Synthesis and Co-ordination Chemistry of Dicobalt-complexed Thiacycloalkynes†

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The reactions of bis(2-mercaptoethyl) sulfide or bis(2-mercaptoethyl) ether with $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(CO)_6]$ in the presence of $HBF_4{\cdot}OEt_2$ afford $[Co_2\{\mu\text{-}C_2(CH_2SCH_2CH_2)_2X\}(CO)_6]$ (X = S or O) respectively together with dimeric products. The structure of the monomer $[Co_2\{\mu\text{-}C_2(CH_2SCH_2CH_2)_2S\}(CO)_6]$ has been established by X-ray crystallography and comprises a hexacarbonyldicobalt unit transversely bridged *via* the alkyne functionality of 1,4,7-trithiacycloundec-9-yne which has an exodentate conformation. Proton NMR studies of the bis(2-mercaptoethyl) sulfide derivatives reveal that the SCH_2CH_2S linkages are predominantly *anti* in solution. The monomers undergo carbonyl substitution by bis(diphenylphosphino)methane (dppm) to afford $[Co_2\{\mu\text{-}C_2(CH_2SCH_2CH_2)_2X\}(\mu\text{-dppm})(CO)_4]$ (X = S or O) which react with $[Mo(CO)_3(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)]$ to afford products in which the macrocycles face cap $Mo(CO)_3$ fragments. Reaction of $[Co_2\{\mu\text{-}C_2(CH_2SCH_2CH_2)_2S\}(CO)_6]$ with $AgBF_4$ and PPh_3 yields $[Co_2\{\mu\text{-}C_2(CH_2SCH_2CH_2)_2S\}(CO)_6\{Ag(PPh_3)\}]BF_4$ for which an X-ray crystallographic study revealed that the $Ag(PPh_3)^+$ fragment is co-ordinated by all three sulfur atoms of the ring which adopts an endodentate conformation. Reaction of $[Co_2\{\mu\text{-}C_2(CH_2SCH_2CH_2)_2S\}(CO)_6]$ with $[Cu(MeCN)_4]PF_6$ affords $[Co_2\{\mu\text{-}C_2(CH_2SCH_2CH_2)_2S\}(CO)_6\{Cu(MeCN)\}]PF_6$ containing a labile acetonitrile ligand which undergoes substitution by phosphines. The dimeric compound $[(OC)_6Co_2\{\mu\text{-}(CCH_2SCH_2CH_2SCH_2CH_2SCH_2C)_2\}Co_2(CO)_6]$ produces a 1:1 adduct when treated with $AgBF_4$. X-Ray crystallography reveals that the silver ion is co-ordinated by four of the six available thioether groups.

Polythioether macrocycles have been extensively studied in recent years due to their ability to co-ordinate transition metals and coinage metals in unusual oxidation states and geometries.[1] Applications of these versatile ligands are being found in nuclear medicine,[2] organometallic chemistry,[3] and sensors for thiophilic metals such as silver.[4] We have recently reported a synthetic route to hexacarbonyldicobalt complexed thiacycloalkynes *via* the acid-catalysed reaction of dithiols with $[Co_2(\mu\text{-}HOCR^1R^2C{\equiv}CCR^1R^2OH)(CO)_6]$ ($R^1 = R^2$ = H or Me; R^1 = H, R^2 = Me).[5] In this paper we describe the application of this methodology to the synthesis of hexacarbonyldicobalt cyclic polythioether and mixed ether-thioether systems containing three or six heteroatoms and a preliminary investigation of their co-ordination chemistry. Motivation for this study came from the previous observation that the structure of $[(Ph_3P)(OC)_5Co_2\{\mu\text{-}(C_2CH_2OSiPh_2OCH_2)_2\}Co_2(CO)_5(PPh_3)]$ could be related to 7,7,16,16-tetraphenyldibenzo[*e*,*l*][1,3,8,10,2,9]tetraoxadisilacyclotetradecine, highlighting the similarity in geometries of benzene-1,2-dimethanol and the co-ordinated but-2-yne-1,4-diol.[6] Therefore the monomeric product of the acid-catalysed reaction of $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(CO)_6]$ with bis(2-mercaptoethyl) sulfide, $[Co_2\{\mu\text{-}C_2(CH_2SCH_2CH_2)_2S\}(CO)_6]$,[7] may reasonably be expected to have a similar geometry and display similar co-ordination chemistry to 2,5,8-trithia[9]-*o*-benzenophane (ttob). The co-ordination chemistry of 1,4,7-trithiacyclononane and related cyclic polythioethers[1] suggests that the best ligating properties are obtained when the sulfur donor atoms are preorganised in an endodentate conformation. Although the conformation of free ttob is exodentate,[8,9] there is considerable strain in the $SCH_2CH_2SCH_2CH_2S$ bracket and the ligand easily converts into an endodentate conformation, as demonstrated by the structures of $[Mo(CO)_3(ttob)]$,[9] $[Cu(PMePh_2)(ttob)]ClO_4$,[10] $[Ag(PPh_3)(ttob)]ClO_4$,[10] $[PdCl_2(ttob)]$[11] and $[Ag(ttob)_2]X$ (X = ClO_4, BPh_4 or CF_3SO_3).[12] It has been observed that incorporation of metallocene redox-active centres into various macrocyclic host structural frameworks is of potential use in the design of sensory devices[13] and the use of dicobalt alkynes in sensor applications is currently being investigated.[14] Parts of this work have appeared in preliminary communications.[7,15]

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Results and Discussion

Reaction of $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(CO)_6]$ with bis(2-mercaptoethyl) sulfide in the presence of $HBF_4{\cdot}OEt_2$ affords the cyclic compounds **1a** and **1b** as well as a small amount of uncyclised $[Co_2\{\mu\text{-}(HOCH_2C{\equiv}CCH_2SCH_2CH_2SCH_2CH_2SH)\}(CO)_6]$. The products were separated by column chromatography and the molecular weights of the monomer and dimer confirmed by mass spectroscopy (see Experimental section). Compounds **2a** and **2b** were similarly prepared by reaction of $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(CO)_6]$ with bis(2-mercaptoethyl) ether. Analytical and IR data for the new compounds are given in Table 1, NMR data in Table 2. Single crystals of **1a** suitable for X-ray diffraction were obtained by cooling a saturated light petroleum solution of the compound to *ca.* 260 K. Selected structural parameters are listed in Table 3 and the molecular structure is shown in Fig. 1.

The complex has crystallographically imposed two-fold symmetry. The central sulfur atom, S(2), and the midpoint of the Co–Co(A) vector lie on the two-fold axis and atoms with a suffix A are generated by symmetry. The molecular structure comprises of a hexacarbonyldicobalt unit transversely bridged by 1,4,7-trithiacycloundec-9-yne. All the bond lengths and angles about the pseudo-tetrahedral Co_2C_2 core are within the

Table 1 Analytical[a] and physical data

Compound	Colour	Yield (%)	$\tilde{\nu}_{\|\|}$(CO)/cm^{-1}	Analysis (%) C	Analysis (%) H
1a	Red	59	2093m, 2056vs, 2031s, 2026m, 2013w[b]	33.6 (34.3)	2.6 (2.5)
1b	Red	20	2093m, 2056vs, 2032s, 2026m, 2014w[b]	33.7 (34.3)	2.6 (2.5)
2a	Red	38	2092m, 2055s, 2031s, 2009(sh), 1981vw[b]	34.9 (35.5)	2.6 (2.6)
2b	Red	29	2092m, 2056s, 2031s, 2026(sh), 2009(sh), 1981vw[b]	35.4 (35.5)	2.8 (2.6)
3·CH_2Cl_2	Pink	57	2023m, 1993s, 1965m, 1947(sh)[c]	50.8 (50.5)	4.0 (4.0)
4	Red	72	2019m, 1986s, 1958m[d]	55.2 (55.4)	4.2 (4.3)
5	Orange	76	2098m, 2060vs, 2028s[c]	41.4 (40.6)	3.0 (2.9)
6	Orange	72	2098m, 2061vs, 2038s[c]	25.3 (26.0)	1.8 (2.0)
7	Red-brown	60	2097m, 2057vs, 2027s[c]	38.1 (40.0)	2.9 (2.8)
8	Red	42	2100m, 2062vs, 2040s, 2034(sh)[c]	36.8 (36.2)	2.7 (2.5)
9	Red	95	2026m, 1997s, 1970m, 1936s, 1832m, 1819(sh)[c]	48.0 (48.1)	3.4 (3.4)
10	Dark red	34	2024m, 1996s, 1969m, 1931s, 1810s[c]	48.3 (48.9)	4.1 (3.5)
11	Red	76	2097m, 2059s, 2031s[e]	28.4 (28.6)	2.1 (2.0)

[a] Calculated values are given in parentheses. [b] In light petroleum. [c] In dichloromethane. [d] In benzene. [e] In acetonitrile.

