Synthesis and Co-ordination Chemistry of Dicobalt-complexed Acetylenic Crown Ethers†

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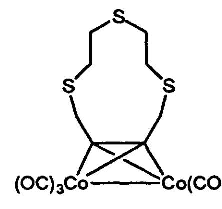
Reactions of $[Co_2(\mu\text{-}HOCHRC{\equiv}CCHROH)(\mu\text{-}dppm)(CO)_4]$ (R = H or Me, dppm = $Ph_2PCH_2PPh_2$) with $HO(CH_2)_nOH$ (n = 4–6) in the presence of $HBF_4{\cdot}OEt_2$ afforded the $Co_2(\mu\text{-}dppm)(CO)_4$-complexed tetraoxacyclodiynes $[(OC)_4(\mu\text{-}dppm)Co_2\{\mu\text{-}CCHRO(CH_2)_nOCHRC\}_2Co_2(\mu\text{-}dppm)(CO)_4]$. The dimeric nature of the products was confirmed by fast atom bombardment mass spectroscopy and the crystal structure of $[(OC)_4(\mu\text{-}dppm)Co_2\{\mu\text{-}CCH_2O(CH_2)_4OCH_2C\}_2Co_2(\mu\text{-}dppm)(CO)_4]$. The acid-catalysed reaction of $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(\mu\text{-}dppm)(CO)_4]$ with triethylene glycol and a $NaBF_4$ template afforded $[Co_2\{\mu\text{-}CCH_2O[(CH_2)_2O]_3CH_2C\}(\mu\text{-}dppm)(CO)_4]$ which can co-ordinate Li^+. The analogous reaction with tetraethylene glycol afforded $[Co_2Na\{\mu\text{-}CCH_2O[(CH_2)_2O]_4CH_2C\}(\mu\text{-}dppm)(CO)_4]BF_4$, in which the sodium template remains co-ordinated by the crown ether. Washing with deionised water removes the Na^+ ion to produce $[Co_2\{\mu\text{-}CCH_2O[(CH_2)_2O]_4CH_2C\}(\mu\text{-}dppm)(CO)_4]$ which forms complexes with $LiBF_4$ and KSCN.

It has been shown previously that acid-catalysed reaction of $[Co_2(\mu\text{-}HC{\equiv}CCH_2OH)(CO)_6]$ with alcohols (ROH) affords ether derivatives $[Co_2(\mu\text{-}HC{\equiv}CCH_2OR)(CO)_6]$.[1] We have demonstrated that this methodology can be used in the preparation of analogous thioether complexes $[Co_2(\mu\text{-}HC{\equiv}CCH_2SR)(CO)_6]$.[2] Treatment of $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(CO)_6]$ with thiols (RSH) in the presence of $HBF_4{\cdot}OEt_2$ affords complexes of the type $[Co_2(\mu\text{-}RSCH_2C{\equiv}CCH_2SR)(CO)_6]$,[2] while treatment with dithiols $HS(CH_2)_nSH$ affords separable mixtures containing predominantly monomeric hexacarbonyldicobalt-complexed dithiacycloalkynes as well as some higher oligomers.[3] By use of bis(2-sulfanylethyl) sulfide, $HSCH_2CH_2SCH_2CH_2SH$, complexes **1** and **2** can be prepared.[4] Although the acetylenic linkages in **1** and **2** are acting as donors to the hexacarbonyldicobalt units, the sulfur atoms are available to co-ordinate further metal–ligand fragments or metal ions. Compound **1** can act as a ligand to soft metal–ligand fragments such as $M(PPh_3)^+$ (M = Ag or Cu) while **2** co-ordinates Ag^+.[4] This paper describes the synthesis, characterisation and co-ordination chemistry of related ether systems.

Results and Discussion

Treatment of $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(CO)_6]$ with an excess of ethanol in the presence of $HBF_4{\cdot}OEt_2$ affords $[Co_2(\mu\text{-}EtOCH_2C{\equiv}CCH_2OEt)(CO)_6]$ in low yield. The yield is not increased by the addition of 4 Å molecular sieves, which would be expected to drive the reaction to completion by removing the water by-product.[1] In an attempt to improve the yield, phosphine substitution was employed to increase the stability of the cationic intermediates.[5] Treatment of $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(\mu\text{-}dppm)(CO)_4]$ **3** (dppm = $Ph_2PCH_2PPh_2$) with ethanol in the presence of $HBF_4{\cdot}OEt_2$ affords $[Co_2(\mu\text{-}EtOCH_2C{\equiv}CCH_2OEt)(\mu\text{-}dppm)(CO)_4]$, but the product was not obtained in a pure form and attempts to purify it by column chromatography failed due to its strong binding to Florisil even at −20 °C. Despite these rather discouraging observations diols were investigated as a means of generating cyclic ether products. Treatment of **3** with ethane-1,2-diol or propane-1,3-diol gives intractable mixtures, but butane-1,4-diol, pentane-1,5-diol and hexane-1,6-diol afford compounds **4**, **5** and **6** in high yield.



