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Synthesis of cobalt-containing cyclophanes, and the formation of an unprecedented seven-membered cyclic diyne†

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The acid-catalysed Nicholas reaction of the bis-propargyl complex $[\{Co_2(CO)_6(\mu\text{-}\eta^2\text{-}HOMe_2CC{\equiv}C\text{–})\}_2]$ **1** in the presence of a variety of nucleophiles leads in each case to $[\{Co_2(CO)_6\}_2\{$*cyclo*-$\mu\text{-}\eta^2\text{:}\mu\text{-}\eta^2\text{-}C({=}CH_2)CH_2CMe_2C{\equiv}C\text{–}C{\equiv}C\}]$, a complex which contains an unprecedented seven-membered macrocyclic diyne ligand. The reactivity of **1** is compared to that of $[\{Co_2(CO)_6\}_2\{\mu\text{-}\eta^2\text{:}\mu\text{-}\eta^2\text{-}1,4\text{-}C_6H_4(C{\equiv}CCMe_2OH)_2\}]$ which does not cyclise on treatment with nucleophiles but instead gives the expected substitution products.

Introduction

In recent years there has been a great deal of interest in the ability of dicobalt coordinated bis-propargyl alcohols to stabilise dications.[1] We have recently reported that the acid-catalysed nucleophilic substitution of such alcohols with dithiols (often called the Nicholas reaction) leads to the synthesis of a hitherto inaccessible range of new thio-macrocycles containing both sulfur atoms and diyne units.[1,2]

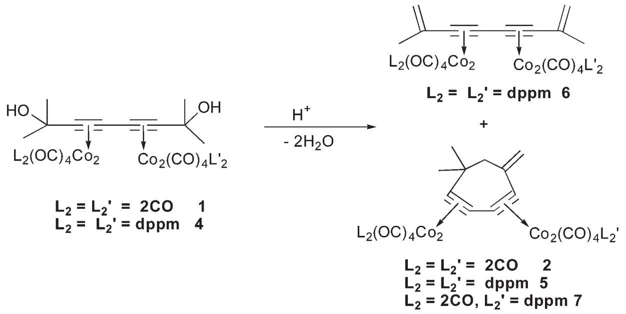
There is considerable current interest both in the synthesis of polymeric materials with acetylenic backbones (due to their important electronic properties) and in the synthesis of small cyclophanes and strained conjugated carbocycles.[3] It seemed possible that a Nicholas reaction between dicobalt-coordinated bis-propargyl alcohols and arene nucleophiles might similarly provide a one-pot route both to unsaturated chains and to cyclophanes. The investigation was stimulated by the recent report of Vollhardt and co-workers that the pyrolysis of dicobalt-stabilised conjugated carbocycles leads to the smooth formation of nano-tubes and nano-onions whereas the analogous uncoordinated carbocycles decompose explosively.[4]

Results and discussion

The acid-catalysed reactions of the dicobalt-coordinated bis-propargylic complex, $[\{Co_2(CO)_6(\mu\text{-}\eta^2\text{-}HOMe_2CC{\equiv}C\text{–})\}_2]$ **1**, with a variety of arene nucleophiles such as PhOH, PhSH, $1,4\text{-}C_6H_4(OH)_2$, and PhOMe were investigated. No substitution products were isolated in any of these reactions. In fact, even when **1** was treated with more potent nucleophilic reagents, such as HSC_3H_6SH, no substitution products were obtained, despite the fact that HSC_3H_6SH has been shown to react readily with the less sterically hindered complex $[\{Co_2(CO)_6(\mu\text{-}\eta^2\text{-}HOCH_2C{\equiv}C\text{–})\}_2]$ to give a thio-macrocycle.[2] Instead, in every case the, complex $[\{Co_2(CO)_6\}_2\{$*cyclo*-$\mu\text{-}\eta^2\text{:}\mu\text{-}\eta^2\text{-}C({=}CH_2)CH_2CMe_2C{\equiv}C\text{–}C{\equiv}C\}]$ **2** was isolated in virtually quantitative yield (Scheme 1).

Complex **2** contains a seven-membered conjugated diyne ring which represents, to our knowledge, the smallest such ring to have been reported. Prior to the synthesis of **2** the smallest reported cyclic diyne in which the two alkyne units are adjacent contained ten carbon atoms.[5] The smallest diyne ring of any kind to have been previously reported is the eight-membered sym-dibenzo-1,5-cycloctadien-3,7-diyne, although the benzo linkers in this latter molecule prevent any ring strain at the alkynic centres.[6] The seven-membered diyne-containing ring present in **2** is particularly noteworthy in view of the conjugation of the two alkyne units and the vinyl group. The severe ring strain that would otherwise have been present in such a small cyclic diyne is, of course, at least partially alleviated by the coordination of the diyne to the dicobalt units.

The reaction presumably involves an intra-molecular self-cyclisation of an intermediate **A** (Scheme 2). Intermediate **A** stems from the dehydration of one of the propargyl moieties to give an ene-yne followed by protonation of the remaining propargyl alcohol and subsequent loss of H_2O. Indeed, if the reaction is quenched after stirring at −78 °C for 30 mins it is possible to isolate $[\{Co_2(CO)_6\}_2\{\mu\text{-}\eta^2\text{:}\mu\text{-}\eta^2\text{-}HOMe_2C{\equiv}CC{\equiv}CC({=}CH_2)Me\}]$ **3** which is the precursor to intermediate **A**.



Scheme 1 Acid catalysed cyclisation of **1** and **4**.

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† Electronic supplementary information (ESI) available: crystallographic data for complexes **8** and **11**. See http://www.rsc.org/suppdata/nj/b3/b310515f/

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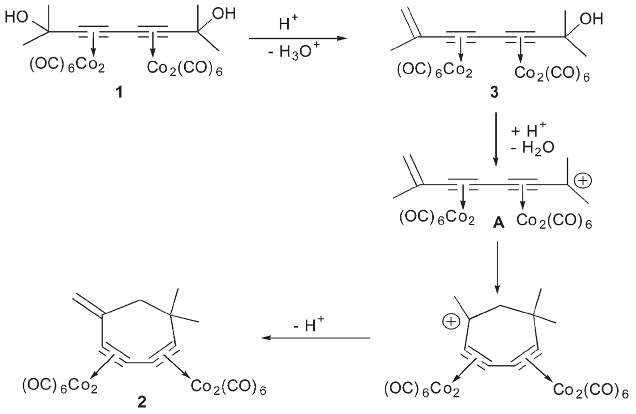


Scheme 2 Proposed pathway leading to formation of **2**.

The cyclisation of **1** to **2** proceeds smoothly on addition of catalytic amounts of HBF_4 in the absence of a nucleophile; the presence of oxygen- or sulfur-based nucleophiles only serves to increase the rate of the reaction, presumably by facilitating proton abstraction (Scheme 2). Alternatively, the reason for the acceleration of the reaction in the presence of Lewis bases is that it proceeds *via* a radical mechanism in a similar way to that reported by Melikyan and co-workers.[1c] However, the isolation of **3** when the reaction was quenched at an early stage, and the lack of other coupled products suggests that this is not the case.

Although dehydration reactions are well known,[7] it is unusual for them to be the sole outcome of a reaction when nucleophiles are also present. It should be noted that the analogous reaction of the mono-propargylic complex $[Co_2(CO)_6(\mu\text{-}\eta^2\text{-}HC{\equiv}CCMe_2OH)]$ in the presence of a nucleophile does not result in dehydration; instead the expected addition of the nucleophile to the propargylic centre takes place.[8] The most striking feature of the diyne reaction reported here is, however, the intramolecular cyclisation step to give **2**, since it might reasonably have been assumed that such a reaction would be disfavoured by the strained cycle which is formed. Obviously the rate of intramolecular addition must be faster than that of the competing E_1 elimination reaction at the second Me_2C^+ centre but, if this is the case, it is surprising that no products derived from standard SN_1 substitution are obtained even when a large excess of a sterically unencumbered nucleophile is used.

