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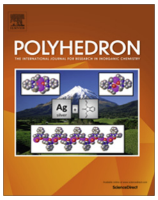

Reactions of a diacetylenic tetracobalt carbonyl complex with monophosphine triphenylphosphine or diphosphines

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ABSTRACT

Five new diacetylenic tetracobalt carbonyl complexes **2**–**6** with monophosphine or diphosphines have been prepared from the parent complex $(\mu\text{-HC}{\equiv}\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}{\equiv}\text{CH-}\mu)[\text{Co}_2(\text{CO})_6]_2$ (**1**), and their structures were fully characterized. Reaction of **1** with PPh_3 in the presence of $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ afforded $(\mu\text{-HC}{\equiv}\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}{\equiv}\text{CH-}\mu)[\text{Co}_2(\text{CO})_5(\text{PPh}_3)]_2$ (**2**) in 59% yield. Similarly, reaction of **1** with dppe ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) in the presence of $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ gave $(\mu\text{-HC}{\equiv}\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}{\equiv}\text{CH-}\mu)[\text{Co}_2(\text{CO})_5]_2(\text{dppe})$ (**3**) and $(\mu\text{-HC}{\equiv}\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}{\equiv}\text{CH-}\mu)[\text{Co}_2(\text{CO})_6][\text{Co}_2(\text{CO})_4(\text{dppe})]$ (**4**), with a bridging diphosphine ligand, in 20% and 16% yields, respectively, whereas $(\mu\text{-HC}{\equiv}\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}{\equiv}\text{CH-}\mu)[\text{Co}_2(\text{CO})_5]_2(\text{dppp})$ (dppp = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2$) (**5**) and $(\mu\text{-HC}{\equiv}\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}{\equiv}\text{CH-}\mu)[\text{Co}_2(\text{CO})_5]_2(\text{dppb})$ (dppb = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2$) (**6**) were prepared by the reactions of **1** with dppp or dppb in the presence of $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ in 29% and 36% yields, respectively. The new complexes **2**–**6** were characterized by elemental analysis, spectroscopy and, for **1**–**3** and **6**, by X-ray crystallography. It is interesting to note that the X-ray crystal structures of **3** and **6** contain 12 and 14 atom macrocycles, respectively.

1. Introduction

The well known complexes $(\mu\text{-RC}{\equiv}\text{CR}')\text{Co}_2(\text{CO})_6$ have been prepared by the reactions of $\text{Co}_2(\text{CO})_8$ with alkynes since 1950s [1]. Studies on these cobalt carbonyl complexes, $(\mu\text{-RC}{\equiv}\text{CR}')\text{Co}_2(\text{CO})_6$, have attracted a great deal of interest due to their applications in organic syntheses [2], the Pauson–Khand reaction [3], the protection of alkynes and the marking of acetylenic steroids [4]. Phosphine ligand substitution in $(\mu\text{-RC}{\equiv}\text{CR}')\text{Co}_2(\text{CO})_6$ has been extensively studied in order to synthesize new complexes containing cobalt carbonyl [5–9]. The parent complex **1** was obtained by the reaction of 1,7-octadiyne with $\text{Co}_2(\text{CO})_8$ [1]. However, substitution reactions of **1** are relatively rare in the literature. As a continuation of our previous work on carbonyl substitution reactions of the transition metal carbonyl complexes [10–13], we have initiated a study on the carbonyl substitution of **1** with a monophosphine or diphosphines and have successfully prepared a series of cobalt carbonyl complexes. In this paper, we will describe the synthesis and characterization of cobalt carbonyl derivatives containing a monophosphine or diphosphines *via* a carbonyl exchange reaction.

2. Experimental

2.1. Materials and methods

All reactions were performed using standard Schlenk and vacuum-line techniques under N_2 atmosphere. PPh_3, dppe, dppp, dppb and $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ were available commercially and used as received. CH_2Cl_2 and MeCN were distilled over CaH_2 under N_2. **1** [1] was prepared according to literature procedures. IR spectra were recorded on a Nicolet MAGNA 560 FTIR spectrometer. ^{1}H, ^{31}P anad ^{13}C NMR spectra were obtained on a Bruker Avance 500 MHz spectrometer. Elemental analyses were performed with a Perkin-Elmer 240C analyzer, while ESI-MS data were obtained on a Bruker Micro TOF Q-II instrument.

2.2. Characterization of *1*

IR (KBr disk, cm^{-1}): $\nu_{\text{C}=\text{O}}$ 2093 (vs), 2049 (vs), 2028 (vs), 2005 (vs), 1995 (vs). ^{1}H NMR (500 MHz, CDCl_3, ppm): 6.09 (s, 2H, $2\text{C}{\equiv}\text{C}H$), 2.96 (s, 4H, $2\text{CH}{\equiv}\text{CC}H_2$), 1.84 (s, 4H, $\text{CH}{\equiv}\text{CCH}_2\text{C}H_2\text{C}H_2\text{CH}_2\text{C}{\equiv}\text{CH}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3, ppm): 199.88 ($\text{C}=\text{O}$), 96.72 ($C{\equiv}\text{CH}$), 73.16 ($\text{C}{\equiv}C\text{H}$), 33.90, 31.47 (2s, CH_2).

