

A comparison between the reaction of P_2Ph_4 with $[\{Co_2(CO)_6\}_2(\mu-\eta^2:\mu-\eta^2-HOCH_2C\equiv C-C\equiv CCH_2OH)]$ and the reaction of $[Co_2(\mu-PPh_2)_2(CO)_6]$ with $HOCH_2C\equiv C-C\equiv CCH_2OH$

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Received 25 January 2005; accepted 16 February 2005

Available online 23 March 2005

Abstract

Reaction of P_2Ph_4 with the diyne–diol complex $[\{Co_2(CO)_6\}_2(\mu-\eta^2:\mu-\eta^2-HOCH_2C\equiv C-C\equiv CCH_2OH)]$ in toluene at 65 °C gives $[\{Co_2(\mu-P_2Ph_4)(CO)_4\}\{Co_2(CO)_6\}(\mu-\eta^2:\mu-\eta^2-HOCH_2C\equiv C-C\equiv CCH_2OH)]$ (**1**). Thermolysis of **1** at 95 °C leads to $[\{Co_2(CO)_5\}_2(\mu-P_2Ph_4)(\mu-\eta^2:\mu-\eta^2-HOCH_2C\equiv C-C\equiv CCH_2OH)]$ (**2**) and $[Co_4\{\mu_4-CH_2=CCC=C(PPh_2)CH_2OCO\}(\mu_2-PPh_2)(\mu_2-CO)(CO)_7]$ (**3**). The structures of **1–3** have been established by X-ray crystallography. In **1**, a pseudoequatorial P_2Ph_4 ligand bridges the cobalt–cobalt bond of a $Co_2(-C\equiv C-)(CO)_4$ unit. By contrast, in isomeric **2**, a pseudoaxial P_2Ph_4 ligand spans two $Co_2(-C\equiv C-)(CO)_5$ units, a new coordination mode for $[\{Co_2(CO)_5L\}_2(\mu-\eta^2:\mu-\eta^2-diyne)]$ complexes. Complex **3** arises from dehydration–cyclocarbonylation of the diyne–diol in **1** to give a 2(5H)-furanone, a process that has not been previously reported. Reaction of $HOCH_2C\equiv C-C\equiv CCH_2OH$ with $[Co_2(\mu-PPh_2)_2(CO)_6]$ at 80 °C in toluene gave $[Co_3(\mu-PPh_2)_3(CO)_6]$, $[Co_2(CO)_6(\mu-\eta^2-HOCH_2C\equiv C-CCCH_2OH)]$ and $[Co_2\{\mu-\eta^4-PPh_2C(CCCH_2OH)C(CH_2OH)CO\}(\mu-PPh_2)(CO)_4]$ (**4**). The regiochemistry of **4** was confirmed by X-ray crystallography.

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Keywords: Cobalt diyne; Tetraphenylbiphosphine; 2,4-hexadiyne-1,6-diol; 2(5H)-furanone

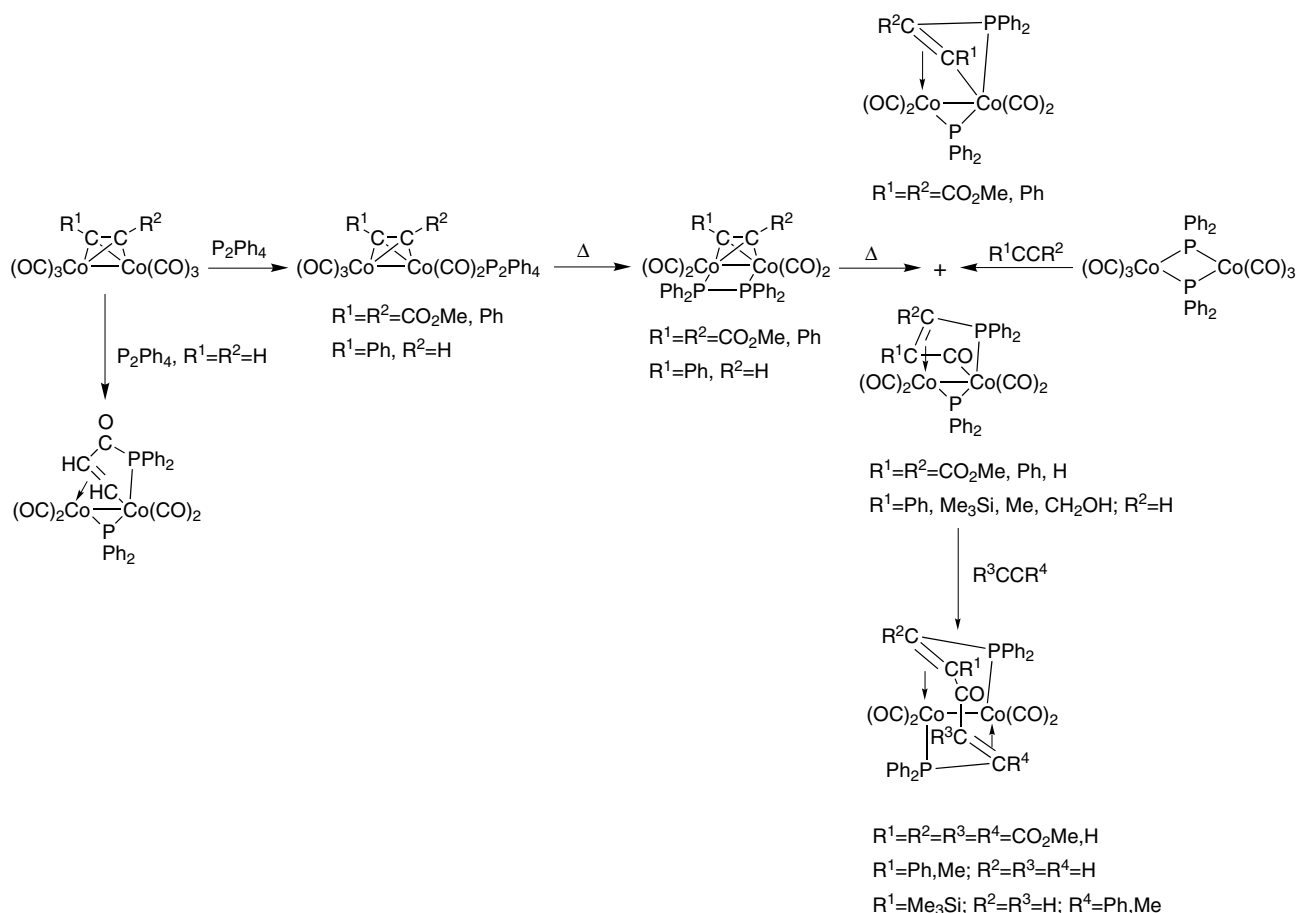
1. Introduction

Phosphorus-donor ligands have been observed to undergo many intramolecular coupling, fragmentation and/or rearrangement reactions in organometallic complexes. Cobalt carbonyl complexes containing phosphorus-donor ligands are amongst the most active in reactions of this type [1–20]. The study of P–C and P–Co bond cleavage and formation in these complexes provides an insight into aspects of the chemistry of cobalt

carbonyl phosphine hydroformylation catalysts [21]. In previous work, we have described the reactions of $[Co_2(\mu-alkyne)(CO)_6]$ complexes with P_2Ph_4 , which lead to new dinuclear cobalt complexes containing four- and five-membered metallacyclic rings [1]. The four-membered metallacyclic rings are derived from the coupling of the alkyne with a PPh_2 group and the five-membered rings from the additional incorporation of CO. We subsequently found an alternative strategy for the synthesis of such compounds involving the reaction of $[Co_2(\mu-PPh_2)_2(CO)_6]$ with alkynes (Scheme 1) [2]. We have now studied the corresponding reactions of cobalt diyne complexes and, in this paper, we report both the reactivity of $[\{Co_2(CO)_6\}_2(\mu-\eta^2:\mu-\eta^2-diyne)]$ with P_2Ph_4 and the reactivity of $[Co_2(\mu-PPh_2)_2(CO)_6]$ with diynes.