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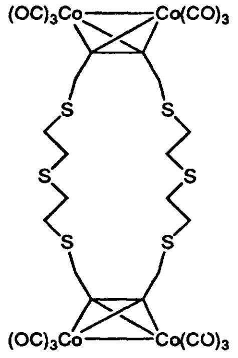

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Analytical and IR data for the new compounds are given in Table 1. The solution IR spectra of the cyclic ethers have absorptions *ca.* 2 cm^{-1} lower than those of **3**, reflecting the change of alcohol to less electronegative ether substituents.[2] The NMR spectra of the products (Table 2) are in accord with their cyclic structures. For example, the ^{13}C NMR spectrum of **4** contains resonances at δ 73.4 and 70.7 due to methylenes adjacent to oxygen, one at δ 26.7 due to the remaining methylenes and one at δ 93.8 due to the acetylenic carbons, as well as resonances assigned to the dppm and carbonyl ligands. Fast atom bombardment (FAB) mass spectrometry (Table 3) indicates that the products are dimeric. The spectrum of **4** is particularly informative, containing peaks assigned to the molecular ion and eight successive carbonyl losses.

Crystals of compound **4** were obtained by diffusion from CH_2Cl_2–Et_2O and used in a single-crystal X-ray diffraction study. Selected structural parameters are listed in Table 4 and the molecular structure is shown in Fig. 1. The complex has a crystallographically imposed inversion centre and atoms with a suffix 'a' are generated by symmetry. The molecule is indeed dimeric and consists of a 1,6,11,16-tetraoxacyclo-

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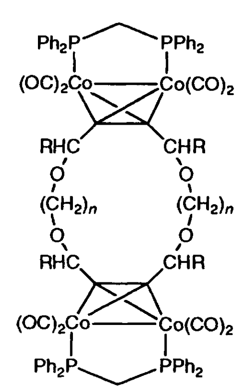
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Analytical[a] and physical data

Complex	Colour	Yield (%)	$\tilde{\nu}_{max}(CO)^b/cm^{-1}$	Analysis (%) C	Analysis (%) H
3	Pink	78	1950 (sh), 1966m, 1994s, 2024m	56.3 (56.6)	3.9 (4.0)
4	Red	95	1952 (sh), 1963s, 1992s, 2021s	58.3 (58.9)	4.4 (4.5)
5	Red	91	1948 (sh), 1963s, 1992s, 2021m	58.7 (59.4)	4.4 (4.7)
6	Red	97	1948 (sh), 1963s, 1992s, 2021s	59.4 (59.8)	4.7 (4.9)
7	Pink	87	1948 (sh), 1966m, 1993s, 2023m	53.7 (53.2)	4.1 (4.2)[c]
8	Red	96	1945 (sh), 1960m, 1989s, 2018m	59.1 (59.9)	4.9 (4.9)
9	Red	93	1946 (sh), 1961m, 1989s, 2018m	59.5 (60.3)	4.9 (5.0)
10	Red	96	1943 (sh), 1960m, 1989s, 2018m	58.1 (57.2)	5.0 (5.0)[d]
11	Red	89	1945 (sh), 1964s, 1992m, 2021m	56.2 (57.5)	4.7 (4.7)
12	Red	77	1944 (sh), 1963m, 1992s, 2020m	56.4 (57.3)	4.9 (4.9)
13	Red	83	1952 (sh), 1972m, 1998s, 2028m, 2056w	51.7 (51.6)	4.3 (4.2)
14	Red	96	1948 (sh), 1970m, 1997s, 2026m	51.2 (51.7)	4.7 (4.5)
15	Red	86	1954 (sh), 1967m, 1995s, 2025m	51.4 (50.9)	4.3 (4.4)
16	Red	94	1950 (sh), 1968m, 1995s, 2025m, 2055w	52.3 (52.8)	4.6 (4.4)

[a] Calculated values given in parentheses. [b] Recorded in CH_2Cl_2. [c] Value for compound **7**·CH_2Cl_2. [d] Value for compound **10**·CH_2Cl_2.



	n	R
4	4	H
5	5	H
6	6	H
8	4	Me
9	5	Me
10	6	Me

icosa-8,18-diyne ring co-ordinated by two $Co_2(\mu\text{-dppm})(CO)_4$ fragments. The dppm ligands occupy equatorial sites as has been previously observed in $[Co_2(\mu\text{-alkyne})(\mu\text{-dppm})(CO)_4]$ complexes.[3] All the bond lengths and angles about the pseudo-tetrahedral Co_2C_2 cores are within those normally expected for this type of structure.[3] The observation of only one acetylenic resonance in the room-temperature ^{13}C NMR spectrum of **4** is consistent with rocking of the alkyne bonds about the cobalt–cobalt vectors.[6] Fig. 2 shows the geometry of the 1,6,11,16-tetraoxacycloicosa-8,18-diyne ring and torsional angles are given in Table 4. The ring is similar to free 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) and like it internal hydrogen bonding appears to be important in determining the shape.[7] The distance O(2) ··· H(5a) is *ca.* 2.46 Å and can be compared with the analogous distance in 18-crown-6 (2.5 Å).[7]