Table 1 Bond lengths (Å) and bond angles (°) for **2**, **5** and **7**

Unit	2	7	5
C1–C2	1.362(6)	1.362(6)	1.360(8)
C2–C3	1.439(8)	1.438(6)	1.42(1)
C3–C4	1.338(5)	1.349(6)	1.364(9)
C4–C5	1.510(6)	1.508(7)	1.50(1)
C8–C9	1.533(6)	1.516(7)	1.538(8)
Mean C_{alkyne}–Co(1)	1.966	1.951	1.980
Mean C_{alkyne}–Co(2)	1.961	1.964	1.972
Mean C_{alkyne}–Co(3)	1.965	1.975	1.985
Mean C_{alkyne}–Co(4)	1.980	1.972	1.98
C1–C9	1.476(6)	1.466(6)	1.475(9)
Co2–Co1	2.4640(9)	2.4831(7)	2.477(1)
Co3–Co4	2.4593(14)	2.4542(9)	2.478(1)
C9–C1–C2	130.3(4)	128.8(4)	128.1(6)
C5–C4–C3	132.5(4)	132.6(4)	127.3(31)
C4–C5–C6	110.0(3)	109.3(4)	114.6(9)
C4–C5–C7	111.0(4)	111.8(4)	116.0(13)
C4–C5–C8	109.1(3)	109.4(4)	111.7(13)
C9–C8–C5	117.7(3)	117.0(4)	111.2(6)
C1–C9–C8	116.2(4)	116.2(4)	111.1(6)
C1–C9–C10	122.5(4)	121.8(5)	120.4(6)

The X-ray crystal structure of **2** (Fig. 1) shows that, although the average bond-lengths and angles (Table 1) within the pseudo-tetrahedral Co_2C_2 cores fall within the normal range, there is a good deal of strain present within the molecule. Thus the alkyne *bend-back* angles of 132.5(4)° and 130.3(4) for C(5)–C(4)–C(3) and C(9)–C(1)–C(2) respectively are very small as compared to those in related acyclic cobalt-alkyne complexes; the mean C–C≡C angle in such alkyne complexes is 141.31°.[9] Indeed, there is only one documented cobalt-complexed alkyne that contains a lower *bend-back* angle than **2**.[10] Furthermore, the bond angles at C(9) and C(8) show a certain amount of distortion as a result of the ring strain present within **2**. Thus the C(1)–C(9)–C(8) angle of 116.2(4)° is smaller than expected for an idealised sp^2 geometry and the C(9)–C(8)–C(5) angle of 117.7(3) is significantly greater than the expected sp^3 angle of 109°.

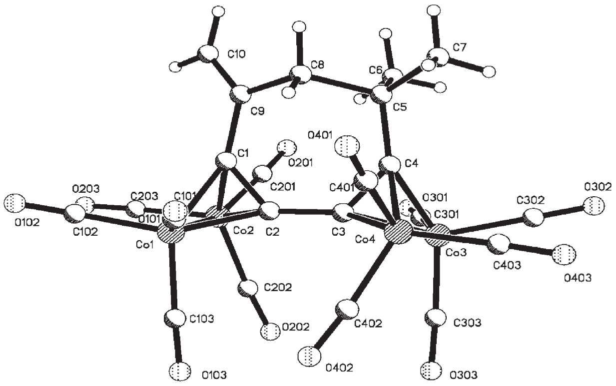
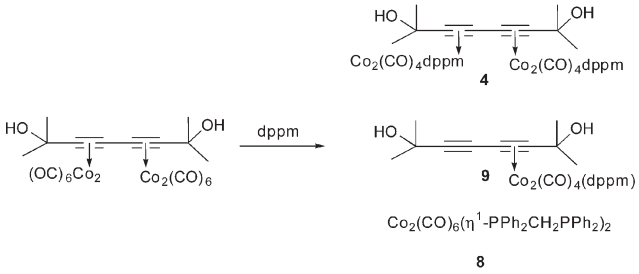


Fig. 1 Molecular Structure of **2**.

The small nature of the seven-membered ring forces the Co_2 units in these cores to adopt a cisoid configuration relative to each other as opposed to the transoid configuration adopted for these units in acyclic or larger macrocyclic 1,3 diyne complexes.[11]

In order to ascertain whether increased steric bulk at the Co_2 moieties would prevent cyclisation the related complex $[\{Co_2(CO)_4(dppm)(\mu\text{-}\eta^2\text{-}HOMe_2CC{\equiv}C\text{–})\}_2]$ **4** was treated with HBF_4 and a range of nucleophiles. In each case $[\{Co_2(CO)_4(dppm)\}_2\{\mathit{cyclo}\text{-}\mu\text{-}\eta^2{:}\mu\text{-}\eta^2\text{-}C({=}CH_2)CH_2CMe_2C{\equiv}C\text{–}C{\equiv}C\}]$ **5** was obtained as the sole product (Scheme 1) in good yield. The precursor **4** was synthesised by refluxing a toluene solution of **1** with 2.2 equivalents of dppm. Interestingly, some $[Co_2(CO)_6(\eta^1\text{-}dppm)_2]$ **8** and $[Co_2(CO)_4(dppm)(\mu\text{-}\eta^2\text{-}HOMe_2CC{\equiv}CCCCMe_2OH)]$ **9** were obtained during work up (Scheme 3).[12] These two species are presumably formed by the phosphine promoted decoordination of a $Co_2(CO)_6$ moiety from an alkyne, in a manner similar to that previously reported by Simpson *et al.*[11]

Compound **5** was initially identified by ^1H and ^{13}C NMR spectroscopic studies. In an attempt to grow crystals of **5** we



Scheme 3 Reaction of **1** with dppm.

also isolated a minute quantity of [{$Co_2(CO)_4$(dppm)(μ-η^2-H_2C=C(Me)C≡C–)}$_2$ **6**, which contains an acyclic bis-eneyne backbone. It is not clear whether **6** was initially present as a minor impurity in the solution of **5** or whether **5** undergoes an acid-catalysed ring–opening reaction on standing in solution open to air. Certainly, the original ^{1}H and ^{13}C NMR spectra of **5** show no resonances due to **6**. The molecular structures of both **6** and **5** (Figs. 2,3 respectively) were obtained by single crystal X-ray analysis. A bulk-powder diffraction study of several batches of crystals obtained by various crystallisation techniques showed that the sample was almost exclusively **5**. It is unclear why **6** should have been formed; certainly the dppm ligands of **5** do not appear to add any undue steric constraints to the core present in cyclic **2** that might warrant an isomerism to the (presumably) less strained acyclic diyne **6**. The unusual *cisoid* configuration of the Co_2 cores present in **2** and **5** means that the dppm ligands are both orientated *exo* to the macrocyclic cavity. We therefore assume that **6** was present as a minor, inseparable impurity in the original reaction mixture rather than being formed by a reverse Nicholas reaction during the crystallisation of **5**.

Interestingly, whilst attempting to form **5** by direct reaction of **2** with two equivalents of dppm, it was noted that, when only a small excess of dppm was used with a short reflux period some [{$Co_2(CO)_4$dppm}($Co_2(CO)_6$)(*cyclo*-μ-η^2:μ-η^2-C(=CH_2)-CH_2CMe_2C≡C–C≡C)] **7** in which **2** has undergone a single dppm substitution was also obtained. This substitution occurred at the Co_2 moiety adjacent to the C=CH_2 group rather than to the CMe_2 group (Fig. 3).