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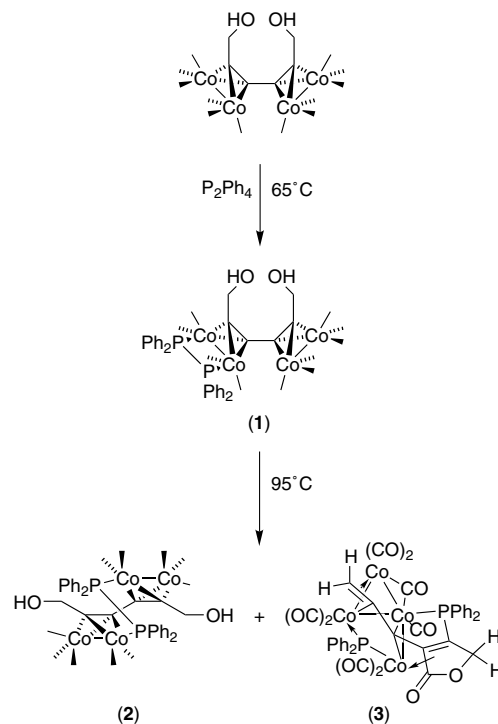


Scheme 1.

2. Results and discussion

2.1. Reactivity of $[\{Co_2(CO)_6\}_2(\mu-\eta^2:\mu-\eta^2-HOCH_2C\equiv C-C\equiv CCH_2OH)]$ towards P_2Ph_4

Reaction of $[\{Co_2(CO)_6\}_2(\mu-\eta^2:\mu-\eta^2-HOCH_2C\equiv C-C\equiv CCH_2OH)]$ with one equivalent of P_2Ph_4 in toluene at 65 °C gave, after purification by column chromatography, $[\{Co_2(\mu-P_2Ph_4)(CO)_4\}\{Co_2(CO)_6\}(\mu-\eta^2:\mu-\eta^2-HOCH_2C\equiv C-C\equiv CCH_2OH)]$ (**1**) in 47% yield as the single major product (Scheme 2). Thermolysis of **1** in toluene at 95 °C gave, after separation by column chromatography, brown crystalline $[\{Co_2(CO)_5\}_2(\mu-P_2Ph_4)(\mu-\eta^2:\mu-\eta^2-HOCH_2C\equiv C-C\equiv CCH_2OH)]$ (**2**) (23% yield) and black crystalline $[Co_4\{\mu_4-CH_2=CCC=C(PPh_2)CH_2OCO\}(\mu_2-PPh_2)(\mu_2-CO)(CO)_7]$ (**3**) (21% yield). Complexes **1–3** have been characterized spectroscopically and their structures confirmed by X-ray diffraction studies (see below). In complex **1**, a bridging P_2Ph_4 ligand replaces two CO groups in pseudoequatorial sites on one $Co_2(-C\equiv C-C)(CO)_6$ unit, leaving the other $Co_2(-C\equiv C-C)(CO)_6$ unit unsubstituted. The alkyne functionalities of the diyne in **1** adopt a relative configuration such that the two CH_2OH substituents are *cis* to each other. Complex



Scheme 2.

2 is isomeric with **1**, but in **2** the P₂Ph₄ ligand bridges the pseudoaxial positions of two non-bonded cobalt atoms on different Co₂(–C≡C–)(CO)₅ units. This ligand coordination mode has not been previously observed for [Co₂(CO)₆]₂(μ-diyne) complexes. Also in contrast to **1**, the two coordinated alkyne functionalities in **2** adopt a relative configuration such that the CH₂OH substituents are *trans*.

The IR spectrum of **1** corresponds closely to that of [Co₂(μ-bma)(CO)₄]{Co₂(CO)₆}(μ-η²:μ-η²-PhC≡C–C≡CPh) (bma = 2,3-bis(diphenylphosphino)maleic anhydride). Yang et al. were unable to unequivocally assign all the ν(CO) bands in this complex [3]. The compound was thermally sensitive (as is **1**) and no X-ray structure could be obtained. Nevertheless, from spectroscopic data, a structure with a bridging bma ligand occupying pseudoequatorial sites was proposed. This structural assignment is now supported by the similarity of the IR spectrum of the bma complex to that of **1**. The ³¹P NMR spectrum of **1** gives a single resonance at δ 7.2, which is within the range of values, δ 3–11, observed for other complexes of the type [Co₂(μ-P₂Ph₄)(μ-η²-R¹C≡CR²)(CO)₄] (R¹ = R² = CO₂ Me, Ph; R¹ = Ph, R² = H) in which a μ-P₂Ph₄ ligand is bonded pseudoequatorially [1]. The ³¹P NMR spectrum of **2** gives a single resonance as in **1**, but shifted to lower field at δ 93.3. The ¹H and ¹³C NMR data for **2** are consistent with the proposed structure, in which a plane of symmetry bisects the molecule through the midpoint of the central C–C bond of the diyne and the midpoint of the P–P bond. The plane of symmetry renders the two inner diyne carbon atoms equivalent, as it does the two outer diyne carbons and the two methylene carbons. As a result, one CH₂, one C≡CCH₂ and one C≡CCH₂ signal are observed in the ¹³C NMR spectrum of **2**. This contrasts with the observation of two signals each for the same pairs of carbon atoms in the ¹³C NMR spectrum of **1**. This latter observation is accounted for by the fact that in **1** the plane of symmetry lies along the diyne ligand rather than perpendicular to it. In the IR spectrum of **3** a ν(CO) band characteristic of a μ-CO ligand is observed at 1824 cm⁻¹. In addition, a ν(CO) band characteristic of a β-γ-unsaturated γ-lactone is observed at 1761 cm⁻¹. The vinyl protons in **3** appear as two doublets centered at δ 4.51 and δ 3.54, each weakly coupled to the μ-PPh₂ phosphorus. No coupling was resolved between the geminal vinyl protons. This correlates with other μ-CR=CH₂ vinyl ligands for which negligible, or only a small coupling is observed [22–28]. The CH₂ protons of the lactone ring are observed as multiplets at δ 4.32 and 4.18 with a geminal H–H coupling of 14 Hz and smaller unresolved coupling to both phosphorus atoms. An HMQC experiment further confirmed the assignments by verifying that the two CH₂ vinyl protons and two CH₂ lac-

tone protons are each, respectively, attached to the same carbon atoms. Two peaks are observed in the ³¹P NMR spectrum of **3**. One peak at δ 81.9 is tentatively assigned to the μ₄-CH₂=CCC=C(PPh₂)CH₂OCO ligand, while a broader resonance at δ 7.1 is assigned to the μ-PPh₂ group. As noted previously, ³¹P NMR signals for phosphido groups bridging metals that are not directly bonded to each other are found substantially upfield of phosphido ligands bridging directly bonded metals [13,29,30].

The formation of **1** from the diyne complex [Co₂(CO)₆]₂(μ-η²:μ-η²-HOCH₂C≡C–C≡CCH₂OH) parallels the initial reactivity of the alkyne complexes [Co₂(μ-alkyne)(CO)₆] with P₂Ph₄. The subsequent thermolysis of **1** (Scheme 2), however, clearly follows a different path from the thermolysis of [Co₂(μ-alkyne)(μ-P₂Ph₄)(CO)₆] (Scheme 1). It also follows a different path from that reported for the thermolysis of other [Co₂(μ-diphosphine)(CO)₄]{Co₂(CO)₆}(μ-η²:μ-η²-(1,3-diyne)) complexes where either partial or full diyne decomplexation has been observed [3,31]. This may be due to the presence of the reactive propargyl alcohol group, CH₂OH, in **1**. The thermolytic transformation of **1** to **2** results in a “*cis*” to “*trans*” conversion of the orientation of the CH₂OH substituents on the diyne. Possible reasons for this conversion include: (a) that pseudoaxial phosphine substitution is thermodynamically favoured over pseudoequatorial substitution; (b) that two units of a phosphine-monosubstituted cobalt pentacarbonyl are thermodynamically favoured over the disproportionated alternative of one unit of a disubstituted tetracarbonyl and one of an unsubstituted hexacarbonyl complex; (c) that a staggered conformation of the bidentate P₂Ph₄ ligand is favoured over an eclipsed conformation.