Similar rings were prepared from $[Co_2\{\mu\text{-HO(Me)CHC}\equiv\text{CCH(Me)OH}\}(\mu\text{-dppm})(CO)_4]$ **7** which was prepared from the reaction of hex-3-yne-2,5-diol with $[Co_2(\mu\text{-dppm})(CO)_6]$. Treatment of **7** with butane-1,4-diol, pentane-1,5-diol and hexane-1,6-diol affords **8**, **9** and **10** respectively. All three compounds would be expected to display a mixture of diastereoisomers in their NMR spectra,[3] but this was not observed possibly due to the broadening of the spectra by the cobalt quadrupole or the cationic propargyl intermediates

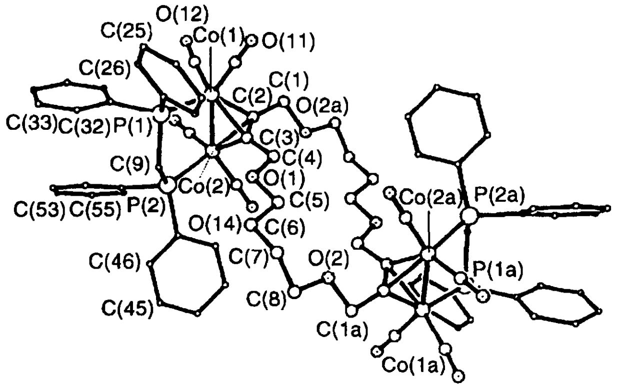


Fig. 1 Molecular structure of compound **4** showing the atom labelling system

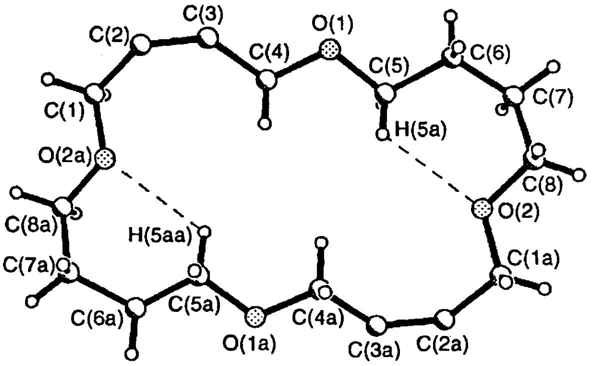


Fig. 2 The 1,6,11,16-tetraoxacycloicosa-8,18-diyne ring

exerting a degree of diastereochemical control.[8] Attempts to use $[Co_2\{\mu\text{-HOMe}_2CC\equiv CCMe_2OH\}(\mu\text{-dppm})(CO)_4]$ resulted in extensive formation of enyne products.[3,9]

Not surprisingly the products derived from diols show very little ability to co-ordinate Group 1 or 2 cations. In order to prepare cyclic polyethers, glycols were used and the procedure modified by the introduction of a template. Reaction of compound **3** with triethylene glycol and an equivalent of $NaBF_4$ in the presence of HBF_4·OEt_2 affords **11**. The analogous reaction using tetraethylene glycol results in the isolation of **15** which has the sodium template co-ordinated in the ring. The free macrocycle **12** is obtained by washing **15** with deionised water. Its FAB mass spectrum indicates that it is monomeric.

