

# Preparation and characterization of cobalt-containing alcohols and diols

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## Abstract

A series of cobalt-containing alcohols and diols were prepared and characterized. Intramolecular hydrogen-bonding was observed for the cobalt-containing diols  $[\text{Co}_2(\text{CO})_6(\mu\text{-}\eta\text{-(HO)R}_1\text{R}_2\text{CC}\equiv\text{CCR}_1\text{R}_2\text{(OH)})]$  (**1**:  $\text{R}_1 = \text{CH}_3$ ,  $\text{R}_2 = \text{C}_2\text{H}_5$ ; **2**:  $\text{R}_1 = \text{CH}_3$ ,  $\text{R}_2 = \text{C}_3\text{H}_7$ ),  $[\text{Co}_2(\text{CO})_6(\mu\text{-}\eta\text{-(HO)Ph}_2\text{CC}\equiv\text{CCPh}_2\text{(OH)})]$  (**3**) and  $[(\mu\text{-PPh}_2\text{CH}_2\text{PPh}_2)\text{Co}_2(\text{CO})_4(\mu\text{-}\eta\text{-(HO)Ph}_2\text{CC}\equiv\text{CCPh}_2\text{(OH)})]$  (**4**). Potentially all the four compounds could serve as chelating O,O-ligands. In principle, it is possible for compounds  $[(\mu\text{-PPh}_2\text{NHPPH}_2)\text{Co}_2(\text{CO})_4(\mu\text{-}\eta\text{-HC}\equiv\text{CCPh}_2\text{(OH)})]$  (**5b**),  $[\text{Co}_2(\text{CO})_6(\mu\text{-}\eta\text{-HC}\equiv\text{CC}_2\text{H}_4\text{OH})]$  (**6**) and  $[\text{Co}_2(\text{CO})_6(\mu\text{-}\eta\text{-HC}\equiv\text{CC}_3\text{H}_6\text{OH})]$  (**7**) in their *syn*-conformations to behave as chelating O,N-ligands. To the best of our knowledge, compounds **5b**, **6** and **7** are the first reported examples of  $\text{PPh}_2\text{NHPPH}_2$ -bridged dicobalt complexes.

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**Keywords:** Cobalt-containing diols; Cobalt-containing alcohols; Alkyne-bridged dicobalt complex; Dppm;  $\text{PPh}_2\text{NHPPH}_2$

## 1. Introduction

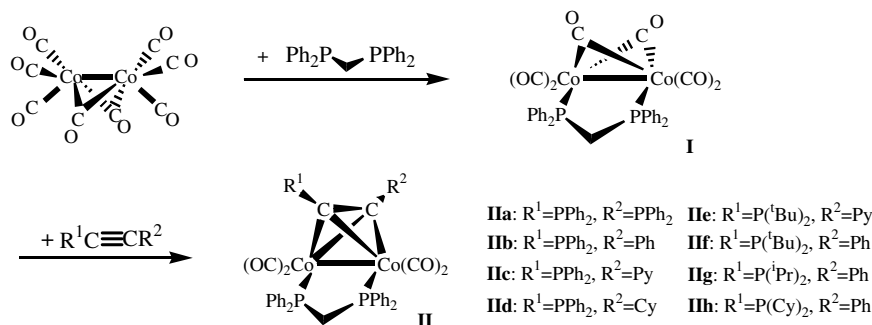
Alkynes are highly reactive building blocks in organic synthesis. The fact that alkyne-bridged dicobalt system has been studied extensively is in part due to its indisputable role played in the Pauson–Khand reaction [1]. Complexes of this class are usually obtained from the direct reaction of dicobalt octacarbonyl ( $\text{Co}_2(\text{CO})_8$ ) with alkynes [2]. The bridging alkyne makes use of both sets of filled  $\pi$ - and unfilled  $\pi^*$ -orbitals in bonding to the dicobalt framework. The former set is responsible for donation of the electron-density to the metal center; meanwhile, the latter one accepts the electron-density from the metal through back-bonding [3]. This synergetic effect enhances the rigidity of the  $\text{Co}_2\text{C}_2$  core. The character and reactivity of the bridging alkyne is significantly changed after the coordination to the metal moiety. A

general methods of preparation of cobalt-containing mono- or bidentate phosphine ligands has been established in our previous studies (Scheme 1) [4]. It has also been revealed that ligands of this type can be characterized as authentic phosphine ligands with bulky, and, in some cases, electron-rich, character [4b]. Moreover, some of the palladium complexes with type II ligands have been demonstrated to perform as effective catalysts in the renowned Suzuki reactions [5].