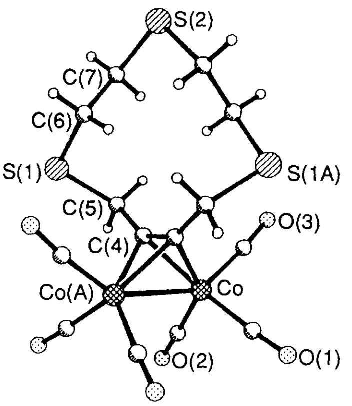
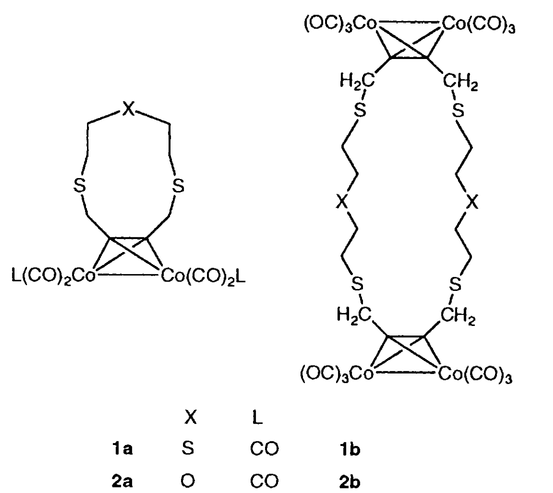


Fig. 1 The molecular structure of compound **1a** showing the atom labelling system



	X	L	
1a	S	CO	**1b**
2a	O	CO	**2b**
3	S	½ dppm	
4	O	½ dppm	

dppm = $Ph_2PCH_2PPh_2$

ranges normally expected for this type of structure.[6,16,17] Dimensions within the ring compare well to those found previously for other macrocyclic thioethers. Sulfur–carbon distances range from 1.803(5) to 1.821(4) Å while the non-bonded distances S(1) ··· S(1A) and S(1) ··· S(2) are 5.536 and 4.442 Å, respectively. The ideal sulfur–sulfur 'bite' of the $SCH_2CH_2SCH_2CH_2S$ bracket has been calculated[9] to be 6.74 Å and may account for angle C(5)–C(4)–C(4A) [149.1(2)°] being higher than in [Co_2(μ-$HOCH_2C{\equiv}CCH_2OH$)$(CO)_6$] [143.9(3)°] despite the formation of a cyclic system. In contrast the eight-membered ring system [Co_2(μ-$CCH_2SCH_2CH_2SCH_2C$)(μ-dppm)$(CO)_4$] (dppm = $Ph_2PCH_2PPh_2$) has corresponding angles of 138.2(7) and 139.3(6)°.[5] The conformations of crown thioethers are usually described in terms of torsional angles, particularly those associated with the $SCH_2CH_2SCH_2CH_2S$ brackets which are formed due to a propensity of S–C bonds to favour *gauche* placement and C–C bonds to favour *anti* placement when part of a $SCH_2CH_2SCH_2CH_2S$ chain. The S(1)–C(6)–C(7)–S(2) torsional angle is −169.1° while the C–S–C–C torsional angles average 63.4° in accord with this general behaviour and the analogous angles found in ttob. The structure of **1a** differs from that of ttob significantly in the relationship of the dicobalt fragment to the ring compared to the relationship of the *o*-benzene fragment to the ring in ttob. The dicobalt unit, although twisted with respect to the plane of the ring, is symmetrically disposed about each side of the ring while the *o*-benzene fragment lies on one side of the ring in ttob. The dihedral angle between the plane defined by the aromatic ring carbon atoms and the plane defined by the three sulfur atoms in ttob is 96.1°. This difference is also reflected in the torsional angle S(1)–C(5)–C(4)–C(4A) (−72.1°), which is significantly different from the corresponding angles in ttob (−138.7 and 128.4°).

Information concerning the conformations of compounds **1a** and **1b** in solution was obtained for the ^1H NMR spectra. The results indicate that the molecules are fluxional, with only one apparent AA'BB' pattern for the $SCH_2CH_2SCH_2CH_2S$ moiety. Although the spectra were broadened by the cobalt quadrupole a simulation of **1a** was obtained using LAOCOON PC[18] with δ 3.07 and 2.90, J 9.1, J' 6.1 and J_{gem} −13.0 Hz, while sufficient resolution was obtained with **1b** recorded in C_6D_6 to perform an iterative fit to obtain δ 2.61(2) and 2.54(2), J 10.47(3), J' 5.50(3) and J_{gem} −12.5(14) Hz. The observed and calculated spectra for **1b** are shown in Fig. 2. The vicinal coupling constants indicate an equilibrium containing predominantly *anti*-SCCS fragments in both **1a** and **1b**.[8] For **2a** and **2b** ^1H NMR spectra of sufficient resolution for detailed analysis were not obtained. The ^{13}C NMR spectra for compounds **1** and **2** were as expected (Table 2) with only small chemical shift differences between the monomers and the dimers.

Surprisingly, reaction of $HS(CH_2CH_2S)_3H$ with [Co_2(μ-$HOCH_2C{\equiv}CCH_2OH$)$(CO)_6$] in the presence of $HBF_4{\cdot}OEt_2$ afforded compounds **1a** and **1b** with only a small amount of the expected [Co_2{μ-$CCH_2(SCH_2CH_2)_3SCH_2C$}$(CO)_6$]. A possible explanation is that having formed one thioether linkage the second cation to be generated *via* protonation and loss of H_2O is stabilised by co-ordination of a thioether in the chain rather than the remaining thiol group. Such co-ordination

Table 2 Hydrogen-1 and carbon-13 NMR data[a]

Compound	$^{1}H(\delta)$	$^{13}C(\delta)$[b]
1a	4.16 (s, 4 H, CCH_2), 3.09–2.85 (m, 8 H, CH_2CH_2)	199.1 (CO), 93.9 (C_2), 35.0, 30.4, 28.5 (CH_2)
1b	4.09 (s, 8 H, CCH_2), 3.01–2.85 (m, 16 H, CH_2CH_2)	199.2 (CO), 94.0 (C_2), 36.9, 33.6, 32.4 (CH_2)
2a	4.4 (s, 4 H, CCH_2), 4.0 [t, 4 H, OCH_2, *J*(HH) 5], 2.9 [t, 4 H, SCH_2, *J*(HH) 5]	199.8 (CO), 96.0 (C_2), 72.3 (OCH_2), 37.4, 33.3 (CH_2)
2b	4.2 (s, 8 H, CCH_2), 3.8 [t, 8 H, OCH_2, *J*(HH) 6], 2.9 [t, 8 H, SCH_2, *J*(HH) 6]	199.5 (CO), 95.3 (C_2), 71.5 (OCH_2), 37.3, 32.9 (CH_2)
3	7.4–7.2 (m, 20 H, Ph), 4.15 (s, 4 H, CCH_2), 3.50 [t, 2 H, PCH_2, *J*(PH) 10], 3.14–2.88 (m, 8 H, CH_2CH_2)[c]	205.6 (CO), 137–128 (Ph), 95.3 (C_2), 42.5 [t, PCH_2, *J*(PC) 20], 36.3, 32.6, 29.9 (CH_2)[c]
4	7.5–7.1 (m, 20 H, Ph), 4.3 [t, 4 H, CCH_2, *J*(PH) 3], 4.1–3.8 (m, 4 H, OCH_2), 3.4 [t, 2 H, PCH_2, *J*(PH) 10], 3.0–2.7 (m, 4 H, SCH_2)	205.0 (CO), 137–128 (Ph), 95.6 (C_2), 71.7 (OCH_2), 42.0 [t, PCH_2, *J*(PC) 19], 38.0, 33.2 (CH_2)
5	7.5–7.3 (m, 15 H, Ph), 4.55 (s, 4 H, CCH_2), 3.3–3.1 (m, 8 H, CH_2CH_2)[c]	200.0 (CO), 135–130 (Ph), 90.4 (C_2), 37.1, 34.2, 31.2 (CH_2)[d]
6	4.57, 4.37 [AB, 4 H, CCH_2, *J*(AB) 15], 3.3–2.9 (m, 8 H, CH_2CH_2), 2.20 (s, 3 H, CH_3)	198.6, 197.7 (CO), 118.3 (CN), 87.1 (C_2), 37.7, 36.7, 33.1 (CH_2)
7	7.6–7.2 (m, 15 H, Ph), 4.63, 4.56 [AB, 4 H, CCH_2, *J*(AB) 16], 3.4–2.8 (m, 8 H, CH_2CH_2)	199.0, 198.2 (CO), 134–129 (Ph), 86.4 (C_2), 38.7, 37.0, 33.6 (CH_2)[c]
8	7.6–7.1 (m, 20 H, Ph), 4.47 (s, 8 H, CCH_2), 3.2–2.9 (m, 16 H, CH_2CH_2)[d]	199.8 (CO), 134–130 (Ph), 103.5 [d, PC≡CP, *J*(PC) 41], 89.1 (C_2), 38.0, 36.8, 33.7 (CH_2)
9	7.44–7.27 (m, 20 H, Ph), 4.53 [d, 2 H, CCH_2, *J*(HH) 15], 4.33 [d of t, 2 H, CCH_2, *J*(HH) 15, *J*(PH) 4], 3.46 [t, 2 H, PCH_2, *J*(PH) 10], 3.01–2.68 (m, 8 H, CH_2CH_2)[c]	221.9 [Mo(CO)], 219.9 [$Mo(CO)_2$], 205.0, 204.3 [$Co(CO)_2$], 137–128 (Ph), 88.1 (C_2), 44.1 (CH_2), 41.3 [t, PCH_2P, *J*(PC) 20], 35.2, 33.5 (CH_2)[d]
10	7.3–7.1 (m, 20 H, Ph), 4.6–2.8 (m, 14 H, CH_2)[c]	227.0 [Mo(CO)], 220.3 [$Mo(CO)_2$], 204.9, 204.6 [$Co(CO)_2$], 138–129 (Ph), 87.9 (C_2), 71.0 (OCH_2), 40.8 [t, PCH_2P, *J*(PC) 20], 42.8, 33.5 (CH_2)[c]
11	4.20 (s, 8 H, CCH_2), 3.06 (s, 16 H, CH_2CH_2)[d]	200.2 (CO), 92.5 (C_2), 37.8, 33.9, 33.2 (CH_2)[d]

