Synthesis of Hexacarbonyldicobalt-complexed Thiacycloalkynes†

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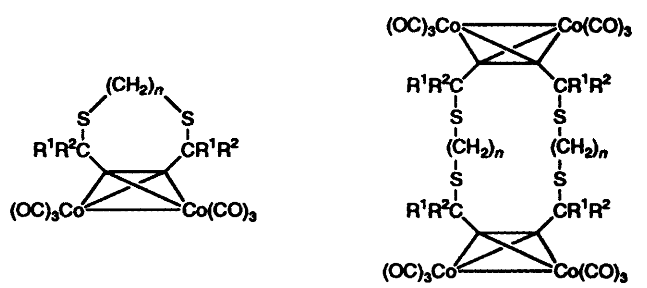
Reaction of $[Co_2(\mu\text{-}HOCR^1R^2C{\equiv}CCR^1R^2OH)(CO)_6]$ ($R^1 = R^2 = H$ or Me; $R^1 = H$, $R^2 = Me$) with $HS(CH_2)_nSH$ (n = 2—5) or $HS(CH_2)_2OH$ in the presence of $HBF_4\cdot OEt_2$ affords predominately monomeric hexacarbonyldicobalt-complexed thiacycloalkynes. In many cases, especially with the longer chain dithiols, dimeric compounds are also formed as minor products and in some cases higher oligomers have also been characterised. Reaction of $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(CO)_6]$ with $HSCH_2CH(OH)CH_2SH$ affords complexed thiacycloalkynes with pendant hydroxyl functionalities. The monomeric complexes undergo carbonyl substitution with bis(diphenylphosphino)methane (dppm) and the X-ray crystal structure of $[Co_2(\mu\text{-}CCH_2SCH_2CH_2SCH_2C)(\mu\text{-}dppm)(CO)_4]$ has been determined. The molecule contains a co-ordinated 1,4-dithiacyclooct-6-yne which adopts two conformations in the solid state. The IR, mass, ^1H and ^{13}C NMR spectra of the new compounds are discussed.

Recently we have demonstrated that the reactions of $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(CO)_6]$ with $SiR^1(R^2)Cl_2$ ($R^1 = R^2 = Me$ or Ph; $R^1 = Me$, $R^2 = Ph$) afford a range of hexacarbonyldicobalt-complexed 1,3-dioxa-2-silacyclohept-5-ynes and dimeric 1,3,8,10-tetraoxa-2,9-disilacyclotetradeca-5,12-diynes.[1] The cyclic nature of these products can be attributed to the adoption of a *cis* bent-back structure by alkynes when co-ordinated to transition-metal centres. The alkyne bend-back angle in $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(CO)_6]$ is 143.9(3)° in the solid state.[2] Dicobalt alkyne fragments have been used as protecting groups to allow geometrically disfavoured cyclisations[3] and to stabilise strained cycloalkynes.[4] We have shown that the modification in the reactivity of the but-2-yne-1,4-diol caused by the well known hexacarbonyldicobalt stabilisation of propargyl cations can be utilised in the synthesis of the dithiaalkyne complexes $[Co_2(\mu\text{-}RSCH_2C{\equiv}CCH_2SR)(CO)_6]$ (R = Et, Bu^n, Bu^t, Ph or CH_2Ph).[5] This paper draws together both the structural and reactivity perturbations engendered by ligation of alkynediols to hexacarbonyldicobalt in the synthesis of hexacarbonyldicobalt-complexed thiacycloalkynes.



	R^1	R^2	n	
1a	H	H	2	**2a**
1b	H	H	3	**2b**
1c	H	H	4	**2c**
1d	H	H	5	**2d**
1e	H	Me	2	
1f	H	Me	3	**2f**
1g	H	Me	4	**2g**
1h	H	Me	5	**2h**
1i	Me	Me	2	
1j	Me	Me	3	**2j**
1k	Me	Me	4	**2k**
1l	Me	Me	5	**2l**

Results and Discussion

Reaction of $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(CO)_6]$ with 1 equivalent of a range of dithiols, $HS(CH_2)_nSH$ (n = 2–5), in the presence of $HBF_4\cdot OEt_2$ affords cyclic hexacarbonyldicobalt thiaalkyne complexes in high overall yields of *ca.* 80% (see Experimental section). Analytical and IR data for the new compounds are given in Table 1. In general both monomeric (compounds **1**) and dimeric (compounds **2**) products are obtained and can be separated by column chromatography on Florisil, in which the monomers are eluted before the dimers. No evidence was found for higher oligomers although normally a small amount of insoluble material was left on top of the Florisil column. In several preparations trace products corresponding to $[Co_2\{\mu\text{-}HS(CH_2)_nSCH_2C{\equiv}CCH_2S(CH_2)_nSH\}(CO)_6]$ and $[Co_2(CO)_6\{\mu\text{-}HOCH_2C{\equiv}CCH_2S(CH_2)_nSCH_2C{\equiv}CCH_2OH\}Co_2(CO)_6]$ were obtained and if the reaction stoichiometry is varied from 1 : 1 these compounds can be prepared in higher yields as expected.[5] The NMR spectra of compounds **1** and **2** (see Table 2) confirm the cyclic nature of the products. For example, the ^1H NMR spectrum of **1a** contains only two resonances: one at δ 4.0, assigned to the acetylenic methylenes, and a second at δ 3.1, assigned to the methylenes derived from the ethane-1,2-dithiol. The ^{13}C NMR spectrum is also very straightforward containing resonances due to the carbonyl ligands at δ 199.6, the acetylenic carbons at δ 98.2, and the methylenes at δ 39.4 and 37.8. Only relatively small differences are observed between the NMR spectra of the monomeric and dimeric compounds. Confirmation of the molecular weights of the products was therefore obtained by mass spectroscopy of selected compounds (see Table 3). For example, the mass spectrum of **1d** contains an isotopic envelope due to the molecular ion centred at *m*/*z* 472 and carbonyl-loss peaks corresponding to all six carbonyl ligands. The dimer **2d** displays an envelope at *m*/*z* 945 assigned to $[M + H]^+$ and peaks due to eleven of the expected twelve carbonyl losses.