Alcohols or diols are readily accessible precursors of alkoxides. The alkoxy ligands have been long known to stabilize metals in high oxidation states [6]. Metal alkoxides are also of great interest due to their current and potential uses in catalysis. For example,  $\text{Al}(\text{O}^i\text{Pr})_3$  has been widely used as a catalyst in organic synthesis as well as in the ring-opening polymerization of aliphatic cyclic esters [7]. Numerous organic alkoxides as well as their metal-containing counterparts were prepared. Their chemical reactivities toward metals were thoroughly examined. Much rich chemistry of the letter were demonstrated [8]. Herein, we

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Scheme 1.

report the preparation and characterization of a series of cobalt-containing alcohols and diols using a methodology similar to the one shown in Scheme 1.

## 2. Results and discussion

### 2.1. Preparation of cobalt-containing diols

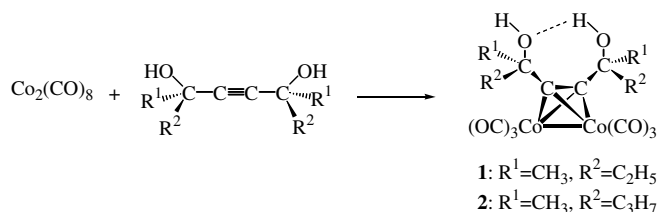
The room temperature reaction of  $(\text{HO})\text{R}_1\text{R}_2\text{CC}\equiv\text{CCR}_1\text{R}_2(\text{OH})$  with  $\text{Co}_2(\text{CO})_8$  in toluene furnished  $[\text{Co}_2(\text{CO})_6(\mu-\eta-(\text{HO})\text{R}_1\text{R}_2\text{CC}\equiv\text{CCR}_1\text{R}_2(\text{OH}))]$  (**1**:  $\text{R}_1=\text{CH}_3$ ,  $\text{R}_2=\text{C}_2\text{H}_5$ ; **2**:  $\text{R}_1=\text{CH}_3$ ,  $\text{R}_2=\text{C}_3\text{H}_7$ ) in good yields in 4 h (Scheme 2). Compounds **1** and **2** were characterized by spectroscopic means as well as by single-crystal X-ray diffraction. The molecular structures of both compounds revealed a pseudo-tetrahedral  $\text{Co}_2\text{C}_2$  core typical for an alkyne-bridged dicobalt complex (Table 1, Figs. 1 and 2). Both substituents of the alkyne are bent away from the dicobalt moiety, as predicted by Dewar–Chatt–Duncanson's model, and reside on the same side [9]. In this regard, **1** and **2** can be considered as potentially chelating metal-containing diols.

All carbonyl ligands of compound **1** and other cobalt-containing alcohols and diols mentioned below are in terminal positions. The  $\text{C}(1)–\text{C}(2)–\text{C}(3)$  and  $\text{C}(2)–\text{C}(1)–\text{C}(7)$  angles are  $138.6(4)^\circ$  and  $139.6(3)^\circ$ , respectively, deviated from the  $180^\circ$  angle characteristic of their free states as predicted. The  $\text{C}–\text{C}$  bond distance of the bridging alkyne is  $1.341(5) \text{ \AA}$ , which is within the regular double bond range. The  $\text{Co}–\text{Co}$  bond distance is  $2.472 \text{ \AA}$ , which is comparable to alkyne-bridging dicobalt complex reported earlier (Table 1, Fig. 1). In general, the cluster core “ $-\text{Co}_2(-\text{C}\equiv\text{C}-)$ ” of a common dicobalt complex of this