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2.3. Synthesis of $(\mu\text{-}HC{\equiv}CCH_2CH_2CH_2CH_2C{\equiv}CH\text{-}\mu)[Co_2(CO)_5(PPh_3)]_2$ (**2**)

To a solution of **1** (0.068 g, 0.1 mmol) and PPh_3 (0.052 g, 0.2 mmol) in CH_2Cl_2 (5 mL) was added a solution of $Me_3NO{\cdot}2H_2O$ (0.022 g, 0.2 mmol) in MeCN (5 mL). The new mixture was stirred for 1 h. The solvent was reduced *in vacuo* and the residue was subjected to TLC separation using CH_2Cl_2/petroleum ether (v/v = 1:5) as the eluent. The main red band afforded 0.068 g (59%) of **2** as a red solid. *Anal.* Calc. for $C_{54}H_{40}Co_4O_{10}P_2$: C, 56.57; H, 3.52. Found: C, 56.88; H, 3.36%. IR (KBr disk, cm^{-1}): $\nu_{C{\equiv}O}$ 2054 (vs), 2000 (vs), 1953 (vs). ^1H NMR (500 MHz, $CDCl_3$, ppm): 7.50–7.29 (m, 30H, Ph*H*), 5.19 (s, 2H, $2C{\equiv}CH$), 1.84–1.76 (m, 4H, $2CH{\equiv}CCH_2$), 1.21–1.08 (m, 4H, $CH{\equiv}CCH_2CH_2CH_2CH_2C{\equiv}CH$). $^{31}P\{^1H\}$ NMR (200 MHz, $CDCl_3$, 85% H_3PO_4, ppm): 54.68 (s). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm): 206.24, 205.14, 202.30 ($C{\equiv}O$), 134.88, 134.55, 132.98, 132.90, 130.25, 128.53, 128.46 (Ph*C*), 94.53 ($C{\equiv}CH$), 71.73 ($C{\equiv}CH$), 32.10, 31.57, 29.71 (CH_2). ESI-MS: *m/z* 1145.9421 [M^+] (Calc. 1145.9425).

2.4. Synthesis of $(\mu\text{-}HC{\equiv}CCH_2CH_2CH_2CH_2C{\equiv}CH\text{-}\mu)[Co_2(CO)_5]_2(dppe)$ (**3**) and $(\mu\text{-}HC{\equiv}CCH_2CH_2CH_2CH_2C{\equiv}CH\text{-}\mu)$ $[Co_2(CO)_6][Co_2(CO)_4(dppe)]$ (**4**)

To a solution of **1** (0.068 g, 0.1 mmol) and dppe (0.040 g, 0.1 mmol) in CH_2Cl_2 (5 mL) was added a solution of $Me_3NO{\cdot}2H_2O$ (0.022 g, 0.2 mmol) in MeCN (5 mL). The new mixture was stirred for 1 h. The solvent was reduced *in vacuo* and the residue was subjected to TLC separation using CH_2Cl_2/petroleum ether (v/v = 1:3) as the eluent. The first red band afforded 0.020 g (20%) of **3** as a red solid, whilst the second red band afforded 0.016 g (16%) of **4** as a red solid. **3**: *Anal.* Calc. for $C_{44}H_{34}Co_4O_{10}P_2$: C, 51.79; H, 3.36. Found: C, 52.02; H, 3.59%. IR (KBr disk, cm^{-1}): $\nu_{C{\equiv}O}$ 2056 (vs), 1999 (vs), 1988 (vs), 1955 (vs). ^1H NMR (500 MHz, $CDCl_3$, ppm): 7.42–7.27 (m, 16H, *o*-Ph*H* and *m*-Ph*H*), 7.15–7.12 (m, 4H, *p*-Ph*H*), 4.94 (s, 2H, $2C{\equiv}CH$), 2.91–2.79 (m, 4H, $2CH{\equiv}CCH_2$), 2.24–2.19 (m, 2H, PCH_2), 2.09–2.04 (m, 2H, PCH_2), 1.87–1.71 (m, 4H, $CH{\equiv}CCH_2CH_2CH_2CH_2CCH$). $^{31}P\{^1H\}$ NMR (200 MHz, $CDCl_3$, 85% H_3PO_4, ppm): 49.46 (s). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm): 207.74, 204.67, 201.70 ($C{\equiv}O$), 136.81, 136.48, 133.68, 133.38, 133.01, 132.97, 130.59, 130.14, 129.84, 128.77 (Ph*C*), 92.63 ($C{\equiv}CH$), 73.20 ($C{\equiv}CH$), 33.01, 30.18 ($HC{\equiv}CCH_2CH_2CH_2CH_2C{\equiv}CH$), 25.64 (t, $J_{P\text{-}C}$ = 9.6 Hz, PCH_2). ESI-MS: *m/z* 1019.8929 [M^+] (Calc. 1019.8955). **4**: *Anal.* Calc. for $C_{44}H_{34}Co_4O_{10}P_2$: C, 51.79; H, 3.36. Found: C, 51.58; H, 3.54%. IR (KBr disk, cm^{-1}): $\nu_{C{\equiv}O}$ 2056 (vs), 1999 (vs), 1986 (vs), 1956 (vs). ^1H NMR (500 MHz, $CDCl_3$, ppm): 7.49–7.39 (m, 12H, *m*-Ph*H* and *p*-Ph*H*), 7.31–7.24 (m, 8H, *o*-Ph*H*), 5.42 (s, 2H, $2C{\equiv}CH$), 3.06, 3.03, 2.86, 2.83 (AB q, J_{AB} = 3.9 Hz, 4H, $2CH{\equiv}CCH_2$), 2.02 (d, *J* = 8.5 Hz, 2H, PCH_2), 1.88, 1.86 (2s, 6H, PCH_2 and $CH{\equiv}CCH_2CH_2CH_2CH_2C{\equiv}CH$). $^{31}P\{^1H\}$ NMR (200 MHz, $CDCl_3$, 85% H_3PO_4, ppm): 48.41 (s). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm): 205.60, 204.17, 201.87 ($C{\equiv}O$), 135.81, 135.49, 134.06, 133.76, 133.00, 132.96, 132.11, 132.08, 131.39, 131.35, 130.68, 130.35, 128.88, 128.84, 128.81 (Ph*C*), 91.15 ($C{\equiv}CH$), 70.56 ($C{\equiv}CH$), 33.46, 28.93 ($HC{\equiv}CCH_2CH_2CH_2CH_2CCH$), 25.41 (d, $J_{P\text{-}C}$ = 13.5 Hz, PCH_2). ESI-MS: *m/z* 1019.8949 [M^+] (calc. 1019.8955).