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

Table 1 Analytical[a] and physical data

Compound	Appearance	Yield (%)	$\nu_{max}(CO)^b/cm^{-1}$	Analysis (%)	
				C	H
1a	Red solid	75	2092m, 2055s, 2029s, 2008w	33.3 (33.5)	1.8 (1.9)
1b	Red oil	71	2091m, 2054s, 2029s, 2027m, 2010w	35.0 (35.1)	2.3 (2.3)
1c	Red solid	86	2092m, 2056s, 2030s, 2025m, 2010w	36.2 (36.7)	2.6 (2.6)
1d	Red-orange solid	9	2092m, 2056s, 2030s, 2026m, 2012w	38.1 (38.2)	2.9 (3.0)
1e	Red solid	64	2090m, 2054s, 2027s, 2005w	36.3 (36.7)	2.7 (2.6)
1f	Red solid	67	2090m, 2053s, 2027s, 2025(sh), 2010w	38.1 (38.2)	2.8 (3.0)
1g	Red-orange solid	28	2090m, 2054s, 2028s, 2026m, 2012w	39.0 (39.5)	3.2 (3.3)
1h	Red-orange solid	70	2091m, 2054s, 2028s, 2025(sh), 2012w	40.3 (40.8)	3.7 (3.6)
1i	Red solid	90	2086m, 2050vs, 2020s[c]	38.8 (39.5)	3.4 (3.3)
1j	Red solid	33	2086m, 2048vs, 2025s, 2017m, 2004w	40.7 (40.8)	3.5 (3.6)
1k	Orange oil	60	2089m, 2053s, 2026s, 2005w	41.5 (42.1)	3.8 (3.9)
1l	Red solid	41	2088m, 2053s, 2024s, 2008w	42.4 (43.2)	4.1 (4.2)
2a	Red oil	20	2093m, 2055s, 2027s	33.3 (33.5)	1.8 (1.9)
2b	Red-orange solid	10	2092m, 2056s, 2031s, 2027m, 2013w	34.0 (35.1)	2.1 (2.3)
2c	Red solid	13	2091w, 2055s, 2029s, 2016(sh)	36.0 (36.7)	2.8 (2.6)
2d	Red solid	13	2091w, 2054s, 2029s, 2016(sh)	38.0 (38.2)	2.9 (3.0)
2f	Red solid	16	2090m, 2055s, 2029s, 2010w	37.0 (38.2)	2.8 (3.0)
2g	Red-orange solid	20	2090m, 2055s, 2028s, 2011w	39.1 (39.5)	3.3 (3.3)
2h	Red solid	17	2090m, 2054s, 2028s, 2010w	41.1 (40.8)	3.7 (3.6)
2j	Red solid	29	2088m, 2053s, 2024s, 2009w	40.5 (40.8)	3.6 (3.6)
2k	Red-orange solid	18	2088m, 2053s, 2026s, 2006w	41.9 (42.1)	4.2 (3.9)
2l	Red oil	20	2088m, 2053s, 2028m, 2024s, 2006w	42.9 (43.2)	4.6 (4.2)
3a	Red solid	65	2093m, 2056s, 2029s, 2010w, 1980vw	34.4 (34.8)	2.5 (2.0)
3b	Red solid	34	2092m, 2057(sh), 2055s, 2028s, 2008w	37.8 (38.0)	2.6 (2.7)
3c	Red solid	71	2088m, 2050s, 2026s, 2019m, 2007w	40.6 (40.9)	3.3 (3.4)
4	Red-orange solid	58	2093m, 2056s, 2031s, 2012w, 1984vw	33.4 (33.9)	2.1 (2.2)
5	Red-orange solid	18	2093m, 2057s, 2032s, 2013(sh), 1983vw	33.2 (33.9)	2.3 (2.2)
6a	Red solid	89	2018s, 1983s, 1958s, 1942w[d]	55.0 (55.4)	4.3 (4.0)
6b	Purple solid	87	2019m, 1991s, 1963m, 1943(sh)[c]	55.8 (56.5)	4.6 (4.4)
6c	Pink solid	38	2026m, 1998s, 1974m, 1962(sh)	56.6 (56.6)	4.4 (4.1)
6d	Pink solid	78	2012m, 1989s, 1974m, 1959s	55.8 (56.5)	4.6 (4.4)
6e	Pink solid	59	2020m, 1990s, 1963m, 1945(sh)[c]	56.7 (57.0)	4.7 (4.5)

[a] Calculated values are given in parentheses. [b] Recorded in light petroleum unless otherwise stated. [c] In dichloromethane. [d] In benzene.

The complex [Co_2(μ-HOCHMeC≡CCHMeOH)$(CO)_6$] was prepared in an analogous manner to [Co_2(μ-$HOCH_2C≡CCH_2OH$)$(CO)_6$] as a red crystalline solid.[6] The ^1H and ^{13}C NMR spectra of [Co_2(μ-HOCHMeC≡CCHMeOH)$(CO)_6$] contain two sets of resonances indicating the presence of the *meso* and D, L diastereomers of the co-ordinated hex-3-yne-2,5-diol. Reactions of [Co_2(μ-HOCHMeC≡CCHMeOH)$(CO)_6$] with the dithiols proceed in a similar fashion to [Co_2(μ-$HOCH_2C≡CCH_2OH$)$(CO)_6$], but the NMR spectra of the products are again complicated inseparable diastereomers allowing an easier distinction to be made between the monomeric and dimeric products. No dimeric products were isolated when ethane-1,2-dithiol was used in this reaction. The monomeric complexes **1e** and **1f** show a doubling of resonances most clearly observed in the ^{13}C NMR spectra corresponding to the *meso* and D, L diastereomers. Curiously **1g** and **1h** only display a single set of resonances in both the ^1H and ^{13}C NMR spectra. The dimeric compounds contain four chiral centres and would be expected to be in five diastereomeric forms[7] with four strong and four weak resonances in each of the methyl, methine and acetylenic regions of the ^{13}C NMR spectra. Not all the expected resonances are resolved in every case but, for example, **2f** displays six acetylene resonances, four methine resonances, four sulfur methylene resonances, five central methylene resonances and five methyl resonances.

