DALTON
FULL PAPER

Synthesis and characterisation of some dimeric η^2-diyne compounds of cobalt

Xue-Nian Chen,[a] Jie Zhang,[a] Shu-Lin Wu,[a] Yuan-Qi Yin,*[a] Wen-Ling Wang[b] and Jie Sun[c]

[a] *State Key Laboratory for Oxo Synthesis and Selected Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China.*
E-mail: hcom@ns.lzb.ac.cn
[b] *Department of Chemistry, Zhengzhou University, Zhengzhou 450052, China*
[c] *Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China*

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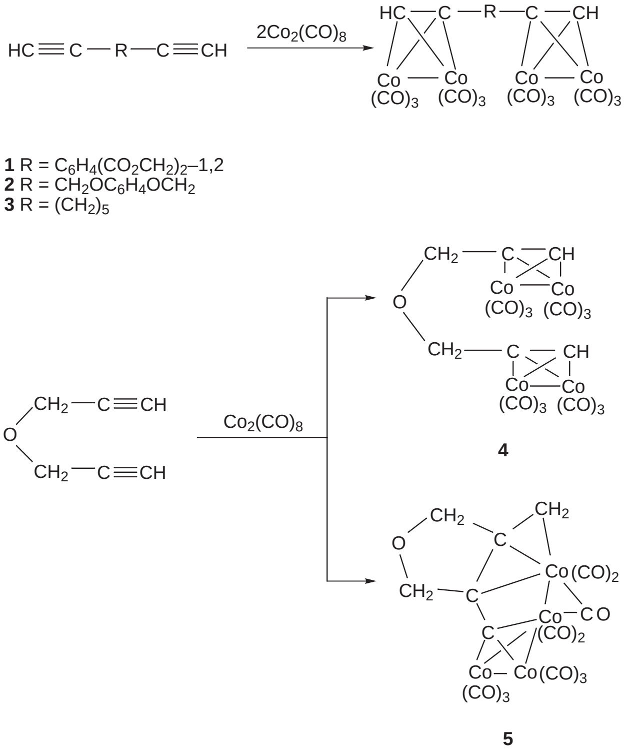
The organometallic dimers [$\{Co_2(CO)_6\}_2$(diyne)] [diyne = $C_6H_4(CO_2CH_2C_2H)_2$-1,2 **1**, $HC_2CH_2OC_6H_4OCH_2C_2H$ **2** or $HC_2(CH_2)_5C_2H$ **3**] have been synthesized from reactions between [$Co_2(CO)_8$] and the appropriate diyne ligands. However, the reaction of [$Co_2(CO)_8$] with diprop-2-ynyl ether $HC_2CH_2OCH_2C_2H$ under similar conditions gave the expected product [$\{Co_2(CO)_6\}_2(\mu$-$HC_2CH_2OCH_2C_2H)$] **4** and the unexpected product [$Co_4(CO)_{10}(\mu$-$CO)\{\mu_4$-$\eta:\eta^3$-$CC(CH_2OCH_2)CCH_2\}$] **5**. The products have been characterised by infrared, ^1H NMR spectroscopy and C/H analyses, and **2**, **4** and **5** also by single-crystal X-ray crystallography. In **2** and **4** both "yne" fragments of the diyne ligand are bonded to a $Co_2(CO)_6$ fragment with the C≡C vector essentially perpendicular to the Co–Co vector. However, in **5** hydrogen migration and new C–C bond formation has led to novel structural features, such as μ_3-CCo_3 and η^3-C_3Co units and a "C_4O" ring.

Octacarbonyldicobalt has been shown to react with alkynes at room temperature to give the μ-alkyne complexes [$Co_2(CO)_6(RC{\equiv}CR')$].[1,2] In other reactions between alkynes and [$Co_2(CO)_8$], cyclic products,[3–5] benzene or their derivatives, bilactones and cyclopentenone are formed by way of dinuclear cobalt intermediates. Recently, diyne clusters have been receiving considerable attention because of their potential application as polymeric materials, moreover also their unusual structures and reactions.[6] A dimer containing two linked $Co_2(CO)_6C_2$ units has been reported previously.[7,8] Seyferth[9] and Rubin[10] and co-workers also synthesized similar polymers containing the $Co_2(CO)_6C_2$ unit. As an extension, we have continued to study the reactions between [$Co_2(CO)_8$] and diyne ligands and found unexpected results.