2.5. Synthesis of $(\mu\text{-}HC{\equiv}CCH_2CH_2CH_2CH_2C{\equiv}CH\text{-}\mu)[Co_2(CO)_5]_2(dppp)$ (**5**)

To a solution of **1** (0.068 g, 0.1 mmol) and dppp (0.041 g, 0.1 mmol) in CH_2Cl_2 (5 mL) was added a solution of $Me_3NO{\cdot}2H_2O$ (0.022 g, 0.2 mmol) in MeCN (5 mL). The new mixture was stirred for 1 h. The solvent was reduced *in vacuo* and the residue was subjected to TLC separation using CH_2Cl_2/petroleum ether (v/v = 1:3) as the eluent. The main red band afforded 0.030 g (29%) of **5** as a red solid. *Anal.* Calc. for $C_{45}H_{36}Co_4O_{10}P_2$: C, 52.25; H, 3.51. Found: C, 51.94; H, 3.27%. IR (KBr disk, cm^{-1}): $\nu_{C{\equiv}O}$ 2060 (vs), 2000 (vs), 1954 (vs). ^1H NMR (500 MHz, $CDCl_3$, ppm): 7.35–7.27 (m, 20H, Ph*H*), 5.24 (s, 2H, $2C{\equiv}CH$), 2.91–2.77 (m, 4H, $2CH{\equiv}CCH_2$), 2.19–2.14 (m, 4H, $2PCH_2$), 2.04–1.99 (m, 2H, $PCH_2CH_2CH_2P$), 1.90–1.85 (m, 4H, $CH{\equiv}CCH_2CH_2CH_2CH_2C{\equiv}CH$). $^{31}P\{^1H\}$ NMR (200 MHz, $CDCl_3$, 85% H_3PO_4, ppm): 45.40 (s). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm): 206.14, 204.31, 202.04 ($C{\equiv}O$), 137.11, 136.76, 135.45, 135.12, 131.53, 131.47, 131.45, 131.34, 131.26, 130.17, 131.01, 128.65, 128.58, 128.55 (Ph*C*), 91.98 ($C{\equiv}CH$), 71.46 ($C{\equiv}CH$), 31.97, 31.87 ($HC{\equiv}CCH_2CH_2CH_2CH_2C{\equiv}CH$), 29.72, 29.17 ($PCH_2CH_2CH_2P$). ESI-MS: *m/z* 1034.9095 [M^++H] (Calc. 1034.9190).