Complex **3** arises from **1** by dehydration–cyclocarbonylation of the diyne–diol, coupled with phosphorus–phosphorus bond cleavage and diyne functionalisation by one phosphido group. A related dehydration of 2,4-hexadiyne-1,6-diol on reaction with H₂O₃(CO)₁₀ has been reported. No CO insertion was observed in this dehydration, however, and furan ring formation occurred yielding [Os₃(μ-H)(μ₂-η³-OCH=CHC=CCCH₃)(CO)₁₀] [32,33]. Dehydration–cyclocarbonylation of a diyne–diol to give a 2(5H)-furanone, as observed here, has not been previously reported. Cyclocarbonylation of propargyl alcohols with carbon monoxide to 2(5H)-furanones is well established, however, and is catalysed by palladium and rhodium complexes [34–40]. Various 4-heterosubstituted 2(5H)-furanones have also been made from propargyl alcohols. These include oxygen, sulphur and selenium substituted lactones [41–43]. Although several 4-phosphorus(V) substituted 2(5H)-furanones have been made, only one phosphorus(III) example has been previously reported [44].

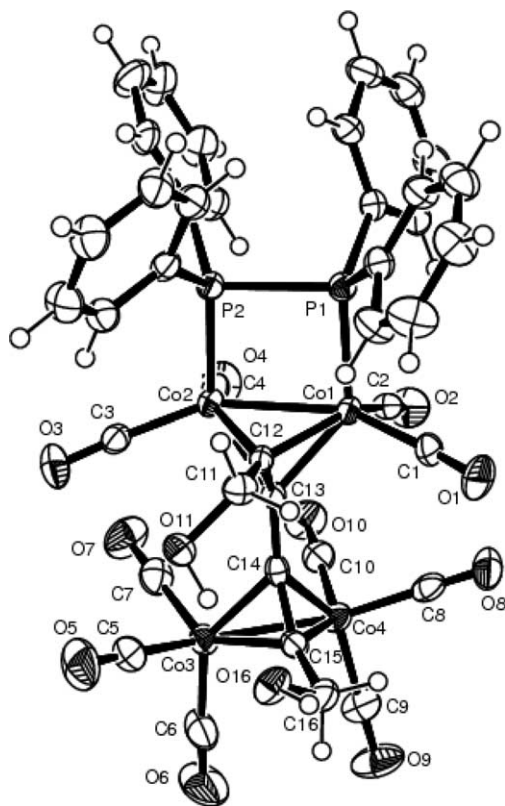


Fig. 1. ORTEP diagram of $[\{\text{Co}_2(\mu\text{-P}_2\text{Ph}_4)(\text{CO})_4\}\{\text{Co}_2(\text{CO})_6\}\{\mu\text{-}\eta^2\text{-}\mu\text{-}\eta^2\text{-HOCH}_2\text{C}\equiv\text{C}-\text{C}\equiv\text{CCH}_2\text{OH}\}]$ (**1**), showing thermal ellipsoids at the 50% probability level.

2.2. Crystal structure of (1)

The structure of **1** is displayed in Fig. 1, and selected bond distances and angles are presented in Table 1. The $[\text{Co}_2(\mu\text{-P}_2\text{Ph}_4)(\mu\text{-}\eta^2\text{-RC}\equiv\text{CR})(\text{CO})_4]$ part of the structure closely resembles that of $[\text{Co}_2(\mu\text{-P}_2\text{Ph}_4)\{\mu\text{-}\eta^2\text{-C}_2(\text{CO}_2\text{Me})_2\}(\text{CO})_4]$ [1]. The two phosphorus donor atoms

Table 1
Selected bond distances (Å) and angles (°) for complex **1**

Co(1)–Co(2)	2.4500(9)	Co(3)–Co(4)	2.4673(9)
Co(1)–C(12)	1.969(4)	Co(1)–C(13)	1.970(4)
Co(1)–P(1)	2.2275(13)	Co(2)–C(12)	1.948(4)
Co(2)–C(13)	1.948(4)	Co(2)–P(2)	2.2206(13)
Co(3)–C(15)	1.959(5)	Co(3)–C(14)	1.973(4)
Co(4)–C(15)	1.949(4)	Co(4)–C(14)	1.984(4)
P(1)–P(2)	2.2651(18)	O(11)–C(11)	1.423(5)
C(11)–C(12)	1.496(6)	C(12)–C(13)	1.348(6)
C(13)–C(14)	1.435(6)	C(14)–C(15)	1.343(6)
C(15)–C(16)	1.491(6)	O(16)–C(16)	1.433(5)
P(1)–Co(1)–Co(2)	87.50(4)	P(2)–Co(2)–Co(1)	87.45(4)
Co(1)–P(1)–P(2)	92.03(6)	Co(2)–P(2)–P(1)	92.43(6)
O(11)–C(11)–C(12)	112.2(4)	C(13)–C(12)–C(11)	133.6(4)
C(12)–C(13)–C(14)	139.7(4)	C(15)–C(14)–C(13)	142.0(4)
C(14)–C(15)–C(16)	140.5(4)	O(16)–C(16)–C(15)	109.4(4)

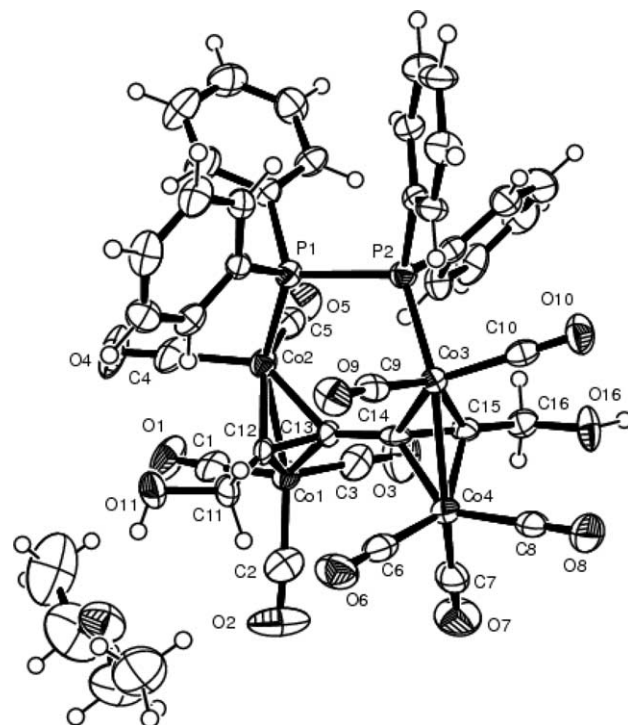


Fig. 2. ORTEP diagram of $[\{\text{Co}_2(\text{CO})_5\}_2(\mu\text{-P}_2\text{Ph}_4)(\mu\text{-}\eta^2\text{-}\mu\text{-}\eta^2\text{-HOCH}_2\text{C}\equiv\text{C}-\text{C}\equiv\text{CCH}_2\text{OH})]$ (**2**), showing thermal ellipsoids at the 50% probability level.

occupy pseudoequatorial positions and the Co–P–P–Co ring is nearly planar (C(23)–P(1)–P(2)–C(35) torsion angle = 3.4°) and close to square. The P–P bond length, 2.2651(18) Å, is also similar to that observed in $[\text{Co}_2(\mu\text{-P}_2\text{Ph}_4)\{\mu\text{-}\eta^2\text{-C}_2(\text{CO}_2\text{Me})_2\}(\text{CO})_4]$, 2.254(2) Å. The “*cis*” orientation of the CH₂OH substituents is illustrated by the C(12)–C(13)–C(14)–C(15) torsion angle of 27.5°. A “*cis*” orientation was also observed for $[\{\text{Co}_2(\text{CO})_6\}_2(\mu\text{-}\eta^2\text{-}\mu\text{-}\eta^2\text{-HOCH}_2\text{C}\equiv\text{C}-\text{C}\equiv\text{CCH}_2\text{OH})]$ [45]. This “*cis*” orientation brings the two OH groups into close proximity, an observation that may be relevant here to the subsequent formation of **3** from **1** by dehydration–decarbonylation upon thermolysis.

