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Preparations of cobalt-containing phosphines and reactions toward dicobalt octacarbonyl

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Abstract

Treatments of bis(diphenylphosphino)methylene (dppm) bridged dicobalt complex, $Co_2(CO)_6(\mu\text{-}Ph_2PCH_2PPh_2)$, with alkynes, $Ph_2PC\equiv CR$ (**2**: R = CMe_3; **3**: R = $SiMe_3$), at 60 °C in THF for 6 h gave alkyne-bridged complexes $[(\mu\text{-}Ph_2PCH_2PPh_2)Co_2(CO)_4][(\mu\text{-}Ph_2PC\equiv CR)]$ (**4**: R = CMe_3; **5**: R = $SiMe_3$). Further reactions of **4** and **5** with $Co_2(CO)_8$ at 80 °C in toluene for 3 h resulted in the formations of unexpected tetra-cobalt clusters, $[(\mu\text{-}Ph_2PCH_2PPh_2)(\mu\text{-}PPh_2)Co_4(CO)_7(\mu_4,\mu_2\text{-}CCR)]$ (**6**: R = CMe_3; **7**: R = $SiMe_3$). All these compounds were characterized by spectroscopic means; **5**, **6** and **7** were studied by X-ray diffraction methods as well. The structure of **6** (or **7**) can be looked upon as a tetra-cobalt *arachno* cluster being coordinated with phosphine ligands and linked by organic moiety.
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Keywords: Alkyne-bridged dicobalt-complex; Metal-containing phosphine; Tetracobalt cluster; *arachno* Cluster

1. Introduction

The exploitation of new and effective phosphine ligands has always been vital to the success of the phosphine-modified, transition-metal based catalytic reactions [1]. In the past, efforts were mainly focused on preparing phosphine ligands derived from pure organic substances, which have done a great job in many designated cases [2]. Nevertheless, reports on the preparations of the metal-containing phosphines are rare and their catalytic potential remained to be explored [3].

We have previously described the preparation of a new type of metal-containing bidentate phosphines, $[(\mu\text{-}Ph_2PCH_2PPh_2)Co_2(CO)_4(\mu\text{-}PPh_2C\equiv CPPh_2)]$ (**1**), which was prepared from the reaction of a bi-functional ligand bis(diphenylphosphino)acetylene (dppa) with one equivalent of a bis(diphenylphosphino)methylene (dppm) bridged dicobalt complex, $Co_2(CO)_6(\mu\text{-}Ph_2PCH_2PPh_2)$. (Diagram 1). The reaction of **1** with

$Mo(CO)_6$ gave a **1**-chelated molybdenum complex, $[(\mu\text{-}Ph_2PCH_2PPh_2)Co_2(CO)_4][(\mu\text{-}P,P\text{-}Ph_2PC\equiv CPPh_2)\text{-}Mo(CO)_4]$ [4]. In this regard, **1** acts as a genuine di-phosphine chelating ligand. It can be looked upon as a modified form of 1,2-bis(diphenylphosphino)ethane (dppe)—a rather frequently used bidentate phosphine ligand [5]. It has also been demonstrated that **1** might act as chelating or bridging di-phosphine ligand toward various transition metals such as tungsten, ruthenium, gold and palladium and form **1**-chelated (or bridged) metal complexes [6].

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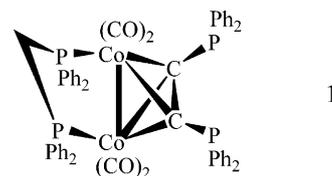
Following the same strategy, cobalt-containing monodentate phosphines might be prepared started with alkynyl phosphines having the formula of $Ph_2PC\equiv CR$. We report herein the preparations of a new type of cobalt-containing monodentate phosphines and their reactions toward dicobalt carbonyls.