The ability of compounds **11** and **12** to co-ordinate other

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

Complex	^1H (δ)	^{13}C (δ)[b]
3	7.40 (br s, 20 H, Ph), 4.75 [m, 4 H, CH_2, J(HH) 3], 3.60 [t, 2 H, PCH_2P, J(PH) 11], 2.60 [t, 2 H, OH, J(HH) 6][c]	205.4 (CO), 138–128 (Ph), 97.2 (C_2), 65.4 (CH_2), 40.7 [t, PCH_2P, J(PC) 21][d]
4	7.36–7.16 (br s, 20 H, Ph), 4.73 (s, 4 H, CCH_2O), 3.57 [br s, 6 H, PCH_2P and $OC\mathit{H}_2(CH_2)_2C\mathit{H}_2O$], 1.65 [br s, 4 H, $OCH_2(C\mathit{H}_2)_2CH_2O$]	205.2 (CO), 138–127 (Ph), 93.8 (C_2), 73.4, 70.7 (OCH_2), 39.0 (br s, PCH_2P), 26.7 [$OCH_2(\mathit{C}H_2)_2CH_2O$]
5	7.37–7.17 (br s, 20 H, Ph), 5.23 (s, 4 H, CCH_2O), 3.55 [br s, 6 H, PCH_2P and $OC\mathit{H}_2(CH_2)_3C\mathit{H}_2O$], 1.60 [s, 4 H, $OCH_2C\mathit{H}_2CH_2C\mathit{H}_2CH_2O$], 1.37 [s, 2 H, $O(CH_2)_2C\mathit{H}_2(CH_2)_2O$]	205.0 (CO), 138–127 (Ph), 93.9 (C_2), 73.4, 70.9 (OCH_2), 38.9 [t, PCH_2P, J(PC) 20], 29.8 [$OCH_2\mathit{C}H_2CH_2\mathit{C}H_2CH_2O$], 22.8 [$O(CH_2)_2\mathit{C}H_2(CH_2)_2O$]
6	7.36–7.16 (br s, 20 H, Ph), 4.73 (s, 4 H, CCH_2O), 3.56 [br s, 6 H, PCH_2P and $OC\mathit{H}_2(CH_2)_4C\mathit{H}_2O$], 1.57 [s, 4 H, $OCH_2C\mathit{H}_2(CH_2)_2C\mathit{H}_2CH_2$], 1.35 [s, 4 H, $O(CH_2)_2(C\mathit{H}_2)_2(CH_2)_2O$]	205.2 (CO), 138–127 (Ph), 93.9 (C_2), 73.4, 71.0 (OCH_2), 38.9 [t, PCH_2P, J(PC) 20], 29.9 [$OCH_2\mathit{C}H_2(CH_2)_2\mathit{C}H_2CH_2O$], 26.3 [$O(CH_2)_2(\mathit{C}H_2)_2(CH_2)_2O$]
7	7.40 (br s, 20 H, Ph), 5.20 (br s, 4 H, CH), 3.75 (m, 2 H, PCH_2P), 2.60 [d, 1 H, OH, J(HH) 4.8], 2.25 [d, 1 H, OH, J(HH) 4.8], 1.50 (s, 6 H, Me)[c]	205.8 (CO), 138–128 (Ph), 102.6 (C_2), 70.8, 70.5 (CH_2), 38.7 (m, PCH_2P), 25.9, 25.5 (Me)[d]
8	7.40 (br s, 20 H, Ph), 4.90 (br s, 2 H, CH), 3.90 [br s, 6 H, PCH_2P and $OC\mathit{H}_2(CH_2)_2C\mathit{H}_2O$], 1.70 [br s, 10 H, $OCH_2(C\mathit{H}_2)_2CH_2O$ and Me][c]	205.5 (CO), 138–127 (Ph), 100.0 (br s, C_2), 78.4 (CH), 62.7 [$O\mathit{C}H_2(CH_2)_2\mathit{C}H_2O$], 37.8 (br s, PCH_2P), 27.7 [$OCH_2(\mathit{C}H_2)_2CH_2O$], 21.7 (Me)
9	7.35 (br s, 20 H, Ph), 4.80 (br s, 2 H, CH), 1.70 (br s, 6 H, PCH_2P and OCH_2), 1.50 [br s, 12 H, Me and $OCH_2(C\mathit{H}_2)_2CH_2O$][c]	205.7 (CO), 138–127 (Ph), 100.0 (C_2), 78.3 (CH), 68.1 (OCH_2), 37.5 (PCH_2P), 30.2 ($OCH_2\mathit{C}H_2CH_2\mathit{C}H_2CH_2O$), 22.9 [$O(CH_2)_2\mathit{C}H_2(CH_2)_2O$], 21.7 (Me)
10	7.30 (br s, 20 H, Ph), 4.80 (br s, 2 H, CH), 3.70 (br s, 6 H, PCH_2P and OCH_2), 1.50 [br s, 14 H, Me and $OCH_2(C\mathit{H}_2)_4CH_2O$][c]	205.7 (CO), 138–127 (Ph), 100.3 (C_2), 78.4 (CH), 69.0 (OCH_2), 37.6 [t, PCH_2P, J(PC) 20], 30.3 [$OCH_2\mathit{C}H_2(CH_2)_2\mathit{C}H_2CH_2$,O], 26.1 [$O(CH_2)_2(\mathit{C}H_2)_2(CH_2)_2O$], 21.6 (Me)
11	7.20 (br s, 20 H, Ph), 4.60 (br s, 4 H, CCH_2O), 3.50 [br s, 14 H, PCH_2P and $O(CH_2CH_2O)_3$][c]	205.0 (CO), 138–127 (Ph), 93.1 (C_2), 73.7, 70.5, 69.1 (CH_2), 38.2 (br s, PCH_2P)
12	7.37–7.18 (br s, 20 H, Ph), 4.96 (s, 4 H, CCH_2O), 3.60 [m, 18 H, PCH_2P and $O(CH_2CH_2O)_4$]	204.9 (CO), 138–127 (Ph), 93.9 (C_2), 73.3, 73.1, 70.8, 70.5, 69.8 (CH_2), 39.6 [t, PCH_2P, J(PC) 21]
13	7.26 (br s, 20 H, Ph), 4.76 (br s, 4 H, CCH_2O), 3.67 [br s, 18 H, PCH_2P and $O(CH_2CH_2O)_3$]	204.5 (CO), 137–128 (Ph), 90.6 (C_2), 72.7, 70.4, 68.8, 68.0 (CH_2), 41.9 (br s, PCH_2P)
14	7.35–7.21 (m, 20 H, Ph), 4.84 (s, 4 H, CCH_2O), 3.72 [br s, 16 H, $O(CH_2CH_2O)_4$], 3.43 [t, 2 H, PCH_2P, J(PH) 10.0 Hz]	204.7 (CO), 137–128 (Ph), 91.7 (C_2), 72.9, 70.6, 70.0, 69.7, 69.2 (CH_2), 41.4 [t, PCH_2P, J(PC) 22]
15	7.37–7.19 (m, 20 H, Ph), 4.77 (s, 4 H, CCH_2O), 3.75–3.57 [br m, 18 H, $O(CH_2CH_2O)_4$ and PCH_2P]	205.0 (CO), 137–128 (Ph), 91.6 (C_2), 72.8, 70.0, 69.5, 69.2, 61.3 (CH_2), 41.1 [t, PCH_2P, J(PC) 20]
16	7.39–7.20 (m, 20 H, Ph), 4.72 (s, 4 H, CCH_2O), 3.72–3.61 [m, 16 H, $O(CH_2CH_2O)_4$], 3.48 [t, 2 H, PCH_2P, J(PH) 10.2]	204.8 (s, CO), 137–128 (Ph), 90.6 (C_2), 72.5, 70.3, 70.1, 69.8, 69.3 (CH_2), 42.5 [t, PCH_2P, J(PC) 20], 29.7 (SCN)