[a] Chemical shifts (δ) in ppm, coupling constants in Hz. Measured in $CDCl_3$ unless otherwise stated. [b] Hydrogen-1 decoupled. [c] Measured in CD_2Cl_2. [d] Measured in CD_3CN.

Table 3 Selected internuclear distances (Å), angles (°) and torsional angles (°) for complex **1a**

Co–C(1)	1.817(6)	C(1)–O(1)	1.123(8)	Co–C(2)	1.824(6)	S(2)–C(7A)	1.821(4)
Co–C(3)	1.806(6)	C(3)–O(3)	1.128(8)	Co–C(4)	1.962(4)	C(2)–O(2)	1.117(9)
Co–Co(A)	2.498(2)	C(4)–Co(A)	1.964(4)	Co–C(4A)	1.964(4)	C(4)–C(5)	1.485(6)
S(1)–C(5)	1.815(4)	C(6)–C(7)	1.509(6)	S(1)–C(6)	1.803(5)	C(4)–C(4A)	1.346(8)
S(2)–C(7)	1.820(4)						
C(1)–Co–C(2)	106.2(3)	C(3)–Co–Co(A)	145.8(2)	S(1)–C(5)–C(4)	115.6(3)	C(4)–Co–C(4A)	40.1(2)
C(2)–Co–C(3)	100.5(3)	C(7)–S(2)–C(7A)	101.1(3)	S(2)–C(7)–C(6)	115.1(3)	C(5)–S(1)–C(6)	101.0(2)
C(2)–Co–C(4)	106.3(2)	C(5)–C(4)–C(4A)	149.1(2)	C(3)–Co–C(4A)	100.5(2)	S(1)–C(6)–C(7)	112.7(3)
C(6)–S(1)–C(5)–C(4)	69.6	C(7A)–S(2)–C(7)–C(6)	54.3	C(5A)–C(4A)–C(4)–C(5)	7.9		
C(4A)–C(4)–C(5)–S(1)	−72.1	S(1)–C(6)–C(7)–S(2)	−169.1	C(5)–S(1)–C(6)–C(7)	72.4		

has been observed by treating the proparglic cationic complex $[Co_2(\mu\text{-}HC{\equiv}CCH_2)(CO)_6]BF_4$ with SR^1R^2 ($R^1 = R^2$ = Me, Et or Pr^i; R^1 = Me, R^2 = Et) to form $[Co_2(\mu\text{-}HC{\equiv}CCH_2SR^1R^2)(CO)_6]BF_4$.[19] Hydrolysis could lead to loss of the fragment $CH_2CH_2SH^+$ and result in the formation of **1a**.[20] We have already shown that under acid conditions monomers and dimers of this type can interconvert and hence **1b** could be obtained.[5]

The bis(diphenylphosphino)methane derivatives **3** and **4** were prepared by substitution of **1a** and **2a** respectively. Compound **3** consistently gave low carbon and hydrogen analyses (Table 1) suggesting the presence of 1 mol equivalent of dichloromethane in the solid. This was also observed in the ^1H NMR spectra. The molecular weight of **3** was confirmed by FAB mass spectroscopy (see Experimental section). The NMR spectra of **3** and **4** are similar to previously prepared compounds[5] and were not sufficiently well resolved to establish the ring conformations.

Reaction of an acetonitrile solution of compound **1a** with equimolar quantities of $AgBF_4$ and PPh_3 affords **5**. Formation of a cationic complex is reflected in the IR spectrum by a small shift of the cobalt carbonyl absorptions to higher wavenumber (*ca.* 4 cm^{-1}). The NMR spectra of **5** show that the compound is fluxional at room temperature and will be discussed in detail after the results of an X-ray crystallographc study which established the solid-state structure. Selected structural parameters are listed in Table 4 and the molecular structure is shown in Fig. 3. The $Ag(PPh_3)^+$ fragment is co-ordinated by all three sulfur atoms of the ring, which now adopts an endodentate conformation. Torsional angles about the C–C bonds are 61.4 and 63.0°. The structure can be compared with that of $[Ag(PPh_3)(ttob)]^+$ with distortions caused by the steric bulk of the dicobalt unit, and the wider angles at the acetylenic carbons [C(2)–C(1)–C(8) 147.6(6) and C(1)–C(8)–C(7) 147.8(5)°] compared with those in the benzenophane (*ca.* 123°).[10] The Ag–S distances are 2.579(2) and 2.595(2) Å for S(1) and S(3) and 2.688(2) Å for the central S(2) atom. These distances are respectively 0.014, 0.041 and 0.088 Å longer than the corresponding distances in $[Ag(PPh_3)(ttob)]^+$. The S–Ag–S angles for the five-membered chelate rings are 82.1(1) and 83.7 (1)°, and the S–Ag–S angle for the seven-membered chelate ring is 104.8(1)°. The silver–phosphorus distance [2.416(2) Å] is longer than the corresponding distance in $[Ag(PPh_3)(ttob)]^+$ [2.382(1) Å].

The room-temperature ^1H NMR spectrum of compound **5** contains a single resonance due to the methylene protons adjacent to the alkyne carbons at δ 4.55, compared to δ 4.16 for **1a**, and broad unresolved multiplets for the backbone methylenes and the aromatic protons. Low-temperature ^1H NMR spectra are in accord with the solid-state structure; the methylene protons adjacent to the alkyne carbons appear as an AB pattern (δ 4.63, 4.56, J_{AB} = 16 Hz) at 212 K, indicating that

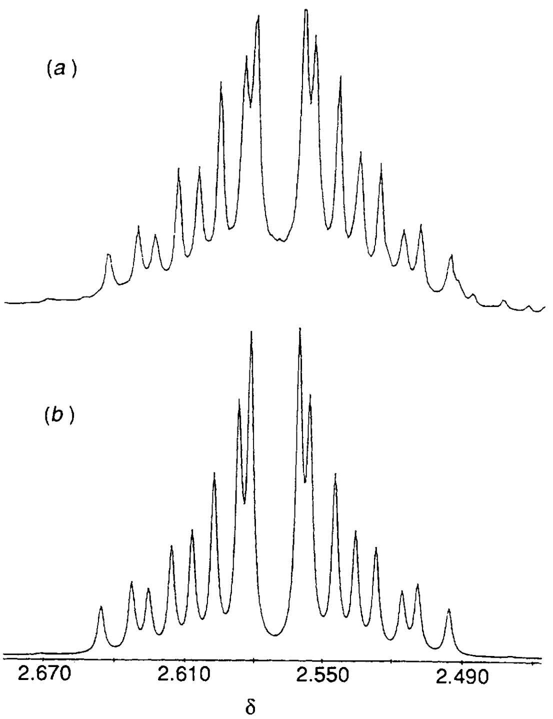
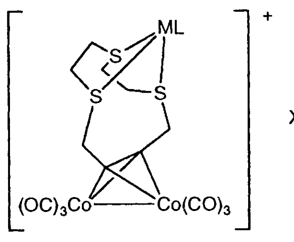
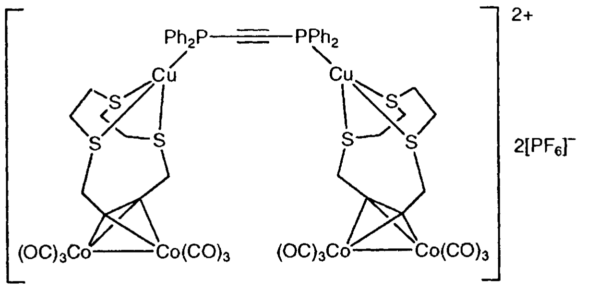