2.6. Synthesis of $(\mu\text{-}HC{\equiv}CCH_2CH_2CH_2CH_2C{\equiv}CH\text{-}\mu)[Co_2(CO)_5]_2(dppb)$ (**6**)

To a solution of **1** (0.068 g, 0.1 mmol) and dppb (0.043 g, 0.1 mmol) in CH_2Cl_2 (5 mL) was added a solution of $Me_3NO{\cdot}2H_2O$ (0.022 g, 0.2 mmol) in MeCN (5 mL). The new mixture was stirred for 1 h. The solvent was reduced *in vacuo* and the residue was subjected to TLC separation using CH_2Cl_2/petroleum ether (v/v = 1:3) as the eluent. The main red band afforded 0.038 g (36%) of **6** as a red solid. *Anal.* Calc. for $C_{46}H_{38}Co_4O_{10}P_2$: C, 52.70; H, 3.65. Found: C, 52.54; H, 3.89%. IR (KBr disk, cm^{-1}): $\nu_{C{\equiv}O}$ 2059 (vs), 2000 (vs), 1954 (vs). ^1H NMR (500 MHz, $CDCl_3$, ppm): 7.65, 7.42 (2s, 20H, Ph*H*), 4.71 (s, 2H, $2C{\equiv}CH$), 2.96–2.72 (m, 4H, $2CH{\equiv}CCH_2$), 2.12–2.06 (m, 8H, $PCH_2CH_2CH_2CH_2P$), 1.87 (s, 4H, $CH{\equiv}CCH_2CH_2CH_2CH_2C{\equiv}CH$). $^{31}P\{^1H\}$ NMR (200 MHz, $CDCl_3$, 85% H_3PO_4, ppm): 46.60 (s). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, ppm): 207.86, 204.20, 201.97 ($C{\equiv}O$), 133.45, 133.36, 131.84, 131.56, 130.74, 129.72, 129.52, 128.62 (Ph*C*), 91.59 ($C{\equiv}CH$), 73.72 ($C{\equiv}CH$), 33.50, 32.58 ($HC{\equiv}CCH_2CH_2CH_2CH_2C{\equiv}CH$), 30.94 (d, $J_{P\text{-}C}$ = 21.9 Hz, PCH_2), 25.62 (d, $J_{P\text{-}C}$ = 12.1 Hz, PCH_2CH_2). ESI-MS: *m/z* 1047.9249 [M^+] (Calc. 1047.9268).

2.7. X-ray structure determination

Single crystals of **1**–**3** and **6** suitable for X-ray diffraction analysis were grown by slow evaporation of CH_2Cl_2/hexane solutions at 4 °C. A single crystal of **1**–**3** or **6** was mounted on a Rigaku MM-007 CCD diffractometer. Data were collected at 113 or 293 K using a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å) in the ω-ϕ scanning mode. Data collection, reduction and absorption corrections were performed by the CRYSTALCLEAR program [14]. The structures were solved by direct methods using the SHELXS-97 program and refined by full-matrix least-squares techniques using SHELXL-97 [15] on F^2. Hydrogen atoms were located using the geometric method. Details of crystal data, data collections and structure refinement are summarized in Table 1.