In order to determine whether this was merely a coincidental result or whether the dppm substitution was in fact selective and occurred preferentially at the Co_2 unit adjacent to the C=CH_2 group **2** was treated with one equivalent of dppm. In these circumstances **7** was obtained in near quantitative yield and none of the possible alternative in which the dppm had coordinated to the Co_2 moiety adjacent to the CMe_2 group. Examination of the crystal structures of **2**, **5** and **7** shows that dppm coordination leads to a decrease in the C(2)–C(1)–C(9) alkyne *bend-back* angles from 130.3(4) in **2** to 129.0(4) in **7** and 128.1(6) in **5**. This apparent decrease is, however, only just larger than experimental error and should be treated with some care. The X-ray structures show a decrease in the C(3)–C(4)–C(5) alkyne *bend-back angle* from 132.5(4) in **2** to 127.3(31)° in **5** on dppm substitution *i.e.* more marked than the corresponding decrease in the C(2)–C(1)–C(9) alkyne *bend-back angle* of 128.8(4) in **7**. Due to the high *esd's* in **5** this result is of low significance, however, it is of interest that this observation is consistent with the anticipated effect of dppm substitution at Co(4)–Co(3) leading to a greater distortion of the compound. The C(3)–C(4)–C(5) alkyne *bend-back* angle in **5** is the lowest recorded for a complex of this type and is a result of the unfavourable steric interactions between the bulky axial P(3)–Ph group and the C(7), C(6) methyl groups. An inspection of the space-filling diagrams of **5** and **7** (Fig. 4) demonstrates these factors. In **7** the single dppm substitution at the C=CH_2 end of the molecule of **2** (Co(1)–Co(2) unit) leads to less steric crowding than would occur were dppm substitution to take place at the other end of the molecule (*i.e.* at the Co(3)–Co(4) unit) where the two methyl groups would be brought into extremely close contact with a phenyl group dppm ligand. Inspection of the Co(3)–Co(4) unit in disubstituted **5** shows that substitution at the Co(3)–Co(4) end of the molecule leads to very close contacts between the ring methyl groups and the dppm ligand.

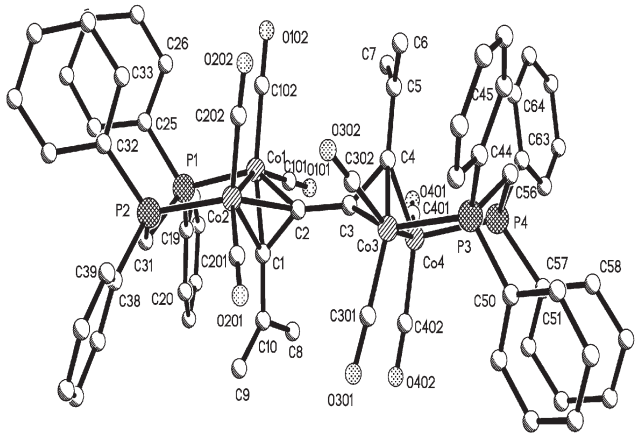


Fig. 2 Molecular structure of **6**; dppm hydrogens removed for clarity.

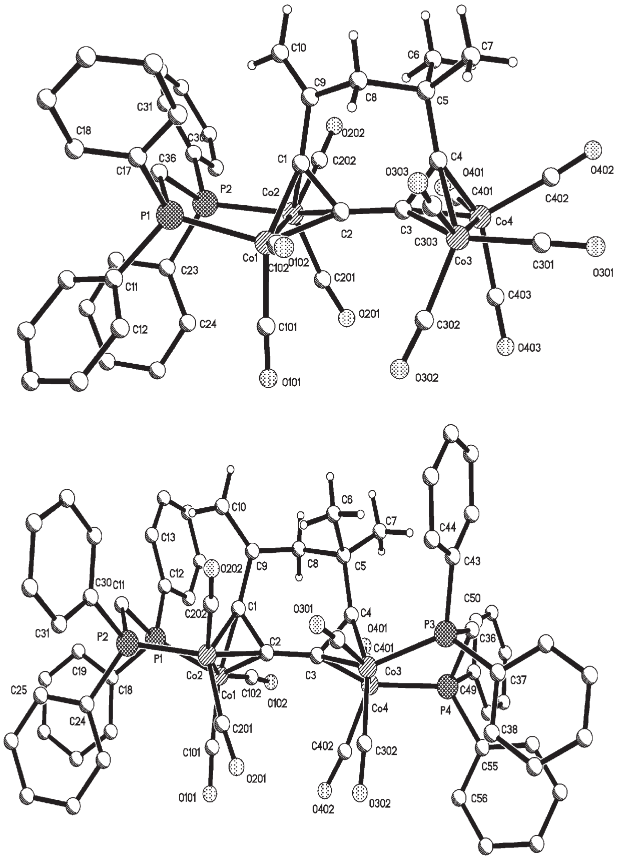


Fig. 3 Molecular structures of **7** (top) and **5** (bottom); dppm hydrogens removed for clarity.

It has previously been shown that treatment of *bis*-$Co_2(CO)_6$ coordinated diynes with an excess of phosphine or phosphite ligand can result in decoordination of one of the Co_2 moieties to yield a mono-coordinated diyne and $Co_2(CO)_4(PR_3)_4$.[11] In the current case prolonged refluxing of a toluene solution of **2** with an excess of dppm resulted only in the formation of **5**. It seems that decoordination of a Co_2 moiety in **5** is disfavoured, presumably because this would necessarily increase the *bend-back* angles at the uncoordinated alkyne carbons from 130° in **2** to near linearity. This increase in the *bend-back* angle would obviously create a lot more strain within the ring.

Given that a Co_2 moiety could not be decoordinated by treatment with dppm, an alternate strategy for the synthesis of a cycle in which one of the alkynes was uncoordinated was conceived. It has been recently demonstrated that only one alkyne of a *fused* diyne (*i.e.* a diyne in which the two alkyne moieties are directly bonded to each other) needs to be coordinated to a Co_2 moiety in order for both propargylic centres to be activated.[13] It was therefore hypothesised that treatment of [$Co_2(CO)_4$(dppm)(μ-η^2-$HOMe_2$CC≡CCCCMe_2OH)] **9** with HBF_4 might result in cyclisation. Accordingly **9** was treated

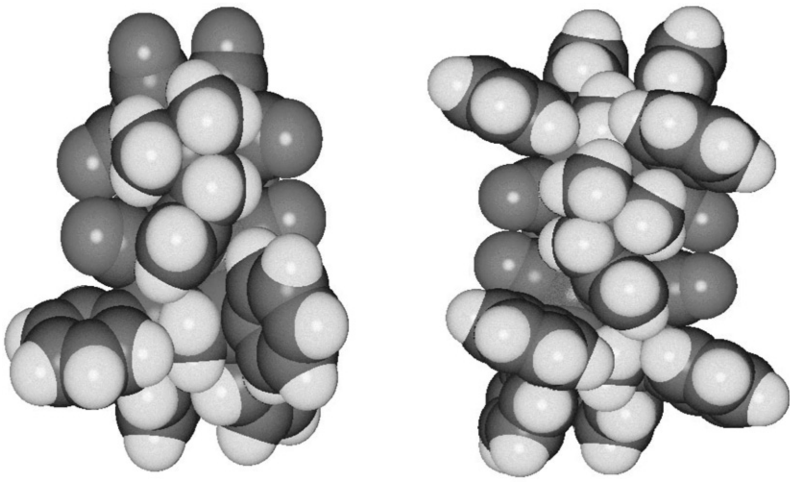


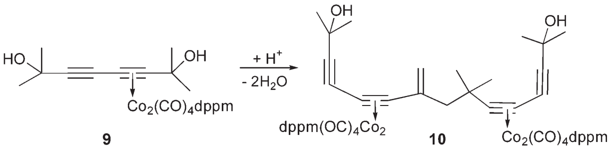
Fig. 4 Space filling diagram of **7** (left) and **5** (right) showing steric clashes between the carbacyclic ring and the dppm groups.

with HBF_4 at −78 °C followed by warming to 0 °C; standard work-up then yielded the dimer $[\{Co_2(CO)_4dppm\}_2\{\mu\text{-}\eta^2\text{:}\mu\text{-}\eta^2\text{-}HOMe_2CCCC{\equiv}CCMe_2CH_2C({=}CH_2)C{\equiv}CCCCMe_2OH]$ **10** (Scheme 4).

It should be noted that **10** contains a similar bridging $Me_2CCH_2C{=}CH_2$ unit to that in **2** and **5**, but now this bridge is inter- rather than intra-molecular. However, the two uncoordinated propargyl alcohols have not reacted, and cyclisation has not occurred. It is not clear why cyclisation does not occur since it has previously been shown that the stabilising effect of a Co_2 unit can be transmitted through an uncoordinated alkyne bond and thus activation of a remote propargyl alcohol is possible.