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2. Results and discussion

Treatments of the dppm-bridged dicobalt complex, $Co_2(CO)_6(\mu\text{-}Ph_2PCH_2PPh_2)$, with alkynyl phosphines, $Ph_2PC\equiv CR$ (**2**: R = CMe$_3$; **3**: R = SiMe$_3$), at 60 °C in THF for 6 h gave alkyne-bridged complexes [(μ-Ph$_2$PCH$_2$PPh$_2$)Co$_2$(CO)$_4$][(μ-Ph$_2$PC$\equiv$CR)] (**4**: R = CMe$_3$; **5**: R = SiMe$_3$) [7] (Scheme 1). Compounds **4** and **5** were characterized by spectroscopic means. The ^{31}P-NMR spectrum of **4** shows two singlets in the ratio of 2:1 at 34.7 and -6.2 ppm, respectively, for all three phosphorous atoms. The matching signals are 34.7 and -11.3 ppm in **5**. The upfielded signal corresponds to the unbound phosphorous atom and they are 5 ppm apart. In ^{1}H-NMR, there are two distinct chemical shifts, 3.32 and 4.25 ppm, being observed for the methylene protons of **4**. The corresponding peaks are 3.15 and 4.85 ppm in **5**. Slightly different chemical shifts were perceived for these two sets of signals. Also, two signals at 203.1 and 207.8 ppm were found and assigned as the carbonyls of **4** in ^{13}C-NMR. The matching signals are 201.1 and 207.8 ppm in **5**.

Suitable crystals of **5** were obtained from mixture solvent (CH$_2$Cl$_2$–hexane = 1:1) at 4 °C and their structures were determined by X-ray diffraction method (Table 1). The ORTEP of **5** is depicted in Fig. 1. The structural study of **5** reveals that the alkyne, Ph$_2$PC$\equiv$CSiMe$_3$, bridges the dicobalt fragment Co$_2$(CO)$_4$(μ-Ph$_2$PCH$_2$PPh$_2$). The bulky substituent, –SiMe$_3$, keeps away from the crowded dppm environs. The bridged dppm takes the axial position of the cobalt center, which is in accord with the common observation for phosphine substituted alkyne-bridged dicobalt complexes [8]. Judging from its structure, **5** is a promising bulky, metal-containing, monodentate phosphine. Unfortunately, attempts to grow crystals for **4** resulted in failure. Although the crystal structure of **4** is not available, it is believed, based on the accumulated spectroscopic data, that a similar framework was held for **4** and **5**.
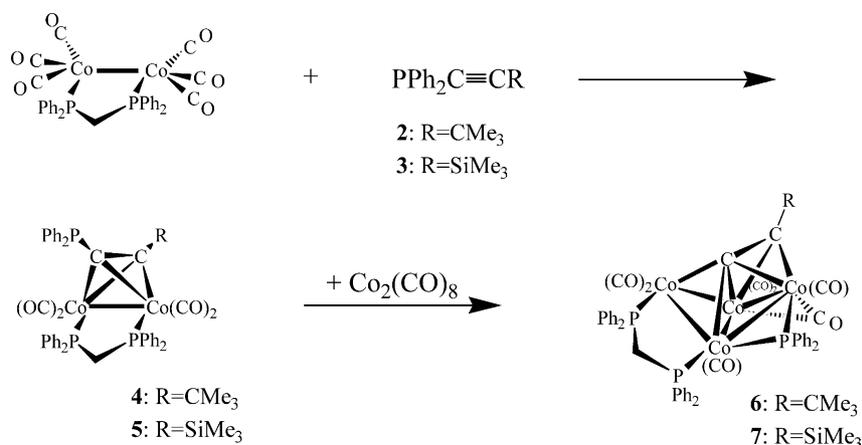
Further reactions of **4** and **5** with Co$_2$(CO)$_8$ at 80 °C in THF for 3 h resulted in the formations of unexpected