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

Table 3 Fast atom bombardment mass spectral data (*m*/*z*)

Complex	Molecular ion $M^{\cdot +}$	$M^{\cdot +} - n$(CO)	n
4	1508	1480, 1452, 1423, 1396, 1368, 1340, 1312, 1283	1–8
5	—	1396, 1341	6, 7
6	—	1536, 1509, 1340	1, 2 (+1), 8
12	859 (+H)	831 (+H), 774	1, 3
14	—	837 ($-BF_4$), 781 ($-BF_4$), 753 ($-BF_4$)	2, 3, 4
15	—	824 ($-BF_4$, $-H$), 769 ($-BF_4$), 858 ($-NaBF_4$), 803 ($-NaBF_4$)	2, 4, 0, 2
16	—	786 ($-SCN$, $+H$)	4

metal ions was investigated. Treatment of **11** with $LiBF_4$ results in co-ordination of Li^+ to afford **13**, but attempts to co-ordinate Na^+ and K^+ failed to give pure products. The presence of the co-ordinated cation was established by elemental analysis and a number of spectroscopic techniques. The IR spectrum of **13** shows a shift of *ca.* 7 cm^{-1} to higher wavenumber for the carbonyl absorptions compared to the spectrum of **11**, as well as an absorption at 1085 cm^{-1} due to the BF_4^- counter ion. The ^7Li NMR spectrum shows a single sharp resonance at δ −0.76 (external reference LiCl in D_2O) which is typical for a solvated Li^+ ion.[10] With the larger macrocycle **12**, Li^+, Na^+ and K^+ were successfully co-ordinated to afford **14**, **15** and **16** respectively. The presence of the metal ions was established by FAB mass spectroscopy (Table 3), elemental analysis (Table 1) and a shift in the carbonyl stretching frequencies to higher wavenumber by *ca.* 5 cm^{-1}. The FAB mass spectrum of a mixture containing equimolar quantities of **12**, $LiBF_4$, $NaBF_4$ and KBF_4 contained strong peaks assigned to **14** and **15**, but only weak peaks due to **16**, suggesting that Li^+ and Na^+ are co-ordinated in preference to K^+. The FAB mass spectrum also suggested that **12** was capable of co-ordinating Ag^+

Experimental

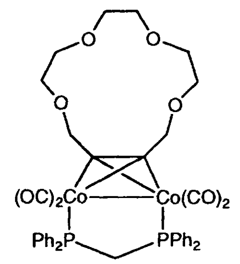
The general experimental procedures have been described previously.[2] The compounds $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(CO)_6]$,[11] $[Co_2\{\mu\text{-}HO(Me)CHC{\equiv}CCH(Me)OH\}(CO)_6]$[11] and $[Co_2(\mu\text{-dppm})(CO)_6]$[12] were prepared by literature methods. Analytical and other data for the new compounds are given in Tables 1–3.

Preparations.—$[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(\mu\text{-dppm})(CO)_4]$ **3**. A solution of $[Co_2(\mu\text{-}HOCH_2C{\equiv}CCH_2OH)(CO)_6]$ (3.81 g, 10.24 mmol) and dppm (3.97 g, 10.24 mmol) in benzene (50 cm^3) was refluxed for an hour and then solvent removed *in vacuo*. The resulting solid was dissolved in CH_2Cl_2 (50 cm^3)