Compound **10** has been fully characterised by IR, ^{13}C, ^1H NMR and FABm/s spectroscopy. In addition **10** has been the subject of a single crystal X-ray diffraction study. The molecular structure of **10** is shown in Fig. 5; relevant bond lengths and angles are given in Table 2. Interestingly the two Co_2 moieties do not adopt the *transoid* geometry common in acyclic diynes, but rather are *cisoid*. Although it was only possible to crystallographically locate one of the O–H hydrogen atoms it seems logical to assume that this *cisoid* conformation is due to an intramolecular H bond between the two O–H groups [O(1)–H(02) 2.107 Å]. Regarding the linking C(5)–C(6)–C(9)–C(10) fragment that joins the two diynes it is interesting to note that the formally sp^2 hybridised C(10) atom shows a significant distortion from the idealised bond angles [*e.g.* C(12)–C(10)–C(9) 115.6(4)°]. Likewise, the adjacent C(9) also shows a significant distortion from its idealised sp^3 geometry [C(10)–C(9)–C(6) 117.7(4)°] and the C(9)–C(6) bond length [1.504(7)Å] is short for a C–C single bond. Within the Co_2 cores there are no unusual features and the alkyne *bend-back* angles fall within their normal range [C(13)–C(12)–C(10) 144.4(4)°; C(14)–C(13)–C(12) 141.8(4)°; C(6)–C(5)–C(4) 139.8(4)°; C(5)–C(4)–C(3) 142.6(4)°].

In an attempt to form further cyclophanes *via* this methodology we synthesised $[\{Co_2(CO)_6\}_2\{\mu\text{-}\eta^2\text{:}\mu\text{-}\eta^2\text{-}1,4\text{-}C_6H_4(C{\equiv}CCMe_2OH)_2\}]$ **11**.[14] We hoped that this might form large cyclophanes on treatment with HBF_4 *via* a dehydration/dimerisation mechanism akin to that leading to the formation of **10**; it seemed unlikely that it would cyclise in an analogous manner to **1** and **4** due to the arene spacer. In fact treatment of **11** with HBF_4 did not lead to any cyclisation or dimerisation; instead $[\{Co_2(CO)_6\}_2\{\mu\text{-}\eta^2\text{-}1,4\text{-}C_6H_4(C{\equiv}CC({=}CH_2)Me)_2\}]$ **12** was isolated as the sole product after standard work-up procedures (Scheme 5).



Scheme 4 Formation of **10**.

The differing reactivity of **11** as compared to **1** and **4** was further highlighted on treatment of **11** with HBF_4 and a range of sulfur-based nucleophiles HSZSH [Z = $(CH_2)_n$ (n = 5,6), $C_2H_4OC_2H_4$ or $C_2H_4SC_2H_4$]. In all cases **11** did react with the nucleophiles to yield $[\{Co_2(CO)_6\}_2\{cyclo\text{-}\mu\text{-}\eta^2\text{-}1,4\text{-}C_6H_4(C{\equiv}CCMe_2SZSCMe_2C{\equiv}C)\}]$ (**14** to **17**) as the sole product after standard work up (Scheme 6). In no case did we find any traces of **12** or of the dimers of compounds **14** to **17**, even though such dimers are among the products of similar reactions involving $[\{Co_2(CO)_6(\mu\text{-}\eta^2\text{-}HOH_2CC{\equiv}C\text{–})\}_2]$ and $[\{Co_2(CO)_6\}_2\{\mu\text{-}\eta^2\text{-}1,4\text{-}C_6H_4(C{\equiv}CCH_2OAc)_2\}]$.[2,15] However, reaction of **11** with HSC_2H_4SH did yield a rather unusual product $[\{Co_2(CO)_6\}_2\{\mu\text{-}\eta^2\text{-}1,4\text{-}C_6H_4(C{\equiv}CCMe_2SC_2H_4SSC_2H_4SCMe_2C{\equiv}C)\}]$ **13** which is derived from substitution of both of the propargylic–OH groups by two molecules of HSC_2H_4SH, followed by coupling of the terminal S–H groups. Such coupling of dithiols to form disulfides is relatively common.[16]

Complexes **13** to **17** have been fully characterised by IR, ^1H NMR, ^{13}C NMR and FABm/s spectroscopy. In addition **17** has been the subject of a single crystal X-ray diffraction study. Compound **17** crystallises with $\frac{1}{2}$ equivalent of $CHCl_3$ and $\frac{1}{4}$ C_6H_{14} within its asymmetric unit; the molecular structure of **17** is shown in Fig. 6 relevant bond angles and lengths are shown in Table 3. The bond angles and lengths of the Co_2C_2 core are all within the expected range. The formation of a macrocycle does not result in any significant deviation from the geometry of the parent complex **11**; thus the C(14)–C(13)–C(12) *bend-back* angle of 141.3(4)° is identical

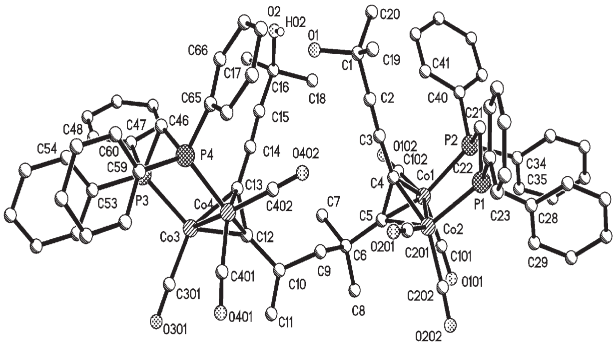


Fig. 5 Molecular structure of **10**; dppm protons removed for clarity.

Table 2 Bond lengths (Å) and bond angles (°) for **10**

Co1–Co2	2.4751(9)	C6–C9	1.504(7)
Co3–Co4	2.4748(8)	C9–C10	1.511(7)
Mean C_{alkyne}–Co1	1.969	C10–C12	1.478(7)
Mean C_{alkyne}–Co2	1.967	C12–C13	1.367(6)
Mean C_{alkyne}–Co3	1.969	C13–C14	1.404(6)
Man C_{alkyne}–Co4	1.960	C14–C15	1.198(6)
C1–C2	1.473(7)	C12–C13–C14	141.8(4)
C2–C3	1.197(6)	C12–C10–C9	115.6(4)
C3–C4	1.399(6)	C10–C9–C6	117.7(4)
C4–C5	1.363(7)	C6–C5–C4	139.8(4)
C5–C6	1.510(7)	C5–C4–C3	142.6(4)

within experimental error to the corresponding *bend-back* angle in **11**.

Regarding the macrocyclic backbone, the oxygen atom is not in its preferred *anti* configuration [C(17)–C(16)–O(1)–C(15) −155.1°; C(16)–O(1)–C(15)–C(14) 129.8°][17] and results in the lone pairs of the oxygen atom not being orientated directly into the macrocyclic cavity. As is to be expected this deviation from the *anti* geometry of the oxygen atom also results in the sulfur atoms not being in their preferred *gauche* geometries [C(1)–C(18)–S(2)–C(17) −56.0°; C(18)–S(2)–C(17)–C(16) −89.5°; C(15)–C(14)–S(1)–C(11) 108.5°; C(14)–S(1)–C(11)–C(10) 54.7°].

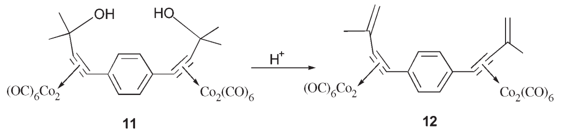
It is possible that this distortion arises from an electronic repulsion between the oxygen lone pairs and the π-cloud of the benzene ring. The separation between the centroid of the ring and the oxygen atom is 4.1 Å.

Conclusion

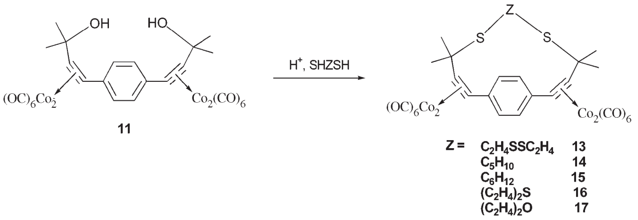
We have provided further evidence that the reactivity of *fused*-diynes is markedly different from that of diynes which contain spacer units between the two alkyne moieties. Most notably, the presence of a direct alkyne–alkyne bond in bis-propargyl alcohols seems to activate the propargylic centres to elimination rather than to nucleophilic attack. In one case this has led to the formation of an unprecedented seven-membered cyclic diyne complex containing a high degree of conjugation. We believe that this result represents an important step forward in the synthesis of small, conjugated carbocycles.