2.3. Crystal structure of (2)

The structure of **2** as its ether solvate is displayed in Fig. 2, and selected bond distances and angles are presented in Table 2. The $\mu\text{-P}_2\text{Ph}_4$ ligand bridges two non-bonded cobalt atoms via pseudoaxial substitution of CO ligands from different $\text{Co}_2(\text{alkyne})(\text{CO})_6$ units. This coordination mode has not been previously observed for a bridging ligand at a *bis* dicobalt-complexed diyne center. The P–P bond length in **2**, 2.283(2) Å, is longer than that observed in **1**. The Ph substituents of the $\mu\text{-P}_2\text{Ph}_4$ ligand are staggered-*gauche*, resulting in a non-planar Co–P–P–Co arrangement (Co(2)–P(1)–P(2)–Co(3) torsion angle = 47.5°). This contrasts with

Table 2
Selected bond distances (Å) and angles (°) for complex **2**

Co(1)–Co(2)	2.4636(10)	Co(3)–Co(4)	2.4787(10)
Co(1)–C(13)	1.984(6)	Co(1)–C(12)	1.999(6)
Co(2)–C(12)	1.934(7)	Co(2)–C(13)	1.968(6)
Co(2)–P(1)	2.2219(16)	Co(3)–C(15)	1.945(6)
Co(3)–C(14)	1.979(6)	Co(3)–P(2)	2.1942(16)
Co(4)–C(15)	1.971(6)	Co(4)–C(14)	2.019(7)
P(1)–P(2)	2.283(2)	O(11)–C(11)	1.413(7)
C(11)–C(12)	1.484(9)	C(12)–C(13)	1.319(9)
C(13)–C(14)	1.431(10)	C(14)–C(15)	1.342(9)
C(15)–C(16)	1.484(9)	O(16)–C(16)	1.426(7)
P(1)–Co(2)–Co(1)	152.02(6)	P(2)–Co(3)–Co(4)	150.44(6)
Co(2)–P(1)–P(2)	113.46(8)	Co(3)–P(2)–P(1)	110.99(8)
O(11)–C(11)–C(12)	113.7(5)	C(13)–C(12)–C(11)	135.7(6)
C(12)–C(13)–C(14)	137.9(6)	C(15)–C(14)–C(13)	151.5(6)
C(14)–C(15)–C(16)	143.6(6)	O(16)–C(16)–C(15)	110.4(5)

the structure of **1** and of $[\text{Co}_2(\mu\text{-P}_2\text{Ph}_4)\{\mu\text{-}\eta^2\text{-C}_2(\text{CO}_2\text{Me})_2\}(\text{CO})_4]$ in which the Co–P–P–Co atoms are planar and the Ph rings are eclipsed. Fully eclipsed, fully staggered and intermediate conformations of P_2Ph_4 ligands have been reported at different metal centers [1,46–54]. Comparison of the structures of **1** and **2** therefore clearly confirms that the P_2Ph_4 ligand is flexible enough to be able to adopt a range of M–P–P–M torsion angles when bridging two atoms of the same metal. Also, in contrast to complex **1**, the diyne ligand in **2** lies in a “trans” configuration with a C(12)–C(13)–C(14)–C(15) torsion angle of 169.7°. Both “cis” and “trans” configurations have been previously reported. To date “cis” complexes [45–55] have been exclusively observed when heteroatoms are present in the β -position and “trans” complexes [31,56–58] when carbon atoms are present in the β -position. The diyne ligand is displaced towards the phosphorus-bonded cobalt atoms, Co(2) and Co(3). Thus, inspection of the Co–C_{diyne} distances shows that C(12) and C(13) lie, respectively, 0.065 and 0.016 Å closer to Co(2) than to Co(1). Likewise, C(14) and C(15) lie, respectively, 0.040 and 0.026 Å closer to Co(3) than to Co(4). It is known that monodentate phosphine ligands prefer the pseudoaxial sites of alkyne dicobalt carbonyl complexes; X-ray structures of both monosubstituted [4,59–64] and disubstituted [65–67] phosphine complexes confirm this. All previous X-ray structures of diphosphine-bridged alkyne dicobalt complexes have, however, exhibited pseudoequatorial substitution [5,56,68–79].

2.4. Crystal structure of (**3**)

The structure of **3** is shown in Fig. 3. Table 3 lists selected bond lengths and angles. The structure consists of a cluster core of four cobalt atoms arranged as a spiked-triangle, coordinated by a 9-electron donor bridging ligand consisting of a 2(5H)-furanone ring substituted at C(13) by a phosphino group and at C(12) by a

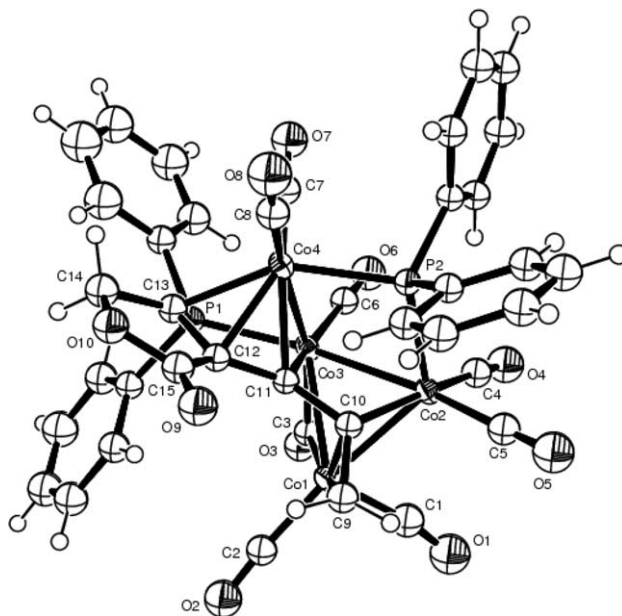


Fig. 3. ORTEP diagram of $[\text{Co}_4\{\mu_4\text{-CH}_2\text{=CC=C}(\text{PPh}_2)\text{CH}_2\text{OCO}\}(\mu_2\text{-PPh}_2)(\mu_2\text{-CO})(\text{CO})_7]$ (**3**), showing thermal ellipsoids at the 50% probability level.

Table 3
Selected bond distances (Å) and angles (°) for complex **3**

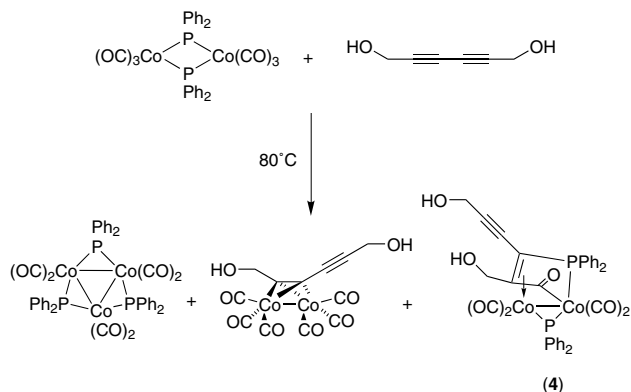
Co(1)–Co(2)	2.4847(4)	Co(1)–Co(3)	2.5234(5)
Co(2)–Co(3)	2.5777(4)	Co(3)–Co(4)	2.5520(5)
Co(2)–P(2)	2.2461(7)	Co(4)–P(2)	2.2676(7)
Co(3)–P(1)	2.2395(7)	Co(1)–C(1)	1.778(3)
Co(1)–C(2)	1.796(3)	Co(1)–C(3)	1.907(2)
Co(2)–C(4)	1.807(3)	Co(2)–C(5)	1.797(3)
Co(3)–C(3)	1.923(3)	Co(3)–C(6)	1.782(3)
Co(4)–C(7)	1.797(3)	Co(4)–C(8)	1.790(3)
Co(1)–C(9)	2.241(3)	Co(1)–C(10)	1.972(2)
Co(2)–C(10)	1.945(2)	Co(3)–C(11)	1.945(2)
Co(4)–C(11)	2.074(2)	Co(4)–C(12)	2.036(2)
Co(4)–C(13)	2.142(2)	P(1)–C(13)	1.806(3)
C(9)–C(10)	1.377(3)	C(10)–C(11)	1.441(3)
C(11)–C(12)	1.410(4)	C(12)–C(13)	1.417(4)
C(12)–C(15)	1.485(3)	C(13)–C(14)	1.509(4)
O(9)–C(15)	1.203(3)		
Co(2)–Co(1)–Co(3)	61.95(2)	Co(1)–Co(2)–Co(3)	59.76(1)
Co(1)–Co(3)–Co(2)	58.29(1)	Co(1)–Co(3)–Co(4)	112.43(2)
Co(4)–Co(3)–Co(2)	89.20(2)	C(13)–P(1)–Co(3)	95.01(8)
Co(2)–P(2)–Co(4)	105.88(3)	Co(1)–C(3)–Co(3)	82.43(10)
O(1)–C(1)–Co(1)	169.3(3)	O(2)–C(2)–Co(1)	175.2(3)
O(3)–C(3)–Co(1)	140.0(2)	O(3)–C(3)–Co(3)	137.6(2)
O(4)–C(4)–Co(2)	176.9(3)	O(5)–C(5)–Co(2)	176.9(3)
O(6)–C(6)–Co(3)	178.4(3)	O(7)–C(7)–Co(4)	174.0(3)
O(8)–C(8)–Co(4)	176.8(3)	C(9)–C(10)–C(11)	123.9(2)
C(9)–C(10)–Co(2)	125.9(2)	Co(2)–C(10)–Co(1)	78.75(9)
C(15)–O(10)–C(14)	111.1(2)	C(12)–C(11)–C(10)	135.2(2)
Co(3)–C(11)–Co(4)	78.75(8)	C(11)–C(12)–C(13)	117.5(2)
C(11)–C(12)–C(15)	133.3(2)	C(13)–C(12)–C(15)	108.8(2)
C(12)–C(13)–C(14)	106.2(2)	C(12)–C(13)–P(1)	112.9(2)
C(14)–C(13)–P(1)	133.5(2)	O(10)–C(14)–C(13)	105.5(2)
O(9)–C(15)–O(10)	122.3(3)	O(9)–C(15)–C(12)	129.6(3)
O(10)–C(15)–C(12)	108.1(2)		