3. Results and discussion

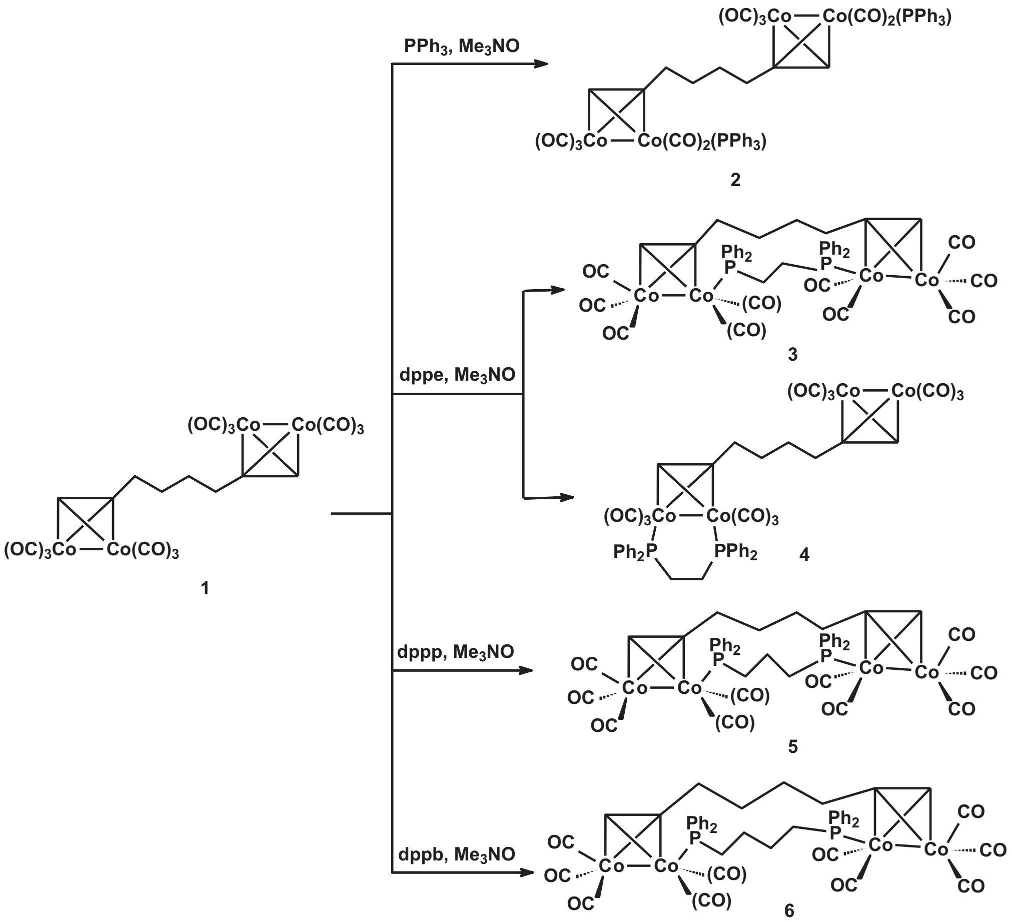
3.1. Synthesis and characterization

As shown in Scheme 1, the reactions of **1** with PPh_3, dppp or dppb in the presence of $Me_3NO{\cdot}2H_2O$ afforded **2**, **5** and **6** in 29–59% yields, respectively, whereas the reaction of **1** with dppe in the presence of $Me_3NO{\cdot}2H_2O$ resulted in the formation of **3** and **4** in 20 and 16% yields, respectively. While complex **2** contains the monophosphine PPh_3, complexes **3**–**6** contain the bridging diphosphines dppe, dppp or dppb.

The new complexes **2**–**6** are air-stable red solids, which have been characterized by elemental analysis and various spectroscopic techniques. The IR spectra of **2**–**6** displayed three to four

Table 1
Crystal data and structure refinements details for **1**–**3** and **6**.

Complex	**1**	**2**	**3**·0.25CH$_2$Cl$_2$	**6**
Empirical formula	$C_{20}H_{10}Co_4O_{12}$	$C_{27}H_{20}Co_2O_5P$	$C_{44.25}H_{34.50}Cl_{0.50}Co_4O_{10}P_2$	$C_{92}H_{76}Co_8O_{20}P_4$
Formula weight	678.00	573.26	1041.60	2096.86
Temperature (K)	113(2)	113(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2(1)/n$
a (Å)	6.857(7)	8.199(7)	9.829(2)	25.289(5)
b (Å)	7.655(7)	9.019(8)	10.983(2)	17.020(3)
c (Å)	12.584(11)	17.782(14)	23.493(5)	28.526(6)
α (°)	98.796(8)	102.896(13)	87.50(3)	90
β (°)	101.490(19)	91.200(13)	78.03(3)	115.52(3)
γ (°)	103.429(16)	100.303(10)	74.34(3)	90
V (Å^3)	615.7(10)	1258.5(17)	2388.9(8)	11 079(4)
Z	1	2	2	4
D_{calc} (g cm^{-3})	1.829	1.513	1.448	1.258
μ (mm^{-1})	2.707	1.417	1.512	1.281
F(000)	334	582	1053	4260
Crystal size (mm^3)	0.20 × 0.18 × 0.12	0.20 × 0.18 × 0.12	0.20 × 0.18 × 0.12	0.28 × 0.24 × 0.20
θ_{min}, θ_{max} (°)	1.69, 27.96	2.35, 25.02	1.77, 25.02	1.42, 25.02
Reflections collected/unique	6377/2895	10 607/4433	19 438/8350	88 916/19 527
R_{int}	0.0408	0.0638	0.0416	0.1527
hkl range	$-8 \leqslant h \leqslant 8$	$-9 \leqslant h \leqslant 9$	$-11 \leqslant h \leqslant 11$	$-30 \leqslant h \leqslant 29$
	$-10 \leqslant k \leqslant 10$	$-10 \leqslant k \leqslant 10$	$-13 \leqslant k \leqslant 13$	$-20 \leqslant k \leqslant 20$
	$-16 \leqslant l \leqslant 16$	$-18 \leqslant l \leqslant 21$	$-27 \leqslant l \leqslant 26$	$-33 \leqslant l \leqslant 30$
Completeness to θ_{max} (%)	98.2	99.8	99.2	99.7
Data/restraints/parameters	2895/0/163	4433/0/317	8350/31/569	19 527/2568/1106
Goodness of fit on F^2	1.049	1.023	1.075	1.219
$R1/wR2$ ($I > 2\sigma(I)$)	0.0289/0.0725	0.0820/0.2263	0.0551/0.1849	0.1641/0.4022
$R1/wR2$ (all data)	0.0305/0.0736	0.1096/0.2492	0.0648/0.1957	0.2881/0.4665
Largest difference in peak and hole (e Å^{-3})	0.449/−0.989	1.431/−0.994	1.409/−0.425	1.196/−0.582



Scheme 1. Preparation of complexes **2**–**6**.