Results and discussion

Treatment of diyne ligands with two molar equivalents of [$Co_2(CO)_8$] in appropriate solvents at room temperature gives tetranuclear clusters [$\{Co_2(CO)_6\}_2$(diyne)] [diyne = $C_6H_4(CO_2CH_2C_2H)_2$-1,2 **1**, $HC_2CH_2OC_6H_4OCH_2C_2H$ **2** or $HC_2(CH_2)_5C_2H$ **3**]. Under the same conditions, reaction of diprop-2-ynyl ether with [$Co_2(CO)_8$] not only produces the expected product [$\{Co_2(CO)_6\}_2(\mu$-$HC_2CH_2OCH_2C_2H)$] **4**, but also the unexpected product [$Co_4(CO)_{10}(\mu$-$CO)\{\mu_4$-$\eta^1:\eta^3$-$CC(CH_2OCH_2)CCH_2\}$] **5** (Scheme 1). High yields are obtained in all reactions at room temperature. In all cases the reactions were monitored by TLC, showing the disappearance of the starting complexes. The products were purified by column chromatography, followed by crystallisation from benzene– or hexane–CH_2Cl_2 at −20 °C to give red or brown crystals. They are stable in air as solids and soluble in common organic solvents.

At the present stage the mechanism concerning the formation of compound **5** remains unclear, but it is certain that the migration of hydrogen and cyclisation are included. This is similar to the reaction of alkynes with triosmium clusters, in which the presence of a terminal hydrogen or CH_2OH group in the molecule of the parent alkyne makes possible a profound rearrangement of the ligand, including hydride transfer to the ligand, subsequent dehydration and cyclisation with the formation of an oxygen-containing "C_4O" ring.[6,11,12] However, no products similar to compound **5** are observed in the other reactions, the possible reason being that a stable pentaatomic ring could not be formed in these cases.



Scheme 1 Formation of complexes **1**–**5**.

The products were characterised by IR spectroscopy, microanalysis and ^1H NMR spectroscopy. In the case of the complexes **2**, **4** and **5** the characterisations have been confirmed and the molecular geometry established by single-crystal X-ray crystallography.

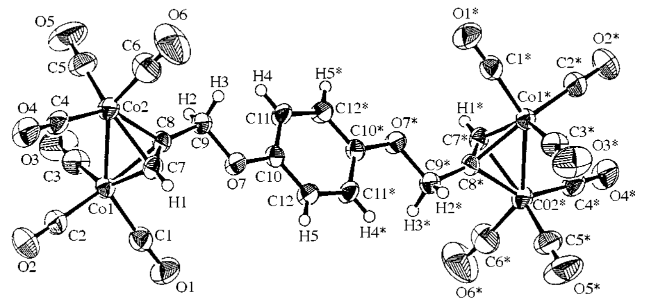


Fig. 1 Molecular structure of complex **2**.

Infrared spectroscopy

The IR spectra of complexes **1**–**4** all show the characteristic carbonyl pattern observed for previously reported cobalt–alkyne compounds[13] with six bands in the terminal carbonyl stretching region. Since these spectra and those of known cobalt–alkyne derivatives are very similar it is reasonable to conclude that a similar co-ordination mode for the alkyne is adopted but in this case that both alkyne linkages are co-ordinated to cobalt atoms. No C≡C stretches were observed in the region of 2100 cm^{-1}, and more importantly no C–H stretch (expected at 3290 cm^{-1}) was present. This we take to indicate the absence of a C≡C triple bond consistent with the view that both alkyne linkages are co-ordinated to Co_2 units. For the IR spectrum of complex **5**, in addition to the absorption bands of terminal carbonyl, those of bridging carbonyl appear at 1838 cm^{-1} and this is consistent with its crystal structure.