type is a tetrahedron where the alkyne unit is almost perpendicular to the metal-metal bond. The structure also shows that the acetylenic ligands fold in upon coordination to the cluster core. The distance between the oxygen and hydrogen atoms of two hydroxyl groups are  $2.052 \text{ \AA}$  for **1**, which is well within the intramolecular hydrogen-bonding range [10]. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **1** are trivial. In contrast with the observed two non-equivalent hydroxyl protons in solid state, two hydroxyl protons are equivalent on the NMR timescale giving rise to a broad signal at 2.99 ppm in  $^1\text{H}$  NMR in  $\text{CDCl}_3$ . In the structure of **2**, the  $\text{C}(2)–\text{C}(1)–\text{C}(3)$  and  $\text{C}(1)–\text{C}(2)–\text{C}(8)$  angles are  $137.5(2)^\circ$  and  $136.9(2)^\circ$ , respectively. The  $\text{C}–\text{C}$  bond distance of the bridged alkyne is  $1.324(3) \text{ \AA}$ . The  $\text{Co}–\text{Co}$  bond distance is  $2.4639(5) \text{ \AA}$ . The distance between oxygen atoms of the two hydroxyl groups are  $2.637 \text{ \AA}$  for **2** (Table 1, Fig. 2). Again, in solution two hydroxyl protons are equivalent and give rise to a broad signal at 2.98 ppm in  $^1\text{H}$  NMR in  $\text{CDCl}_3$ .

As seen above, the two hydroxyl groups of the coordinated alkyne come closer in a well-defined rigid geometry in these alkyne dinuclear clusters. This observable fact suggests that any charged functional groups at these positions will be disposed in a clamp-like fashion and are potentially capable of binding ions of the opposite charge [11]. Unfortunately, attempts to isolate the expected aluminum complexes were not successful (Scheme 3). The reactions of both **1** and **2** with trimethyl aluminum always led to precipitation of compounds of unknown composition. Besides, the complex would undergo an elimination reaction in acidic medium and produce the related olefinic compounds [12].

Subsequently, the heating  $\text{Co}_2(\text{CO})_8$  with  $(\text{HO})\text{Ph}_2\text{CC}\equiv\text{CCPh}_2(\text{OH})$  in toluene at  $60^\circ\text{C}$  for 3 h produced  $[\text{Co}_2(\text{CO})_6(\mu-\eta-(\text{HO})\text{Ph}_2\text{CC}\equiv\text{CCPh}_2(\text{OH}))]$  (**3**). Further reaction of **3** with  $\text{PPh}_2\text{CH}_2\text{PPh}_2$  (dppm) in toluene at  $100^\circ\text{C}$  for 16 h yielded  $[(\mu-\text{PPh}_2\text{CH}_2\text{PPh}_2)\text{Co}_2(\text{CO})_4(\mu-\eta-(\text{HO})\text{Ph}_2\text{CC}\equiv\text{CCPh}_2(\text{OH}))]$  (**4**) (Scheme 4). In several occasions, the bridging dppm is a necessity, especially when the reaction is conducted at elevated temperatures. Without the protection provided by the bridging dppm, intermolecular attacks among  $\text{Co}_2(\text{CO})_6(\mu-\eta-\text{RC}\equiv\text{CR})$



Scheme 2.