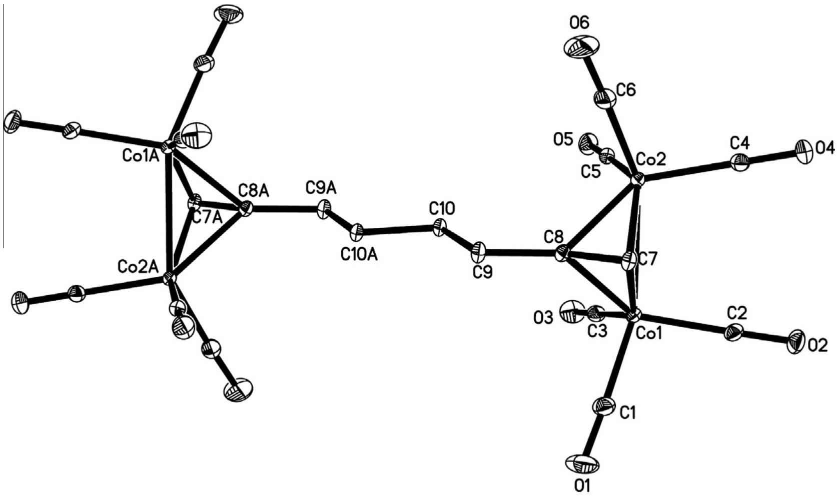


Fig. 1. ORTEP view of **1** with 30% probability level ellipsoids.

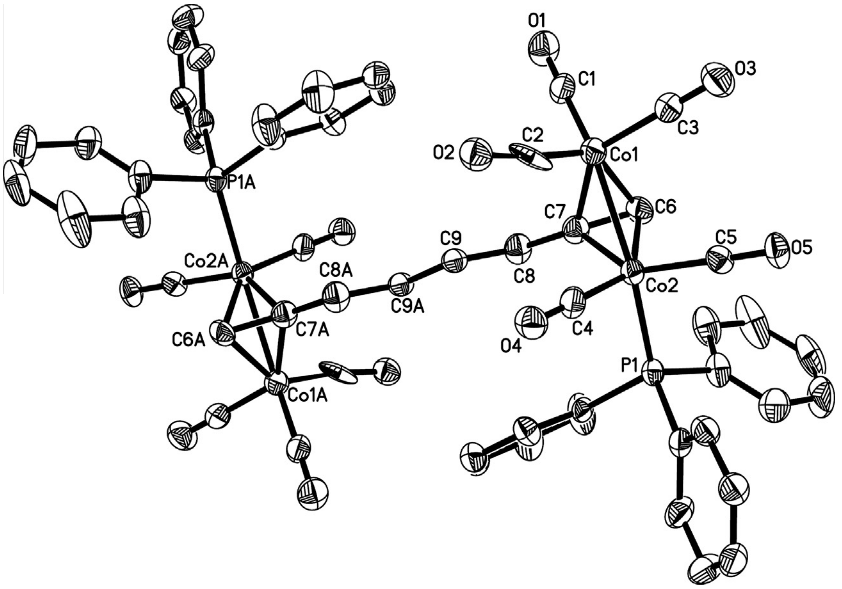


Fig. 2. ORTEP view of **2** with 30% probability level ellipsoids.

absorption bands in the region 2060–1953 cm^{-1} for their terminal carbonyls and the $\nu_{C\equiv O}$ values moved towards lower frequencies with respect to **1** (2093, 2049, 2028, 2005 and 1995 cm^{-1}) but were very close to the bands for (μ-FcC≡CH)$Co_2(CO)_5(PPh_3)$ (Fc = ferrocene) (2055, 1999 and 1963 cm^{-1}) [16]. The ^{1}H NMR spectra of **2**–**6** showed a singlet at 5.42–4.71 ppm for the acetylenic protons. The ^{31}P{^{1}H} NMR spectra of **2**–**6** exhibited a singlet at 54.68–45.40 ppm for the phosphorus atoms of PPh_3, dppe, dppp or dppb coordinated to the cobalt atoms. The ^{13}C{^{1}H} NMR spectra of **2**–**6** demonstrated three singlets at about 200 ppm for the terminal carbonyls and two singlets at about 90 and 70 ppm for the acetylenic carbons.

3.2. X-ray crystal structures

The molecular structures of **1**–**3** and **6** were determined by single crystal X-ray diffraction analysis. While ORTEP views of **1**–**3** and **6** are shown in Figs. 1–4, selected bond lengths and angles are presented in Table 2. As shown in Figs. 1 and 2, complexes **1** and **2** consist of two pseudo-tetrahedral [C_2Co_2] clusters with twelve terminal carbonyls or ten terminal carbonyls and two PPh_3 ligands, which are joined together through a zigzag chain, C8C9C10C10AC9AC8A or C7C8C9C9AC8AC7A. The molecules of **1** and **2** are centrosymmetric, with the midpoint of C10–C10A or C9–C9A as an inversion center. The Co–Co bond lengths [2.482(2) Å for **1** and 2.4602(19) Å for **2**] and the triple bond lengths [C7–C8 = 1.345(2) Å for **1** and C6–C7 = 1.341(9) Å for **2**] are comparable to the previously reported complexes $C_{20}H_8[Co_2(CO)_6]_2$ [17] and (μ-FcC≡CH)$Co_2(CO)_4$(dppm) (dppm = $Ph_2PCH_2PPh_2$) [18]. The phosphorus atom of PPh_3 in **2** resides in an apical position of the square-pyramidal coordination sphere of the cobalt atom, consistent with the crystal structure of (μ-FcC≡CH)$Co_2(CO)_5(PPh_3)$ [16].

