Et)$ and norbornadiene with Me_3NO at 0°C, and subsequent stirring at room temperature affords the cyclopentanones 3–10. Yields for the monothiaalkynes were reasonable (see Table 2), but those of the dithiaalkynes were poor. This is in

accord with the observation that internal alkynes typically give lower yields of cyclopentenones [17]. Exo-isomers were formed exclusively by norbornene, while the norbornadiene products were formed as exo- and endo-isomers in the ratios exo:endo 94:6 (6) and 92:8 (7). These ratios were determined from the ^{1}H-NMR spectra by means of the 5,6-H signals, which appear separated by ca. 0.2 ppm from each other, with the signal of the endo-isomer highfield shifted relative to the exo-isomer signal, and by the appearance of the significantly downfield shifted 8-H signal of the endo-form relative to the exo-form [19]. The ^{13}C-NMR spectra also showed a second set of low intensity signals due to the endo-isomer.

Free thiaalkyne was found in the product mixture when the dithiaalkyne complexes were used, but not in the case of the monothiaalkyne complexes. Since we have already shown Me_3NO to be a demetallating agent in these systems this result was not surprising, but has not been observed previously for Me_3NO promoted reactions [16]. An explanation might be that cyclisation in these cases proceeds so slowly that demetallation, amongst other side reactions, becomes favoured over cyclisation. The products derived from the dithiaalkynes were difficult to purify even after being subjected several times to chromatography, and satisfactory elemental analyses were not obtained for compounds 5, 8–10. However the IR and NMR spectra and the observation of the expected molecular ions in the electron impact mass spectra (see Tables 2–6) confirmed the identities of the products. All the cyclopentenones showed a strong IR absorption band between 1698 and 1684 (C=O stretching band) and a weaker band at 1636–1624 cm^{-1} (C=C stretching band), and these are typical for α,β-unsaturated ketones.

Assignment of the NMR resonances was made by use of ^{13}C DEPT, ^{1}H-^{1}H COSY and ^{13}C-^{1}H COSY spectra. Confirmation that the products were in the

TABLE 5. ^{1}H-NMR data for the cyclic thioether cyclopentenones[a]

	3a-H	4-H	5-H endo	6-H endo	5,6-H exo	7-H	7a-H	8-H	9-H	11-H	SCH$_2$	CH$_2$
8 [b]	2.78d	2.39d	1.73–1.68m	1.63–1.57m	1.37–1.28m	2.47d	2.27d	1.03–0.98m	3.50, 3.46 AB	3.78, 3.49 AB	2.96–2.84m	
9	2.89d	2.33d	1.73–1.66m	1.64–1.54m	1.40–1.27m	2.46d	2.31d	1.03–0.95m	3.20, 2.91 AB	3.50, 3.15 AB	2.94–2.85 m,2H 2.68–2.54 m,2H	2.01–1.72m
10 [b]	2.50d	2.28d	1.74–1.49m,2H		1.37–1.23	2.41s, br	2.20d	0.95s	3.36–3.27m,3H [c]	3.48–3.40 s,1H 3.36–3.27 m,3H [c]	2.96–2.66m	

[a] Chemical shifts (δ) in ppm. Measured at 270 MHz in $CDCl_3$ unless otherwise stated. [b] Measured at 500 MHz. [c] Overlapping signals

TABLE 6. ^{13}C-NMR data for the cyclic thioether cyclopentenones [a]

	1	2	3	3a	4	5	6	7	7a	8	9	11	SCH$_2$	CH$_2$
8	208.1	141.5	169.9	50.1	37.8	28.4	29.1	38.9	53.8	31.7	22.95	29.2	33.6, 33.1	
9	208.5	143.7	169.5	49.0	37.7	28.6 [c]	29.1	38.9	53.9	31.8	25.2	28.4	31.3, 31.2 [c]	33.6 [c]
10 [b]	208.9	140.6	173.6	52.9	37.4	29.1	28.6	38.8	53.5	32.6 [c]	22.9	31.4 [c]	32.1, 31.9, 31.8, 31.6 [c]	