Table 1  
Crystal data of **1**, **2**, **3**, **5a**, **5b**, **6**, and **7**

Compound	<b>1</b>	<b>2</b>	<b>3</b>	<b>5a</b>	<b>5b</b>	<b>6</b>	<b>7</b>
Formula	C <sub>32</sub> H <sub>36</sub> Co <sub>4</sub> O <sub>16</sub>	C <sub>18</sub> H <sub>22</sub> Co <sub>2</sub> O <sub>8</sub>	C <sub>68</sub> H <sub>44</sub> Co <sub>4</sub> O <sub>16</sub>	C <sub>21</sub> H <sub>12</sub> Co <sub>2</sub> O <sub>7</sub>	C <sub>43</sub> H <sub>33</sub> Co <sub>2</sub> NO <sub>5</sub> P <sub>2</sub>	C <sub>62</sub> H <sub>50</sub> Co <sub>4</sub> N <sub>2</sub> O <sub>10</sub> P <sub>4</sub>	C <sub>64</sub> H <sub>54</sub> Co <sub>4</sub> N <sub>2</sub> O <sub>10</sub> P <sub>4</sub>
Formula weight	912.36	484.22	1352.75	494.17	823.50	1342.64	1370.69
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	triclinic	orthorhombic
Space group	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> $\bar{1}$	<i>Pbca</i>
<i>a</i> (Å)	9.7269(7)	8.9360(9)	15.3065(13)	6.6972(8)	10.9974(7)	11.1751(10)	17.6826(12)
<i>b</i> (Å)	32.247(2)	11.0808(11)	20.3771(17)	10.8070(13)	17.5744(12)	16.5038(15)	20.3498(13)
<i>c</i> (Å)	12.6768(9)	22.386(2)	20.1655(17)	14.9215(17)	20.1312(14)	18.1966(17)	34.949(3)
$\alpha$ (°)				104.299(2)		100.689(2)	
$\beta$ (°)	91.1600(10)	90.850(2)	101.572(2)	98.911(2)	102.9600(10)	105.976(2)	
$\gamma$ (°)						98.860(2)	
<i>V</i> (Å <sup>3</sup> )	3975.5(5)	2216.4(4)	6161.8(9)	1008.7(2)	3094.8(5)	12576.0(15)	
<i>Z</i>	4	4	4	2	4	2	8
<i>D<sub>c</sub></i> (Mg/m <sup>3</sup> )	1.585	1.451	1.458	1.627	1.443	1.441	1.448
$\lambda$ (Mo K $\alpha$ ) (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
$\mu$ (mm <sup>−1</sup> )	3.416	1.534	1.128	1.685	1.006	1.214	1.197
$\theta$ Range (°)	2.04–25.99	1.82–26.02	1.44–26.01	1.99–25.99	1.56–26.04	1.53–26.03	1.63–25.99
Observed reflections ( <i>F</i> > 4 $\sigma$ ( <i>F</i> ))	7787	4353	12080	3918	7465	11979	12344
Number of refined parameters	469	253	809	271	478	747	757
<sup>a</sup> <i>R</i> <sub>1</sub> for significant reflections	0.0459	0.0411	0.0393	0.0437	0.0408	0.0502	0.0461
<sup>b</sup> <i>wR</i> <sub>2</sub> for significant reflections	0.1139	0.0993	0.0872	0.1071	0.0791	0.1306	0.0827
<sup>c</sup> Goodness-of-fit	0.995	1.019	0.927	0.949	0.901	0.981	0.808

<sup>a</sup>  $R_1 = |\sum(|F_o| - |F_c|)/\sum F_o|$ .

<sup>b</sup>  $wR_2 = \{\sum[w(F_o^2 - F_c^2)]^2 / \sum[w(F_o^2)]\}^{1/2}$ ; *w* = 0.0668, 0.0622, 0.0540, 0.0704, 0.0405, 0.0919, and 0.0386 for **1**, **2**, **3**, **5a**, **5b**, **6**, and **7**, respectively.

<sup>c</sup> Goodness-of-fit =  $[\sum[w(F_o^2 - F_c^2)]^2 / (N_{\text{reflms}} - N_{\text{params}})]^{1/2}$ .

