



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



Xu-Feng Liu*

Department of Chemical Engineering, Ningbo University of Technology, Ningbo 315016, China

ARTICLE INFO

Article history:

Received 28 November 2013

Accepted 27 January 2014

Available online 10 February 2014

Keywords:

Cobalt carbonyl complex

Phosphine ligand

Carbonyl substitution

Synthesis

Crystal structure

ABSTRACT

Five new diacetylenic tetracobalt carbonyl complexes **2–6** with monophosphine or diphosphines have been prepared from the parent complex $(\mu\text{-HC}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}\text{-}\mu)[\text{Co}_2(\text{CO})_6]_2$ (**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 $(\mu\text{-HC}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}\text{-}\mu)[\text{Co}_2(\text{CO})_5(\text{PPh}_3)]_2$ (**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 $(\mu\text{-HC}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}\text{-}\mu)[\text{Co}_2(\text{CO})_5]_2$ (dppe) (**3**) and $(\mu\text{-HC}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}\text{-}\mu)[\text{Co}_2(\text{CO})_6][\text{Co}_2(\text{CO})_4(\text{dppe})]$ (**4**), with a bridging diphosphine ligand, in 20% and 16% yields, respectively, whereas $(\mu\text{-HC}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}\text{-}\mu)[\text{Co}_2(\text{CO})_5]_2(\text{dpppp})$ (dpppp = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2$) (**5**) and $(\mu\text{-HC}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}\text{-}\mu)[\text{Co}_2(\text{CO})_5]_2(\text{dpppb})$ (dpppb = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2$) (**6**) were prepared by the reactions of **1** with dpppp or dpppb 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.

© 2014 Elsevier Ltd. All rights reserved.

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, dpppb 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. ^1H , ^{31}P and ^{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}): $\nu_{\text{C}\equiv\text{O}}$ 2093 (vs), 2049 (vs), 2028 (vs), 2005 (vs), 1995 (vs). ^1H NMR (500 MHz, CDCl_3 , ppm): 6.09 (s, 2H, $2\text{C}\equiv\text{CH}$), 2.96 (s, 4H, $2\text{CH}\equiv\text{CCH}_2$), 1.84 (s, 4H, $\text{CH}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , ppm): 199.88 (C=O), 96.72 (C $\equiv\text{CH}$), 73.16 (C $\equiv\text{CH}$), 33.90, 31.47 (2s, CH_2).

* Tel./fax: +86 574 87089989.

E-mail address: nkxfliu@126.com

2.3. Synthesis of $(\mu\text{-HC}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}\text{-}\mu)[\text{Co}_2(\text{CO})_5(\text{PPh}_3)]_2$ (**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 $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ (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 $\text{C}_{54}\text{H}_{40}\text{Co}_4\text{O}_{10}\text{P}_2$: C, 56.57; H, 3.52. Found: C, 56.88; H, 3.36%. IR (KBr disk, cm^{-1}): $\nu_{\text{C}\equiv\text{O}}$ 2054 (vs), 2000 (vs), 1953 (vs). ^1H NMR (500 MHz, CDCl_3 , ppm): 7.50–7.29 (m, 30H, PhH), 5.19 (s, 2H, $2\text{C}\equiv\text{CH}$), 1.84–1.76 (m, 4H, $2\text{CH}\equiv\text{CCH}_2$), 1.21–1.08 (m, 4H, $\text{CH}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (200 MHz, CDCl_3 , 85% H_3PO_4 , ppm): 54.68 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , ppm): 206.24, 205.14, 202.30 ($\text{C}\equiv\text{O}$), 134.88, 134.55, 132.98, 132.90, 130.25, 128.53, 128.46 (PhC), 94.53 ($\text{C}\equiv\text{CH}$), 71.73 ($\text{C}\equiv\text{CH}$), 32.10, 31.57, 29.71 (CH_2). ESI-MS: m/z 1145.9421 [M^+] (Calc. 1145.9425).