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

Co(1)–Co(2)	2.465(1)	Co(1)–P(1)	2.227(1)	Co(1)–C(2)	1.943(4)	Co(1)–C(3)	1.970(3)
Co(1)–C(11)	1.768(4)	Co(1)–C(12)	1.795(3)	Co(2)–P(2)	2.226(1)	Co(2)–C(2)	1.940(3)
Co(2)–C(3)	1.959(3)	Co(2)–C(13)	1.763(3)	Co(2)–C(14)	1.769(5)	P(1)–C(9)	1.849(3)
P(1)–C(21)	1.836(3)	P(1)–C(31)	1.834(3)	P(2)–C(9)	1.834(3)	P(2)–C(41)	1.837(3)
P(2)–C(51)	1.827(3)	C(1)–C(2)	1.485(4)	C(1)–O(2a)	1.421(5)	C(2)–C(3)	1.339(3)
C(3)–C(4)	1.493(3)	C(4)–O(1)	1.418(3)	C(5)–C(6)	1.508(4)	C(5)–O(1)	1.430(3)
C(6)–C(7)	1.518(4)	C(7)–C(8)	1.504(7)	C(8)–O(2)	1.408(4)	C(11)–O(11)	1.132(6)
C(12)–O(12)	1.134(4)	C(13)–O(13)	1.144(4)	C(14)–O(14)	1.123(7)		
Co(2)–Co(1)–P(1)	94.7(1)	Co(1)–P(1)–C(9)	110.9(1)	P(2)–Co(2)–C(13)	103.9(1)	C(11)–Co(1)–C(12)	100.6(2)
Co(2)–Co(1)–C(3)	50.9(1)	Co(1)–P(1)–C(31)	121.3(1)	Co(1)–Co(2)–C(14)	149.9(1)	P(2)–Co(2)–C(2)	139.7(1)
Co(2)–Co(1)–C(11)	149.6(1)	Co(2)–P(2)–C(9)	109.2(1)	C(3)–Co(2)–C(14)	102.3(2)	C(2)–Co(2)–C(3)	40.2(1)
C(3)–Co(1)–C(11)	99.3(2)	Co(2)–Co(1)–C(2)	50.5(1)	Co(1)–P(1)–C(21)	113.9(1)	C(2)–Co(2)–C(13)	105.4(1)
C(2)–Co(1)–C(12)	100.8(2)	P(1)–Co(1)–C(3)	102.4(1)	C(9)–P(1)–C(31)	101.4(1)	P(2)–Co(2)–C(14)	100.8(1)
Co(1)–Co(2)–P(2)	99.2(1)	P(1)–Co(1)–C(11)	98.6(1)	Co(2)–P(2)–C(41)	117.5(1)	C(13)–Co(2)–C(14)	100.5(2)
Co(1)–Co(2)–C(3)	51.3(1)	Co(2)–Co(1)–C(12)	100.8(1)	P(1)–Co(1)–C(2)	138.4(1)	C(9)–P(1)–C(21)	104.1(1)
Co(1)–Co(2)–C(13)	96.3(2)	C(3)–Co(1)–C(12)	139.7(2)	C(2)–Co(1)–C(3)	40.0(1)	C(21)–P(1)–C(31)	103.3(1)
C(3)–Co(2)–C(13)	141.6(2)	Co(1)–Co(2)–C(2)	50.7(1)	C(2)–Co(1)–C(11)	104.1(2)	C(9)–P(2)–C(41)	103.3(1)
C(2)–Co(2)–C(14)	100.4(2)	P(2)–Co(2)–C(3)	101.7(1)	P(1)–Co(1)–C(12)	108.8(1)		

C(3)–C(2)–C(1)–O(2a)	55.1	C(5)–C(6)–C(7)–C(8)	−70.2	C(4)–O(1)–C(5)–C(6)	−179.2
C(4)–C(3)–C(2)–C(1)	2.1	O(2)–C(8)–C(7)–C(6)	72.3	C(7)–C(8)–O(2)–C(1a)	170.1
C(2)–C(3)–C(4)–O(1)	177.7	C(5)–O(1)–C(4)–C(3)	170.2	C(8a)–O(2a)–C(1)–C(2)	176.7
C(7)–C(6)–C(5)–O(1)	−175.3				



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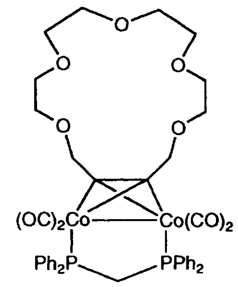

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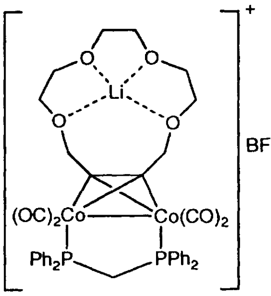

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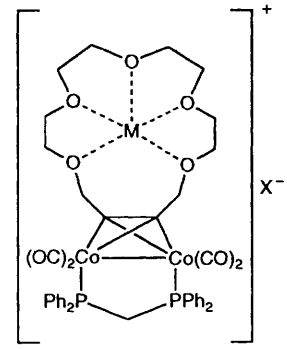

	M	X
14	Li	BF_4
15	Na	BF_4
16	K	SCN

and light petroleum (b.p. = 40–60 °C; 100 cm^3) was added to precipitate the product. This mixture was left at −25 °C overnight after which time the product was filtered off and dried *in vacuo* (6.24 g, 8.91 mmol).

[{Co_2[μ-$CCH_2O(CH_2)_4OCH_2C$](μ-dppm)$(CO)_4$}$_2$] **4**. To a solution of compound **3** (0.56 g, 0.80 mmol) in CH_2Cl_2 (30 cm^3) was added butane-1,4-diol (0.07 g, 0.80 mmol) and two drops of HBF_4·OEt_2. This mixture was stirred overnight and then an excess of $NaHCO_3$ was added. The solvent was removed *in vacuo* and the residue was dissolved in CH_2Cl_2 (20 cm^3) and passed through a plug of magnesium sulfate (5 × 1.5 cm). Removal of the solvent *in vacuo* yielded **4** as a dark red solid (0.57 g, 0.76 mmol). Compounds **5** and **6** were prepared *via* similar procedures.