Proton NMR spectroscopy

The ^1H NMR spectroscopic data for the complexes **1**–**5** are consistent with the overall geometry established in the solid state for **2**, **4** and **5**, and with the IR spectroscopy studies.

For complexes **1**–**4** which contain a terminal alkyne hydrogen a single resonance is observed in the region δ 6.14–6.02. As expected,[14,15] because of the reduction in the C≡C triple-bond character, there is a downfield shift in the position of these terminal protons with respect to the "free" ligand (at around δ 2.50–1.90). Similarly, they possess methylene protons which exhibit a singlet in the region δ 5.52–2.89 in their ^1H NMR spectra, which also undergo a distinct downfield shift when the C≡C group is co-ordinated to Co–Co. Complexes **1** and **2** have aromatic rings and consequently their ^1H NMR spectra contain peaks in the region δ 7.81–6.90. For **2** the appearance of a singlet at δ 6.90 (integral 4 H) indicates that the four aromatic protons are equivalent and that the aromatic ring must be rotating about the C(10)–O(7) bond (Fig. 1). The ^1H NMR spectrum for **1** reveals non-equivalent aromatic protons and appears as a multiplet in the region δ 7.81–7.57.

In the ^1H NMR spectrum of complex **5** no signals due to protons of a terminal alkyne are observed. The multiplet at δ 5.03 is assignable to two protons of the $C(12)H_2$ group.[16] Since **5** is asymmetric the four protons of the two CH_2 groups in the "C_4O" ring are in different environments. This results in the CH_2 protons giving rise to two sets of peaks.[17]

Crystal and molecular structures of $[\{Co_2(CO)_6\}_2(\mu\text{-}HC_2CH_2OC_6H_4OCH_2C_2H)]$ 2 and $[\{Co_2(CO)_6\}_2(\mu\text{-}HC_2CH_2OCH_2C_2H)]$ 4

Table 1 Selected bond lengths (Å) and angles (°) for complex **2** with estimated standard deviations (e.s.d.s) in parentheses

Co(1)–Co(2)	2.4746(8)	Co(1)–C(7)	1.944(4)
Co(1)–C(8)	1.953(3)	Co(2)–C(7)	1.953(3)
Co(2)–C(8)	1.943(3)	C(7)–C(8)	1.309(4)
Co(2)–Co(1)–C(7)	50.7(1)	Co(2)–Co(1)–C(8)	50.38(9)
C(7)–Co(1)–C(8)	39.3(1)	Co(1)–Co(2)–C(7)	50.4(1)
Co(1)–Co(2)–C(8)	50.75(10)	C(7)–Co(2)–C(8)	39.3(1)
Co(1)–C(7)–Co(2)	78.9(1)	Co(1)–C(7)–C(8)	70.7(2)
Co(2)–C(7)–C(8)	69.9(2)	Co(1)–C(8)–Co(2)	78.9(1)
Co(1)–C(8)–C(7)	70.0(2)	Co(2)–C(8)–C(7)	70.8(2)
C(7)–C(8)–C(9)	107.1(3)		

Table 2 Selected bond lengths (Å) and angles (°) for complex **4** with e.s.d.s in parentheses