Table 1
Crystal data of **5**, **6** and **7**

Compound	5	6	7
Formula	C$_{46}$H$_{41}$Co$_2$O$_4$P$_3$Si	C$_{51}$H$_{41}$Co$_4$O$_8$P$_3$	C$_{50}$H$_{41}$Co$_4$O$_8$P$_3$Si
Formula weight	896.65	1110.47	1126.55
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2(1)/n$	$P\bar{1}$	$P2(1)/n$
a (Å)	13.0289(11)	11.198(4)	12.5584(10)
b (Å)	25.793(2)	11.977(4)	21.4358(16)
c (Å)	13.1245(11)	20.023(6)	24.4529(10)
α (°)	–	103.807(6)	–
β (°)	97.556(2)	101.029(6)	103.5980(10)
γ (°)	–	101.574(6)	–
V (Å^3)	4372.2(6)	2472.8(13)	5090.2(7)
Z	4	2	4
D_{calc} (Mg m^{-3})	1.362	1.491	1.470
λ(Mo–K$_\alpha$) (Å)	0.71073	0.71073	0.71073
μ (mm^{-1})	0.937	1.467	1.449
2θ range (°)	2.07–26.01	1.82–26.09	1.90–26.04
Observed reflections ($F > 4\sigma(F)$)	4859	3284	5564
Number of refined parameters	505	585	603
[a]R_1 for significant reflections	0.0396	0.0884	0.0350
[b]wR_2 for significant reflections	0.0793	0.2238	0.0958
[c]Goodness-of-fit	0.883	0.954	1.036

[a] $R_1 = |\Sigma(|F_o| - |F_c|)/|\Sigma F_o||$.
[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 0.10, 0.0727, 0.1081$ for **4**, **6** and **7**.
[c] GoF $= [\Sigma w(F_o^2 - F_c^2)^2/(N_{rflns} - N_{params})]^{1/2}$.
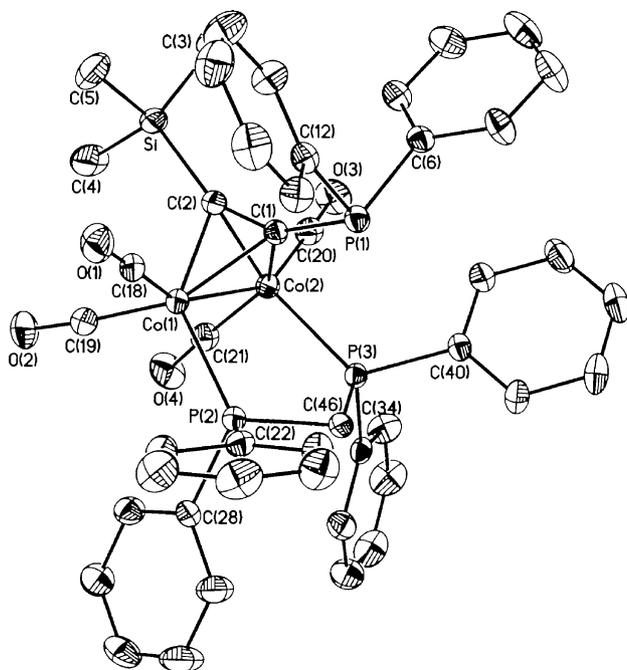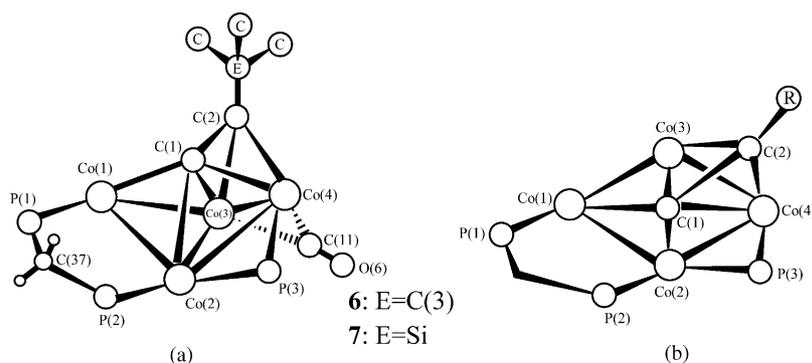

Scheme 1.