Reactions of [Co_2(μ-$HOCMe_2C≡CCMe_2OH$)$(CO)_6$] with dithiols followed the established trends, with again no dimeric products being isolated with ethane-1,2-dithiol. Careful chromatography of the products obtained by reaction with propane-1,3-dithiol afforded a third band eluted with CH_2Cl_2–light petroleum (2:3). Fast atom bombardment (FAB) mass spectroscopy confirmed that the third band was a trimeric product {*m*/*z* 1501 $[M + H]^+$, 1444, 1360, 1276, 1248, 1220, 1108, 1080 $[M - n\text{CO}]^+$ (n = 2,5,8–10,14,15)} isolated in 10% yield. The NMR spectra of the trimer are as expected very similar to the monomer **1j** and the dimer **2j** (Table 2). For example, the ^{13}C NMR spectrum contains resonances at δ 200.1, 106.7, 48.7, 32.8, 29.4 and 29.1 corresponding to the carbonyl, alkyne, quaternary carbon, methyl, and the two methylene environments respectively. Similarly the reaction with pentane-1,5-dithiol afforded small amounts of trimeric and tetrameric products as well as **1l** and **2l**. Occasionally trace amounts of side products were obtained when using [Co_2(μ-$HOCMe_2C≡CCMe_2OH$)$(CO)_6$] which were postulated to have undergone rearrangement giving enyne functionalities.[8] Interestingly the electron impact mass spectra of **1j** and **1l** do not show peaks due to the expected molecular ions or carbonyl-loss peaks thereof. Instead both spectra contain an envelope at *m*/*z* 392 followed by six carbonyl-loss peaks corresponding to [Co_2(μ-$H_2C{=}CMeC≡CCMe{=}CH_2$)$(CO)_n$] (n = 0–6), suggesting that the dithiol is easily lost to afford the dienyne.

The yields of cyclic compounds are unusually high considering that high dilution or template techniques are not employed. This suggests that the product distribution is under thermodynamic rather than kinetic control and that the monomers and dimers can interconvert. This suggestion was tested by treating CH_2Cl_2 solutions of pure **1c** and **2c** with $HBF_4{\cdot}OEt_2$ for 24 h. In both cases mixtures of **1c** and **2c** were obtained which could be separated as described above, although the overall yield of material recovered was low (*ca.* 25%). Protonation of thioether functionalities leading to exchange reactions has been observed previously in dicobalt thiaalkyne systems.[5]

Reaction of [Co_2(μ-$HOCR_2C≡CCR_2OH$)$(CO)_6$] with $HS(CH_2)_2OH$ affords the monomeric products **3a**–**3c**, in an analogous fashion to **1a**, **1e**, **1i**, which were characterised by