As shown in Figs. 3 and 4, complexes **3** and **6** consist of two pseudo-tetrahedral [C_2Co_2] clusters with ten terminal carbonyls and dppe or dppb. The macrocycles of **3** and **6** have 12 and 14 atoms, respectively, which are joined together by a zigzag chain, C38C39C40C41C42C43 or C40C41C42C43C44C45, and a

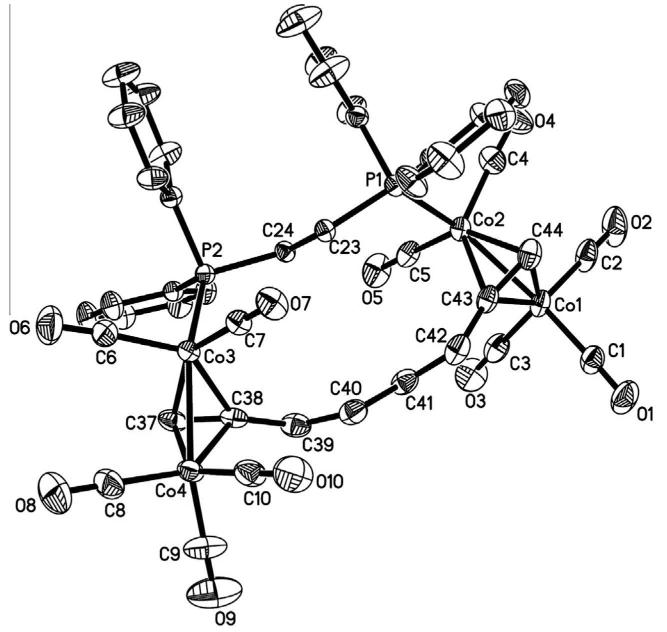


Fig. 3. ORTEP view of **3** with 30% probability level ellipsoids.

diphosphine ligand, dppe or dppb. The Co–Co bond lengths [2.4890(13) and 2.4882(13) Å for **3**, and 2.487(3) and 2.441(3) Å for **6**] are close to that of **1**, whereas the triple bond lengths [C37–C38 = 1.328(8) Å and C43–C44 = 1.321 (8) Å for **3**, and C39–C40 = 1.27(2) Å and C45–C46 = 1.26(2) Å for **6**] are somewhat shorter than that of **1**. It should be noted that the two phosphorus atoms of dppe or dppb both reside in an apical position of the square-pyramidal coordination sphere of the cobalt atoms, in good agreement with **2** and analogous dicobalt complexes [19]. In addition, the structure of **6** is of lower quality than **3** and there are 2568 restraints in the crystal refinement because of so many disordered

Table 2
Selected bond lengths (Å) and angles (°) for **1**–**3** and **6**.

1			
Co(1)–C(7)	1.9571(2)	Co(2)–C(8)	1.975(2)
Co(1)–C(8)	1.972(2)	C(7)–C(8)	1.345(2)
Co(1)–Co(2)	2.482(2)	C(8)–C(9)	1.489(2)
Co(2)–C(7)	1.956(2)	C(9)–C(10)	1.524(3)
C(7)–Co(1)–C(8)	40.04(7)	C(8)–Co(2)–Co(1)	51.00(7)
C(7)–Co(1)–Co(2)	50.63(7)	C(8)–C(7)–Co(2)	70.73(1)
C(8)–Co(1)–Co(2)	51.09(5)	C(8)–C(7)–Co(1)	70.60(1)
C(7)–Co(2)–C(8)	40.02(6)	Co(2)–C(7)–Co(1)	78.71(8)
C(7)–Co(2)–Co(1)	50.66(5)	Co(1)–C(8)–Co(2)	77.91(8)
2			
Co(1)–C(7)	1.982(8)	Co(2)–C(7)	1.956(8)
Co(1)–C(6)	2.000(9)	Co(2)–P(1)	2.212(2)
Co(1)–Co(2)	2.4602(2)	C(6)–C(7)	1.341(9)
Co(2)–C(6)	1.950(7)	C(7)–C(8)	1.511(1)
C(7)–Co(1)–C(6)	39.3(3)	C(7)–Co(2)–P(1)	102.4(2)
C(7)–Co(1)–Co(2)	50.9(2)	C(6)–Co(2)–Co(1)	52.4(3)
C(6)–Co(1)–Co(2)	50.6(2)	C(7)–Co(2)–Co(1)	51.8(2)
C(6)–Co(2)–C(7)	40.2(3)	P(1)–Co(2)–Co(1)	153.13(7)
C(6)–Co(2)–P(1)	104.1(3)	C(7)–C(6)–Co(1)	69.6(5)
3			
Co(1)–C(44)	1.984(6)	Co(2)–C(43)	1.953(5)
Co(1)–C(43)	1.992(5)	Co(3)–Co(4)	2.4882(1)
Co(1)–Co(2)	2.4890(1)	C(43)–C(44)	1.321(8)
Co(2)–C(44)	1.934(5)	C(37)–C(38)	1.328(8)
C(44)–Co(1)–C(43)	38.8(2)	C(43)–Co(2)–P(1)	99.02(2)
C(44)–Co(1)–Co(2)	49.67(2)	C(44)–Co(2)–Co(1)	51.47(2)
C(43)–Co(1)–Co(2)	50.19(2)	C(43)–Co(2)–Co(1)	51.59(1)
C(44)–Co(2)–C(43)	39.7(2)	P(1)–Co(2)–Co(1)	150.07(5)
C(44)–Co(2)–P(1)	103.64(2)	C(37)–C(38)–C(39)	141.7(5)
6			
Co(1)–C(40)	1.983(1)	Co(2)–C(39)	1.987(2)
Co(1)–C(39)	2.010(2)	C(45)–C(46)	1.26(2)
Co(1)–Co(2)	2.487(3)	Co(3)–Co(4)	2.441(3)
Co(2)–C(40)	1.939(2)	C(39)–C(40)	1.27(2)
C(40)–Co(1)–C(39)	37.2(6)	C(46)–Co(3)–C(45)	37.8(6)
C(40)–Co(1)–Co(2)	49.9(5)	P(2)–Co(3)–Co(4)	151.85(2)
C(39)–Co(1)–Co(2)	51.1(5)	C(39)–C(40)–C(41)	130.3(2)
C(40)–Co(2)–C(39)	37.9(6)	C(46)–C(45)–C(44)	144.0(2)
P(1)–Co(2)–Co(1)	147.06(1)	C(23)–C(24)–C(25)	111.9(1)