CCCH₂ group. There are seven carbonyl ligands in terminal positions, two bonded to each of Co(1), Co(2) and Co(4), and one bonded to Co(3). The remaining carbonyl bridges the Co(1)–Co(3) bond. Although **3** obeys the 18 electron rule overall, Co(4) is electron-rich and Co(2) electron-poor. This is reflected in the slight asymmetry of the Co–P_{phosphido}–Co bridge. The Co(2)–P(2) bond distance, 2.2461(7) Å, is thus shorter than the Co(4)–P(2) distance, 2.2676(7) Å, and the Co(2)–P(2)–Co(4) bond angle is 105.88(3)°. The Co(1)–Co(2)–Co(3) triangle is not equilateral with the Co(2)–Co(3) bond, 2.5777(4) Å, being longer than the Co(1)–Co(2) and Co(1)–Co(3) bonds (2.4847(4) and 2.5234(5) Å, respectively). The vinyl bond length of 1.377(3) Å is similar to those observed for other μ-vinyl ligands [25–28,80,81]. Diyne functionalization by the phosphino group has taken place at one of the two outer diyne carbons as in the reaction of [$\{\text{Co}_2(\text{CO})_6\}_2(\mu-\eta^2:\mu-\eta^2\text{-PhC}\equiv\text{C}-\text{C}\equiv\text{CPh})$] with bma [3].

In light of the long P–P bond in **2**, an attempt was made to induce P–P cleavage in this molecule by further thermolysis. Refluxing a solution of **2** in toluene, however, led only to extensive decomposition. Decomposition of other phosphine-substituted alkyne cobalt carbonyl complexes tends to be fast at these temperatures. Thus, unlike in the thermolysis of [$\text{Co}_2(\mu\text{-P}_2\text{Ph}_4)(\mu-\eta^2\text{-RC}\equiv\text{CR})(\text{CO})_4$], alkyne insertion into the Ph₂P–PPh₂ bond of **2** is not observed. This may be due to the inherent rigidity of the core of complex **2** not allowing the phosphorus and alkyne carbon atoms to come into close enough proximity to couple. The fact that the P₂Ph₄ ligand occupies a pseudoaxial position in **2** rather than the pseudoequatorial positions it occupies in **1** and [$\text{Co}_2(\mu\text{-P}_2\text{Ph}_4)(\mu-\eta^2\text{-RC}\equiv\text{CR})(\text{CO})_4$] may also be significant.

2.5. Reaction of [$\text{Co}_2(\mu\text{-PPh}_2)_2(\text{CO})_6$] with HOCH₂C≡C–C≡CCH₂OH

Reaction of [$\text{Co}_2(\mu\text{-PPh}_2)_2(\text{CO})_6$] with HOCH₂C≡C–C≡CCH₂OH at 80 °C in toluene produced a range



Scheme 3.

of products (Scheme 3), in moderate yields (see Section 4): Unreacted [$\text{Co}_2(\mu\text{-PPh}_2)_2(\text{CO})_6$], [**13**] [$\text{Co}_3(\mu\text{-PPh}_2)_3(\text{CO})_6$], [**13**] [$\text{Co}_2(\text{CO})_6(\mu-\eta^2\text{-HOCH}_2\text{C}\equiv\text{C}-\text{CCCH}_2\text{OH})$] [**32**] and [$\text{Co}_2\{\mu-\eta^4\text{-PPh}_2\text{C}(\text{CCCH}_2\text{OH})\text{C}(\text{CH}_2\text{OH})\text{CO}\}(\mu\text{-PPh}_2)(\text{CO})_4$] (**4**) were isolated. The identity of these complexes (except **4**) was confirmed by comparison of their ¹H, ³¹P NMR and IR spectra with the literature values. The formula of complex **4** was assigned on the basis that its spectroscopic properties are closely similar to those of [$\text{Co}_2(\mu-\eta^4\text{-PPh}_2\text{CR}^1\text{CR}^2\text{CO})(\mu\text{-PPh}_2)(\text{CO})_4$] (R¹ = R² = H, CO₂Me; R¹ = H, R² = Ph, SiMe₃, Me, CH₂OH) [1,2]. In addition, the regiochemistry of **4** was established by a single crystal X-ray diffraction study.

2.6. Crystal structure of (4)

The structure of **4** is displayed in Fig. 4, and selected bond distances and angles are presented in Table 4. The molecular structure of **4** is similar to that of [$\text{Co}_2(\mu-\eta^4\text{-PPh}_2\text{CHCPhCO})(\mu\text{-PPh}_2)(\text{CO})_4$], reported by us [1]. One difference is that the diphenylphosphido ligand bridges the Co–Co bond symmetrically in **4**. In [$\text{Co}_2(\mu-\eta^4\text{-PPh}_2\text{CHCPhCO})(\mu\text{-PPh}_2)(\text{CO})_4$], a slight asymmetry of the Co–P_{phosphido} bonds presumably compensates for the formally uneven electron distribution over

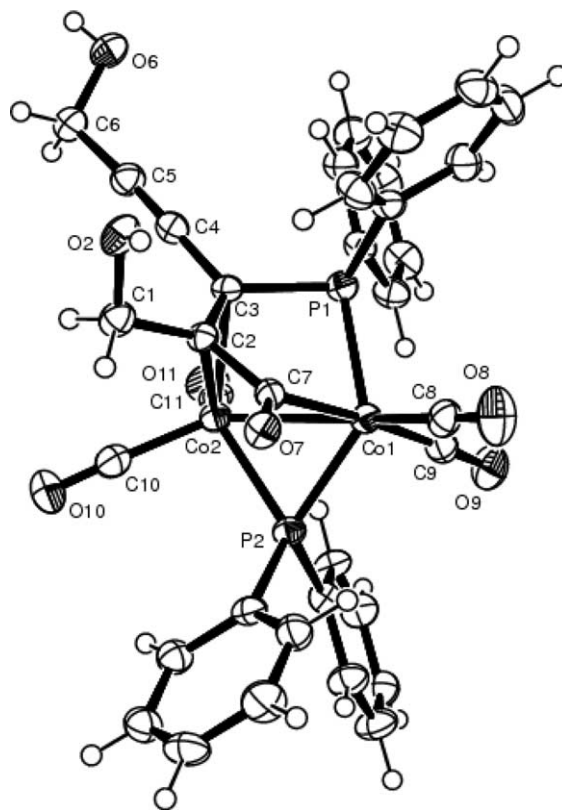


Fig. 4. ORTEP diagram of [$\text{Co}_2\{\mu-\eta^4\text{-PPh}_2\text{C}(\text{CCCH}_2\text{OH})\text{C}(\text{CH}_2\text{OH})\text{CO}\}(\mu\text{-PPh}_2)(\text{CO})_4$] (**4**), showing thermal ellipsoids at the 50% probability level.