Fig. 1. ORTEP drawing with the numbering scheme of **5**. Some carbon and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Co(1)–C(2) 1.988(3); Co(1)–C(1) 1.993(3); Co(1)–P(2) 2.2371(9); Co(1)–Co(2) 2.4825(6); Co(2)–C(1) 1.986(3); Co(2)–C(2) 1.995(3); Co(2)–P(3) 2.2181(9); Si–C(2) 1.859(3); P(1)–C(1) 1.800(3); P(2)–C(46) 1.843(3); P(3)–C(46) 1.827(3); C(1)–C(2) 1.344(4); C(2)–Co(1)–C(1) 39.48(12); C(2)–Co(1)–P(2) 136.86(10); C(1)–Co(1)–P(2) 100.70(9); C(2)–Co(1)–Co(2) 51.57(9); C(1)–Co(1)–Co(2) 51.26(8); P(2)–Co(1)–Co(2) 93.64(3); C(1)–Co(2)–C(2) 39.48(11); C(1)–Co(2)–P(3) 95.56(9); C(2)–Co(2)–P(3) 134.55(9); C(1)–Co(2)–Co(1) 51.53(8); C(2)–Co(2)–Co(1) 51.31(8); P(3)–Co(2)–Co(1) 100.45(3); C(46)–P(2)–Co(1) 112.50(10); C(46)–P(3)–Co(2) 110.76(10); C(2)–C(1)–P(1) 150.1(2); Co(2)–C(1)–Co(1) 77.21(11); C(1)–C(2)–Si 152.5(3); C(1)–C(2)–Co(1) 70.48(17); C(1)–C(2)–Co(2) 69.89(18); Co(1)–C(2)–Co(2) 77.13(11); P(3)–C(46)–P(2) 113.12(16).

tetra-cobalt clusters, [(μ-Ph$_2$PCH$_2$PPh$_2$)(μ-PPh$_2$)Co$_4$(CO)$_7$(μ$_4$,μ$_2$-CCR)] (**6**: R = CMe$_3$; **7**: R = SiMe$_3$) with high yield [9] (Scheme 1). Actually, the reaction can be started from a lower temperature such as 55 °C and with moderate yield. Interestingly, we did not

simply find the expected **4**- (or **5**-) coordinated dicobalt complex. Compound **6** and **7** were characterized by spectroscopic means as well as X-ray diffraction methods. There are three singlets in the ratio of 1:1:1 at 39.3, 44.9 and 194.7 ppm, respectively, being observed for all three phosphorous atoms of **6** in ^{31}P-NMR spectrum. The matching signals are 44.3, 48.3 and 193.5 ppm in **7**. The highly downfielded signal corresponds to the bridged phosphido atom; while the other two signals represent the bridged dppm. One triplet at 3.37 ppm was found for the methylene protons of **6** in ^{1}H-NMR. Nevertheless, two distinct chemical shifts at 3.31 and 3.39 ppm were observed for the methylene protons in **7**. It indicates that the thermal motion of the coordinated dppm, which swings back and forth around the dicobalt fragment, in **6** is faster than that of **7** [4]. Slow decompositions of compounds **6** and **7** were observed while taking long hours NMR, which is in contrast with the robustness of **4** or **5** in solution.

The reddish-black crystals of **6** and **7** were grown in mixed solvent (CH$_2$Cl$_2$–hexane = 1:1) at 4 °C and were sampled and subjected for the X-ray crystal structural determination (Table 1). The ORTEPs of **6** and **7** are depicted in Figs. 2 and 3. There is one CH$_3$OH molecule in each asymmetric unit of **7**. Their corresponding geometrical data are quite close except for some small variations. The structure of **6** (or **7**) can be regarded as a tetra-cobalt *arachno* cluster being coordinated with phosphines as well as connected with organic moiety [10]. The dppm remains bridging on the two cobalt atoms, Co(1) and Co(2), of the newly formed tetra-cobalt *arachno* cluster. It is obvious that the two cobalt atoms, Co(3) and Co(4), must come from the latterly added reactant, Co$_2$(CO)$_8$. Interestingly, a phosphido ligand, bridging Co(2) and Co(4), is found on the cluster. It has to come from the breaking of the C–PPh$_2$ bond of the original bridging alkynyl phosphines, Ph$_2$PC≡CR.