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

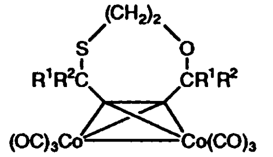
Compound	^{1}H(δ)[b]	^{13}C-{^{1}H} (δ)
1a	4.0 (s, 4 H, CCH_2), 3.1 (s, 4 H, SCH_2)	199.6 (CO), 98.2 (C_2), 39.4, 37.8 (CH_2)
1b	4.12 (s, 4 H, CCH_2), 2.93 [t, 4 H, SCH_2, *J*(HH) 6], 2.11 [qnt, 2 H, CH_2, *J*(HH) 6][c]	199.5 (CO), 95.9 (C_2), 37.7 (CCH_2), 31.3 (SCH_2), 29.4 (CH_2)
1c	4.1 (s, 4 H, CCH_2), 3.0–2.7 (m, 4 H, SCH_2), 2.2–1.9 (m, 4 H, CH_2)	199.4 (CO), 96.2 (C_2), 36.7 (CCH_2), 33.7 (SCH_2), 23.3 (CH_2)
1d	4.1 (s, 4 H, CCH_2), 2.8–2.5 (m, 4 H, SCH_2), 2.2–1.7 (m, 6 H, CH_2)	199.5 (CO), 95.0 (C_2), 35.0 (CCH_2), 28.7, 25.7, 25.3 (CH_2)
1e	4.08 [q, 1 H, CH, *J*(HH) 6], 4.06 [q, 1 H, CH, *J*(HH) 6], 3.6–2.8 (m, 4 H, CH_2), 1.68 [d, 3 H, CH_3, *J*(HH) 6], 1.66 [d, 3 H, CH_3, *J*(HH) 6]	199.8 (CO), 107.1, 105.4 (C_2), 47.8, 44.6 (CH), 39.6, 34.9 (CH_2), 24.6, 23.6 (Me)
1f	4.38 [q, 1 H, CH, *J*(HH) 6], 4.20 [q, 1 H, CH, *J*(HH) 6], 3.36–2.60 (m, 4 H, CH_2), 2.48–1.84 (m, 2 H, CH_2), 1.68 [d, 3 H, CH_3, *J*(HH) 6], 1.66 [d, 3 H, CH_3, *J*(HH) 6]	199.9 (CO), 105.7, 103.8 (C_2), 43.9, 43.2 (CH), 33.5, 31.5 (SCH_2), 30.3, 28.8 (CH_2), 25.2, 24.7 (Me)
1g	4.2 [q, 2 H, CH, *J*(HH) 6], 3.5–2.0 (m, 8 H, CH_2), 1.8 [d, 6 H, CH_3, *J*(HH) 7]	199.8 (CO), 104.6 (C_2), 41.3 (CH), 33.4 (SCH_2), 25.6 (CH_2), 22.4 (Me)
1h	4.35 [q, 2 H, CH, *J*(HH) 7], 2.72 [t, 4 H, SCH_2, *J*(HH) 6], 2.40–2.30 (m, 2 H, CH_2), 1.82–1.65 (m, 10 H, CH_2 and CH_3)[c]	199.8 (CO), 103.2 (C_2), 41.6 (CH), 32.1 (SCH_2), 27.4, 26.7 (CH_2), 24.3 (Me)
1i	3.2 (s, 4 H, CH_2), 1.7 (s, 12 H, CH_3)	200.2 (CO), 111.4 (C_2), 45.7 (*C*Me), 34.0 (Me), 33.0 (CH_2)
1j	3.20–3.16 (m, 4 H, SCH_2), 1.99–1.65 (m, 14 H, CH_2 and CH_3)[c]	200.2 (CO), 106.9 (C_2), 47.3 (*C*Me), 35.2 (Me), 27.8 (SCH_2), 27.7 (CH_2)
1k	2.9–2.6 (m, 4 H, SCH_2), 1.9–1.5 (m, 16 H, CH_2 and CH_3)[d]	200.8 (CO), 107.7 (C_2), 48.6 (*C*Me), 33.1 (Me), 30.9, 29.3 (CH_2)[d]
1l	3.06–2.56 (m, 4 H, SCH_2), 2.22–1.40 (m, 18 H, CH_2 and CH_3)	200.2 (CO), 107.7 (C_2), 48.1 (*C*Me), 32.9 (Me), 30.7 (SCH_2), 28.8, 28.3 (CH_2)
2a	4.1 (s, 8 H, CCH_2), 3.0 (s, 8 H, SCH_2)	199.3 (CO), 94.6 (C_2), 36.9, 33.7 (CH_2)
2b	4.07 (s, 8 H, CCH_2), 2.86 [t, 4 H, SCH_2, *J*(HH) 7], 2.05 [qnt, 2 H, CH_2, *J*(HH) 7][c]	199.3 (CO), 94.5 (C_2), 37.0 (CCH_2), 32.4 (SCH_2), 29.4 (CH_2)
2c	4.1 (s, 8 H, CCH_2), 3.0–2.8 (m, 8 H, CH_2), 2.1–1.7 (m, 8 H, CH_2)	199.4 (CO), 94.6 (C_2), 36.6, 33.0, 28.8 (CH_2)
2d	4.0 (s, 8 H, CCH_2), 2.9–2.6 (m, 8 H, SCH_2), 1.9–1.5 (m, 12 H, CH_2)	199.5 (CO), 95.2 (C_2), 36.9 (CCH_2), 33.5, 29.3, 28.2 (CH_2)
2f	4.29–4.11 (m, 4 H, CH), 3.01–2.73 (m, 8 H, SCH_2), 2.08–1.99 (m, 4 H, CH_2), 1.75–1.68 (m, 12 H, CH_3)[c]	199.7 (CO), 101.9, 101.6, 101.4, 101.3, 101.2, 101.1 (C_2), 43.8, 43.62, 43.59, 42.1 (CH), 31.4, 31.3, 31.2, 30.9 (SCH_2), 30.3, 29.8, 29.7, 29.6, 29.5 (CH_2), 24.7, 24.4, 23.9, 23.83, 23.78 (Me)
2g	4.5–3.8 (m, 4 H, CH), 3.2–2.5 (m, 8 H, SCH_2), 2.4–1.4 (m, 20 H, CH_2 and CH_3)	199.7 (CO), 102.0–101.3 (m, C_2), 43.1–41.6 (m, CH), 31.9–31.6 (m, SCH_2), 29.0–28.6 (m, CCH_2), 24.5–22.6 (m, CH_2, CH_3)
2h	4.44–3.88 (m, 4 H, CH), 3.14–2.48 (m, 8 H, SCH_2), 2.12–1.38 (m, 24 H, CH_2 and CH_3)	199.8 (CO), 102.3, 102.2, 102.11, 102.06, 101.9, 101.8, 101.7, 101.6 (C_2), 43.3, 42.9, 42.0, 41.8 (CH), 32.4, 32.2, 32.14, 32.08 (SCH_2), 29.9, 29.7, 29.5, 29.4, 28.9, 28.7, 28.5, 28.4 (CH_2), 24.6, 24.5, 23.9, 23.8, 23.7 (Me)
2j	3.04–2.94 (m, 8 H, SCH_2), 2.05–1.93 (m, 4 H, CH_2), 1.75 (s, 24 H, CH_3)[d]	200.1 (CO), 107.1 (C_2), 48.2 (*C*Me), 32.7 (Me), 29.4 (SCH_2), 28.0 (CH_2)
2k	2.9–2.6 (m, 8 H, SCH_2), 1.9–1.5 (m, 32 H, CH_2 and CH_3)[d]	200.2 (CO), 107.0 (C_2), 48.6 (*C*Me), 32.8 (Me), 30.2, 29.1 (CH_2)[d]
2l	2.96–2.48 (m, 8 H, SCH_2), 2.08–1.48 (m, 36 H, CH_2 and CH_3)	200.1 (CO), 107.1 (C_2), 48.5 (*C*Me), 32.8 (Me), 30.4 (SCH_2), 29.2, 28.8 (CH_2)
3a	4.9 (s, 2 H, CH_2O), 4.1–3.9 (m, 2 H, $OC\mathit{H}_2CH_2$), 4.0 (s, 2 H, CH_2S), 3.0–2.8 (m, 2 H, $SC\mathit{H}_2CH_2$)	199.4 (CO), 98.2, 95.6 (C_2), 74.3, 74.1 (OCH_2), 38.9, 36.5 (SCH_2)
3b	5.00–4.32 (m, 2 H, CH), 4.28–3.46 (m, 2 H, OCH_2), 3.26–2.82 (m, 2 H, SCH_2), 1.82–1.50 (m, 6 H, CH_3)	199.7 (CO), 105.9, 105.8, 103.0, 102.2 (C_2), 81.0, 76.6 (OCH), 75.7, 69.8 (OCH_2), 47.3, 45.4 (SCH), 38.3, 34.4 (SCH_2), 24.1, 23.8, 23.2, 22.7 (Me)
3c	4.28–4.00 (m, 2 H, OCH_2), 3.12–2.80 (m, 2 H, SCH_2), 1.74 (s, 6 H, CH_3), 1.64 (s, 6 H, CH_3)	199.8 (CO), 109.5, 106.3 (C_2), 78.2 (OCMe), 66.3 (OCH_2), 46.6 ($SCMe_2$), 32.9, 32.3 (Me)
4	4.2 (s, 5 H, CCH_2 and CH), 3.3–3.0 (m, 4 H, SCH_2), 2.6 (s, br, 1 H, OH)	199.2 (CO), 94.6 (C_2), 71.9 (CH), 37.9, 37.8 (CH_2)
5	4.2 (s, 10 H, CCH_2 and CH), 3.0–2.8 (m, 10 H, SCH_2 and OH)	199.2 (CO), 93.6, 93.5 (C_2), 70.2, 70.1 (CH), 39.6, 39.5 (SCH_2), 37.6, 37.4 (CCH_2)
6a	7.6–7.2 (m, 20 H, Ph), 4.1 [t, 4 H, CCH_2, *J*(PH) 3], 3.4 [t, 2 H, PCH_2, *J*(PH) 10], 3.1 (s, 4 H, CH_2)	205.1 (CO), 137–128 (Ph), 98.4 (C_2), 41.7 [t, PCH_2, *J*(PC) 20], 40.2, 37.7 (CH_2)
6b	7.7–7.1 (m, 20 H, Ph), 4.5–4.0 (m, 2 H, CH), 3.6–2.8 (m, 6 H, CH_2 and PCH_2), 1.6 [d, 6 H, CH_3, *J*(HH) 7]	205.7, 205.2 (CO), 138–127 (Ph), 106.1, 105.9 (C_2), 47.4, 46.2 (CH), 38.8 [t, PCH_2, *J*(PC) 20], 37.6 [t, PCH_2, *J*(PC) 21], 35.5, 34.9 (CH_2), 25.2, 24.7 (Me)
6c	7.5–7.2 (m, 20 H, Ph), 4.9 [t, 2 H, CCH_2O, *J*(PH) 4], 4.1–3.9 (m, 4 H, CCH_2S and CH_2O), 3.3 [t, 2 H, PCH_2, *J*(PH) 11], 3.0–2.8 (m, 2 H, SCH_2)	205.0 (CO), 137–128 (Ph), 98.2, 95.7 (C_2), 75.7, 73.6 (OCH_2), 41.3 [t, PCH_2, *J*(PC) 20], 39.4, 36.3 (SCH_2)
6d	7.5–7.2 (m, 20 H, Ph), 4.2 [t, 4 H, CCH_2, *J*(PH) 3], 3.5 [t, 2 H, PCH_2, *J*(PH) 10], 2.8–2.1 (m, 8 H, SCH_2)	205.7 (CO), 137–128 (Ph), 97.8 (C_2), 42.0 [t, PCH_2, *J*(PC) 20], 37.0, 33.7, 23.5 (CH_2)
6e	7.4–7.2 (m, 20 H, Ph), 4.1 (s, 4 H, CCH_2), 3.4 [t, 2 H, PCH_2, *J*(PH) 10], 2.7–2.0 (m, 10 H, CH_2)	205.0 (CO), 137–128 (Ph), 95.8 (C_2), 42.5 [t, PCH_2, *J*(PC) 19], 35.8, 30.0, 27.1, 25.8 (CH_2)