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

Co(1)–Co(2)	2.5305(6)	Co(1)–P(1)	2.1943(9)
Co(1)–P(2)	2.1916(9)	Co(2)–P(2)	2.1921(9)
Co(2)–C(2)	2.071(3)	Co(2)–C(3)	2.110(3)
Co(1)–C(7)	2.008(3)	Co(1)–C(8)	1.796(4)
Co(1)–C(9)	1.814(4)	Co(2)–C(10)	1.772(3)
Co(2)–C(11)	1.799(4)	P(1)–C(3)	1.817(3)
C(1)–O(2)	1.426(4)	C(1)–C(2)	1.507(4)
C(2)–C(3)	1.417(4)	C(2)–C(7)	1.467(4)
C(3)–C(4)	1.431(4)	C(4)–C(5)	1.189(4)
C(5)–C(6)	1.473(5)	O(6)–C(6)	1.395(4)
O(7)–C(7)	1.238(3)	O(8)–C(8)	1.133(4)
O(9)–C(9)	1.131(4)	O(10)–C(10)	1.141(4)
O(11)–C(11)	1.138(4)		
P(1)–Co(1)–Co(2)	75.37(3)	P(2)–Co(1)–Co(2)	54.75(2)
P(2)–Co(2)–Co(1)	54.73(2)	C(3)–P(1)–Co(1)	96.54(10)
Co(1)–P(2)–Co(2)	70.51(3)	C(3)–C(2)–C(7)	116.5(3)
C(3)–C(2)–C(1)	121.5(3)	C(7)–C(2)–C(1)	120.8(3)
C(2)–C(3)–C(4)	121.9(3)	C(2)–C(3)–P(1)	110.7(2)
C(4)–C(3)–P(1)	123.7(2)	C(5)–C(4)–C(3)	178.2(4)
C(4)–C(5)–C(6)	176.8(4)	O(7)–C(7)–C(2)	122.2(3)
O(7)–C(7)–Co(1)	124.1(2)	C(2)–C(7)–Co(1)	113.5(2)
O(8)–C(8)–Co(1)	178.3(3)	O(9)–C(9)–Co(1)	174.8(3)
O(10)–C(10)–Co(2)	177.9(3)	O(11)–C(11)–Co(2)	172.5(3)

the two Co atoms. The two cobalt and two phosphorus atoms are close to co-planar, with a P(1)–Co(1)–Co(2)–P(2) torsion angle of 169.3°. The structure confirms that phosphido-diyne coupling has occurred regioselectively, such that the carbon bearing the free diyne substituent, C≡CCH₂OH is adjacent to the phosphido group. Similar regioselectivity was observed in the reaction of bma with [$\{\text{Co}_2(\text{CO})_6\}_2(\mu\text{-}\eta^2\text{:}\mu\text{-}\eta^2\text{-PhC}\equiv\text{CC}\equiv\text{CPh})$] [3]. Regioselectivity has previously been observed in the reaction of unsymmetrical alkynes with [$\text{Co}_2(\mu\text{-PPh}_2)_2(\text{CO})_6$] and has been rationalized on the basis of the steric demands of the substituents. Of particular note is that HC≡CCH₂OH reacted with [$\text{Co}_2(\mu\text{-PPh}_2)_2(\text{CO})_6$] to give exclusively [$\text{Co}_2\{\mu\text{-}\eta^4\text{-PPh}_2\text{CHC}(\text{CH}_2\text{OH})\text{CO}\}\{\mu\text{-PPh}_2\}(\text{CO})_4$] [2]. Thus, the observation that **4** is formed regioselectively indicates that the CH₂OH group is more sterically demanding than C≡CCH₂OH. The relatively modest yield of **4** can also be attributed to steric factors. It has previously been noted that bulky internal alkynes, when reacted with [$\text{Co}_2(\mu\text{-PPh}_2)_2(\text{CO})_6$], gave lower yields of [$\text{Co}_2\{\mu\text{-}\eta^4\text{-PPh}_2\text{CRCRCO}\}\{\mu\text{-PPh}_2\}(\text{CO})_4$] than less bulky internal and terminal alkynes [2,6]. [$\text{Co}_3(\mu\text{-PPh}_2)_3(\text{CO})_6$] is known to be produced during the thermolysis of [$\text{Co}_2(\mu\text{-PPh}_2)_2(\text{CO})_6$] under N₂, and therefore, its formation here is not surprising [13]. The production of [$\text{Co}_2(\text{CO})_6(\mu\text{-}\eta^2\text{-HOCH}_2\text{C}\equiv\text{C}\text{-CCCH}_2\text{OH})$], however, involving complete loss of the cobalt-bonded phosphido ligands, was more unexpected. Related processes are known; for example, alkynes have been reported to cause phosphido loss, reacting with [$\text{Co}(\mu\text{-H})(\mu\text{-PPh}_2)(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)(\text{CO})_4$] to yield [$\text{Co}_2(\mu\text{-alkyne})(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)(\text{CO})_4$] [7].

3. Conclusions

It is clear that the reactions of diynes with phosphido-bridged cobalt carbonyl complexes and the reaction of biphosphines with diyne-bridged cobalt carbonyl complexes are more complicated than the corresponding monoynone reactions. With the monoynone systems many of the same complexes are obtained in both types of reaction. This is not the case with the diyne chemistry described here. Reaction of [$\{\text{Co}_2(\text{CO})_6\}_2(\mu\text{-}\eta^2\text{:}\mu\text{-}\eta^2\text{-diyne})$] with P₂Ph₄ initially follows a similar pathway to that of [$\text{Co}_2(\text{CO})_6(\mu\text{-alkyne})$]. In both cases, $\mu\text{-P}_2\text{Ph}_4$ complexes can be isolated. Complexes **2** and **3**, however, formed on thermolysis of the $\mu\text{-P}_2\text{Ph}_4$ substituted complex **1**, do not have analogues in monoynone chemistry. Complex **2** is isomeric with **1**, whereas complex **3** arises from **1** by dehydration–cyclocarbonylation of the cobalt-complexed diyne–diol, accompanied by coupling of a phosphido group derived from the $\mu\text{-P}_2\text{Ph}_4$ ligand. A study of the reaction of [$\text{Co}_2(\mu\text{-PPh}_2)_2(\text{CO})_6$] with the 2,4-hexadiyne-1,6-diol showed some similarities as well as some differences as compared to the previously studied reactions of [$\text{Co}_2(\mu\text{-PPh}_2)_2(\text{CO})_6$] with monoynes [2,6]. As in the reaction with monoynes a 5-membered ring complex, **4**, was formed, though in lower yield; phosphido loss, however, was also observed yielding [$\text{Co}_2(\text{CO})_6(\mu\text{-}\eta^2\text{-HOCH}_2\text{C}\equiv\text{C}\text{-CCCH}_2\text{OH})$].