Experimental

Unless otherwise stated all experiments were carried out under an atmosphere of dry, oxygen-free nitrogen, using conventional Schlenk line techniques, and solvents freshly distilled from the appropriate drying agent. Except where otherwise indicated NMR spectra were recorded in $CDCl_3$ using a Bruker DRX 400 spectrometer, with TMS as an external standard for ^1H and ^{13}C spectra and H_3PO_4 as an external standard for ^{31}P NMR spectra. Infrared spectra were, unless otherwise stated, recorded in dichloromethane solution in 0.5 mm NaCl solution cells, using a Perkin Elmer 1710 Fourier Transform spectrometer. FAB mass spectra were obtained using a Kratos MS 890 instrument, using 3-nitrobenzyl alcohol as a matrix. Preparative TLC was carried out on 1 mm silica plates prepared at the University of Cambridge. Column chromatography was performed on Kieselgel 60 (70–230 mesh ASTM). All products are listed in order of decreasing R_f. Unless otherwise stated, all reagents were obtained from commercial suppliers and used without further purification. 1,4-C_6H_4(C≡CCMe$_2$OH)$_2$ and [{$Co_2(CO)_6$(μ-η^2-HOMe$_2$-CC≡C–)}$_2$] were prepared by the literature methods.[18,19]



Scheme 5 Dehydration of **11**.



Scheme 6 Formation of **13** to **17**.

Crystal structure determinations

Single-crystal X-ray diffraction data were collected using a Nonius-Kappa CCD diffractometer, equipped with an Oxford Cryosystems cryostream and employing MoKα (0.71069 Å) irradiation from a sealed tube X-ray source. Cell refinement, data collection and data reduction were performed with the programs DENZO[20] and COLLECT[21] and multi-scan absorption corrections were applied to all intensity data with the program SORTAV.[22] All structures were solved and refined with the programs SHELXS97 and SHELXL97[23] respectively. The structure of complex **5** shows disorder about a pseudo C_2 axis located approximately between the mid-point of the C(2)–C(3) bond and the C(5)–C(9) atoms of the carbacyclic ring. This leads to two positions of the C(2), C(3), C(6) and C(8) atoms being observed in an approximately 6:4 ratio. The two positions were refined with the total occupancy of the site summing to unity. One of the phenyl rings in compound **6** is disordered over two sites and the n-hexane solvent molecule is disordered about an inversion centre. The n-hexane and chloroform solvent molecules in compound **7** are disordered about the same site in a 1:1 ratio.

The bulk powder diffraction experiment PXRD profiles were measured at room temperature on a STOE STADI-P high-resolution powder diffractometer using graphite-monochromated Cu Kα radiation (λ = 1.5148 Å). Relatively high backgrounds (plots displaced upwards from zero on the y-scale) arises from fluorescence of Co in Cu Kα radiation, simulated patterns are from *Cerius*^{2} (Accelrys Inc.).

A summary of data collection and data refinement details is given in Table 4.

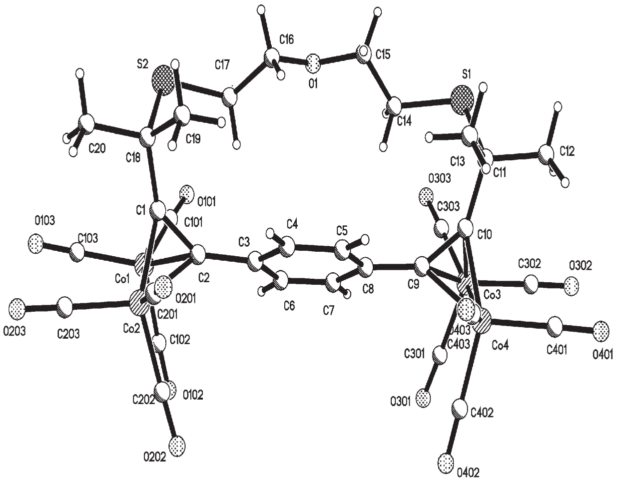


Fig. 6 Molecular structure of **17**.

Table 3 Bond lengths (Å) and bond angles (°) for **17**

Co1–Co2	2.4561(9)	C2–C1–C18	141.3(4)
Co3–Co4	2.4638(8)	C1–C2–C3	143.0(4)
C1–C2	1.374(6)	C8–C9–C10	143.9(4)
C9–C10	1.347(6)	C9–C10–C11	143.5(4)
C2–C3	1.462(6)	C11–S1–C14–C15	108.5
C6–C9	1.459(6)	C10–C11–S1–C14	54.7
Mean C_{alkyne}–Co1	1.964	C18–S2–C17–C16	−89.5
Mean C_{alkyne}–Co2	1.980	C1–C18–S2–C17	−56.0
Mean C_{alkyne}–Co3	1.964	C17–C16–O1–C15	−155
Mean C_{alkyne}–Co4	1.990	C16–O1–C15–C14	129.8

Preparation of $[\{Co_2(CO)_4(dppm)(\mu\text{-}\eta^2\text{-}HOMe_2CC{\equiv}C\text{–})\}_2]$ 4

To a solution of **1** (982 mg, 1.33 mmol) in toluene (200 cm^3) was added dppm (1.093 g, 2.15 eq, 2.85 mmol). The mixture was stirred for 1 hour at 80 °C and the solvent was then removed on a rotary evaporator. The residue was dissolved in dichloromethane and the solution was adsorbed onto silica; the silica was then pumped dry and added to the top of a chromatography column. Elution with hexane:ethyl acetate 7:1 afforded an orange band of $[Co_2(CO)_6(\eta^1\text{-}PPh_2CH_2PPh_2)_2]$ **8** (102 mg). Further elution with hexane:ethyl acetate 2:1 afforded red-orange crystalline **9**, which was crystallised from hexane:ethyl acetate (683 mg, 0.88 mmol, 65.8%). Further elution with ethyl acetate afforded green crystalline **4** (213 mg, 0.15 mmol, 11.5%).

Data for 4

IR νCO (cm^{-1}): 2024.0 w, 1999.4 vs, 1986.0 sh; ^{1}H NMR (CD_3COCD_3) δ: 7.73–7.05 (m, 40H, C_6H_5), 5.21 (dd, 2H, $^2J_{H\text{–}P}$ 12 Hz, $^2J_{H\text{–}H}$ 13 Hz, PC*H*H), 3.49 (dd, 2H, $^2J_{H\text{–}P}$ 11 Hz, $^2J_{H\text{–}H}$ 13 Hz, PCH*H*), 1.74 (s, 12H, CH_3); ^{13}C NMR (THF-d_8) δ: 202.31, 206.19 (*C*O), 137.99–125.57 (Ph), 110.05, 97.25 (C≡C), 73.96 (*C*Me_2OH), 33.57 (v.br., P*C*P), 31.24 (CH_3); ^{31}P NMR (THF-d_8) δ: 38.53; LSIMSm/s: 1417 MNa^+, 1394 MH^+, $M^+ - n$CO ($n = 1$ to 6).

Data for 8

IR νCO (cm^{-1}): 2083.3 vw, 2045.4 vs, 2011.2 vs, 1985.6 vs, 1820.8 s, 1793.0 s; ^{1}H NMR δ: 7.25–7.74 (m, 20 H, C_6H_5), 3.1 (vb,s, 2H, PCH_2P); ^{31}P NMR δ: 60.93; LSIMSm/s: 693 MNa^+-dppm, 670 M^+-dppm; M^+ -dppm $- n$CO ($n = 1$ to 6); 1226 $M^+ - 6$CO.