[a] Chemical shifts (δ) in ppm, coupling constants in Hz. Measured in $CDCl_3$ unless otherwise stated. [b] Recorded at 60 MHz unless otherwise stated. [c] Recorded at 270 MHz. [d] Measured in CD_2Cl_2.

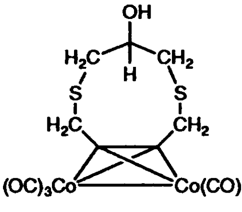
Table 3 Mass spectrometric data (m/z) for selected compounds

			$[M - n\text{CO}]^+$											
Compound	$[M + H]^+$	$[M]^+$	$n = 1$	2	3	4	5	6	7	8	9	10	11	12
1d[a]	—	472	444	416	388	360	332	304						
1i[a]	—	486	—	430	—	374	346	—						
2c[b]	—	—	—	—	832	804	776	748	720	692	664	636	608	580
2d[b]	945	—	916	—	860	832	804	776	748	720	692	664	636	608
3a[a]	—	—	386	358	330	302	274	246						
4[b]	461	—	432	404	376	348	320	292						

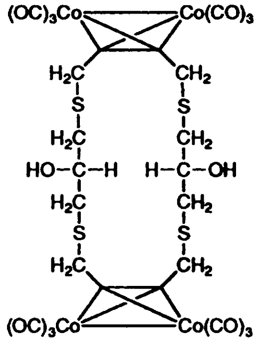
[a] Electron impact. [b] Fast atom bombardment obtained from a 3-nitrobenzyl alcohol matrix