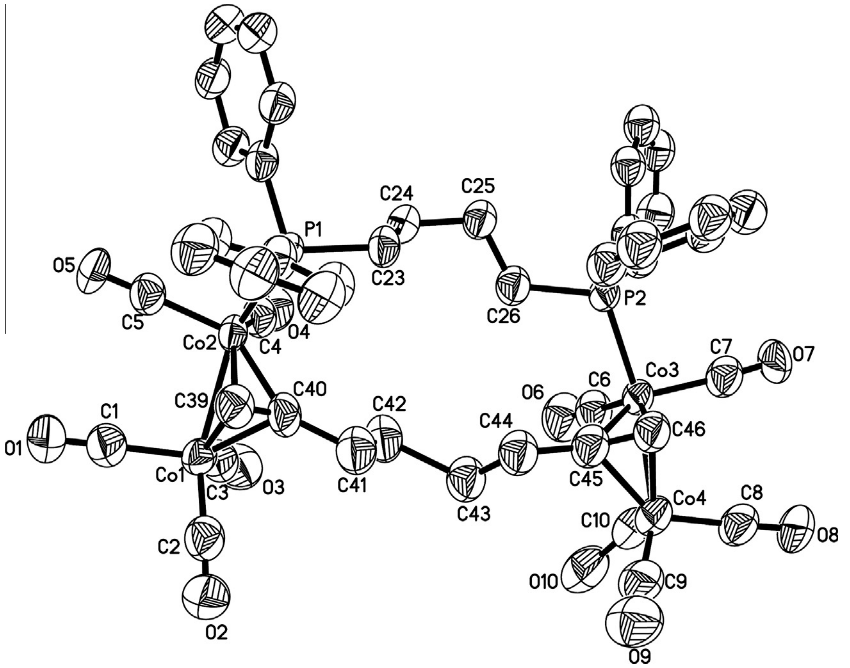


Fig. 4. ORTEP view of **6** with 30% probability level ellipsoids.

solvent molecules in the crystal structure. The room temperature analysis and poor crystal quality may lead to such results.

3.3. Discussion

The present work reports a novel series of diacetylenic tetracobalt carbonyl complexes with the monophosphine ligand PPh_3 or bridging diphosphine ligands, dppe, dppp or dppb. The reactions of the starting material **1** with dppe, dppp or dppb resulted in the formation of two coordination modes: macrocycle and intramolecular bridging. The macrocyclic complex **3** and intramolecular bridging complex **4** were obtained from the reaction of dppe at the same time and the structure of **3** was determined by X-ray crystallography, whereas the structure of **4** was deduced from ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR and ESI-MS spectroscopy. It is very interesting that when dppe was replaced by dppp or dppb, the same type of reactions yielded products with only one coordination mode: the macrocyclic complexes **5** and **6**. X-ray analysis also revealed the structure of **6**. Unfortunately, all attempt to grow suitable single crystals of **4** and **5** failed. A detailed mechanism for the reactions is still uncertain and will need deeper study.

4. Summary

In summary, the reactions of complex **1** with PPh_3, dppe, dppp or dppb afforded diacetylenic tetracobalt carbonyl complexes **2**–**6** in moderate yields. The new complexes **2**–**6** were characterized by elemental analysis, spectroscopy and, in some cases, by X-ray crystallography. These macrocyclic complexes may have potential applications in supramolecular chemistry.

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Appendix A. Supplementary material

CCDC 971422–971425 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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