Data for 9

IR νCO (cm^{-1}): 2027.2 s, 2000.9 vs, 1973.1 s, 1952.6 sh; ^{1}H NMR δ: 7.51–6.98 (m, 20H, C_6H_5), 3.60 (dd, 1H, $^2J_{H\text{–}P}$ 10 Hz, $^2J_{H\text{–}P}$ 13 Hz, PC*H*HP), 3.23 (dd, 1H, $^2J_{H\text{–}P}$ 11 Hz, $^2J_{H\text{–}P}$ 13 Hz, PCH*H*P), 2.01(s, 1H, O*H*), 1.77 (s, 1H, O*H*), 1.66 (s, 6H, CH_3) 1.57 (s, 6H, CH_3; ^{13}C NMR δ: 201.94, 206.40 (CO), 137.93 to 128.17 (Ph), 113.8, 93.00 (C≡C coordinated to Co_2), 100.00, 83.4 (free C≡C), 74.304 (*C*(OH)Me_2), 66.4 (*C*(OH)Me_2), 36.15 (t, $^1J_{P\text{–}C}$ 20.2Hz, P*C*H_2P), 31.67 (CH_3); ^{31}P NMR δ: 38.81; LSIMSm/s 802 MNa^+, $M^+ - n$CO (n = 1,3,4), $M^+ - 4CO - nH_2O$ (n = 1,2).

Preparation of $[\{Co_2(CO)_4L_2\}_2\{\mu\text{-}\eta^2\text{:}\mu\text{-}\eta^2\text{-}(cyclo\text{-}C(=CH_2)\text{-}CH_2CMe_2C{\equiv}C\text{–}C{\equiv}C\text{–})\}]$ L_2 = 2CO 2; L_2 = dppm 5

To a solution of **1** or **4** (1.36 mmol) in 200 cm^3 dichloromethane at −78 °C was added 0.1 ml of 48% HBF_4 in ether. After warming to room temperature and further stirring for 2 hours an excess of $NaHCO_3$ was added to the mixture. The resulting mixture was filtered through a plug of $MgSO_4$ and the solvent was carefully removed on a rotary evaporator. Purification by flash chromatography (hexane:ethyl acetate) yielded $[\{Co_2(CO)_6\}_2\{\mu\text{-}\eta^2\text{:}\mu\text{-}\eta^2\text{-}[cyclo\text{-}C(=CH_2)CH_2CMe_2\text{-}C{\equiv}C\text{–}C{\equiv}C\text{–}]\}]$ **2** (930 mg, 1.32 mmol); $[\{Co_2(CO)_4(dppm)\}_2\text{-}\{\mu\text{-}\eta^2\text{:}\mu\text{-}\eta^2\text{-}[cyclo\text{-}C(=CH_2)CH_2CMe_2C{\equiv}C\text{–}C{\equiv}C\text{–}]\}]$ **5** (528 mg, 43%).

Table 4 X-Ray crystallographic data for the new complexes

Complex	2	5	6	7	10	17
Empirical formula	$C_{22}H_{10}Co_4O_{12}$	$C_{68}H_{54}Co_4O_8P_4$	$C_{75}H_{70}Cl_2Co_4O_8P_4$	C_{45} $H_{32}Co_4O_{10}P_2$	$C_{79.5}H_{70}Cl_4Co_4O_{10}P_4$	$C_{34}H_{28}Cl_{1.5}Co_4O_{13}S_2$
Weight	702.02	1358.71	1529.81	1030.37	1686.7	997.58
Crystal system	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
Crystal size	0.21 × 0.16 × 0.09	0.23 × 0.07 × 0.05	0.35 × 0.35 × 0.23	0.28 × 0.28 × 0.23	0.19 × 0.12 × 0.05	0.12 × 0.12 × 0.10
Space group	$P2_12_12_1$	Cc	$P\bar{1}$	$C2/c$	$C2/$c	$P1$-
a (Å)	9.369(2)	9.9757(2)	11.3551(1)	39.7446(5)	40.5806(5)	12.4650(4)
b (Å)	16.409(2)	35.2755(8)	13.8087(2)	15.4562(2)	11.9801(2)	12.9587(5)
c (Å)	16.632(2)	17.6562(4)	23.8944(3)	16.7757(3)	36.1936(5)	13.8733(4)
α(°)	90	90	73.855(2)	90	90	69.498(2)
β(°)	90	106.167(9)	80.770(2)	91.171(1)	118.245(8)	73.291(2)
γ(°)	90	90	82.120(2)	90	90	81.816(2)
V/Å^3	2556.9(7)	5967.5(2)	3535.32(7)	10 303.2(3)	15 500.8(4)	2008.22(12)
Z	4	4	2	8	8	2
D_c Mg/m^3	1.824	1.512	1.437	1.328	1.446	1.650
Abs coefficient mm^{-1}	2.611	1.257	1.143	1.376	1.119	1.887
F(000)	1384	2776	1572	4160	6904	1003
θ range/°	3.52 to 27.49	3.59 to 27.49	3.52 to 27.45	3.54 to 27.49	3.55 to 25.05	3.70 to 27.46
Index ranges	$7 \le h \le 12$ $-21 \le k \le 13$ $-18 \le l \le 21$	$-10 \le h \le 12$ $-42 \le k \le 45$ $-22 \le ll \le 17$	$-14 \le h \le 14$ $-17 \le k \le 17$ $-30 \le ll \le 31$	$-51 \le h \le 50$ $-18 \le k \le 20$ $-21 \le ll \le 21$	$-48 \le h \le 47$ $-13 \le k \le 14$ $-42 \le ll \le 43$	$-15 \le h \le 16$ $-16 \le k \le 16$ $-17 \le ll \le 17$
Reflections measured	9560	22 460	43 652	45 396	52 975	18 407
Independent reflections	5431	10 401	16 067	11 771	13 600	9128
R_{int}	0.0584	0.0466	0.0429	0.0449	0.1132	0.0415
Goodness of fit on F^2	1.071	1.131	1.019	1.048	1.052	1.046
Final R indices $R1$	0.0448	0.0458	0.0565	0.0585	0.0582	0.0549
$wR2$	0.0804	0.0997	0.1404	0.1882	0.1535	0.1278
R indices (all data) R1	0.0602	0.0595	0.0798	0.0842	0.0822	0.1009
$wR2$	0.0872	0.2710	0.1545	0.2091	0.1813	0.1477
Largest diff peak and hole	0.795 and −0.658	0.758 and −0.515	1.653 and −2.592	1.711 and −0.507	1.496 and −1.385	0.950 and −1.253

2 was also the sole product when the reaction was carried out in a manner identical to the above procedure but with 1 equivalent of a nucleophile added immediately after the addition of HBF_4.

Data for 2

^1H NMR: δ: 5.40 (s,br, 1H, C=C*H*H), 5.35 (s,br, 1H, C=CH*H*), 2.93 (s, 2H, Me_2CCH_2), 1.55 (s, 3H. $CMeCH_3$), 1.35 s, 3H. CCH_3Me); ^{13}C NMR: δ: 198.9 (CO), 116.7 (C=CH_2), 110.2 (*C*=CH_2), 93.4 (br, external *C*≡C–C≡C), 88.5 (br, internal C≡*C*–C≡C), 60.9 (Me_2C–CH_2), 58.2 (Me_2C–CH_2), 44.2 (Me), 38.2 (Me); FAB m/s: 702 (M^+), $M^+ - n$CO ($n = 1$ to 12); Analytical calculated for $C_{22}H_{10}O_{12}Co_4$: C 37.64, H 1.44; Found C 38.01, H 1.62

Data for 5

IR νCO (cm^{-1}): 2029.9 w, 2002.9 vs, 1979.5 s, 1957.0 w; ^1H NMR δ 7.49–7.00 (m, 40 H, C_6H_5), 5.29 (s, 2H, C=CH_2), 3.79 (dd, $^2J_{H-P}$ 10 Hz, $^2J_{H-P}$ 13 Hz, 1H PCH*H*P), 3.59 (dd, $^2J_{H-P}$ 10 Hz, $^2J_{H-P}$ 12 Hz, 1H, PC*H*HP),3.39 (dd, $^2J_{H-P}$ 10 Hz, $^2J_{H-P}$ 12 Hz, 1H PCH*H*P), 3.20 (dd, $^2J_{H-P}$ 10 Hz, $^2J_{H-P}$ 12 Hz, 1H PC*H*HP), 2.37 (s, 2H, CH_2), 1.18 (s, 6H, CH_3); ^{13}C NMR δ: 207.57, 207.35, 205.47, 203.49 (CO), 150.54 (*C*=CH_2), 136–128 (aromatic C of dppm), 119.29 (C=CH_2), 105.99, 103.90, 102.79, 86.87 (C≡C), 47.04 (CH_2), 39.57 (*C*Me_2), 39.03 (t, $^1J_{P-C}$ 16.1Hz, PCH_2P), 37.77 (t, $^1J_{P-C}$ 16.1Hz, PCH_2P), 33.32 (CH_3); ^{31}P NMR δ:38.44, 34.68; MS (LSIMS): 1381 MNa^+, 1359 MH^+, $M^+ - n$CO ($n = 1$, 3, 5–8); Analytical Calculated. for $C_{75}H_{70}O_8P_4Cl_2Co_4$ (as for crystals from DCM: hexane): C, 58.88; H, 4.61; P, 8.10; Found: C, 59.33; H, 4.15; P, 5.13.