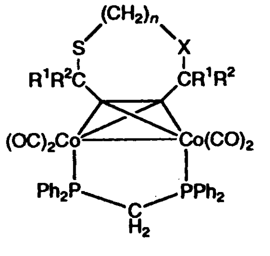
	R^1	R^2
3a	H	H
3b	H	Me
3c	Me	Me



4



5



	R^1	R^2	n	X
6a	H	H	2	S
6b	H	Me	2	S
6c	H	H	2	O
6d	H	H	4	S
6e	H	H	5	S

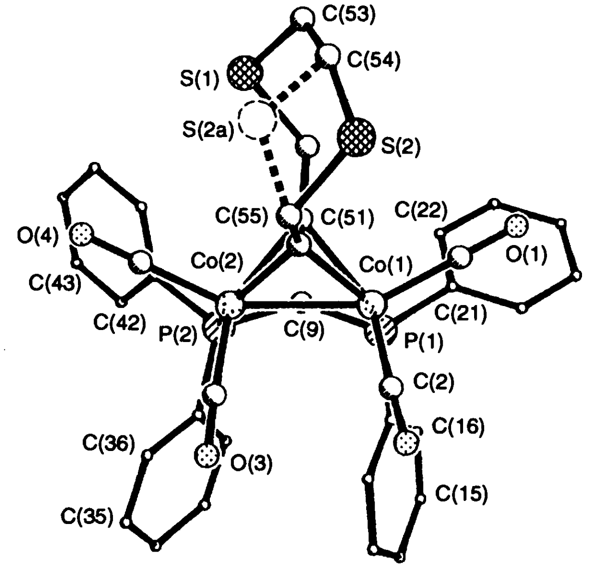


Fig. 1 The molecular structure of **6a** showing the atom labelling system

NMR analysis and shown to be monomeric in the case of **3a** by mass spectrometry (Table 3) and in the case of **3b** by a doubling of resonances in the ^{13}C NMR spectrum.

Reaction of $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(CO)_6]$ with $HSCH_2CH(OH)CH_2SH$ could in principle afford products based on a nine-membered dithioether ring analogous to **1b** and **2b** with a pendant hydroxyl group or an eight-membered ring analogous to compound **3** with a pendant thiol group. Only the former products are observed. The monomer **4** contains a resonance at δ 2.6 in the ^1H NMR spectrum corresponding to the hydroxyl functionality and the ^{13}C NMR spectrum also indicates that the more symmetrical nine-membered ring has been formed as it only contains one acetylenic and two methylenic resonances. The dimeric product **5** is formed in two isomeric forms as indicated by the ^{13}C NMR spectrum which contains two resonances for each carbon type, apart from the carbonyls which appear as one broad peak. The two isomers could not be separated by column chromatography and are most likely due to the hydroxyl functionalities disposed either mutually *cis* or *trans* with respect to the eighteen-membered ring.

Reactions of **1a**, **1e**, **3a**, **1c** and **1d** with dppm afford **6a**–**6e** in which two carbonyl ligands are substituted by the bidentate phosphine.[5] Attempts to substitute dimeric compounds led to decomposition and no products could be isolated. Compounds **6** are more crystalline than the unsubstituted compounds and suitable crystals for X-ray diffraction of **6a** were obtained by slow crystallisation from CH_2Cl_2–light petroleum. Selected structural parameters are listed in Table 4 and the molecular structure is shown in Fig. 1. The molecular structure comprises a $Co_2(\mu\text{-dppm})(CO)_4$ unit transversely bridged by 1,4-dithiacyclooct-6-yne. The dppm occupies two equatorial sites as has been previously observed in $[Co_2(\mu\text{-alkyne})(\mu\text{-dppm})(CO)_4]$ complexes.[9] The 1,4-dithiacyclooct-6-yne was found to be partially disordered and it was possible to resolve two distinct sites [S(2) and S(2A), 60 : 40] for the sulfur atom furthest from the dppm. The disordered components of the remaining portion of the ring could not be resolved and were best approximated by atoms with correspondingly large anisotropic thermal parameters. All the bond lengths and angles about the pseudo-tetrahedral Co_2C_2 core are within the ranges normally expected for this type of structure.[1,2,9,10] The alkyne bend-back angles [C(52)–C(51)–C(56) 138.2(7) and C(51)–C(56)–C(55) 139.3(6)°] are within the expected range and the ring does not appear to be strained.