2.4. Synthesis of $(\mu\text{-HC}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}\text{-}\mu)[\text{Co}_2(\text{CO})_5]_2(\text{dppe})$ (**3**) and $(\mu\text{-HC}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}\text{-}\mu)[\text{Co}_2(\text{CO})_6][\text{Co}_2(\text{CO})_4(\text{dppe})]$ (**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 $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ (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 $\text{C}_{44}\text{H}_{34}\text{Co}_4\text{O}_{10}\text{P}_2$: C, 51.79; H, 3.36. Found: C, 52.02; H, 3.59%. IR (KBr disk, cm^{-1}): $\nu_{\text{C}\equiv\text{O}}$ 2056 (vs), 1999 (vs), 1988 (vs), 1955 (vs). ^1H NMR (500 MHz, CDCl_3 , ppm): 7.42–7.27 (m, 16H, *o*-PhH and *m*-PhH), 7.15–7.12 (m, 4H, *p*-PhH), 4.94 (s, 2H, $2\text{C}\equiv\text{CH}$), 2.91–2.79 (m, 4H, $2\text{CH}\equiv\text{CCH}_2$), 2.24–2.19 (m, 2H, PCH_2), 2.09–2.04 (m, 2H, PCH_2), 1.87–1.71 (m, 4H, $\text{CH}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CCH}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (200 MHz, CDCl_3 , 85% H_3PO_4 , ppm): 49.46 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , ppm): 207.74, 204.67, 201.70 ($\text{C}\equiv\text{O}$), 136.81, 136.48, 133.68, 133.38, 133.01, 132.97, 130.59, 130.14, 129.84, 128.77 (PhC), 92.63 ($\text{C}\equiv\text{CH}$), 73.20 ($\text{C}\equiv\text{CH}$), 33.01, 30.18 ($\text{HC}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$), 25.64 (t, $J_{\text{P-C}} = 9.6$ Hz, PCH_2). ESI-MS: m/z 1019.8929 [M^+] (Calc. 1019.8955). **4**: *Anal. Calc.* for $\text{C}_{44}\text{H}_{34}\text{Co}_4\text{O}_{10}\text{P}_2$: C, 51.79; H, 3.36. Found: C, 51.58; H, 3.54%. IR (KBr disk, cm^{-1}): $\nu_{\text{C}\equiv\text{O}}$ 2056 (vs), 1999 (vs), 1986 (vs), 1956 (vs). ^1H NMR (500 MHz, CDCl_3 , ppm): 7.49–7.39 (m, 12H, *m*-PhH and *p*-PhH), 7.31–7.24 (m, 8H, *o*-PhH), 5.42 (s, 2H, $2\text{C}\equiv\text{CH}$), 3.06, 3.03, 2.86, 2.83 (AB q, $J_{\text{AB}} = 3.9$ Hz, 4H, $2\text{CH}\equiv\text{CCH}_2$), 2.02 (d, $J = 8.5$ Hz, 2H, PCH_2), 1.88, 1.86 (2s, 6H, PCH_2 and $\text{CH}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (200 MHz, CDCl_3 , 85% H_3PO_4 , ppm): 48.41 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , ppm): 205.60, 204.17, 201.87 ($\text{C}\equiv\text{O}$), 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 (PhC), 91.15 ($\text{C}\equiv\text{CH}$), 70.56 ($\text{C}\equiv\text{CH}$), 33.46, 28.93 ($\text{HC}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CCH}$), 25.41 (d, $J_{\text{P-C}} = 13.5$ Hz, PCH_2). ESI-MS: m/z 1019.8949 [M^+] (Calc. 1019.8955).

2.5. Synthesis of $(\mu\text{-HC}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}\text{-}\mu)[\text{Co}_2(\text{CO})_5]_2(\text{dppp})$ (**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 $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ (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 $\text{C}_{45}\text{H}_{36}\text{Co}_4\text{O}_{10}\text{P}_2$: C, 52.25; H, 3.51. Found: C, 51.94; H, 3.27%. IR (KBr disk, cm^{-1}): $\nu_{\text{C}\equiv\text{O}}$ 2060 (vs), 2000 (vs), 1954 (vs). ^1H NMR (500 MHz, CDCl_3 , ppm): 7.35–7.27 (m, 20H, PhH), 5.24 (s, 2H, $2\text{C}\equiv\text{CH}$), 2.91–2.77 (m, 4H, $2\text{CH}\equiv\text{CCH}_2$), 2.19–2.14 (m, 4H, 2PCH_2), 2.04–1.99 (m, 2H, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$), 1.90–1.85 (m, 4H, $\text{CH}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (200 MHz, CDCl_3 , 85% H_3PO_4 , ppm): 45.40 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , ppm): 206.14, 204.31, 202.04 ($\text{C}\equiv\text{O}$), 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 (PhC), 91.98 ($\text{C}\equiv\text{CH}$), 71.46 ($\text{C}\equiv\text{CH}$), 31.97, 31.87 ($\text{HC}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$), 29.72, 29.17 ($\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$). ESI-MS: m/z 1034.9095 [M^+H] (Calc. 1034.9190).

2.6. Synthesis of $(\mu\text{-HC}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}\text{-}\mu)[\text{Co}_2(\text{CO})_5]_2(\text{dppb})$ (**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 $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ (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 $\text{C}_{46}\text{H}_{38}\text{Co}_4\text{O}_{10}\text{P}_2$: C, 52.70; H, 3.65. Found: C, 52.54; H, 3.89%. IR (KBr disk, cm^{-1}): $\nu_{\text{C}\equiv\text{O}}$ 2059 (vs), 2000 (vs), 1954 (vs). ^1H NMR (500 MHz, CDCl_3 , ppm): 7.65, 7.42 (2s, 20H, PhH), 4.71 (s, 2H, $2\text{C}\equiv\text{CH}$), 2.96–2.72 (m, 4H, $2\text{CH}\equiv\text{CCH}_2$), 2.12–2.06 (m, 8H, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{P}$), 1.87 (s, 4H, $\text{CH}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (200 MHz, CDCl_3 , 85% H_3PO_4 , ppm): 46.60 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , ppm): 207.86, 204.20, 201.97 ($\text{C}\equiv\text{O}$), 133.45, 133.36, 131.84, 131.56, 130.74, 129.72, 129.52, 128.62 (PhC), 91.59 ($\text{C}\equiv\text{CH}$), 73.72 ($\text{C}\equiv\text{CH}$), 33.50, 32.58 ($\text{HC}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$), 30.94 (d, $J_{\text{P-C}} = 21.9$ Hz, PCH_2), 25.62 (d, $J_{\text{P-C}} = 12.1$ 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 K α radiation ($\lambda = 0.71073$ 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 $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ afforded **2**, **5** and **6** in 29–59% yields, respectively, whereas the reaction of **1** with dppe in the presence of $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ 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

Download English Version:

<https://daneshyari.com/en/article/1335403>

Download Persian Version:

<https://daneshyari.com/article/1335403>

[Daneshyari.com](https://daneshyari.com)