Selected structural parameters of **6** and **7** were shown in Table 2 for comparison. The geometrical data of these

6: E=C(3)
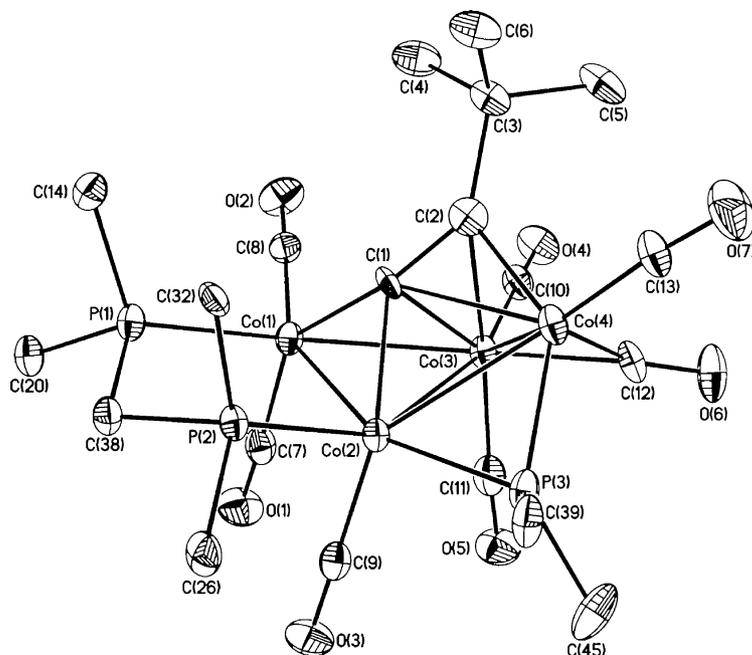**7**: E=Si

(a)   (b)

Fig. 2. ORTEP drawing with the numbering scheme of **6**. Some carbon and hydrogen atoms are omitted for clarity.

two compounds' main frameworks are rather close. The bond angle of the C(1)–C(2)–Si in **7** is much steeper than that of C(1)–C(2)–C(3) in **6**. The dihedral angels for the Co$_4$ butterfly structures, Co(1)–Co(2)–Co(3)–Co(4), are 135.1° and 132.8° for **6** and **7**, respectively. They are much wilder than the common observed Co$_4$C$_2$ butterfly structures, which range from 100° to 120° [11].

Diagrams of simplified structures of **6** and **7** were drawn (Diagram 2). The atom numbering of the main

structures of these two compounds has been kept the same. Looking from the top, the C(1) atom is above the center of the four cobalt atoms. The C(2) atom is connected to C(1) on the left and ascending up to the right. The C(1)–C(2) bond bisects the Co(3)–Co(4) bond. The dppm ligand is above the Co(1)–Co(2)–Co(3) plane; while the phosphido ligand is below the Co(2)–Co(3)–Co(4) plane. As shown from the side view, this cluster can be regarded as a tetra-cobalt
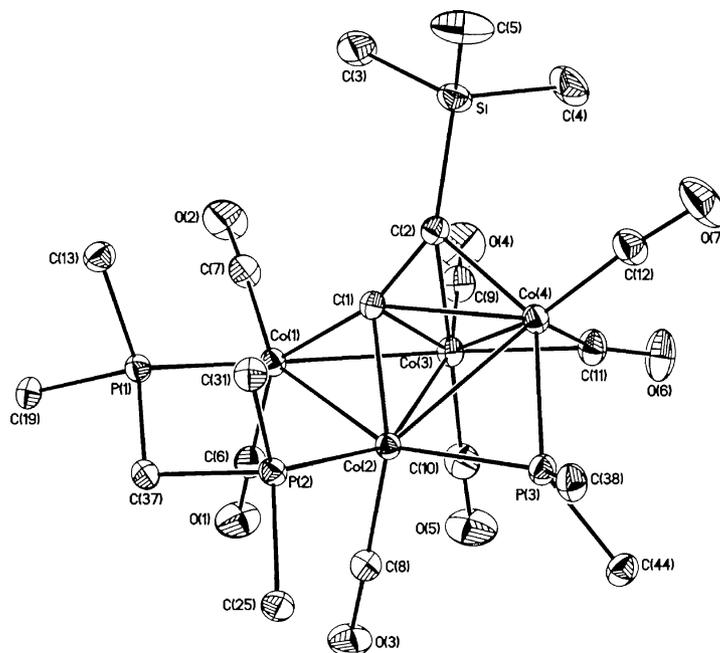

Fig. 3. ORTEP drawing with the numbering scheme of **7**. Some carbon and hydrogen atoms are omitted for clarity.