A variable-temperature NMR experiment was run on a

Table 4 Selected internuclear distances (Å) and angles (°) for complex **6a**

Co(1)–Co(2)	2.474(1)	Co(1)–P(1)	2.220(2)	Co(1)–C(1)	1.751(8)	Co(1)–C(2)	1.792(8)
Co(1)–C(51)	1.972(6)	Co(1)–C(56)	1.948(7)	Co(2)–P(2)	2.218(2)	Co(2)–C(3)	1.778(6)
Co(2)–C(4)	1.778(7)	Co(2)–C(51)	1.981(6)	Co(2)–C(56)	1.948(7)	P(1)–C(9)	1.849(6)
P(2)–C(9)	1.828(5)	C(1)–O(1)	1.148(11)	C(2)–O(2)	1.131(10)	C(3)–O(3)	1.143(8)
C(4)–O(4)	1.117(8)	S(1)–C(52)	1.782(7)	S(1)–C(53)	1.844(16)	S(2)–C(54)	1.589(20)
S(2)–C(55)	1.715(10)	S(2A)–C(54)	1.681(20)	S(2A)–C(55)	1.647(11)	C(51)–C(52)	1.482(9)
C(51)–C(56)	1.334(10)	C(53)–C(54)	1.419(26)	C(55)–C(56)	1.483(12)		
Co(2)–Co(1)–P(1)	95.1(1)	Co(2)–Co(1)–C(1)	150.5(3)	P(1)–Co(1)–C(1)	99.0(3)	Co(2)–Co(1)–C(2)	100.7(3)
P(1)–Co(1)–C(2)	109.8(3)	C(1)–Co(1)–C(2)	98.7(4)	Co(2)–Co(1)–C(51)	51.4(2)	P(1)–Co(1)–C(51)	99.2(2)
C(1)–Co(1)–C(51)	100.5(3)	C(2)–Co(1)–C(51)	142.0(3)	Co(2)–Co(1)–C(56)	50.6(2)	P(1)–Co(1)–C(56)	136.1(2)
C(1)–Co(1)–C(56)	103.1(3)	C(2)–Co(1)–C(56)	103.7(3)	C(51)–Co(1)–C(56)	39.8(3)	Co(1)–Co(2)–P(2)	98.7(1)
Co(1)–Co(2)–C(3)	96.6(2)	P(2)–Co(2)–C(3)	105.9(2)	Co(1)–Co(2)–C(4)	149.5(2)	P(2)–Co(2)–C(4)	101.9(2)
C(3)–Co(2)–C(4)	99.0(3)	Co(1)–Co(2)–C(51)	51.1(2)	P(2)–Co(2)–C(51)	99.8(2)	C(3)–Co(2)–C(51)	141.7(3)
C(4)–Co(2)–C(51)	102.9(3)	Co(1)–Co(2)–C(56)	50.6(2)	P(2)–Co(2)–C(56)	137.8(2)	C(3)–Co(2)–C(56)	105.9(3)
C(4)–Co(2)–C(56)	99.7(3)	C(51)–Co(2)–C(56)	39.7(3)	Co(1)–P(1)–C(9)	110.8(2)	Co(2)–P(2)–C(9)	109.1(2)
P(1)–C(9)–P(2)	109.9(3)	C(52)–S(1)–C(53)	102.4(5)	C(54)–S(2)–C(55)	105.5(8)	C(54)–S(2A)–C(55)	104.5(10)
Co(1)–C(51)–Co(2)	77.5(2)	Co(1)–C(51)–C(52)	134.0(4)	Co(2)–C(51)–C(52)	139.5(5)	Co(1)–C(51)–C(56)	69.1(4)
Co(2)–C(51)–C(56)	68.8(4)	C(52)–C(51)–C(56)	138.2(7)	S(1)–C(52)–C(51)	114.4(5)	S(1)–C(53)–C(54)	120.3(9)
S(2)–C(54)–S(2A)	58.6(7)	S(2)–C(54)–C(53)	156.3(16)	S(2A)–C(54)–C(53)	114.9(16)	S(2)–C(55)–S(2A)	56.9(4)
S(2)–C(55)–C(56)	118.3(6)	S(2A)–C(55)–C(56)	125.7(7)	Co(1)–C(56)–Co(2)	78.8(3)	Co(1)–C(56)–C(51)	71.1(4)
Co(2)–C(56)–C(51)	71.5(4)	Co(1)–C(56)–C(55)	138.6(6)	Co(2)–C(56)–C(55)	130.2(5)	C(51)–C(56)–C(55)	139.3(6)
Co(1)–C(1)–O(1)	178.6(7)	Co(1)–C(2)–O(2)	175.7(9)	Co(2)–C(3)–O(3)	177.4(7)	Co(2)–C(4)–O(4)	176.9(6)

sample of complex **6a** in an attempt to observe in the NMR spectra the two conformers observed in the solid-state structure. This was not observed down to 183 K, the lowest temperature at which spectra were recorded. At this temperature the ^{13}C NMR spectrum contained two acetylenic resonances at δ 104.0 and 94.0 consistent with the rock of the alkyne bond about the cobalt–cobalt vector becoming slow on the NMR time-scale and upon warming the resonances coalesced at 213 ± 10 K. The activation energy (ΔG_{T_c}) for this process was calculated[11] and found to be *ca.* 38 ± 4 kJ mol^{-1}, which can be compared with *ca.* 48 kJ mol^{-1} determined for [$Co_2(\mu$-dppm)(μ-PhC_2Ph)($CO)_4$].[12]

The NMR spectra of **6b** show that like **1e** two diastereoisomers are present. In an attempt to separate the *meso* and D, L isomers **6b** was chromatographed on a long Florisil column (30 cm), eluting with light petroleum–dichloromethane (4:1). This produced one very slowly moving red band which spread over the whole length of the column and was collected as two fractions. By comparison of the ^{13}C NMR spectra of these two fractions with that of the mixed isomer spectrum, it was established that in one fraction the intensity of one peak of each pair of resonances was much greater than the other, while in the second fraction the intensity ratio was reversed. Therefore partial separation of the two diastereomers had been achieved.

In conclusion the results presented in this paper demonstrate that the acid catalysed reaction of hexacarbonyldicobalt alkynediol compounds with a range of dithiols represents a convenient high yield route to thiacycloalkyne complexes.

Experimental

The general experimental procedures have been described previously.[5] Proton NMR spectra were recorded with JEOL PMX 60 and JEOL GX 270 instruments and were often found to be better resolved by the lower-field instrument. A JEOL GX 270 instrument was used to record the ^{13}C-{^1H} NMR spectra. The dicobalt alkyne starting materials were prepared by the method of Sternberg *et al.*[6] Light petroleum used has fraction of boiling point 40–60 °C. Analytical and other data for the new compounds are given in Tables 1–3.

Reaction of [$Co_2(\mu$-$HOCR_2C{\equiv}CCR_2OH)(CO)_6$] *with Dithiols*.—The compounds of the type **1**–**5** were all prepared in a similar manner which will be described in detail for **1b** and **2b**. To a solution of [$Co_2(\mu$-$HOCH_2C{\equiv}CCH_2OH)(CO)_6$] (0.50 g, 1.3 mmol) in CH_2Cl_2 (100 cm^3) was added propane-1,3-dithiol (0.13 cm^3, 1.4 mmol) and 3 drops of $HBF_4{\cdot}OEt_2$. The resulting mixture was stirred for 48 h, after which time an excess of $NaHCO_3$ was added and the solvent was removed *in vacuo*. The residue was extracted with CH_2Cl_2 (20 cm^3) and filtered through a plug of magnesium sulfate (5 × 1.5 cm). The solvent was removed *in vacuo* and the residue chromatographed on a Florisil column (15 × 1.5 cm). Elution with light petroleum–CH_2Cl_2 (9:1) produced a red band which upon removal of the solvent *in vacuo* afforded **1b** (0.28 g, 0.63 mmol). Elution with light petroleum–CH_2Cl_2 (3:2) produced a second red band which upon removal of the solvent *in vacuo* afforded **2b** (0.04 g, 0.05 mmol). Complexes **1a**, **1c**, **2c**, **1d** and **2d** were isolated in a similar manner. As the degree of methyl substitution in the product is increased the chromatographic step of the work-up can be performed with more polar solvent mixtures. For example, **1k** was eluted with light petroleum–CH_2Cl_2 (3:1) and **2k** with CH_2Cl_2. Compound **4** was eluted with CH_2Cl_2 and **5** with CH_2Cl_2–tetrahydrofuran (19:1).