Fig. 2 The AA'BB' ^1H NMR spectrum of the $SCH_2CH_2SCH_2CH_2S$ section of compound **1b**: (*a*) observed and (*b*) simulated with LAOCOON PC



	M	L	X
5	Ag	PPh_3	BF_4
6	Cu	MeCN	PF_6
7	Cu	PPh_3	PF_6



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at room temperature a fluxional process equivalences both sides of the macrocyclic ring. This is not observed in $[Ag(PPh_3)(ttob)]^+$ where the chemical shift difference between the benzylic protons is larger.[10] Fluxionality in compound **5** could be achieved by the $Ag(PPh_3)^+$ pivoting about the unique sulfur and hence migrating between the two faces or by intermolecular exchange of $Ag(PPh_3)^+$ fragments.

Reaction of equimolar quantities of compounds **1a** and $[Cu(MeCN)_4]PF_6$ at room temperature affords **6** containing a co-ordinated $Cu(MeCN)^+$ fragment. The NMR spectra of **6** reveal that it is static on the NMR time-scale at room temperature. The acetylenic methylenes appear as an AB pattern and two resonances are observed in the ^{13}C-{^1H} NMR spectrum for the carbonyl ligands. The acetonitrile ligand is very labile and the highest-mass fragment observed in the FAB mass spectrum corresponds to $[M - PF_6 - MeCN]^+$. The analysis for nitrogen was consistently low, also suggesting ready loss of the acetonitrile.

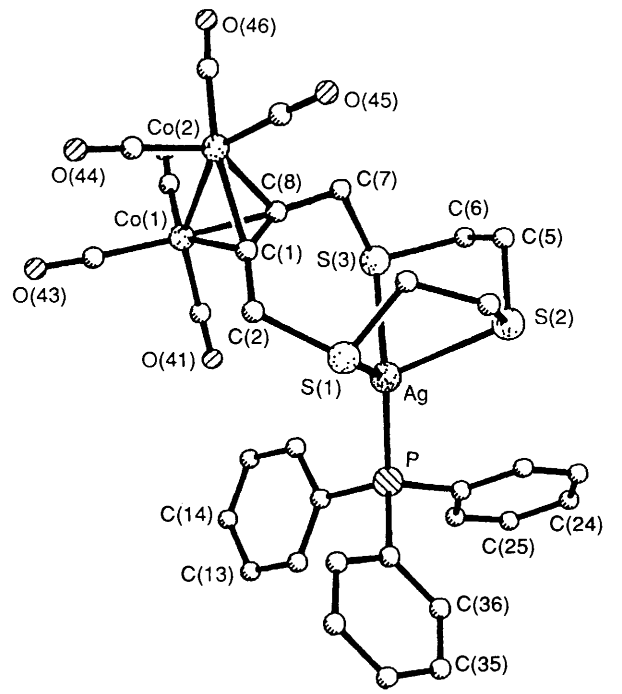


Fig. 3 The molecular structure of compound **5** showing the atom labelling system

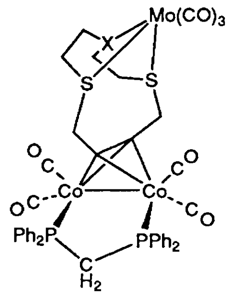
Reaction of compound **6** with triphenylphosphine results in substitution of the acetonitrile with triphenylphosphine to produce **7** in a similar manner to the reactions of $[Cu(MeCN)(ttob)]^+$.[10] Reaction of **6** with 1,2-bis(diphenylphosphino)ethane (dppe) abstracts the copper ion to afford $[Cu(dppe)_2]^+$ and **1a** is released. This contrasts with the observation that 2,5,8,17,20,23-hexathia[9](1,2)[9](4,5)cyclophane (L) reacts with $[Cu(MeCN)_4]PF_6$ and dppe to afford $[Cu_2L(\mu\text{-dppe})][PF_6]_2$ in which the dppe bridges between the two copper atoms.[21] Reaction of **6** with bis(diphenylphosphino)acetylene (dppa) which is incapable of chelation affords $[Co_2\{\mu\text{-}C_2(CH_2SCH_2CH_2)_2S\}(CO)_6\{Cu(\mu\text{-dppa})Cu\}Co_2\{\mu\text{-}C_2(CH_2SCH_2CH_2)_2S\}(CO)_6][PF_6]_2$ **8** in which the two copper centres are linked by dppa.

Attempts to prepare molybdenum tricarbonyl derivatives of **1a** were hampered by its thermal instability, which rapidly decomposes above 60 °C. Compounds **3** and **4** in which the metal–metal bond is supported by a dppm ligand are more stable and were treated with $[Mo(CO)_3(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)]$ in refluxing tetrahydrofuran to afford **9** and **10** which are not stable to chromatography on Florisil and were purified by filtration and crystallisation. The NMR spectra of **9** revealed that the mesitylene had been displaced by the three thioether functionalities of the macrocyclic ring. In the ^1H NMR spectrum the methylenic hydrogens appear as a doublet and a doublet of triplets, indicating that the $Mo(CO)_3$ fragment is co-ordinated to one face of the ring and is static on the NMR time-scale. The small triplet coupling of 4 Hz is ascribed to long-range phosphorus coupling. The ^{13}C-{^1H} NMR spectrum contains resonances due to the molybdenum carbonyl ligands at δ 221.9 and 219.9 in the ratio 1 : 2 and two broader peaks assigned to the cobalt carbonyls. Only one alkyne carbon resonance is observed indicating that alkyne rocking about the cobalt–cobalt vector is fast on the NMR time-scale at room temperature.[5] Compound **10** is analogous to **9**, but considerably less stable.

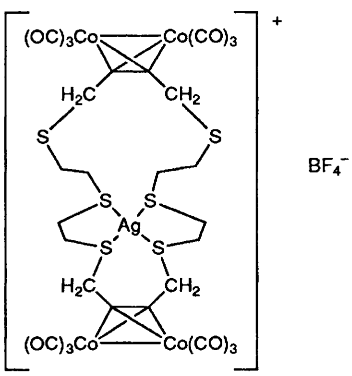
Table 4 Selected internuclear distances (Å), angles (°) and torsional angles (°) for complex **5**

Ag–S(1)	2.579(2)	Ag–S(2)	2.688(2)	Ag–S(3)	2.595(2)	Ag–P	2.416(2)
Co(1)–Co(2)	2.466(2)	Co(1)–C(1)	1.968(4)	Co(1)–C(8)	1.949(5)	Co(1)–C(41)	1.766(7)
Co(1)–C(42)	1.817(6)	Co(1)–C(43)	1.821(7)	Co(2)–C(1)	1.970(5)	Co(2)–C(8)	1.958(5)
Co(2)–C(44)	1.816(7)	Co(2)–C(45)	1.794(5)	Co(2)–C(46)	1.826(7)	S(1)–C(2)	1.822(7)
S(1)–C(3)	1.826(5)	S(2)–C(4)	1.820(6)	S(2)–C(5)	1.819(7)	S(3)–C(6)	1.837(8)
S(3)–C(7)	1.836(6)	C(1)–C(2)	1.492(7)	C(1)–C(8)	1.328(7)	C(3)–C(4)	1.506(10)
C(5)–C(6)	1.499(7)	C(7)–C(8)	1.482(8)	C(41)–O(41)	1.127(10)	C(42)–O(42)	1.132(8)
C(43)–O(43)	1.132(10)	C(44)–O(44)	1.132(9)	C(45)–O(45)	1.130(6)	C(46)–O(46)	1.114(9)