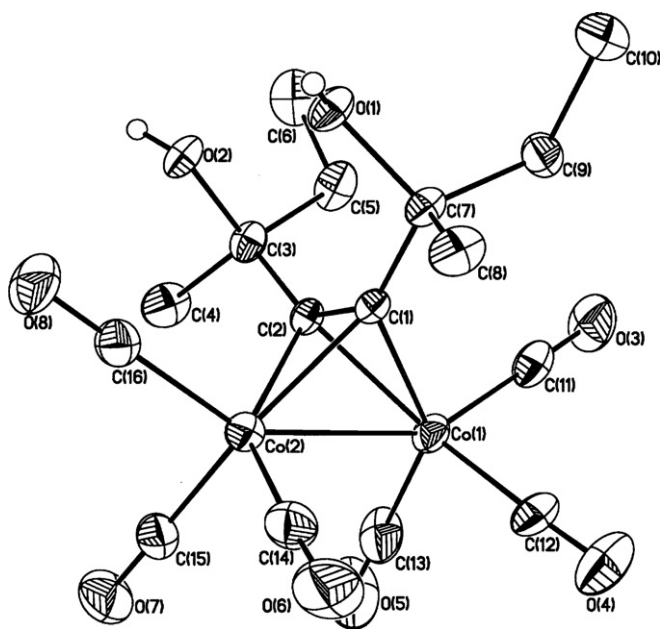
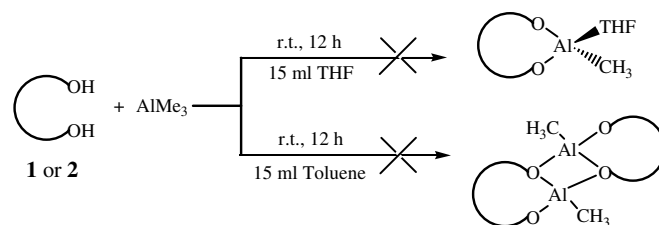
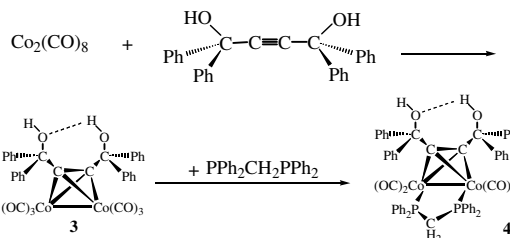


Fig. 1. ORTEP drawing of **1**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Co(1)–C(2) 1.965(4); Co(1)–C(1) 1.965(4); Co(1)–Co(2) 2.4720(8); Co(2)–C(1) 1.968(4); Co(2)–C(2) 1.969(4); O(1)–C(7) 1.444(4); O(2)–C(3) 1.438(5); C(1)–C(2) 1.341(5); C(1)–C(7) 1.497(5); C(2)–C(3) 1.508(5); C(3)–C(5) 1.531(6); C(3)–C(4) 1.538(6); C(7)–C(8) 1.532(6); C(7)–C(9) 1.538(6); C(2)–Co(1)–C(1) 39.89(15); C(1)–Co(2)–C(2) 39.81(15); C(2)–C(1)–C(7) 139.6(3); Co(1)–C(1)–Co(2) 77.87(14); Co(1)–C(2)–Co(2) 77.87(14); C(1)–C(2)–C(3) 138.6(4); O(2)–C(3)–C(2) 106.5(3); O(1)–C(7)–C(1) 105.7(3); C(1)–C(7)–C(8) 112.7(3); C(1)–C(7)–C(9) 110.0(3).



Scheme 3.



Scheme 4.