Reactions with Bis(diphenylphosphino)methane.—A similar procedure was used to prepare compounds of type **6** which will be described in detail for **6a**. Complex **1a** (0.68 g, 1.80 mmol) and dppm (0.71 g, 1.85 mmol) were dissolved in benzene (45 cm^3) and the resulting solution refluxed for 1.5 h, after which time the solution was cooled to room temperature and the solvent removed *in vacuo*. The resulting dark red residue was then chromatographed on a Florisil column (15 × 1.5 cm). Elution with CH_2Cl_2–light petroleum (1:1) produced a red band which upon removal of the solvent under reduced pressure afforded a red solid. This was purified by recrystallisation from CH_2Cl_2–light petroleum (1:25) to afford **6a** (1.21 g, 1.60 mmol).

Crystal Structure Determination.—Crystals of **6a** were obtained by solvent diffusion from CH_2Cl_2–light petroleum as deep red prisms with crystal dimensions of *ca.* 0.60 × 0.35 × 0.10 mm. Data were collected using a Nicolet P3 diffractometer (293 K, Mo-Kα X-radiation, graphite monochromator, $\bar{\lambda}$ = 0.710 69 Å). Of the 5922 data collected (Wyckoff ω-scans, $2\theta \leqslant 50°$), 3697 unique data had $F \geqslant 4\sigma(F)$, and only these were used for the structure refinement. The data were corrected for Lorentz, polarisation and X-ray absorption effects, the latter by a method based upon azimuthal scan data.[13]

Table 5 Atomic coordinates (× 10^4) for complex **6a**

Atom	*x*	*y*	*z*
Co(1)	−31(1)	493(1)	2076(1)
Co(2)	−189(1)	1606(1)	2555(1)
P(1)	−2311(2)	156(1)	2338(1)
P(2)	−2527(2)	1525(1)	2881(1)
C(1)	68(11)	−27(4)	1379(4)
O(1)	116(11)	−359(3)	913(4)
C(2)	1568(10)	157(4)	2674(5)
O(2)	2639(8)	−41(3)	3025(4)
C(3)	1227(9)	1482(3)	3311(3)
O(3)	2173(7)	1390(3)	3782(3)
C(4)	7(8)	2467(3)	2470(3)
O(4)	199(7)	3004(3)	2415(3)
C(9)	−3635(7)	858(3)	2405(3)
S(1)	−1531(4)	2213(1)	555(1)
S(2)	2588(7)	1316(2)	757(2)
S(2A)	2295(10)	2072(4)	914(3)
C(51)	−747(8)	1310(3)	1588(3)
C(52)	−1894(9)	1462(3)	960(3)
C(53)	−202(21)	1957(6)	−38(5)
C(54)	1300(24)	1687(13)	221(8)
C(55)	2253(10)	1557(5)	1553(4)
C(56)	813(9)	1315(3)	1792(3)
C(11)	−2354(8)	−285(3)	3142(3)
C(12)	−1109(8)	−205(3)	3687(3)
C(13)	−1167(11)	−525(3)	4304(3)
C(14)	−2433(13)	−899(4)	4387(3)
C(15)	−3670(10)	−979(3)	3845(3)
C(16)	−3611(8)	−674(3)	3229(3)
C(21)	−3495(8)	−378(3)	1708(3)
C(22)	−4822(11)	−186(4)	1266(4)
C(23)	−5575(13)	−617(5)	779(5)
C(24)	−5083(11)	−1236(4)	729(4)
C(25)	−3766(11)	−1431(3)	1157(4)
C(26)	−2948(9)	−1008(3)	1640(3)
C(31)	−2622(8)	1377(3)	3791(3)
C(32)	−3750(9)	987(3)	4023(3)
C(33)	−3769(11)	933(4)	4726(4)
C(34)	−2697(12)	1267(5)	5189(4)
C(35)	−1583(12)	1661(5)	4963(3)
C(36)	−1520(8)	1706(3)	4269(3)
C(41)	−3897(7)	2220(2)	2686(3)
C(42)	−4969(8)	2400(3)	3112(3)
C(43)	−5973(8)	2921(3)	2939(3)
C(44)	−5904(9)	3274(3)	2341(4)
C(45)	−4843(8)	3107(3)	1922(3)
C(46)	−3826(8)	2581(3)	2099(3)

Crystal data for **6a**. $C_{35}H_{30}Co_2O_4P_2S_2$, $M = 758.6$, monoclinic, space group $P2_1/n$, $a = 8.602(1)$, $b = 20.428(4)$, $c = 19.724(4)$ Å, $\beta = 99.67(1)°$, $U = 3417(1)$ Å^3, $Z = 4$, $D_c = 1.48$ g cm^{-3}, $F(000) = 1552$, μ(Mo-Kα) = 12.1 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 μ-$CCH_2S(CH_2)_2SCH_2C$ ring was partially disordered and it was possible to resolve two distinct sites [S(2) and S(2A), 60 : 40] for one of the S atoms. The disordered components of the remaining portion of the chain could not be resolved and were best approximated by atoms with correspondingly large anisotropic thermal parameters. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were not included for the methylene groups C(53) and C(54) in the disordered portion of the heterocyclic ring but all other 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 $R = 0.052$ ($R' = 0.057$) and a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.0001|F|^2]$ gave a satisfactory analysis of variance. The final electron density difference synthesis showed no peaks > 0.5 or < -0.75 e Å^{-3}. All calculations were performed on a Digital MicroVax computer with the SHELXTL system of programs.[14] Scattering factors with corrections for anomalous dispersion were taken from ref. 15. Atomic coordinates are listed in Table 5.

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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