S(1)–Ag–S(2)	82.1(1)	S(1)–Ag–S(3)	104.8(1)	S(2)–Ag–S(3)	83.7(1)
S(1)–Ag–P	126.8(1)	S(2)–Ag–P	118.9(1)	S(3)–Ag–P	124.5(1)
Ag–S(1)–C(2)	113.8(1)	Ag–S(1)–C(3)	99.7(2)	C(2)–S(1)–C(3)	100.0(3)
Ag–S(2)–C(4)	100.3(2)	Ag–S(2)–C(5)	100.1(2)	C(4)–S(2)–C(5)	102.5(3)
Ag–S(3)–C(6)	97.7(2)	Ag–S(3)–C(7)	114.7(2)	C(6)–S(3)–C(7)	100.2(3)
Ag–P–C(11)	118.6(2)	Ag–P–C(21)	114.7(1)	C(11)–P–C(21)	103.8(2)
Ag–P–C(31)	109.7(1)	C(11)–P–C(31)	103.6(2)	C(21)–P–C(31)	105.0(3)
Co(1)–C(1)–Co(2)	77.5(2)	Co(1)–C(1)–C(2)	131.8(3)	Co(2)–C(1)–C(2)	132.0(3)
Co(1)–C(1)–C(8)	69.4(3)	Co(2)–C(1)–C(8)	69.8(3)	C(2)–C(1)–C(8)	147.6(6)
S(1)–C(2)–C(1)	117.0(4)	S(1)–C(3)–C(4)	111.7(4)	S(2)–C(4)–C(3)	116.3(3)
S(2)–C(5)–C(6)	115.9(4)	S(3)–C(6)–C(5)	116.0(5)	S(3)–C(7)–C(8)	113.4(4)
Co(1)–C(8)–Co(2)	78.3(2)	Co(1)–C(8)–C(1)	71.0(3)	Co(2)–C(8)–C(1)	70.7(3)
Co(1)–C(8)–C(7)	133.5(3)	Co(2)–C(8)–C(7)	127.6(3)	C(1)–C(8)–C(7)	147.8(5)
C(1)–C(2)–S(1)–C(3)	62.7	C(8)–C(1)–C(2)–S(1)	−3.8	C(4)–C(3)–S(1)–C(2)	−171.4
C(5)–S(2)–C(4)–C(3)	70.8	S(2)–C(4)–C(3)–S(1)	63.0	C(6)–C(5)–S(2)–C(4)	−133.8
C(5)–C(6)–S(3)–C(7)	64.7	S(3)–C(6)–C(5)–S(2)	61.4	C(8)–C(7)–S(3)–C(6)	−148.4
C(7)–C(8)–C(1)–C(2)	−7.5	S(3)–C(7)–C(8)–C(1)	63.3		



	X
9	S
10	O



11

The dimeric compound **1b** has six thioether functionalities and was treated with $AgBF_4$ to establish whether a soft metal ion could be encapsulated. Analytical data and FAB mass spectroscopy established that the product **11** was a 1 : 1 adduct. Compound **11** has poor solubility in most solvents and only a relatively weak $^{13}C-\{^1H\}$ NMR spectrum could be obtained in acetonitrile. The NMR spectra indicated that **11** was either very symmetrical or fluxional. Variable-temperature studies were made impractical by the low solubility, but fortunately it was possible to obtain single crystals for X-ray crystallography. Selected structural parameters are listed in Table 5 and the molecular structure is shown in Fig. 4. The silver ion is co-ordinated by four of the thioether groups leaving two uncomplexed. The effect of complexation on the macrocycle conformation is demonstrated by the *anti* arrangements of S(1)–C(53)–C(54)–S(2) and S(5)–C(63)–C(64)–S(6) compared to the *gauche* arrangements of S(2)–C(55)–C(56)–S(3) and S(4)–C(61)–C(62)–S(5). The silver ion is in a severely distorted tetrahedral co-ordination sphere and is displaced towards the centre of the macrocycle. Hence the distances Ag–S(3) [2.635(3) Å] and Ag–S(4) [2.634(3) Å] are considerably longer than Ag–S(2) [2.493(3) Å] and Ag–S(5) [2.493(3) Å] and the angle S(2)–Ag–S(5) [144.2(1)°] is large. The S–Ag–S angles for the five-membered chelate rings [86.4(1) and 85.5(1)°] and for the seven-membered chelate ring [101.8(1)°] are consistent with other silver thiamacrocycle structures.[12] At the uncomplexed end of the macrocycle the alkyne angles C(52)–C(51)–C(66) [149.1(11)°] and C(65)–C(66)–C(51) [145.8(11)°] are similar to that in **1a** [149.1(2)°], while the analogous angles at the complexed end are considerably reduced [142.0(10) and 141.7(10)°]. A possible explanation of the appearance of only one acetylenic resonance, one carbonyl resonance and three methylenic resonances in the $^{13}C-\{^1H\}$ NMR spectrum of **11** is that the silver ion migrates between the two ends of the macrocycle.

In conclusion it has been shown that, despite their endodentate conformations and increased steric bulk compared to simpler thiamacrocycles, dicobalt-complexed thiacycloalkynes can act as ligands for silver(I), copper(I) and molybdenum(0) centres. The use of such compounds in sensors is currently being explored.[14]

Experimental

The general experimental procedures have been described previously.[22] The compounds $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(CO)_6]$[23] and $[Cu(MeCN)_4]PF_6$[24] were prepared by literature methods. Analytical and other data for the new compounds are given in Tables 1 and 2.

Reaction of $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(CO)_6]$ *with* Bis(2-*mercaptoethyl) Sulfide*.—To a solution of $[Co_2(\mu\text{-}HOCH_2\text{-}$

Table 5 Selected internuclear distances (Å), angles (°) and torsional angles (°) for compex **11**

Ag-S(2)	2.493(3)	Ag-S(3)	2.635(3)	Ag-S(4)	2.634(3)	Ag-S(5)	2.493(3)
Co(1)-Co(2)	2.465(2)	Co(1)-C(51)	1.973(11)	Co(1)-C(66)	1.964(10)	Co(2)-C(51)	1.961(10)
Co(2)-C(66)	1.960(11)	Co(3)-Co(4)	2.469(2)	Co(3)-C(58)	1.967(11)	Co(3)-C(59)	1.950(10)
Co(4)-C(58)	1.940(10)	Co(4)-C(59)	1.999(11)	C(51)-C(52)	1.492(16)	C(51)-C(66)	1.318(15)
C(52)-S(1)	1.824(11)	S(1)-C(53)	1.771(12)	C(53)-C(54)	1.535(17)	C(54)-S(2)	1.833(11)
S(2)-C(55)	1.804(13)	C(55)-C(56)	1.502(15)	C(56)-S(3)	1.814(12)	S(3)-C(57)	1.823(11)
C(57)-C(58)	1.481(15)	C(58)-C(59)	1.361(16)	C(59)-C(60)	1.473(16)	C(60)-S(4)	1.841(11)
S(4)-C(61)	1.828(13)	C(61)-C(62)	1.485(15)	C(62)-S(5)	1.823(13)	S(5)-C(63)	1.830(11)
C(63)-C(64)	1.534(16)	C(64)-S(6)	1.821(11)	S(6)-C(65)	1.814(12)	C(65)-C(66)	1.499(17)

S(2)-Ag-S(3)	86.4(1)	S(2)-Ag-S(4)	119.2(1)	S(3)-Ag-S(4)	101.8(1)
S(2)-Ag-S(5)	144.2(1)	S(3)-Ag-S(5)	115.3(1)	S(4)-Ag-S(5)	85.5(1)
Co(1)-C(51)-Co(2)	77.6(4)	Co(1)-C(51)-C(52)	131.7(7)	Co(2)-C(51)-C(52)	130.1(8)
Co(1)-C(51)-C(66)	70.1(7)	Co(2)-C(51)-C(66)	70.3(6)	C(52)-C(51)-C(66)	149.1(11)
C(51)-C(52)-S(1)	114.6(8)	C(52)-S(1)-C(53)	103.8(5)	S(1)-C(53)-C(54)	110.7(8)
C(53)-C(54)-S(2)	110.3(8)	Ag-S(2)-C(54)	115.2(4)	Ag-S(2)-C(55)	101.5(4)
C(54)-S(2)-C(55)	100.3(6)	S(2)-C(55)-C(56)	116.9(8)	C(55)-C(56)-S(3)	116.3(9)
Ag-S(3)-C(56)	94.4(4)	Ag-S(3)-C(57)	102.1(4)	C(56)-S(3)-C(57)	99.9(5)
S(3)-C(57)-C(58)	110.6(7)	Co(3)-C(58)-Co(4)	78.4(4)	Co(3)-C(58)-C(57)	130.0(7)
Co(4)-C(58)-C(57)	137.2(8)	Co(3)-C(58)-C(59)	69.0(6)	Co(4)-C(58)-C(59)	72.1(6)
C(57)-C(58)-C(59)	142.0(10)	Co(3)-C(59)-Co(4)	77.4(4)	Co(3)-C(59)-C(58)	70.3(6)
Co(4)-C(59)-C(58)	67.5(6)	Co(3)-C(59)-C(60)	139.0(8)	Co(4)-C(59)-C(60)	131.2(7)
C(58)-C(59)-C(60)	141.7(10)	C(59)-C(60)-S(4)	107.6(7)	Ag-S(4)-C(60)	103.3(4)
Ag-S(4)-C(61)	94.8(4)	C(60)-S(4)-C(61)	100.2(5)	S(4)-C(61)-C(62)	116.9(9)
C(61)-C(62)-S(5)	116.3(8)	Ag-S(5)-C(62)	103.0(4)	Ag-S(5)-C(63)	115.1(3)
C(62)-S(5)-C(63)	101.2(6)	S(5)-C(63)-C(64)	107.5(8)	C(63)-C(64)-S(6)	110.4(8)
C(64)-S(6)-C(65)	103.9(5)	S(6)-C(65)-C(66)	113.9(8)	Co(1)-C(66)-Co(2)	77.8(4)
Co(1)-C(66)-C(51)	70.8(6)	Co(2)-C(66)-C(51)	70.4(7)	Co(1)-C(66)-C(65)	132.1(8)
Co(2)-C(66)-C(65)	132.1(7)	C(51)-C(66)-C(65)	145.8(11)		