Co(1)–Co(2)	2.4686(9)	Co(3)–Co(4)	2.4866(9)
C(13)–C(14)	1.308(6)	C(17)–C(18)	1.316(6)
Co(1)–C(13)	1.948(5)	Co(3)–C(17)	1.959(4)
Co(1)–C(14)	1.939(4)	Co(3)–C(18)	1.938(5)
Co(2)–C(13)	1.939(5)	Co(4)–C(17)	1.952(4)
Co(2)–C(14)	1.958(5)	Co(4)–C(18)	1.961(4)
Co(2)–Co(1)–C(13)	50.4(1)	Co(4)–Co(3)–C(17)	50.4(1)
Co(2)–Co(1)–C(14)	51.0(1)	Co(4)–Co(3)–C(18)	50.8(1)
C(13)–Co(1)–C(14)	39.3(2)	C(17)–Co(3)–C(18)	39.5(2)
Co(1)–Co(2)–C(13)	50.7(1)	Co(3)–Co(4)–C(17)	50.6(1)
Co(1)–Co(2)–C(14)	50.3(1)	Co(3)–Co(4)–C(18)	50.0(1)
C(13)–Co(2)–C(14)	39.2(2)	C(17)–Co(4)–C(18)	39.3(2)
Co(1)–C(13)–C(14)	69.9(3)	Co(3)–C(17)–C(18)	69.4(3)
Co(2)–C(14)–C(13)	69.6(3)	Co(4)–C(18)–C(17)	70.0(3)

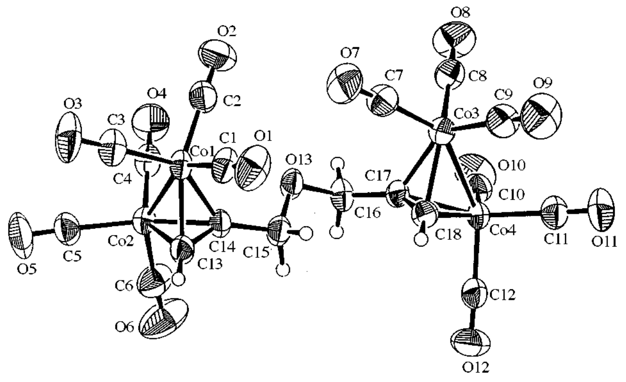


Fig. 2 Molecular structure of complex **4**.

The crystal structures of complexes **2** and **4** consist of discrete molecules of $[\{Co_2(CO)_6\}_2(\mu\text{-}HC_2CH_2OC_6H_4OCH_2C_2H)]$ and $[\{Co_2(CO)_6\}_2(\mu\text{-}HC_2CH_2OCH_2C_2H)]$ in which the two $Co_2(CO)_6$(alkyne) fragments are linked by the $CH_2OC_6H_4$-OCH_2 and CH_2OCH_2 groups, respectively. The molecular structures are shown in Figs. 1 and 2; selected bond lengths and angles are listed in Tables 1 and 2, respectively. As seen in Fig. 1, the molecule sits on a crystallographic centre of symmetry which lies at the centre of the aryl ring. The Co_2C_2 core adopts a pseudo-tetrahedral geometry with the C(7)–C(8) alkyne bond lying essentially perpendicular to the Co(1)–Co(2) vector. Each of the cobalt atoms is co-ordinated to three terminal carbonyl ligands which display linear geometries. The Co(1)–Co(2) bond length found in **2** lies within the range 2.460–2.477 Å observed for other dicobalt systems that are bridged by perpendicular alkyne ligands,[7,18–20] but is shorter than the value of 2.52 Å found in the parent carbonyl $[Co_2(CO)_8]$. The C(1)–C(8) length is slightly shorter than the range 1.33–1.36 Å of values for the alkynic C–C bond in the same set of related dicobalt complexes.[7,18–20] This C–C distance shows a lengthening of *ca.* 0.13 Å from the value of 1.18 Å found in the free alkyne, an observation that is consistent with the delocalisation of electron density into the Co_2 unit. As seen in Fig. 2, the Co_2C_2 core also adopts a pseudo-tetrahedral geometry and the overall conformations of the two Co_2C_2 moieties in **4** resemble each other and are similar to that found in **2**. The two Co–Co and C–C bond lengths are slightly longer than the value found in **2** but still lie within the normal range. The Co–C bond distances in the Co_2C_2 cores are in the range 1.938(6)–1.961(4) Å, comparable with those of related dicobalt complexes.[7,18–20] No

Table 3 Selected bond lengths (Å) and angles (°) for complex **5** with e.s.d.s in parentheses