Table 2
Comparison of selected structural parameters of **6** and **7**

	6	**7**
Bond length		
Co(1)–Co(2)	2.4936(16)	2.5180(6)
Co(2)–Co(3)	2.5691(15)	2.5890(5)
Co(3)–Co(4)	2.4470(16)	2.4517(6)
Co(3)–Co(1)	2.5528(17)	2.5472(6)
Co(1)–P(1)	2.197(2)	2.1888(9)
Co(2)–P(2)	2.217(2)	2.2101(8)
C(1)–C(2)	1.301(11)	1.330(4)
C(1)–Co(1)	1.932(7)	1.899(3)
C(1)–Co(2)	2.001(8)	1.982(3)
C(1)–Co(3)	2.001(8)	1.991(3)
C(1)–Co(4)	2.306(8)	2.268(3)
C(2)–Co(3)	2.242(3)	2.205(3)
C(2)–Co(4)	1.912(9)	1.946(3)
C(2)–Si	–	1.859(3)
C(2)–C(3)	1.547(13)	–
P(3)–Co(4)	2.160(3)	2.1451(9)
P(3)–Co(2)	2.217(2)	2.2246(8)
Bond angle		
C(1)–C(2)–Si	–	148.9(2)
C(1)–C(2)–C(3)	138.2(9)	–
C(1)–C(2)–Co(3)	62.3(5)	62.94(16)
C(1)–C(2)–Co(4)	89.7(6)	85.42(19)
Co(1)–Co(2)–Co(3)	60.54(3)	59.817(15)
Co(2)–Co(3)–Co(4)	61.65(4)	61.491(15)
Co(1)–C(1)–Co(2)	78.7(3)	80.88(11)
Co(1)–C(1)–Co(3)	80.9(3)	81.78(10)
Co(1)–C(1)–Co(4)	141.3(4)	144.65(14)
Co(2)–C(1)–Co(3)	79.9(3)	81.33(10)
Co(4)–C(1)–Co(3)	68.8(2)	69.95(8)
Co(3)–C(1)–Co(1)	80.9(3)	81.78(10)
Co(4)–C(2)–Co(3)	71.7(3)	72.09(9)
Co(2)–P(3)–Co(4)	71.97(8)	72.34(3)
P(1)–Co(1)–Co(2)	97.61(7)	97.04(3)
P(2)–Co(2)–Co(1)	96.32(7)	95.85(2)

arachno cluster with Co$_4$ butterfly framework or as a C–EMe$_3$ (E:Si or C) triangular face capped Co$_4$C trigonal bipyramidal cluster [12].

3. Summary

Two cobalt-containing bulky, monodentate phosphines **4** and **5** were synthesized. Their reactions with Co$_2$(CO)$_8$ yielded unexpected tetra-cobalt clusters **6** and **7**. It is a new pathway of making tetra-cobalt *arachno* clusters with butterfly framework.

4. Experimental

4.1. General

All operations were performed in a nitrogen flushed glove box or in a vacuum system. Freshly distilled solvents were used. All processes of separations of the products were performed by Centrifugal Thin Layer Chromatography (CTLC, Chromatotron, Harrison model 8924). ^{1}H-NMR spectra were recorded (Varian VXR-300S spectrometer) at 300.00 MHz; chemical shifts are reported in ppm relative to internal CHCl$_3$ or CH$_2$Cl$_2$. ^{31}P- and ^{13}C-NMR spectra were recorded at 121.44 and 75.46 MHz, respectively. ^{1}H-NMR spectra of variable temperature experiments were recorded by the same instrument. Some other routine ^{1}H-NMR spectra were recorded at Gemini-200 spectrometer at 200.00 MHz or Varian-400 spectrometer at 400.00 MHz. IR spectra of sample powder in KBr were recorded on a Hitachi 270-30 spectrometer. Mass spectra were recorded on JEOL JMS-SX/SX 102A GC/MS/MS spectrometer. Elemental analyses were recorded on Heraeus CHN-O-S-Rapid.