C(66)-C(51)-C(52)-S(1)	77.8	C(53)-S(1)-C(52)-C(51)	−90.9	C(54)-C(53)-S(1)-C(52)	−94.8
S(1)-C(53)-C(54)-S(2)	−161.2	C(55)-S(2)-C(54)-C(53)	−179.6	C(54)-S(2)-C(55)-C(56)	88.9
S(2)-C(55)-C(56)-S(3)	59.6	C(55)-C(56)-S(3)-C(57)	54.0	C(58)-C(57)-S(3)-C(56)	−176.1
C(59)-C(58)-C(57)-S(3)	53.4	C(60)-C(59)-C(58)-C(57)	−18.3	S(4)-C(60)-C(59)-C(58)	59.4
C(61)-S(4)-C(60)-C(59)	−177.8	C(60)-S(4)-C(61)-C(62)	54.4	S(4)-C(61)-C(62)-S(5)	56.6
C(61)-C(62)-S(5)-C(63)	93.6	C(64)-C(63)-S(5)-C(62)	−177.1	S(5)-C(63)-C(64)-S(6)	−158.2
C(63)-C(64)-S(6)-C(65)	−94.0	C(66)-C(65)-S(6)-C(64)	−93.9	C(65)-C(66)-C(51)-C(52)	0.5
S(6)-C(65)-C(66)-C(51)	67.5				

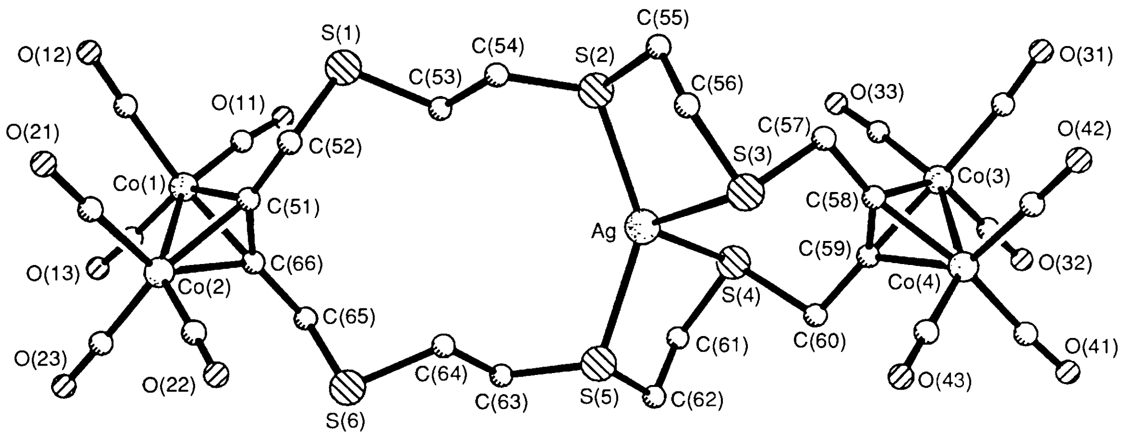


Fig. 4 The molecular structure of compound **11** showing the atom labelling system

$C{\equiv}CCH_2OH)(CO)_6]$ (11.16 g, 30.0 mmol) in CH_2Cl_2 (200 cm^3) was added bis(2-mercaptoethyl) sulfide (4.62 g, 30.0 mmol) and four drops of $HBF_4{\cdot}OEt_2$. The resulting mixture was stirred for 24 h, after which time an excess of $NaHCO_3$ (*ca.* 1 g) was added and the solvent reduced to *ca.* 50 cm^3 *in vacuo*. The solution was dried over sodium sulfate and filtered through a short plug of Celite (1.5 × 3 cm). The solvent was removed *in vacuo* and the residue chromatographed on a Florisil column (10 × 2.0 cm) eluting with light petroleum (b.p. 40–60 °C)-CH_2Cl_2 (4:1) to produce a red band. Removal of the solvent *in vacuo* afforded compound **1a** (8.64 g, 17.63 mmol). Mass spectrum (FAB): *m/z* 491, $[M+H]^+$; 434, 406, 378, 350 and 322 $[M - n\text{CO}]^+$ (n = 2–6). Elution of the column with light petroleum-CH_2Cl_2 (1:1) produced a second red band which after removal of the solvent afforded **1b** (2.99 g, 3.05 mmol). Mass spectrum (FAB): *m/z* 812, 728, 700, 672 and 644, $[M - n\text{CO}]^+$ (n = 6, 9–12). Finally elution with a 9:1 solvent mixture produced a third red band of $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2SCH_2CH_2SCH_2CH_2SH)(CO)_6]$ (1.30 g, 2.56 mmol).

Reaction of $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(CO)_6]$ *with Bis*(2-*mercaptoethyl*) *Ether*.—To a solution of $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(CO)_6]$ (0.8 g, 2.20 mmol) in CH_2Cl_2 (60 cm^3) was added bis(2-mercaptoethyl) ether (0.30 g, 2.20 mmol) and four drops of $HBF_4{\cdot}OEt_2$. The resulting mixture was stirred for 30 h, after which time an excess of $NaHCO_3$ (*ca.* 0.25 g) was added and the solvent removed *in vacuo*. The residue was extracted with light petroleum (5 × 10 cm^3) and filtered through a short plug of magnesium sulfate (1.5 × 3 cm). The solvent was removed *in vacuo* and the residue chromato-

Table 6 Atomic coordinates (× 10^4) for compound **1a**, with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Co	434(1)	1709(1)	1119(1)
S(1)	−2053(1)	3389(1)	2712(2)
S(2)	0	5298(1)	2500
C(1)	1583(5)	1224(3)	1572(9)
O(1)	2314(4)	963(3)	1894(8)
C(2)	−376(5)	1048(3)	77(9)
O(2)	−893(5)	653(3)	−545(8)
C(3)	825(4)	2257(3)	−646(7)
O(3)	1039(3)	2640(3)	−1695(5)
C(4)	−442(3)	2455(2)	2105(5)
C(5)	−1260(3)	2873(2)	1301(5)
C(6)	−1214(3)	4101(2)	3392(5)
C(7)	−1010(3)	4663(2)	2047(5)

graphed on a Florisil column (10 × 1.5 cm). Elution with light petroleum–CH_2Cl_2 (3:2) produced a red band which after removal of the solvent *in vacuo* afforded compound **2a** (0.40 g, 0.84 mmol). Mass spectrum (electron impact, EI): *m/z* 474, 446, 418, 390, 362, 334 and 306, $[M - n\text{CO}]^+$ (*n* = 0–6). Further elution of the column with CH_2Cl_2–tetrahydrofuran (thf) (98:2) yielded a second red band which upon removal of the solvent afforded **2b** (0.30 g, 0.32 mmol).

Carbonyl-substitution Reactions.—Complex **1a** (0.24 g, 0.49 mmol) and dppm (0.19 g, 0.49 mmol) were dissolved in benzene (15 cm^3), the resulting solution refluxed for 20 min and then the solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2 and filtered through a plug of Florisil (5 × 1.5 cm) before crystallisation by addition of light petroleum to afford compound **3** (0.23 g, 0.28 mmol). Mass spectrum (FAB): *m/z* 819 $[M + H]^+$. Complex **4** was prepared in a similar manner.