Preparation of [{$Co_2(CO)_6$}$_2${μ-η^2:μ-η^2-$HOMe_2C$≡CC≡CC-(=CH_2)Me}] 3

To a solution of **1** (740 mg, 1.0 mmol) in dichloromethane (200 cm^3) at −78 °C under argon was added three drops of 48% HBF_4 in ether. The mixture was stirred at −78 °C for 9 h. After slow warming to *ca.* 0 °C during 1 h an excess of $NaHCO_3$ was added to the mixture. The resulting mixture was filtered through a plug of $MgSO_4$ and the solvent was carefully removed on a rotary evaporator. The residue was dissolved in the minimum amount of dichloromethane and the solution was applied to the base of TLC plates. Elution with hexane: dichloromethane 2:1 afforded complex **2** (137 mg, 0.20 mmol, 31.3%), deep green [{$Co_2(CO)_4$dppm}$_2${μ-η^2:μ-η^2-MeC-(=CH_2)C≡CC≡CMe_2OH]}] **3** (150 mg, 0.21 mmol, 33.4%), and starting material **1** (280 mg).

3 IR νCO (cm^{-1}): 2099.7 s, 2079.4 vs, 2059.1 vs, 2032.5 vs, 2023.1 vs, 1975 sh.; ^1H NMR δ: 5.31 (s, 2H, C=CH_2), 2.18 (s, 3H, CH_3), 1.86 (s, 1H, *OH*), 1.71 (s, 6H, CH_3,); ^{13}C NMR δ: 198.9 (CO), 142.4 (*C*=CH_2), 116.4 (C=CH_2), 111.8, 102.9, 92.2, 89.9 (C≡C), 73.6 (*C*Me_2OH), 30.9 (C(CH_3)$_2$OH), 26.7 (C(=CH_2)CH_3); FABm/s 742.6 MNa^+; 702.66 $MH^+ - H_2O$; $MNa^+ - n$CO (n = 1–3, 5), $MH^+ - H_2O - n$CO (n = 1,3,4).

Alternative preparation of 5

To a solution of **2** (930 mg, 1.32 mmol) in toluene (200 cm^3) was added dppm (1.046 mg, 2.72 mmol, 2.06 eq). The mixture was stirred for 3 hours at 70 °C, the solvent removed *in vacuo* and the residue dissolved in dichloromethane and adsorbed onto silica. The silica was pumped dry and added to the top of a chromatography column. Elution with hexane: dichloromethane 6:4 afforded green [$Co_2(CO)_4$(dppm)(*cyclo*-μ-η^2:μ-η^2-C(=CH_2)CH_2CMe_2C≡C–C≡C)$Co_2(CO)_6$] **7** (70 mg). Further elution with hexane:dichloromethane 6:4 afforded complex **5** as a deep dark green crystalline material which was crystallised from hexane:dichloromethane (1.673 g, 1.23 mmol, 93.2%).

Alternative preparation of [{$Co_2(CO)_4$(dppm)}{$Co_2(CO)_6$}(*cyclo*-μ-η^2:μ-η^2-C(=CH_2) CH_2CMe_2C≡C–C≡C)] 7

To a solution of **2** (1.824 g, 2.58 mmol) in toluene (200 cm^3) was added dppm (1.013 g, 2.64 mmol, 1.02 eq.). The mixture was stirred at 70 °C for 2 hours and allowed to cool down to room temperature. The solvent removed *in vacuo* and the residue dissolved in the minimum of dichloromethane and adsorbed onto silica. The silica was pumped dry and added to the top of a chromatography column. Elution with hexane afforded first a green band, which corresponded to the unreacted starting material (372 mg, 0.53 mmol). Further elution with hexane:dichloromethane 3:1 afforded the deep green-brown major product **7** (1.572 g, 1.52 mmol, 74.15% yield based on reacted starting material) and green **5** (620 mg, 0.46 mmol, 22.44% yield on reacted starting material).

IR νCO (cm^{-1}): 2084.8 vs, 2068.4 w, 2048.1 vs, 2027.0 vs, 2013.4 vs, 1990.1 sh, 1970.2 s, 1955.8 sh.; ^1H NMR δ: 7.30–7.05 (m, 20 H, C_6H_5), 5.44 (broad s, 2H, C=CH_2), 3.50 (broad s, 1H, PCH_2P), 3.31 (broad s, 1H, PCH_2P), 2.41 (broad s, 2H, C(CH_3)$_2$$CH_2$C=$CH_2$), 1.32 (broad s, 6H, CH_3); ^{13}C NMR δ: 206.02, 202.68, 200.20 (CO), 149.03 (*C*=CH_2), 138–128 (aromatic, dppm), 120.88 (C=CH_2), 106.52, 100.10, 96.25, 87.61 (C≡C), 45.53 (CH_2), 39.80 (PCH_2P), 38.14 (*C*Me_2), 32.93 (CH_3); MS (LSIMS): $M^+ - n$CO (n = 3–10); Analytical Calculated for $C_{45}H_{32}O_{10}P_2Co_4$: C, 52.45; H, 3.13; P, 6.01; Found: C, 52.36; H, 4.05; P, 3.49.

Preparation of [{$Co_2(CO)_4$dppm}$_2${μ-η^2:μ-η^2-$HOMe_2$CCC≡$CCMe_2CH_2$C(=CH_2)C≡$CCCMe_2$OH] 10

To a solution of the complex **9** (495 mg, 0.21 mmol) in 200 m^3 dichloromethane at −78 °C under argon were added three drops of 48% HBF_4 in ether. After slow warming to 0 °C an excess of $NaHCO_3$ was added to the mixture. The resulting mixture was filtered through a plug of $MgSO_4$. The solvent was removed under reduced pressure and the residue absorbed on silica and applied to the top of a column. Elution with hexane: ethyl acetate 4:1 produced a first band of the orange-red crystalline complex **10** (108 mg, 0.07 mmol, 34.3%), and a second band proved to be the starting material **9** (334 mg). Complex **10** was crystallised as red-orange crystals by slow evaporation of a dichloromethane:hexane solution.