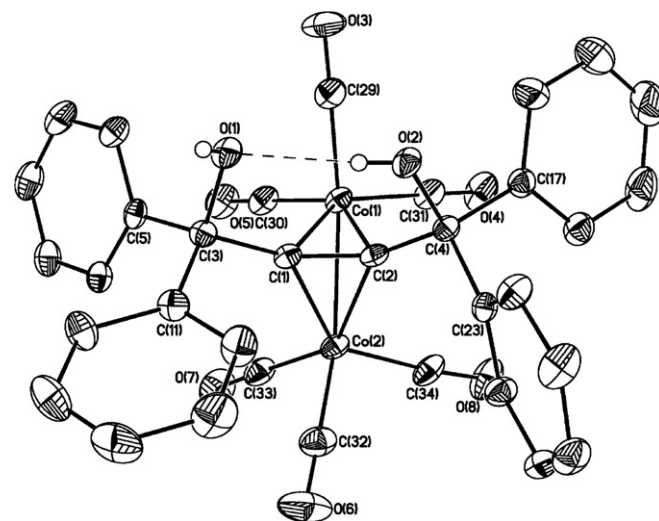


Fig. 3. ORTEP drawing of **3**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Co(1)–C(1) 1.972(3); Co(1)–C(2) 1.978(3); Co(1)–Co(2) 2.4472(6); Co(2)–C(1) 1.952(3); Co(2)–C(2) 1.985(3); O(1)–C(3) 1.445(4); O(2)–C(4) 1.435(3); C(1)–C(2) 1.346(4); C(1)–C(3) 1.521(4); C(2)–C(4) 1.536(4); C(1)–Co(1)–C(2) 39.84(11); C(1)–Co(2)–C(2) 39.98(11); Co(2)–C(1)–Co(1) 77.15(10); Co(1)–C(2)–Co(2) 76.28(10); C(2)–C(1)–C(3) 140.4(3); C(1)–C(2)–C(4) 138.2(3); O(1)–C(3)–C(1) 102.8(2); O(2)–C(4)–C(2) 106.9(2).

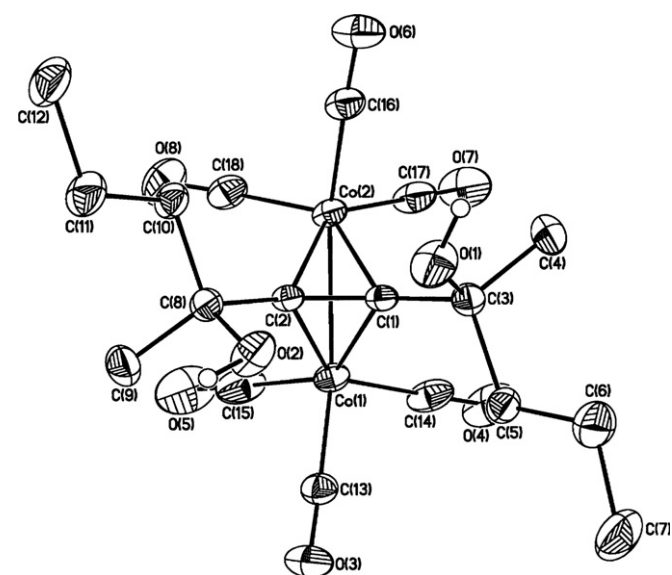


Fig. 2. ORTEP drawing of **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Co(1)–Co(2) 2.4639(5); C(1)–C(2) 1.324(3); Co(1)–C(1) 1.965(2); Co(1)–C(2) 1.971(2); Co(2)–C(2) 1.951(3); Co(2)–C(1) 1.972(2); C(1)–C(3) 1.522(4); C(2)–C(8) 1.526(4); O(1)–C(3) 1.445(3); O(2)–C(8) 1.434(3); C(2)–C(1)–C(3) 137.5(2); C(1)–C(2)–C(8) 136.9(2); O(1)–C(3)–C(1) 106.4(2); O(2)–C(8)–C(2) 103.4(2); C(1)–Co(1)–C(2) 39.30(10); C(2)–Co(2)–C(1) 39.44(10); Co(1)–C(1)–Co(2) 77.49(9); Co(2)–C(2)–Co(1) 77.86(9).

molecules do occur and the self-aggregation process always lead to a great amount of precipitation. The sequence of reactions shown in Scheme 1 is reversed in the synthesis of **4**. Firstly, the alkynyl alcohol is allowed to bridge to the dicobalt fragment. As predicted by the Dewar–Chatt–Duncanson's model, bulky substituents of the alkyne bend away from the dicobalt center. Then, the dppm is added to the alkyne bridged dicobalt fragment. The dppm-alkynyl alcohol sequence will not lead to **4**

due to the bulkiness of the latter. Compounds **3** and **4** were characterized by spectroscopic means. In addition, the molecular structure of **3** was determined by a single-crystal X-ray diffraction method. As revealed from the crystal structure, there is an intramolecular hydrogen-bonding between the oxygen atom of one and the hydrogen atom of another hydroxyl group. The H $\cdots$ O distance is 1.934 Å for **3**. Two hydroxyl protons of **3** and **4** are equivalent resulting in broad signals at 4.31 ppm and 2.51 ppm, respectively, in their  $^1\text{H}$  NMR spectra in  $\text{CDCl}_3$ . A triplet signal at 3.69 ppm ( $J_{\text{P-H}} = 10.5$  Hz) observed in the  $^1\text{H}$  NMR spectra of **4** is assigned to the methylene protons (Figs. 3 and 4).