Preparation of $[Co_2\{\mu\text{-}C_2(CH_2SCH_2CH_2)_2S\}(CO)_6\{Ag(PPh_3)\}]BF_4$ **5**.—To a solution of $[Co_2\{\mu\text{-}C_2(CH_2SCH_2CH_2)_2S\}(CO)_6]$ (3.23 g, 6.6 mmol) in MeCN (200 cm^3) was added dropwise a solution of $AgBF_4$ (1.27 g, 6.6 mmol) and PPh_3 (1.72 g, 6.6 mmol) in MeCN (50 cm^3) over a period of 10 min and allowed to stir for 24 h. After reduction of the solvent volume to *ca.* 50 cm^3 under reduced pressure the solution was filtered through a Celite pad (5 × 1.5 cm) and then the solvent removed *in vacuo*. The residue was recrystallised from CH_2Cl_2 by addition of Et_2O to afford compound **5** (4.74 g, 5.0 mmol). Mass spectrum (FAB): *m/z* 859, 775, 719 and 691, $[M - BF_4 - n\text{CO}]^+$ (*n* = 0, 3, 5 *or* 6).

Preparation of $[Co_2\{\mu\text{-}C_2(CH_2SCH_2CH_2)_2S\}(CO)_6\{Cu(MeCN)\}]PF_6$ **6**.—To a solution of $[Co_2\{\mu\text{-}C_2(CH_2SCH_2CH_2)_2S\}(CO)_6]$ **1a** (3.23 g, 6.6 mmol) in MeCN (200 cm^3) was added dropwise a solution of $[Cu(MeCN)_4]PF_6$ (2.46 g, 6.6 mmol) in MeCN (50 cm^3) over a period of 15 min and allowed to stir for 24 h. After reduction of the solvent volume to *ca.* 40 cm^3 under reduced pressure the solution was filtered through a Celite pad (5 × 1.5 cm) and then further reduced to *ca.* 5 cm^3. Addition of Et_2O (80 cm^3) afforded a crystalline product after 2 h at 263 K which was washed with Et_2O (10 cm^3) to afford compound **6** (3.51 g, 4.8 mmol). Mass spectrum (FAB): *m/z* 553, 525, 497, 469, 441, 413 and 385, $[M - \text{MeCN} - n\text{CO}]^+$ (*n* = 0–6).

Reaction of $[Co_2\{\mu\text{-}C_2(CH_2SCH_2CH_2)_2S\}(CO)_6\{Cu(MeCN)\}]PF_6$ *with Phosphines.*—To a solution of $[Co_2\{\mu\text{-}C_2(CH_2SCH_2CH_2)_2S\}(CO)_6\{Cu(MeCN)\}]PF_6$ **6** (0.10 g, 0.14 mmol) in MeCN (40 cm^3) was added dropwise a solution of PPh_3 (0.035 g, 1.4 mmol) in MeCN (10 cm^3). The resulting mixture was stirred for 2 h and then the solvent was removed *in vacuo*. The red-brown product was washed with Et_2O (3 × 20 cm^3) and dried under vacuum to afford $[Co_2\{\mu\text{-}C_2(CH_2SCH_2CH_2)_2S\}(CO)_6\{Cu(PPh_3)\}]PF_6$ **7** (0.081 g, 0.08 mmol). Mass spectrum (FAB): *m/z* 815, 787, 759, 731, 703, 675 and 647, $[M - PF_6 - n\text{CO}]^+$ (*n* = 0–6). $^{31}P\text{-}\{^1H\}$ NMR (CD_2Cl_2): δ 3.98. Compound **8** was prepared in a similar manner. Mass spectrum (FAB): *m/z* 1647, $[M - PF_6]^+$.

Reactions with $[Mo(CO)_3(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)]$.—A solution of compound **3** (0.13 g, 0.16 mmol) and $[Mo(CO)_3(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)]$ (0.05 g, 0.17 mmol) in thf (20 cm^3) was refluxed for 30 min. The solvent was removed *in vacuo* and the residue dissolved in CH_2Cl_2 (20 cm^3) before filtering through a plug of Celite (5 × 1.5 cm). Reduction of the solvent volume *in vacuo* and addition of light petroleum afforded compound **9** (0.15 g, 0.015 mmol).

To a solution of complex **4** (0.95 g, 1.27 mmol) in thf (40 cm^3) was added $[Mo(CO)_3(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)]$ (0.38 g, 1.27 mmol) and the resulting solution refluxed for 0.75 h, after which time the solution was cooled to room temperature and the solvent removed *in vacuo*. The resulting dark red residue was dissolved in CH_2Cl_2–light petroleum (1:1) then filtered through a plug of Celite (7 × 1.5 cm). The solvent was again removed *in vacuo* and then the residue recrystallised four times from CH_2Cl_2 (2.5 cm^3) by addition of light petroleum (80 cm^3) to afford compound **10** as a dark red precipitate (0.40 g, 0.43 mmol).

Reaction of Compound **1b** *with* $AgBF_4$.—To solution of compound **1b** (0.14 g, 0.14 mmol) in MeCN (20 cm^3) was added $AgBF_4$ (0.028 g, 0.14 mmol). The mixture was stirred for 3 h at room temperature and then the solvent reduced *in vacuo* to *ca.* 2 cm^3. Diethyl ether was added to precipitate the product, which was recrystallised by slow diffusion of Et_2O into a CH_2Cl_2 solution to afford red crystals of compound **11** (0.13 g, 0.11 mmol). Mass spectrum (FAB): *m/z* 1089, $[M - BF_4]^+$

Crystal Structure Determinations.—Crystals of compound **1a** were obtained from light petroleum as deep red prisms with dimensions *ca.* 0.62 × 0.60 × 0.45 mm. Data were collected using a Nicolet *P*3 diffractometer (295 K, Mo-Kα X-radiation, graphite monochromator, $\bar{\lambda}$ = 0.710 73 Å). Of the 1997 data collected (Wyckoff ω scans, 2θ ⩽ 50°), 1192 unique data had $F \geqslant 5\sigma(F)$, and only these were used for the structure solution and refinement. The data were corrected for Lorentz, polarisation and X-ray absorption effects, the latter by a method based upon azimuthal scan data.[25]

Crystal data for **1a**: $C_{14}H_{12}Co_2O_6S_3$, *M* = 490.3, orthorhombic, space group *Pbcn*, *a* = 13.458(4), *b* = 18.195(5), *c* = 7.996(2) Å, *U* = 1958.1(9) $Å^3$, *Z* = 4, D_c = 1.66 g cm^{-3}, *F*(000) = 984, μ(Mo-Kα) = 20.2 cm^{-1}.

The structure was solved by conventional heavy-atom methods and successive Fourier difference syntheses were used to locate all non-hydrogen atoms. The complex has crystallographically imposed two-fold symmetry. The central sulfur atom, S(2), and the midpoint of the Co–Co(A) vector lie on the two-fold axis and atoms with a suffix 'A' are generated by symmetry. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions (C–H 0.96 Å) with fixed isotropic thermal parameters (*U* = 0.08 $Å^2$). Refinement by full-matrix least squares led to *R* = 0.038 (*R'* = 0.042) and a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.0005|F|^2]$ gave a satisfactory analysis of variance. The final electron-density difference synthesis showed no peaks >0.4 or < −0.4 e $Å^{-3}$. Atomic coordinates are listed in Table 6.

Crystals of compound **5** were obtained by solvent diffusion from CH_2Cl_2–light petroleum as deep red prisms with crystal dimensions *ca.* 0.62 × 0.50 × 0.45 mm. Data were collected using a Siemens R3m/V diffractometer (295 K, Mo-Kα X-radiation, graphite monochromator, $\bar{\lambda}$ = 0.710 73 Å). Of the 6825 data collected (Wyckoff ω scans, 2θ ⩽ 50°), 5131 unique data had $F \geqslant 5\sigma(F)$, and only these were used for the structure solution and refinement. The data were corrected as above.