4. Experimental

4.1. General procedures

All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Solvents were freshly distilled from the appropriate drying agent. NMR spectra were recorded in CDCl₃ using a Bruker DRX 400, 500 CryoProbe and AV 700 spectrometers with TMS as an external standard for the ¹H and ¹³C NMR spectra. The quoted ³¹P NMR data are referenced to external 85% H₃PO₄ with downfield shifts positive. Infrared spectra were recorded in dichloromethane solution in 0.5 mm NaCl solution cells, using a Perkin–Elmer 1710 Fourier Transform spectrometer. Low resolution FAB mass spectra were obtained using a Kratos MS 890 instrument, using 3-nitrobenzyl alcohol as a matrix. High resolution FAB mass spectra were obtained using a Bruker Daltonics, Apex III instrument and Apollo ESI source. Samples were run as NaCl adducts using methanol/dichloromethane 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). Elemental analyses were performed at Cambridge. Unless otherwise stated, all reagents were obtained from commercial suppliers and used without

further purification. [$\{\text{Co}_2(\text{CO})_6\}_2(\mu\text{-}\eta^2\text{:}\mu\text{-}\eta^2\text{-HOCH}_2\text{C}\equiv\text{C}\text{-C}\equiv\text{CCH}_2\text{OH})$] was prepared by the literature method [32,82]. [$\text{Co}_2(\mu\text{-PPh}_2)_2(\text{CO})_6$] was generated in situ from [$\text{Co}_2(\text{CO})_8$] and PPh_2H using our previously reported modification of Geoffroy's procedure [2,13].

4.2. Reaction of [$\{\text{Co}_2(\text{CO})_6\}_2\{\mu\text{-}\eta^2\text{:}\mu\text{-}\eta^2\text{-HOCH}_2\text{C}\equiv\text{C}\text{-C}\equiv\text{CCH}_2\text{OH}\}$] with P_2Ph_4

2.26 g (3.31 mmol) of [$\{\text{Co}_2(\text{CO})_6\}_2(\mu\text{-}\eta^2\text{:}\mu\text{-}\eta^2\text{-HOCH}_2\text{C}\equiv\text{C}\text{-C}\equiv\text{CCH}_2\text{OH})$] and 1.23 g (3.32 mmol) of P_2Ph_4 were dissolved in 120 mL of toluene in a three-necked round bottomed flask. The mixture was heated at 65 °C for 2 h and monitored by spot TLC. The solution was then cooled and the solvent was removed on a rotary evaporator. The residue was dissolved in the minimum quantity of ethyl acetate and adsorbed on to silica. The silica was pumped dry and added to the top of a chromatography column. Elution with ethyl acetate/hexane (1:4) gave 0.47 g of unreacted [$\{\text{Co}_2(\text{CO})_6\}_2(\mu\text{-}\eta^2\text{:}\mu\text{-}\eta^2\text{-HOCH}_2\text{C}\equiv\text{C}\text{-C}\equiv\text{CCH}_2\text{OH})$]. Further elution with ethyl acetate/hexane (1:3) gave 1.22 g (yield 47%, conversion 80%) of grey [$\{\text{Co}_2(\mu\text{-P}_2\text{Ph}_4)(\text{CO})_4\}\{\text{Co}_2(\text{CO})_6\}\{\mu\text{-}\eta^2\text{:}\mu\text{-}\eta^2\text{-HOCH}_2\text{C}\equiv\text{C}\text{-C}\equiv\text{CCH}_2\text{OH}\}$] (**1**). Complex **1**: Anal. Calc. for $\text{C}_{40}\text{H}_{26}\text{Co}_4\text{O}_{12}\text{P}_2$ (**1**): C, 48.19; H, 2.61. Found: C, 47.46; H, 2.80%. FAB MS (*m/e*): 996 (M^+) and $\text{M}^+ - n\text{CO}$ ($n = 3\text{--}10$). HRMS calculated for $\text{C}_{39}\text{H}_{24}\text{Co}_4\text{NaO}_{10}\text{P}_2$ ($\text{M}^+ + \text{Na}$) 1018.8120, found 1018.8170. IR (CH_2Cl_2) 2085 (s), 2050 (vs), 2022 (vs), 1995 (m, sh), 1968 (m) cm^{-1} . NMR: ^1H (CDCl_3) δ 7.4–7.0 (m, 20H, Ph), 5.1–4.9 (m, 4H, CH_2), 1.6 (m, 2H, OH); ^{13}C (CDCl_3) δ 204.9, 204.1, 199.4, 198.6 (br, CO's), 134–128 (m, Ph), 102.4, 95.0, 87.2, 83.6 (s, C \equiv), 64.4, 64.0 (s, CH_2); ^{31}P (CDCl_3) δ 7.2 (s, $\mu\text{-P}_2\text{Ph}_4$).

4.3. Thermolysis of [$\{\text{Co}_2(\mu\text{-P}_2\text{Ph}_4)(\text{CO})_4\}\{\text{Co}_2(\text{CO})_6\}\{\mu\text{-}\eta^2\text{:}\mu\text{-}\eta^2\text{-HOCH}_2\text{C}\equiv\text{C}\text{-C}\equiv\text{CCH}_2\text{OH}\}$]

0.60 g (0.60 mmol) of (**1**) was dissolved in 70 mL of toluene and heated at 95 °C for 2.5 h. The mixture was cooled and the solvent removed. The residue was dissolved in the minimum of ethyl acetate and separated by preparative TLC. Elution with ethyl acetate/hexane (1:3) gave 0.13 g (yield 21%) of black [$\text{Co}_4\{\mu_4\text{-CH}_2\text{=C}\equiv\text{C}(\text{PPh}_2)\text{CH}_2\text{OCO}\}$] (**3**) and 0.14 g (yield 23%) of brown [$\{\text{Co}_2(\text{CO})_5\}_2(\mu\text{-P}_2\text{Ph}_4)(\mu\text{-}\eta^2\text{:}\mu\text{-}\eta^2\text{-HOCH}_2\text{C}\equiv\text{C}\text{-C}\equiv\text{CCH}_2\text{OH})$] (**2**). Complex **2**: Anal. Calc. for $\text{C}_{44}\text{H}_{36}\text{Co}_4\text{O}_{13}\text{P}_2$ (**2**): Et_2O : C, 49.37; H, 3.39. Found: C, 49.36; H, 3.39%. FAB MS (*m/e*): 996 (M^+) and $\text{M}^+ - n\text{CO}$ ($n = 1\text{--}10$). IR (CH_2Cl_2) 2067 (m), 2052 (s), 2018 (sh), 2008 (s), 1968 (w) cm^{-1} . NMR: ^1H (CDCl_3) δ 7.5–7.2 (m, 20H, Ph), 4.6–4.3 (m, 4H, CH_2), 1.6 (m, 2H, OH); ^{13}C (CDCl_3) δ 205.0, 203.8, 200.4 (s, CO's), 134–128 (m, Ph), 101.4, 80.0 (s,

C \equiv), 63.7 (s, CH_2); ^{31}P (CDCl_3) δ 93.3 (s, $\mu\text{-P}_2\text{Ph}_4$). Complex **3**: FAB MS (*m/e*): 950 (M^+) and $\text{M}^+ - n\text{CO}$ ($n = 1\text{--}8$). HRMS calculated for $\text{C}_{39}\text{H}_{24}\text{Co}_4\text{NaO}_{10}\text{P}_2$ ($\text{M}^+ + \text{Na}$) 972.8065, found 972.8157. IR (CH_2Cl_2) 2056 (m), 2029 (s), 2012 (vs), 1824 (br), 1761 (br) cm^{-1} . NMR: ^1H (CDCl_3) δ 7.8–6.9 (m, 20H, Ph), 4.51 (d, $^3J_{\text{PH}} = 4.7$ Hz, 1H, =CHH), 4.32 (m, $^2J_{\text{HH}} = 14$ Hz, 1H, CHH), 4.18 (m, $^2J_{\text{HH}} = 14$ Hz, 1H, CHH), 3.54 (d, $^3J_{\text{PH}} = 3.9$ Hz, 1H, =CHH); ^{31}P (CDCl_3) δ 81.9 ($\mu\text{-PPh}_2\text{CR}=\text{C}$), 7.1 ($\mu\text{-PPh}_2$).