Co(1)–Co(2)	2.502(2)	Co(1)–Co(3)	2.478(2)
Co(2)–Co(3)	2.519(2)	Co(3)–Co(4)	2.649(2)
Co(1)–C(17)	1.93(1)	Co(2)–C(17)	1.93(1)
Co(3)–C(17)	1.97(1)	Co(4)–C(12)	2.17(1)
Co(4)–C(13)	2.11(1)	Co(4)–C(16)	2.15(1)
Co(3)–C(9)	1.90(1)	Co(4)–C(9)	1.98(1)
C(12)–C(13)	1.37(2)	C(13)–C(14)	1.51(2)
C(13)–C(16)	1.45(1)	C(15)–C(16)	1.49(2)
C(16)–C(17)	1.42(1)		
Co(2)–Co(1)–Co(3)	60.76(5)	Co(2)–Co(1)–C(17)	49.7(3)
Co(3)–Co(1)–C(17)	51.4(3)	Co(1)–Co(2)–Co(3)	59.16(5)
Co(1)–Co(2)–C(17)	49.7(3)	Co(3)–Co(2)–C(17)	50.6(3)
Co(1)–Co(3)–Co(2)	60.07(5)	Co(1)–Co(3)–C(17)	49.9(3)
Co(2)–Co(3)–C(17)	49.1(3)	Co(4)–Co(3)–C(17)	63.4(3)
Co(2)–Co(3)–Co(4)	105.46(6)	Co(1)–Co(3)–Co(4)	99.75(6)
Co(3)–Co(4)–C(16)	79.6(3)	C(12)–Co(4)–C(13)	37.4(4)
C(13)–Co(4)–C(16)	39.8(4)	C(12)–Co(4)–C(16)	70.3(4)
O(12)–C(14)–C(13)	105.8(9)	O(12)–C(15)–C(16)	106.4(9)
Co(4)–C(13)–C(12)	73.9(7)	Co(4)–C(13)–C(14)	121.5(8)
Co(4)–C(13)–C(16)	71.9(6)	C(12)–C(13)–C(16)	123(1)
C(12)–C(13)–C(14)	129(1)	C(14)–C(13)–C(16)	106.4(10)
Co(4)–C(16)–C(13)	68.4(8)	Co(4)–C(16)–C(15)	123.3(8)
Co(4)–C(16)–C(17)	86.1(6)	C(13)–C(16)–C(15)	107.4(8)
C(15)–C(16)–C(17)	127.5(9)	C(13)–C(16)–C(17)	124.5(10)
C(16)–C(17)–Co(1)	127.8(8)	C(16)–C(17)–Co(2)	137.2(8)
C(16)–C(17)–Co(3)	130.9(8)	Co(1)–C(17)–Co(2)	80.6(4)
Co(1)–C(17)–Co(3)	78.7(4)	Co(2)–C(17)–Co(3)	80.3(4)
Co(4)–C(12)–C(13)	68.7(6)		