[Co_2{μ-HO(Me)CHC≡CCH(Me)OH}(μ-dppm)$(CO)_4$] **7**. A solution of [Co_2(μ-dppm)$(CO)_6$] (3.40 g, 5.07 mmol) and hex-3-yne-2,5-diol (0.58 g, 5.07 mmol) in benzene (50 cm^3) was refluxed for 2 h after which the solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2 (20 cm^3) and light petroleum (b.p. = 40–60 °C; 100 cm^3) added to precipitate the product. This mixture was left at −25 °C overnight after which the product was filtered off and dried *in vacuo* to yield compound **7** (2.72 g, 3.73 mmol).

[{Co_2[μ-CCH(Me)O$(CH_2)_4$OCH(Me)C](μ-dppm)$(CO)_4$}$_2$] **8**. Complex **7** (0.56 g, 0.80 mmol) was dissolved in CH_2Cl_2 (40 cm^3). To this solution butane-1,4-diol (0.07 g, 0.80 mmol) and two drops of HBF_4·OEt_2 were added. This mixture was stirred overnight and then an excess of $NaHCO_3$ was added to neutralise the acid. The solvent was removed *in vacuo* and the residue was dissolved in CH_2Cl_2 (20 cm^3) and passed through a magnesium sulfate plug (5 × 1.5 cm). After this the solvent was again removed *in vacuo* to yield **8** as a dark red solid (0.57 g, 0.38 mmol). Compounds **9** and **10** were prepared by a similar procedure.

[Co_2{μ-$CCH_2O[(CH_2)_2O]_3CH_2C$}(μ-dppm)$(CO)_4$] **11**. Complex **3** (0.80 g, 1.14 mmol) was dissolved in CH_2Cl_2 (150 cm^3). To this triethylene glycol (0.17 g, 1.14 mmol), $NaBF_4$ (0.13 g, 1.14 mmol) and five drops of HBF_4·OEt_2 were added. The mixture was stirred for 5 d after which an excess of $NaHCO_3$ was added. The solvent was then removed *in vacuo* and the residue dissolved in CH_2Cl_2 (20 cm^3) and passed through a plug of magnesium sulfate (4 × 1.5 cm). The solvent was removed again *in vacuo* to yield compound **11** as a dark red solid (0.83 g, 1.02 mmol).

[Co_2{μ-$CCH_2O[(CH_2)_2O]_4CH_2C$}(μ-dppm)$(CO)_4$] **12**. Complex **3** (1.19 g, 1.70 mmol) was dissolved in CH_2Cl_2 (150 cm^3). To this tetraethylene glycol (0.33 g, 1.70 mmol), $NaBF_4$ (0.19 g, 1.70 mmol) and five drops of HBF_4·OEt_2 were added. The mixture was stirred for 5 d after which an excess of $NaHCO_3$ was added. The solvent was removed *in vacuo* and the residue dissolved in CH_2Cl_2 (20 cm^3) and passed through a magnesium sulfate plug (4 × 1.5 cm). Removal of the solvent *in vacuo* afforded [Co_2Na{μ-$CCH_2O[(CH_2)_2O]_4CH_2C$}(μ-dppm)$(CO)_4$]BF_4 **15**, as a dark red solid (1.42 g, 1.48 mmol). This was dissolved in CH_2Cl_2 (40 cm^3) and washed with deionised water (4 × 100 cm^3) to remove the $NaBF_4$. The

Table 5 Atomic coordinates ($\times 10^4$) for complex **4**, with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Co(1)	1257(1)	1494(1)	3011(1)	C(23)	3455(5)	−3056(3)	2659(3)
Co(2)	2567(1)	2675(1)	2884(1)	C(24)	2733(5)	−3346(4)	2244(3)
P(1)	2366(1)	635(1)	1821(1)	C(25)	1951(4)	−2459(4)	1664(3)
P(2)	4060(1)	1959(1)	1745(1)	C(26)	1853(3)	−1267(3)	1491(2)
C(1)	819(3)	2600(3)	4730(2)	C(31)	1813(3)	1362(2)	743(2)
C(2)	1589(3)	2101(3)	3915(2)	C(32)	2412(3)	753(3)	27(2)
C(3)	2701(3)	1140(2)	3667(2)	C(33)	2060(3)	1329(3)	−799(2)
C(4)	3709(3)	45(3)	4157(2)	C(34)	1118(3)	2527(3)	−919(2)
C(5)	5789(3)	−1693(3)	4031(2)	C(35)	514(3)	3149(3)	−214(2)
C(6)	6800(3)	−2485(3)	3378(2)	C(36)	859(3)	2572(3)	615(2)
C(7)	7959(3)	−3585(3)	3772(3)	C(41)	5810(3)	1536(3)	1812(2)
C(8)	8917(3)	−3277(3)	4074(2)	C(42)	6271(3)	970(3)	2607(2)
O(1)	4703(2)	−757(2)	3593(1)	C(43)	7589(4)	653(4)	2699(3)
O(2)	8303(2)	−2743(2)	4840(1)	C(44)	8407(3)	940(4)	2010(3)
C(9)	4083(2)	510(2)	1610(2)	C(45)	7961(3)	1498(3)	1212(3)
C(11)	750(3)	328(3)	3595(2)	C(46)	6662(3)	1802(3)	1108(2)
O(11)	425(3)	−415(3)	3977(2)	C(51)	3838(3)	2972(3)	688(2)
C(12)	−315(3)	2719(3)	2754(2)	C(52)	3995(3)	2588(3)	−100(2)
O(12)	−1325(3)	3506(3)	2645(2)	C(54)	3797(5)	3451(5)	−863(3)
C(13)	1389(3)	4103(3)	2420(2)	C(53)	3500(5)	4669(5)	−842(3)
O(13)	614(3)	5031(3)	2130(2)	C(55)	3370(4)	5037(4)	−79(3)
C(14)	3436(4)	3187(3)	3375(2)	C(56)	3535(3)	4204(3)	683(2)
O(14)	3977(4)	3521(3)	3687(2)	O(61)	4901(19)	5445(12)	4845(11)
C(21)	2584(3)	−959(3)	1911(2)	C(61)	6054(15)	4223(16)	4633(14)
C(22)	3382(4)	−1879(3)	2496(2)	C(62)	7011(11)	3188(14)	4800(8)