[a] Hydrogen-1 decoupled, chemical shifts (δ) in ppm. Measured at 67.8 MHz in CDCl$_3$ unless otherwise stated. [b] Measured at 125.6 MHz. [c] Interchangeable values.

exo-form was obtained by comparison with literature data for related compounds [19,20] and by the observation of crosspeaks between the 3a- and 7a-protons and the 8-H signal due to the Cassiopeia effect [21]. This effect occurs in rigidly-held saturated four-bond systems, and coupling is observed if the bonds line up in an M or W shape.

In conclusion, we have shown that propargylic monothioethers undergo the Pauson-Khand reaction with norbornene and norbornadiene in good yield. Cyclodithioethers, however, are less effective in forming cyclopentenone derivatives. The decrease of yields with increasing ring size suggests a dependence upon steric hindrance around the triple bond, as is known to be the case for heavily substituted internal alkynes. Demetallation affords cyclic acetylenic thioethers in good yield, and the coordination chemistry of 1,4,7-trithiacycloundec-9-yne will be the subject of a future paper.

3. Experimental details

The hexacarbonyldicobalt alkyne complexes were prepared by published methods [6–8]. Infra-red spectra were obtained with Mattson Alpha Centauri or Perkin Elmer 983G spectrophotometers. Raman spectra were recorded with a SA multichannel Raman spectrometer model HR640 with a CCD detector. ^{1}H NMR and ^{13}C-{^{1}H} spectra were recorded with JEOL GX 270 and ALPHA 500 instruments. The EI mass spectra were obtained with an AEI MS902 instrument and the FAB mass spectra were obtained by the SERC mass spectrometry service at Swansea with a VG ZAB-E instrument. Elemental analyses were performed by Mr. A.J. Fassam at the University of Kent. The $Me_3NO \cdot H_2O$ was dehydrated by several sublimations under vacuum. Column chromatography and filtrations were performed on silica gel (grade 62, 60-200 mesh) supplied by Aldrich Chemicals.

3.1. Preparation of 1,4,7-trithiacycloundec-9-yne

Toluene (20 ml) was added to a mixture of [Co$_2${μ-C$_2$(CH$_2$SCH$_2$CH$_2$)$_2$S}(CO)$_6$] (0.37 g, 0.76 mmol) and Me$_3$NO (0.57 g, 7.60 mmol) and the resulting solution was stirred for 48 h and then filtered through a pad of Celite. The solvent was then removed in vacuo, and recrystallisation of the residue from light petroleum afforded 1,4,7-trithiacycloundec-9-yne as white crystals (0.10 g, 65%). Raman (C≡C) 2227 cm^{-1}. ^{1}H NMR 500 MHz (CDCl$_3$): δ 3.45 (s, 4H, CCH$_2$); 2.941, 2.926 [AA′BB′, 8H, J 11.14, J' 5.13, J_{gem} − 12.32]. ^{13}C-{^{1}H} NMR 67.8 MHz (CDCl$_3$): 79.6 (C$_2$); 31.4, 30.2, 20.0 (CH$_2$).

3.2. Preparation of 1,4,7,12,15,18-hexathiacyclodocos-9,20-diyne

Toluene (30 ml) was added to a mixture of [Co$_2$-(CO)$_6${μ-(CCH$_2$SCH$_2$CH$_2$SCH$_2$CH$_2$SCH$_2$C)$_2$}Co$_2$-(CO)$_6$] (0.11 g, 0.11 mmol) and Me$_3$NO (0.10 g, 1.33 mmol), and the resulting solution was stirred for 24 h and then filtered. The solvent was removed in vacuo to afford 1,4,7,12,15,18-hexathiacyclodocos-9,20-diyne as a white powder (0.03 g, 65%). ^{1}H NMR 270 MHz (CDCl$_3$): δ 3.38 (s, 8H, CCH$_2$); 2.93 (s br, 16H, SCH$_2$). ^{13}C-{^{1}H} NMR 67.8 MHz (CDCl$_3$): 79.2 (C$_2$); 31.8, 29.7, 19.9 (CH$_2$).