4.4. Reaction of [$\text{Co}_2(\mu\text{-PPh}_2)_2(\text{CO})_6$] with $\text{HOCH}_2\text{C}\equiv\text{C}\text{-C}\equiv\text{CCH}_2\text{OH}$

A solution of 1.60 g (2.25 mmol) of [$\text{Co}_2(\mu\text{-PPh}_2)_2(\text{CO})_6$] in 30 mL of toluene was heated with 0.25 g (2.25 mmol) of $\text{HOCH}_2\text{C}\equiv\text{C}\text{-C}\equiv\text{CCH}_2\text{OH}$ at 80 °C for 1 h. The solution was cooled and the solvent removed. The residue was dissolved in the minimum of ethyl acetate and separated by preparative TLC. Elution with ethyl acetate/hexane (1:2) gave 0.11 g of orange [$\text{Co}_2(\mu\text{-PPh}_2)_2(\text{CO})_6$], 0.10 g (yield 7%) of green [$\text{Co}_3(\mu\text{-PPh}_2)_3(\text{CO})_6$], 0.02 g (yield 2%) of red [$\text{Co}_2(\text{CO})_6(\mu\text{-}\eta^2\text{-HOCH}_2\text{C}\equiv\text{C}\text{-CCCH}_2\text{OH})$], 0.12 g (yield 7%) of dark orange [$\text{Co}_2\{\mu\text{-}\eta^4\text{-PPh}_2\text{C}(\text{CCCH}_2\text{OH})\text{C}(\text{CH}_2\text{OH})\text{CO}\}\{\mu\text{-PPh}_2(\text{CO})_4\}$] (**4**). A number of other minor bands were observed but not isolated. Complex **4**: FAB MS (*m/e*): 738 (M^+) and $\text{M}^+ - n\text{CO}$ ($n = 1\text{--}5$). HRMS calculated for $\text{C}_{35}\text{H}_{26}\text{Co}_2\text{NaO}_7\text{P}_2$ ($\text{M}^+ + \text{Na}$) 760.9709, found 760.9775. IR (CH_2Cl_2) 2052 (m), 2022 (s), 1982 (m), 1610 (w, br) cm^{-1} . NMR: ^1H (CDCl_3) δ 8.33–7.20 (m, 20H, Ph), 4.38 (d, $^3J_{\text{HH}} = 6$ Hz, 2H, C $\equiv\text{CCH}_2\text{OH}$), 3.60 (d, $^3J_{\text{HH}} = 7$ Hz, 2H, PCCH_2OH), 2.29 (t, 1H, PCCH_2OH), 1.86 (t, 1H, C $\equiv\text{CCH}_2\text{OH}$); ^{13}C (CDCl_3) δ 220.3 (s, CCO), 206.1 (s, 1CO), 203.3 (s, 1CO), 200.5 (s, 2CO) 142–128 (m, Ph), 89.2 (s, C \equiv), 87.8 (d, $^2J_{\text{CP}} = 33$ Hz, $\text{PC}=\text{CCO}$), 84.5 (s, C \equiv), 62.3 (s, PCCH_2OH), 51.8 (s, C $\equiv\text{CCH}_2\text{OH}$), 40.8 (dd, $^1J_{\text{CP}} = 38$ Hz, $^2J_{\text{CP}} = 8$ Hz, $\text{PC}=\text{CCO}$); ^{31}P (CDCl_3) δ 163.2 (br, $\mu\text{-PPh}_2$), 55.3 (br, $\mu\text{-PPh}_2\text{CR}=\text{CRCO}$).

4.5. X-ray crystallography

Intensity data were collected on a Nonius Kappa CCD diffractometer using Mo $\text{K}\alpha$ radiation (graphite crystal monochromator $\lambda = 0.71073$ Å) and an Oxford Cryosystems Cryostream. The structures were solved using *SIR-92* [83] and refined against all F^2 data using *SHELXL-97* [84]. Hydrogen atoms were included in calculated positions. Black blocks of **1** were grown from CH_2Cl_2 /pentane. The OH hydrogen atoms were located and refined successfully. Repeated attempts were made to grow crystals of **2** suitable for X-ray analysis from CH_2Cl_2 /pentane, but the crystals obtained did not diffract. Crystals grown by vapor diffusion of pentane into ether solution did produce fragile, crumbly brown

Table 5

Crystallographic data for $[\{\text{Co}_2(\mu\text{-P}_2\text{Ph}_4)(\text{CO})_4\}\{\text{Co}_2(\text{CO})_6\}\{\mu\text{-}\eta^2\text{-}\eta^2\text{-HOCH}_2\text{C}\equiv\text{C}\text{-C}\equiv\text{CCH}_2\text{OH}\}]$ (**1**), $[\{\text{Co}_2(\text{CO})_5\}_2(\mu\text{-P}_2\text{Ph}_4)(\mu\text{-}\eta^2\text{-}\eta^2\text{-HOCH}_2\text{C}\equiv\text{C}\text{-C}\equiv\text{CCH}_2\text{OH})]\cdot\text{Et}_2\text{O}$ (**2**), $[\text{Co}_4\{\mu_4\text{-CH}_2\text{=CC=C(C(PPH}_2\text{)CH}_2\text{OCO})\}(\mu_2\text{-PPH}_2)(\mu_2\text{-CO})(\text{CO})_7]$ (**3**) and $[\text{Co}_2\{\mu\text{-PPH}_2\text{C}(\text{CCCH}_2\text{OH})\text{C}(\text{CH}_2\text{OH})\text{CO}\}(\mu\text{-PPH}_2)(\text{CO})_4]$ (**4**).

	1	2 · Et ₂ O	3	4
Formula	C ₄₀ H ₂₆ Co ₄ O ₁₂ P ₂	C ₄₄ H ₃₆ Co ₄ O ₁₃ P ₂	C ₃₉ H ₂₄ Co ₄ O ₁₀ P ₂	C ₃₅ H ₂₆ Co ₂ O ₇ P ₂
Fw	996.27	1070.39	950.24	738.36
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	13.0354(2)	17.6615(4)	11.1304(2)	10.0494(3)
<i>b</i> (Å)	8.7724(1)	10.5836(3)	11.7000(2)	12.5260(3)
<i>c</i> (Å)	36.0487(7)	24.3700(5)	15.9757(4)	14.4778(5)
α (°)			88.110(1)	67.998(1)
β (°)	95.895(1)	92.334(2)	80.419(1)	80.891(1)
γ (°)			66.293(1)	67.751(2)
<i>V</i> (Å ³)	4100.4(1)	4551.5(2)	1876.99(7)	1563.63(8)
<i>Z</i>	4	4	2	2
ρ_{calcd} (g cm ⁻³)	1.614	1.562	1.681	1.568
<i>F</i> (0 0 0)	2000	2168	952	752
Crystal size (mm)	0.16 × 0.05 × 0.01	0.18 × 0.07 × 0.05	0.35 × 0.16 × 0.10	0.18 × 0.12 × 0.10
μ (mm ⁻¹)	1.729	1.565	1.881	1.213
Radiation (λ) (Å)	0.71073	0.71073	0.71073	0.71073
Temperature (K)	180	180	180	180
θ range (°)	3.67–25.01	3.58–17.66	3.52–27.52	3.52–27.49
Reflections collected	23,414	12,391	16,995	15,565
Independent reflections	7148	2927	8562	7101
Number of parameters	529	573	496	421
Goodness of fit	1.011	1.182	1.147	1.007
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0498	0.0276	0.0345	0.0467
<i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0772	0.0744	0.0955	0.0897

crystals. These crystals diffracted but, although analyzing exactly for carbon and hydrogen (see Section 4), resulted in poor quality data (99% complete at $2\theta = 17.5^\circ$). The OH hydrogen atoms were not located. Instead they were placed in chemically reasonable positions (with SHELXL/AFIX-83). Black blocks of **3** were grown from CH₂Cl₂/pentane. Red blocks of **4** were grown from CH₂Cl₂/pentane. Crystal data collection and refinement details are summarized in Table 5.

5. Supplementary material

Crystallographic data for the structural analyses has been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 260112, 260111, 260110 and 260113 for compounds **1**, **3** and **4**, respectively. Copies of this information may be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk or by contacting The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033.

Acknowledgements

We acknowledge the financial support of the EPSRC for the purchase of the Nonius Kappa CCD diffracto-

meter. We thank Dr. John E. Davies for determining the crystal structures of **1**, **2**, **3** and **4**. The ERSRC mass spectrometry service is thanked for collection of low resolution FAB MS data. Dr. A. Abdul-Sada at The University of Sussex, UK is thanked for collection of high resolution FAB MS data. We also thank Dr. Vladimir B. Golovko, University of Cambridge, for helpful discussions.

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