4.2. Synthesis of 4 and 5

Into a 100 cm^3 flask was placed dicobalt octacarbonyl, Co$_2$(CO)$_8$ (0.342 g, 1.000 mmol) and dppm (0.385 g, 1.000 mmol) in 10 ml of THF. The solution was stirred at 65 °C for 6 h and yielded yellow-colored Co$_2$(CO)$_6$(μ-P,P-PPh$_2$CH$_2$PPh$_2$]. Further reaction with Ph$_2$PC≡CCMe$_3$ **2** (0.266 g, 1.000 mmol) in 5 ml of THF at 45 °C for 8 h yields a red solution. The solvent was removed, and the resulting residue was chromatography by CTLC. Complex [(μ-Ph$_2$PCH$_2$PPh$_2$)Co$_2$(CO)$_4$][(μ-Ph$_2$PC≡CCMe$_3$] (**4**) was obtained from red band eluted by mixed solvent (CH$_2$Cl$_2$–hexane = 1:1) in the yield of 60.0% (0.528 g, 0.600 mmol). Crystals were obtained from the CH$_2$Cl$_2$–hexane solution of **4** at 4 °C. The same procedures were followed for the preparation of **5** with **3** as the alkyne source. Red colored compound was obtained and identified as **5** in the yield of 63.0% (0.565 g, 0.630 mmol).

4.2.1. Characterization of 4
^{1}H-NMR (CDCl$_3$, δ/ppm): 1.29 (s, 9H, CMe$_3$), 3.32, 4.25 (m, 2H, dppm), 7.01–7.47 (30H, arene); ^{13}C-NMR (CDCl$_3$, δ/ppm): 33.18 (s, 3C, CH$_3$), 37.65 (t, 1C, dppm), 203.06, 207.75 (s, 2C, CO), 127.35–138.52 (36C, arene); ^{31}P-NMR (CDCl$_3$, δ/ppm): 34.7 (s, 2P, dppm), −6.2 (s, 1P, PPh$_2$); E.A.: Calc.: C, 64.10; H, 4.69. Found: C, 63.92; H, 5.07%; IR(KBr): $\nu_{(CO)}$ 2009(s), 1984(s), 1962(s); ESIMS: 880.93.

4.2.2. Characterization of 5
^{1}H-NMR (CDCl$_3$, δ/ppm): 0.60 (s, 9H, SiMe$_3$), 3.15, 4.85 (m, 2H, dppm), 6.83–7.42 (30H, arene); ^{13}C-NMR (CDCl$_3$, δ/ppm): 1.83 (s, 3C, SiMe$_3$), 37.56 (t, 1C, dppm), 201.05, 207.74 (s, 2C, CO), 127.63–137.71 (36C, arene); ^{31}P-NMR (CDCl$_3$, δ/ppm): 34.7 (s, 2P, dppm), −11.3 (s, 1P, PPh$_2$); E.A.: Calc.: C, 70.51; H, 6.78.

Found: C, 72.30; H, 6.41%; FABMS: 896; IR (KBr): $v_{(CO)}$ 2015(s), 1990(s), 1955(s).

4.3. Synthesis of 6 and 7

Into a 100 cm^3 flask was placed dicobalt octacarbonyl, $Co_2(CO)_8$ (0.047 g, 0.136 mmol) and **4** (0.120 g, 0.136 mmol) in 20 cm^3 of toluene at 80 °C stirred for 3 h. The solvent was removed under reduced pressure and the resulting black residue was chromatographed by Centrifugal Thin Layer Chromatography. A reddish-black band was eluted out by mixed solvent (CH_2Cl_2–hexane = 1:1) and was identified as **5** in the yield of 90.4% (0.133 g, 0.123 mmol). The same procedures were followed for the preparation of **7** started with $Co_2(CO)_8$ (0.077 g, 0.226 mmol) and **5** (0.202 g, 0.226 mmol). A reddish-black band was eluted out by mixed solvent (CH_2Cl_2–hexane = 1:1) and was identified as **6** in the yield of 93.8% (0.239 g, 0.212 mmol).