3.3. Pauson-Khand reactions of hexacarbonyldicobalt thioalkyne complexes with norbornene and norbornadiene

A typical experimental procedure is described below for preparation of cyclopentenone 4.

To a solution of [Co$_2$(μ-MeC≡CCH$_2$SEt)(CO)$_6$] (1.42 g, 3.55 mmol) and norbornene (1.67 g, 17.75 mmol) in dichloromethane (40 ml) 4 equiv of dry Me$_3$NO (1.07 g, 14.25 mmol) were added in one portion at −78°C with oxygen bubbling into the mixture. The mixture was stirred for 1 h at −78°C and then allowed to warm to room temperature. During the first 30 min of stirring at room temperature, formation of a violet precipitate started. An infrared spectrum of the reaction mixture after 3.5 h showed a carbonyl stretching band at 1690 cm^{-1} as well as characteristic adsorptions of the starting material. Two more equivalents of Me$_3$NO (0.53 g, 7.06 mmol) were added, and the starting material was completely consumed after 6.25 h of reaction. The mixture was then filtered through a short plug of silica gel and the filtrate evaporated to dryness in vacuo to leave a brown residue. This was redissolved in light-petroleum/CH$_2$Cl$_2$ (1 : 1) and chromatographed on silica gel to afford compound 4 as a yellow oil (0.32 g, 1.35 mmol) in 38% yield.

3.4. Crystal structure determination

Crystals of 1 were obtained from CDCl$_3$-light petroleum as colourless prisms, and a crystal of dimensions ca. 0.30 × 0.25 × 0.25 mm was used. Data were collected on a Enraf-Nonius FAST area detector diffractometer (293 K, Mo-Kα X-radiation, graphite monochromator, λ = 0.710 69 Å) by the SERC X-ray crystallographic service using procedures described elsewhere [22]. Of the 10 090 data collected ($2\theta \leq 50°$), 1643 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.

TABLE 7. Atomic positional (fractional coordinates) parameters with estimated standard deviations in parentheses for compound 1

Atom	x	y	z
S(1)	0.4218(0)	0.1930(1)	0.7701(1)
S(2)	0.2710(0)	0.4476(1)	0.8884(1)
S(3)	0.3827(0)	0.8340(1)	0.9751(1)
C(1)	0.4506(1)	0.4912(3)	0.8175(3)
C(2)	0.4534(1)	0.3701(3)	0.7071(3)
C(3)	0.3632(1)	0.2630(3)	0.8701(3)
C(4)	0.3229(1)	0.3528(3)	0.7761(3)
C(5)	0.3100(1)	0.5886(3)	0.9892(3)
C(6)	0.3324(1)	0.7115(3)	0.8877(3)
C(7)	0.4348(1)	0.6977(3)	1.0294(3)
C(8)	0.4457(1)	0.5858(3)	0.9122(3)

Crystal data for 1: $C_8H_{12}S_3$, M = 204.4, orthorhombic, space group $Pccn$, $a = 24.5974(21), b = 8.7979(6)$, $c = 8.9043(6)$ Å, $U = 1926.9$ Å^3, $Z = 8$, $D_c = 1.41$ gcm^{-3}, $F(000) = 864.0$, $\mu = (Mo-K\alpha) = 0.08$ 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 and the hydrogen atoms with a common isotropic thermal parameter. 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 $R = 0.037$ ($R_w = 0.040$) [23]. A final difference Fourier map calculation showed no peaks of chemical significance. Scattering factors with corrections for anomalous dispersion were taken from reference 24. Atomic co-ordinates are listed in Table 7. A complete list of bond lengths and angles and tables of hydrogen atom coordinates and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre.

Acknowledgments

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