IR νCO (cm^{-1}): 2183.4 vw, 2023.4 s, 2000.2 s, 1968.5 s, 1603.1 w; ^1H NMR δ: 7.48–7.03 (m, 40 H, C_6H_5), 6.00 (d, $^2J_{H-H}$ 1.91 Hz, 1H, C=C*H*H), 5.54 (d, $^2J_{H-H}$ 1.91 Hz, 1H, C=CH*H*), 3.74 (dd, $^2J_{H-P}$ 11 Hz, $^2J_{H-P}$ 13 Hz, 1H, PCH*H*P) 3.56 (dd, $^2J_{H-P}$ 11 Hz, $^2J_{H-P}$ 13 Hz, 1H, PC*H*HP), 3.46 (s, 1H, *OH*), 3.25 (m, 2H, PCH_2P) 2.90 (s, 2H, CCH_2C), 2.41 (s, 1H, *OH*, 1.59 (s, 6H, CH_3), 1.50 (s, 6H, CH_3), 1.43 (s, 6H, CH_3); ^{13}C NMR δ: 207.20, 202.25 (CO), 147.68 (*C*=CH_2), 138.69–129 (m, aromatic C of dppm) 120.97 (C=CH_2), 101.63, 100.25, 84.91, 84.54 (C≡C), 66.26 (*C*–OH), 66.06 (*C*–OH), 49.34 (CCH_2C), 42.03 (C*C*Me_2), 35.18 (PCH_2P), 33.73 (PCH_2P), 31.45 (CH_3), 31.34 (CH_3), 30.28 (CH_3); ^{31}P NMR δ: 38.99 (s, br), 38.85 (s, br); LSIMSm/s 1548.1 MNa^+, 1526.4 MH^+, $M^+ - n$CO (n = 1–8): 1497–1301, 1507 $M^+ - H_2O$; Analytical Calculated for $C_{78}H_{69}O_{10}P_4Co_4$: C, 61.39; H, 4.56; P, 8.11; Found: C, 61.70; H, 4.70; P, 5.21%.

Preparation of [{$Co_2(CO)_6$}$_2${μ-η^2-1,4-C_6H_4(C≡$CCMe_2$OH)$_2$}] 11

To a solution of 1,4-C_6H_4(C≡$CCMe_2$OH)$_2$(1 eq., 0.0146 mol) in toluene (100 cm^3) and DCM (40 cm^3) was added $Co_2(CO)_8$

(10 g, 0.029 mol). The reaction mixture was stirred under N_2 at RT for 3 h. The solvent was removed *in vacuo* and the residue purified by flash chromatography on silica to yield red crystalline **11** (10 g, 85%).

IR νCO (cm^{-1}): 2090.0 m, 2054.2 s, 2026 vs; ^{1}H NMR δ:7.30 (s, 4H, C_6H_4), 1.6 (s, 12H, CH_3); ^{13}C NMR δ: 199 (CO), 131.50, 122.6 (C_6H_4), 95.4, 81.7 (C≡C), 65.51 (CMe$_2$OH), 31.4 (CH$_3$); LSIMS m/s: 814 M$^+$; M$^+ - n$CO (n = 1 to 12).

Reactions of $[\{Co_2(CO)_6\}_2\{\mu\text{-}\eta^2\text{-}1,4\text{-}C_6H_4(C\equiv CCMe_2OH)_2\}]$ 11

To a solution of **11** (0.17 g, 0.21 mmol) in DCM (50 cm^3) was added 54%wt $HBF_4{\cdot}OEt_2$(0.05 ml, 0.0034 mmol) at −78 °C and the appropriate dithiol HSZSH (0.24 mmol, 1.2 eq.). The resultant mixture was stirred for 10 mins at −78 °C, then allowed to warm to RT and stirred for a further 2 hours. The reaction was quenched with an excess of $NaHCO_3$ and dried with $MgSO_4$. The mixture was filtered through a silica plug, the solvent removed *in vacuo*, the residue redissolved in the minimum DCM and applied to the base of TLC plates. The reaction mixtures were separated as follows:

a) No thiol:

Elution with 3:1 DCM:hexane afforded brown crystalline **12** (0.13 g, 92%).

IR νCO (cm^{-1}): 2087.6 m, 2055.8 vs, 2026.1 s; ^{1}H NMR δ 7.50 (s, 4H, C_6H_4), 5.50 (s, 4H, $C{=}CH_2$), 2.20 (s, 6H, CH_3); ^{13}C NMR δ199.26 (CO), 141.92 ($C{=}CH_2$), 138.02, 129.56 (C_6H_4), 116.96 ($C{=}CH_2$), 95.47, 92.19 (C≡C), 23.94 (CH_3); MS (LSIMS): M$^+ - n$CO (n = 3–6): M$^+ - n$CO − 2Co, (n = 7–12).

b) Z = C_2H_4

Elution in 9:1 hexane:ethyl acetate afforded red solid **11** (0.017 g, 10%) and brown solid **13** (0.04 g, 22%).

IR νCO (cm^{-1}): 2088.2(m), 2054.2(s), 2025.9(s); ^{1}H NMR δ: 7.5 (s, 4H, C_6H_4), 3.2 (m, 4H, SCH_2), 2.8 (m, 4H, CH_2), 1.8 (s, 12H, CH_3); ^{13}C NMR δ: 199.1 (b, CO), 138.6, 129.6 (C_6H_4), 110.4, 94.2 (C≡C), 49.5 (Me$_2$$C$S), 32.6 ($CH_3$), 29.6 ($CH_2CH_2S$); FABm/s 966 M$^+$; M$^+ - n$CO ($n$ = 6, 12).

c) Z = C_5H_{10}

Elution in 8:1 hexane:ethyl acetate afforded red solid **11** (0.031 g, 20%) and brown solid **14** (0.059 g, 31%).

IR νCO (cm^{-1}): 2087.3(m), 2054.2(s), 2025.6(s).

^{1}H NMR δ: 7.4 (s, 4H, C_6H_4), 2.2 (m, 4H CH_2S), 1.75 (s, 12H, CH_3), 1.15 (m, 4H, CH_2), 1.1 (m, 2H, CH_2); ^{13}C NMR δ: 199.5 (br, CO), 138.8, 129.4 (C_6H_4), 111.8, 94.5 (C≡C), 48.7 (C≡CCMe$_2$S), 33.1 (SCH_2CH_2), 32.8 (CH$_3$) 30.6 (CH$_2$), 28.0 (CH$_2$); FABm/s 915 MH$^+$, M$^+ - n$CO (n = 1–4, 11).

d) Z = C_6H_{12}

Elution in 4:1 hexane:ethyl acetate afforded brown solid **15** (0.1 g, 50%).

IR νCO (cm^{-1}): 2087.4(m), 2053.4(s), 2025.4(s); ^{1}H NMR δ 7.4 (s, 4H, C_6H_4), 2.7 (m, 8H, CH_2S), 2.25 (m 4H, CH_2S), 1.8 (s, 12H, CH_3); ^{13}C NMR δ 200.0 (s, CO), 138.5 (C_6H_4), 129.6 (C_6H_4), 110.6 (C≡C), 94.0 (C≡C), 49.2 (C≡CCMe$_2$S), 38.9 (SCH_2), 31.0 (CCH_3), 28 (br, CH_2); FABm/s 929 MH$^+$, M$^+ - n$CO (n = 1,3–10,12).

e) Z = $(C_2H_4)_2S$

Elution afforded red solid **11** (0.075 g, 40%) and dark brown solid **16** (0.099 g, 53%).

IR νCO (cm^{-1}): 2088.0(m), 2055.0(s), 2027.0(s); ^{1}H NMR δ 7.6 (s, 4H, Ph), 3.1 (m, 4H, CH_2), 2.4 (m, 4H, CH_2S), 1.75 (s, 12H, CH_3); ^{13}C NMR δ 199.2 (CO), 141.9 (C_6H_4), 129.3 (C_6H_4), 110.9 (C≡C), 94.1 (C≡C), 45.1 (CMe$_2$S), 33.2 (CH_3), 31.4 (CH_2) 30.1(CH_2); FABm/s M$^+ - n$CO (n = 4,5,7–11).

f) Z = $(C_2H_4)_2O$

Elution afforded red solid **11** (0.040 g, 25%) and dark brown solid **17** (0.093 g, 50%).

IR νCO (cm^{-1}): 2088.0(m), 2054.8(s), 2028.0(s); ^{1}H NMR δ 7.4 (s, 4H, Ph), 3.2 (t$^3J_{HH}$ 8Hz, 4H, CH_2O), 2.4 (t$^3J_{HH}$ 8Hz, 4H, CH_2S), 1.7 (s, 12H, CH_3); ^{13}C NMR δ199.4 (CO), 139.0 (C_6H_4), 129.3 (C_6H_4), 111.9 (C≡C), 94.9 (C≡C), 69.5 (CH$_2$O), 49.1 (CMe$_2$S), 33.0 (CH_3), 30.1 (CH_2S); FABm/s M$^+ - n$CO (n = 3–12).

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