4.3.1. Characterization of 6
^{1}H-NMR (CDCl$_3$, δ/ppm):1.86 (s, 9H, CMe$_3$), 3.37 (t, 2H, dppm), 6.44–7.85 (30H, arene); ^{13}C-NMR (CDCl$_3$, δ/ppm): 32.40 (s, 3C, CH$_3$), 39.26 (t, 1C, dppm), 127.51–140.31 (36C, arene); ^{31}P-NMR (CDCl$_3$, δ/ppm): 39.3, 44.9 (s, 2P, dppm), 194.7 (s, 1P, μ-PPh$_2$); E.A.: Calc.: C, 55.48; H, 3.82. Found: C, 55.06; H, 4.03%; IR (KBr): $v_{(CO)}$ 2033(s), 1981(s), 1941(s), 1933(s).

4.3.2. Characterization of 7
^{1}H-NMR (CDCl$_3$, δ/ppm): 0.72 (s, 9H, SiMe$_3$), 3.31, 3.39 (m, 2H, dppm), 6.38–7.73 (30H, arene); ^{13}C-NMR (CDCl$_3$, δ/ppm): 0.97 (s, 3C, SiMe$_3$), 127.22–136.31 (36C, arene); ^{31}P-NMR (CDCl$_3$, δ/ppm): 44.3, 48.3 (s, 2P, dppm), 193.5 (s, 1P, μ-PPh$_2$); E.A.: Calc.: C, 53.29; H, 3.64. Found: C, 52.07; H, 4.16%.

4.4. X-ray crystallographic studies

Suitable crystals of **5**, **6**, and **7** were sealed in thin-walled glass capillaries under nitrogen atmosphere and mounted on a Bruker AXS SMART 1000 diffractometer. Intensity data were collected in 1350 frames with increasing ω (width of 0.3° per frame). The absorption correction was based on the symmetry equivalent reflections using SADABS program. The space group determination was based on a check of the Laue symmetry and systematic absences, and was confirmed using the structure solution. The structure was solved by direct methods using a SHELXTL package [13]. All non-H atoms were located from successive Fourier maps and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms [14]. Crystallographic data of **5**, **6**, and **7** are summarized in Table 1.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC nos. 211706, 211707, and 211708 for compounds **5**, **6** and **7**, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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[7] The synthesis of Ph$_2$PC≡CCMe$_3$ (**2**) or Ph$_2$PC≡CSiMe$_3$ (**3**) was carried out by modifying the literature procedures. A.J. Carty, N.K. Hota, T.W. Ng, H.A. Patel, T.J. O'Connor, Can. J. Chem. 49 (1971) 2706. Into a 100 cm^3 round flask was placed 3,3-dimethyl-1-butyne (0.822 g, 10.000 mmol) with 10 ml of dimethyl ether. The solution was stirred at −78 °C before one molar equivalent of *n*-butyllithium (2.0 M in cyclohexane), which was dissolved in 5 ml of dimethyl ether, was slowly added. It remained at −78 °C for 1 h before one molar equivalent of diphenylchlorophosphine (2.206 g, 10.000 mmol), which was dissolved in 5 ml

of dimethyl ether, was again slowly added. The reaction mixture was then allowed to warm to room temperature and stirred for another hour. The solvent was removed under reduced pressure and toluene was added to precipitate lithium chloride. After filtration, the resulting solution was further purified through chromatography. White needle solid was obtained and identified as **2** in the yield of 78.0% (2.077 g, 7.800 mmol). The same procedures were followed for the preparation of **3**. The reaction started with trimethylsilylacetylene (1.423 g, 10.000 mmol) as the alkyne source. White colored compound was obtained and identified as **3** in the yield of 72.0% (2.033 g, 7.200 mmol). **2**: ^{1}H-NMR (CDCl$_3$, δ/ppm): 1.43 (s, 9H, CMe$_3$), 7.37–7.71 (10H, arene); ^{31}P-NMR (CDCl$_3$, δ/ppm): $-$33.6 (s, 1P, C≡CP); **3**: [1]H-NMR (CDCl$_3$, δ/ppm): 0.19 (s, 9H, SiMe$_3$), 7.55–7.56 (10H, arene); [31]P-NMR (CDCl$_3$, δ/ppm): $-$32.4 (s, 1P, C≡CP).

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