solvent was then removed *in vacuo* and the residue dissolved in CH_2Cl_2 (20 cm^3) and passed through a plug of magnesium sulfate (4 × 1.5 cm). Removal of the solvent *in vacuo* afforded compound **12** as a dark red solid (1.12 g, 1.30 mmol).

$[Co_2Li\{\mu\text{-}CCH_2O[(CH_2)_2O]_3CH_2C\}(\mu\text{-dppm})(CO)_4]BF_4$ **13**. To a solution of compound **11** (0.24 g, 0.29 mmol) in a mixture of CH_2Cl_2 (10 cm^3) and MeOH (5 cm^3) was added $LiBF_4$ (0.03 g, 0.29 mmol). The mixture was stirred overnight after which time the solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2 (20 cm^3) and then passed through a plug of Celite (2 × 1.5 cm). The solvent was again removed *in vacuo* to afford compound **13** as a dark red solid (0.22 g, 0.24 mmol).

$[Co_2Li\{\mu\text{-}CCH_2O[(CH_2)_2O]_4CH_2C\}(\mu\text{-dppm})(CO)_4]BF_4$ **14**. To a solution of compound **12** (0.43 g, 0.50 mmol) in a mixture of CH_2Cl_2 (10 cm^3) and MeOH (10 cm^3) was added $LiBF_4$ (0.05 g, 0.50 mmol). This mixture was stirred overnight after which the solvent was removed *in vacuo*. The residue was then dissolved in CH_2Cl_2 (20 cm^3) and passed through a plug of Celite (2 × 1.5 cm). The solvent was again removed *in vacuo* to yield compound **14** as a dark red solid (0.46 g, 0.48 mmol).

$[Co_2K\{\mu\text{-}CCH_2O[(CH_2)_2O]_4CH_2C\}(\mu\text{-dppm})(CO)_4]SCN$ **16**. Complex **12** (0.34 g, 0.40 mmol) was dissolved in a mixture of CH_2Cl_2 (10 cm^3) and MeOH (10 cm^3). To this KSCN (0.04 g, 0.40 mmol) was added and the mixture was stirred overnight. The solvent was then removed *in vacuo* and the residue dissolved in CH_2Cl_2 and passed through a Celite plug (2 × 1.5 cm). The solvent was again removed *in vacuo* to yield compound **16** as a dark red solid (0.35 g, 0.38 mmol).

Crystal Structure Determination.—Crystals of compound **4** were obtained by solvent diffusion from CH_2Cl_2–Et_2O as very large deep red prisms. The crystal used was an irregular block (crystal dimensions *ca.* 0.62 mm) cut from a much larger crystal. Data were collected using a Siemens R3m/V diffractometer (295 K, Mo-Kα X-radiation, graphite monochromator, $\bar{\lambda}$ = 0.710 69 Å). Of the 7119 data collected (Wyckoff ω scans, $2\theta \leqslant 50°$), 5328 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.[13]

Crystal data. $C_{74}H_{68}Co_4O_{12}P_4 \cdot Et_2O$, M = 1583.0, triclinic, space group $P\bar{1}$, a = 11.386(4), b = 12.305(6), c = 15.883(7) Å, α = 76.13(4), β = 77.01(3), γ = 62.93(3)°, U = 1906.4(15) $Å^3$, Z = 1, D_c = 1.38 g cm^{-3}, $F(000)$ = 818, μ(Mo-Kα) = 10.0 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 $\bar{1}$ symmetry and atoms with the suffix 'a' are generated by symmetry. In addition, the unit cell also has a molecule of Et_2O which is disordered about the inversion centre. 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 = 0.034 (R' = 0.037) 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 > 0.34 or < −0.44 e $Å^{-3}$. Atomic coordinates are listed in Table 5.

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.

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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