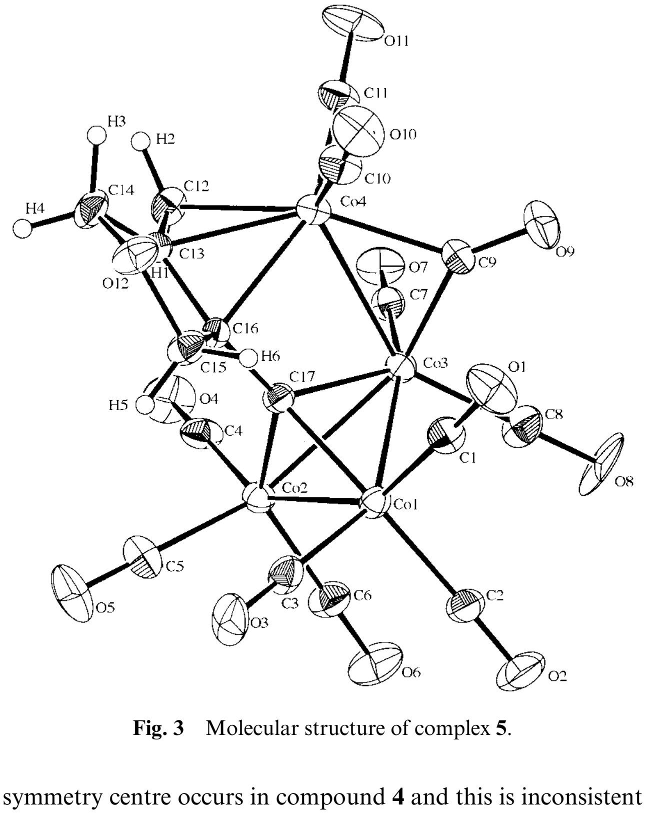


Fig. 3 Molecular structure of complex **5**.

symmetry centre occurs in compound **4** and this is inconsistent with **2**.

Crystal and molecular structure of [$Co_4(CO)_{10}(\mu$-CO){μ_4-η : η^3-$CC(CH_2OCH_2)CCH_2$}] 5

In order to establish the structure of complex **5** a suitable crystal of it was subjected to X-ray diffraction analysis. The molecular structure is shown in Fig. 3, while selected lengths and angles are collected in Table 3. It is confirmed that the complex contains a "C_4O" ring and μ_3-CCo_3 and η^3-C_3Co units. The formation of the "C_4O" ring and asymmetric molecule are consistent with the ^1H NMR spectrum of **5** showing several peaks from δ 5.03 to 2.59. All of the Co–Co and C–C bond lengths are in the normal region. The C(12)–C(13) distance is 1.37(2) Å in the range of C–C double-bond distances, but the C(16)–C(17) distance of 1.42(1) Å is shorter than C–C single-bond distances of 1.53 Å and is longer than C–C double-bond distances of 1.337 Å. The C–Co bond lengths in the μ_3-CCo_3 unit are also in the normal region but are longer than that in the η^3-C_3Co. It is possible that a σ-coordinated form occurs in the μ_3-CCo_3 unit and a π-coordinated form in the η^3-C_3Co unit. The C(9)O(9) carbonyl is bridging and the others are terminal; this coexistence of both terminal and bridging carbonyls is consistent with the IR spectrum of complex **5** showing several strong absorption bands from 2092 to 1838 cm^{-1}.

Experimental

All reactions were carried out under pure nitrogen using standard Schlenk techniques. Hexane, benzene and light petroleum (60–90 °C) were dried by sodium while dichloromethane was distilled from CaH_2. Chromatographic separations were performed on silica columns (160–200 mesh) of varying length. Thin-layer chromatography (TLC) was carried out on commercial Merck plates coated with a 0.20 mm layer of silica.

Infrared spectra were recorded in NaCl cells on a Nicolet FT-IR 10 DX spectrometer. Spectra of compounds in the solid state were recorded as pressed KBr discs. Proton NMR spectra were recorded on a Bruker Am 300 (300 MHz) in $CDCl_3$ deuteriated solvent. Chemical shifts are given on the δ scale relative to $SiMe_4$ (0.0 ppm). Elemental analyses were carried out on a Carlo Erba 1106 type analyzer.

Nona-1,8-diyne was purchased from Aldrich Chem. Co. Dicobalt octacarbonyl[21] and diynes $C_6H_4(CO_2CH_2C_2H)_2$-1,2,[22] $HC_2CH_2OC_6H_4OCH_2C_2H$,[22] $HC_2CH_2OCH_2C_2H$[23] were prepared by literature methods or slight modifications thereof.