Table 7 Atomic coordinates (× 10[4]) for compound **5**, with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ag	4957(1)	1371(1)	3024(1)	C(46)	8032(5)	4474(5)	674(4)
Co(1)	5032(1)	3188(1)	875(1)	O(46)	8531(5)	4266(5)	52(4)
Co(2)	7239(1)	4767(1)	1708(1)	C(11)	1530(4)	−738(4)	1972(3)
S(1)	5675(1)	3627(1)	3976(1)	C(12)	237(5)	−1022(5)	2094(4)
S(2)	7300(1)	1802(1)	4135(1)	C(13)	−839(5)	−1560(6)	1285(5)
S(3)	6222(1)	1037(1)	1630(1)	C(14)	−586(6)	−1838(6)	348(5)
P	2971(1)	−89(1)	2997(1)	C(15)	653(6)	−1553(7)	226(4)
C(1)	5985(4)	3924(4)	2263(3)	C(16)	1725(5)	−1002(5)	1051(4)
C(2)	5530(5)	4342(4)	3193(3)	C(21)	3219(4)	−1363(4)	3060(3)
C(3)	7481(5)	4033(5)	4279(4)	C(22)	4405(5)	−1193(4)	3631(4)
C(4)	7887(6)	3399(5)	4812(4)	C(23)	4632(6)	−2124(5)	3692(4)
C(5)	8283(5)	1585(5)	3217(5)	C(24)	3696(6)	−3249(5)	3168(4)
C(6)	7531(6)	705(5)	2186(5)	C(25)	2530(5)	−3431(4)	2597(4)
C(7)	7237(5)	2387(4)	1586(4)	C(26)	2295(5)	−2486(4)	2543(4)
C(8)	6544(4)	3224(4)	1699(3)	C(31)	2338(4)	559(4)	4067(3)
C(41)	3739(6)	1991(6)	852(6)	C(32)	2130(5)	1595(4)	4240(4)
O(41)	2926(5)	1230(6)	852(7)	C(33)	1636(6)	2118(5)	5032(4)
C(42)	5272(6)	2479(5)	−354(4)	C(34)	1423(6)	1655(5)	5703(4)
O(42)	5437(6)	2005(5)	−1108(3)	C(35)	1648(6)	647(5)	5541(4)
C(43)	4087(5)	4084(5)	779(4)	C(36)	2095(5)	87(4)	4720(3)
O(43)	3527(5)	4654(4)	706(3)	B	1280(7)	3414(6)	2745(6)
C(44)	6765(5)	6004(5)	1813(4)	F(1)	481(6)	3906(5)	2886(10)
O(44)	6462(5)	6770(4)	1873(4)	F(2)	1968(13)	3681(7)	3573(5)
C(45)	8696(5)	5503(4)	2703(4)	F(3)	2189(7)	3818(6)	2329(7)
O(45)	9593(4)	5968(4)	3346(3)	F(4)	653(5)	2239(4)	2258(3)

Table 8 Atomic coordinates (× 10[4]) for compound **11**, with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ag	6 052(1)	2 004(1)	2 980(1)	O(43)	10 887(13)	961(3)	4 385(7)
Co(1)	4 285(2)	4 133(1)	2 662(1)	C(51)	6 231(14)	3 786(3)	2 731(7)
Co(2)	7 345(2)	4 166(1)	3 532(1)	C(52)	6 906(15)	3 587(3)	2 007(7)
Co(3)	4 786(2)	620(1)	2 406(1)	S(1)	5 184(5)	3 376(1)	1 172(2)
Co(4)	7 834(2)	603(1)	3 301(1)	C(53)	4 980(16)	2 948(3)	1 626(8)
C(11)	2 361(19)	3 880(4)	2 163(9)	C(54)	6 130(15)	2 679(3)	1 227(7)
O(11)	1 123(12)	3 720(3)	1 857(9)	S(2)	5 380(4)	2 226(1)	1 387(2)
C(12)	4 562(17)	4 394(4)	1 674(9)	C(55)	6 944(15)	1 978(3)	874(8)
O(12)	4 835(15)	4 531(3)	1 050(7)	C(56)	8 655(16)	1 873(3)	1 480(8)
C(13)	3 202(18)	4 426(4)	3 375(9)	S(3)	8 464(4)	1 599(1)	2 449(2)
O(13)	2 541(13)	4 609(3)	3 793(7)	C(57)	7 119(14)	1 238(3)	1 876(7)
C(21)	8 324(17)	4 431(4)	2 746(8)	C(58)	6 660(14)	982(3)	2 545(7)
O(21)	8 928(13)	4 586(3)	2 237(7)	C(59)	5 921(14)	963(3)	3 301(7)
C(22)	9 365(18)	3 963(4)	4 122(9)	C(60)	5 472(15)	1 184(3)	4 036(7)
O(22)	10 655(12)	3 837(3)	4 478(7)	S(4)	3 932(4)	1 531(1)	3 509(2)
C(23)	6 902(16)	4 459(3)	4 430(8)	C(61)	3 634(16)	1 778(3)	4 519(8)
O(23)	6 522(14)	4 632(3)	4 969(7)	C(62)	5 269(15)	1 906(3)	5 126(7)
C(31)	5 199(16)	369(3)	1 436(8)	S(5)	6 731(4)	2 188(1)	4 605(2)
O(31)	5 571(13)	229(3)	822(7)	C(63)	5 934(15)	2 629(3)	4 840(7)
C(32)	3 672(18)	294(4)	3 044(9)	C(64)	6 988(15)	2 900(3)	4 392(7)
O(32)	3 056(14)	114(3)	3 470(7)	S(6)	6 939(4)	3 332(1)	4 927(2)
C(33)	2 847(17)	864(3)	1 881(8)	C(65)	5 087(16)	3 557(3)	4 222(8)
O(33)	1 649(12)	1 016(3)	1 530(7)	C(66)	5 608(14)	3 783(3)	3 493(7)
C(41)	7 507(16)	268(3)	4 119(8)	B	6 013(13)	2 288(3)	8 035(6)
O(41)	7 197(16)	64(3)	4 614(6)	F(1)	4 564(18)	2 089(5)	7 767(13)
C(42)	8 952(16)	361(3)	2 499(8)	F(2)	7 368(18)	2 081(4)	8 416(9)
O(42)	9 544(13)	221(3)	1 974(7)	F(3)	5 687(21)	2 528(3)	8 642(9)
C(43)	9 708(17)	820(3)	3 955(8)	F(4)	6 435(25)	2 455(5)	7 316(9)

Crystal data for **5**. $C_{32}H_{27}AgBCo_2F_4O_6PS_3$, $M = 947.2$, triclinic, space group $P\bar{1}$, $a = 10.820(5)$, $b = 13.293(7)$, $c = 15.273(9)$ Å, $\alpha = 113.49(4)$, $\beta = 95.17(4)$, $\gamma = 107.24(4)°$, $U = 1869(2)$ Å^3, $Z = 2$, $D_c = 1.68$ g cm^{-3}, $F(000) = 944$, μ(Mo-Kα) = 16.7 cm^{-1}.

The structure was solved and refined as above, leading to $R = 0.039$ ($R' = 0.045$), and a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.0007|F|^2]$ gave a satisfactory analysis of variance. The final electron-density difference synthesis showed no peaks >0.87 or <-0.75 e Å^{-3}. Atomic coordinates are listed in Table 7.

Crystals of compound **11** were grown from CH_2Cl_2–OEt_2 as thin red needles and that used was cut from a needle and had dimensions *ca.* 0.60 × 0.20 × 0.10 mm. Data were collected using a Siemens R3m/v diffractometer (291 K, Mo-Kα X-radiation, graphite monochromator, $\bar{\lambda} = 0.710\,73$ Å). Of the 6159 data collected (Wyckoff ω scans, $2\theta \leqslant 45°$), 3614 unique data had $F \geqslant 4\sigma(F)$, and only these were used for the structure solution and refinement. The data were corrected as above.

Crystal data for **11**. $C_{28}H_{24}AgBCo_4F_4O_{12}S_6$, $M = 1175.2$, monoclinic, space group $P2_1/n$, $a = 7.666(3)$, $b = 37.736(12)$, $c = 14.997(5)$ Å, $\beta = 100.78(3)°$, $U = 4262(2)$ Å^3, $Z = 4$, $D_c = 1.83$ g cm^{-3}, $F(000) = 2320$, μ(Mo-Kα) = 23.4 cm^{-1}.

The structure was solved by conventional heavy-atom methods and successive Fourier difference syntheses were used to locate all non-hydrogen atoms. The crystal diffracted comparatively poorly, and the relatively long *b* axis led to difficulty in adequately resolving some of the most intense low-angle reflections. Owing to the limited data, carbon atoms were refined with isotropic thermal parameters. Hydrogen atoms were included in calculated positions with fixed isotropic thermal parameters. The asymmetric unit contains a disordered BF_4^- counter ion which was refined as an idealised rigid group with correspondingly large anisotopic thermal parameters for the constituent atoms. Attempts to model the positions of the disordered fluorine atoms in more detail were less satisfactory and led to unstable refinements. Final $R = 0.057$ ($R' = 0.057$) with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.001|F|^2]$. The final electron-density difference synthesis showed no peaks > 1.14 or < -0.59 e $Å^{-3}$, the former being in the vicinity of the BF_4^- anion. Given these problems the final level of refinement achieved was surprisingly good. Atomic coordinates are listed in Table 8.

All calculations were performed on a Digital MicroVax II computer with the SHELXTL PLUS system of programs.[25] Scattering factors with corrections for anomalous dispersion were taken from ref. 26.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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