Preparations

[{$Co_2(CO)_6$}$_2${μ-$C_6H_4(CO_2CH_2C_2H)_2$-1,2}] 1. In a typical reaction [$Co_2(CO)_8$] (684 mg, 2 mmol) and $C_6H_4(CO_2CH_2C_2H)_2$-1,2 (242 mg, 1 mmol) were dissolved in benzene (40 cm^3). The solution was stirred at room temperature for 2 h. A change from brown to red was observed and TLC monitoring showed the disappearance of the starting material [$Co_2(CO)_8$]. After addition of a small amount of silica the solvent was removed and the residue chromatographed. Elution with benzene produced red bands and the volume of the resulting solution was reduced to *ca.* 10 cm^3. Crystallisation at −20 °C yielded a reddish purple crystalline material (648 mg, 79.6%) (Found: C, 38.38; H, 1.20. Calc. for $C_{13}H_5Co_2O_8$: C, 38.36; H, 1.24%) mp 82–84 °C. IR: ν(CO) 2098s, 2055vs, 2031vs, 2022vs, 2016vs, 2002vs and ν(C=O) 1737m and 1715 cm^{-1}. ^1H NMR: δ 7.81–7.57 (m, 4 H, C_6H_4), 6.14 (s, 2 H, 2CH) and 5.52 (s, 4 H, $2CH_2$).

[{$Co_2(CO)_6$}$_2$(μ-$HC_2CH_2OC_6H_4OCH_2C_2H$)] 2. Dicobalt octacarbonyl (684 mg, 2 mmol) and $HC_2CH_2OC_6H_4OCH_2C_2H$ (186 mg, 1 mmol) were dissolved in dichloromethane (30 cm^3). The solution was stirred at room temperature for 3 h then separated on a silica gel column using CH_2Cl_2–light petroleum (1 : 5) as eluent. Only one red band was collected. Crystallisation at −20 °C yielded a reddish purple crystalline material (445 mg, 58.7%) which was separated by filtration at room temperature. Recrystallisation from hexane–CH_2Cl_2 at −20 °C gave red crystals suitable for single-crystal X-ray analysis (Found: C, 38.08; H, 1.30. Calc. for $C_{12}H_5Co_2O_7$: C, 38.02; H, 1.33%), mp 102–104 °C. IR: ν(CO) 2096s, 2058vs, 2024vs, 2002vs(sh), 2000vs(sh) and 1976m cm^{-1}. ^1H NMR: δ 6.90 (s, 4 H, C_6H_4), 6.04 (s, 2 H, 2CH) and 5.15 (s, 4 H, $2CH_2$).

[{$Co_2(CO)_6$}$_2${μ-$HC_2(CH_2)_5C_2H$}] 3. In a similar reaction, a solution of [$Co_2(CO)_8$] (684 mg, 2 mmol) and nona-1,8-diyne

Table 4 Summary of the crystallographic data for compounds **2**, **4** and **5**

	2	**4**	**5**
Molecular formula	$C_{24}H_{10}Co_4O_{14}$	$C_{18}H_6Co_4O_{13}$	$C_{17}H_6Co_4O_{12}$
M	758.07	665.97	637.96
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	*Cc* (no. 9)
a/Å	8.567(2)	18.149(2)	14.808(2)
b/Å	11.476(1)	7.0111(7)	10.346(3)
c/Å	8.088(2)	20.897(2)	14.401(5)
α/°	102.44(1)		
β/°	104.15(2)	115.318(7)	105.591
γ/°	102.55(1)		
V/Å^3	721.7(2)	2403.7(5)	2125.0801
Z	1	4	4
D_c/g cm^{-3}	1.744	1.840	1.994
Crystal size/mm	0.20 × 0.20 × 0.30	0.20 × 0.20 × 0.30	0.60 × 0.60 × 0.40
Crystal habit	Red	Red	Brown
T/K	293	293	288
F(000)	374	1304	1248
μ/cm^{-1}	23.25	27.76	31.31
No. measured reflections	2726	3977	2256
No. observed reflections	1846 [$I > 2.50\sigma(I)$]	2372 [$I > 2.00\sigma(I)$]	1943 [$I > 3.00\sigma(I)$]
No. variables	191	316	299
R	0.030	0.030	0.046
R′	0.035	0.031	0.066
Goodness of fit	1.15	1.20	1.21
Largest peak in final difference map/e Å^{-3}	0.29	0.25	0.85

(120 mg, 1 mmol) in hexane (30 cm^3) was stirred for 3 h. The solution was separated on a silica gel column using light petroleum as eluent. Crystallisation at −20 °C yielded a red oil (489 mg, 69.7%) (Found: C, 36.39; H, 1.80. Calc. for $C_{21}H_{12}Co_4O_{12}$: C, 36.44; H, 1.75%). IR: ν(CO) 2093s, 2049vs, 2017vs, 1976(sh), 1940m and 1873w cm^{-1}. ^{1}H NMR: δ 6.02 (s, 2 H, 2CH), 2.89 (s, 4 H, $2CH_2$) and 1.68 (m, 6 H, $CH_2CH_2CH_2$).

[{$Co_2(CO)_6$}$_2$(μ-$HC_2CH_2OCH_2C_2H$)] 4 and [$Co_4(CO)_{10}$(μ-CO){μ_4-η:η^3-CC(CH_2OCH_2)CCH_2}] 5. Stirring a solution of [$Co_2(CO)_8$] (684 mg, 2 mmol) and $HC_2CH_2OCH_2C_2H$ (94 mg, 1 mmol) in hexane (40 cm^3) for 2 h and TLC monitoring showed the disappearance of the starting material [$Co_2(CO)_8$]. Chromatography as above produced a major red and minor brown band, respectively. The solution of the major red band was reduced in volume to *ca.* 10 cm^3. Crystallisation at −20 °C yielded a red-purple crystalline material **4** (406 mg, 61.0%). Recrystallisation by slow layer diffusion of hexane into a hexane–CH_2Cl_2 mixture at −20 °C gave red prismatic crystals of **4** suitable for single-crystal X-ray analysis (Found: C, 32.42; H, 0.98. Calc. for $C_{18}H_6Co_4O_{13}$: C, 32.46; H, 0.91%), mp 52–54 °C. IR: ν(CO) 2095s, 2060vs, 2039vs, 2022vs, 2010vs and 1995s cm^{-1}. ^{1}H NMR: δ 6.07 (s, 2 H, 2CH) and 4.85 (s, 4 H, $2CH_2$). The solution of the minor brown band was reduced in volume to *ca.* 5 cm^3. Crystallisation at −20 °C yielded a brown crystalline material **5** (140 mg, 22.0%). Recrystallisation from hexane at −20 °C gave crystals of **5** suitable for single-crystal X-ray analysis (Found: C, 31.96; H, 1.02. Calc. for $C_{17}H_6Co_4O_{12}$: C, 32.00; H, 0.95%), mp 158 °C (decomp.). IR: ν(CO) 2092s, 2057vs, 2036vs, 2024vs, 2009vs, 1989s and 1838s cm^{-1}. ^{1}H NMR: δ 5.03 (m, 2 H, CH_2), 4.52 (br s, 1 H, C*H*H), 4.30 (br s, 1 H, CH*H*), 3.59 (s, 1 H, C*H*H) and 2.59 (s, 1 H, CH*H*).

Crystal structure determination and refinements

Suitable crystals of the compounds **2**, **4** and **5** were mounted on glass fibers with epoxy resin. Details of crystal data, data collection and refinement parameters are given in Table 4. Data were collected by the ω–2θ scan method on a Rigaku AFC7R diffractometer (**2**, **4**) or AXIS-IV imaging plate area detector (**5**) with Mo-Kα radiation.

The cobalt atoms in each of the three structures were located by centrosymmetric direct methods, and the remaining non-hydrogen atoms from subsequent Fourier-difference syntheses. The structures were refined to convergence by full-matrix least squares with all non-hydrogen atoms assigned anisotropic displacement parameters. Weighting schemes were applied. All atoms were assigned neutral-atom scattering factors taken from ref. 24. Calculations were performed using TEXSAN.[25]

CCDC reference number 186/1426.

See http://www.rsc.org/suppdata/dt/1999/1987/ for crystallographic files in .cif format.

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