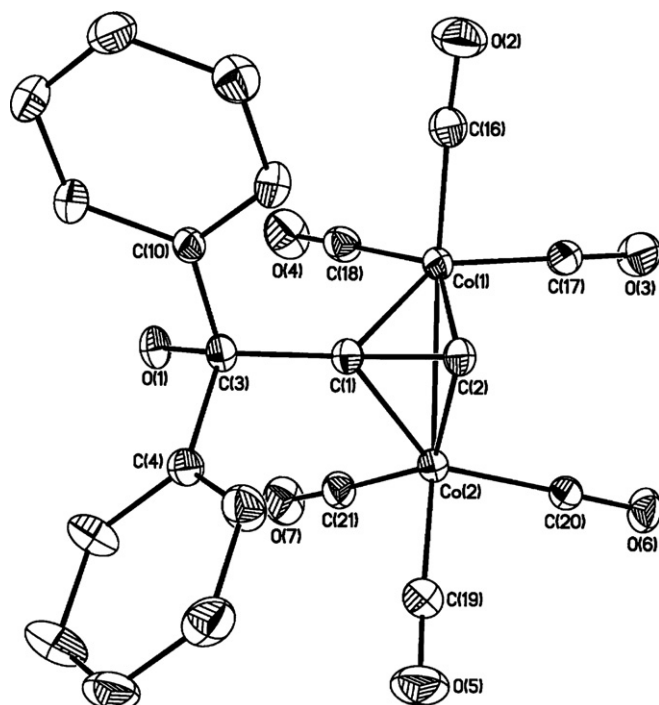


Fig. 4. ORTEP drawing of **5a**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles ( $^\circ$ ): Co(1)–C(2) 1.969(4); Co(1)–C(1) 1.986(4); Co(1)–Co(2) 2.4729(8); Co(2)–C(2) 1.951(4); Co(2)–C(1) 1.977(4); O(1)–C(3) 1.436(4); C(1)–C(2) 1.340(5); C(1)–C(3) 1.499(5); C(2)–Co(1)–C(1) 39.60(15); C(2)–Co(2)–C(1) 39.88(15); C(2)–C(1)–C(3) 146.5(4); Co(2)–C(2)–Co(1) 78.21(15); Co(2)–C(1)–Co(1) 77.22(13); O(1)–C(3)–C(1) 109.3(3).

## 2.2. Preparation of cobalt-containing alcohols

Several cobalt-containing alcohols were prepared using a procedure similar to the one for synthesis of diols. The reaction of  $\text{Co}_2(\text{CO})_8$  with  $\text{HCC}\equiv\text{CCPh}_2\text{OH}$  in toluene at 60  $^\circ\text{C}$  for 2 h furnished  $[\text{Co}_2(\text{CO})_6(\mu-\eta\text{-HC}\equiv\text{CCPh}_2\text{OH})]$  (**5a**). Further reaction of **5a** with  $\text{PPh}_2\text{NHPPH}_2$  in toluene at 80  $^\circ\text{C}$  for 16 h produced  $[(\mu\text{-PPh}_2\text{NHPPH}_2)\text{Co}_2(\text{CO})_4(\mu-\eta\text{-HC}\equiv\text{CCPh}_2\text{OH})]$  (**5b**) (Scheme 5). The alkynyl alcohol was first allowed to bridge to the dicobalt fragment. Then,  $\text{PPh}_2\text{NHPPH}_2$  was added to alkyne-bridged dicobalt fragment. Again, reversing the sequence did not lead to the formation of **5b**. Here  $\text{PPh}_2\text{NHPPH}_2$  was chosen

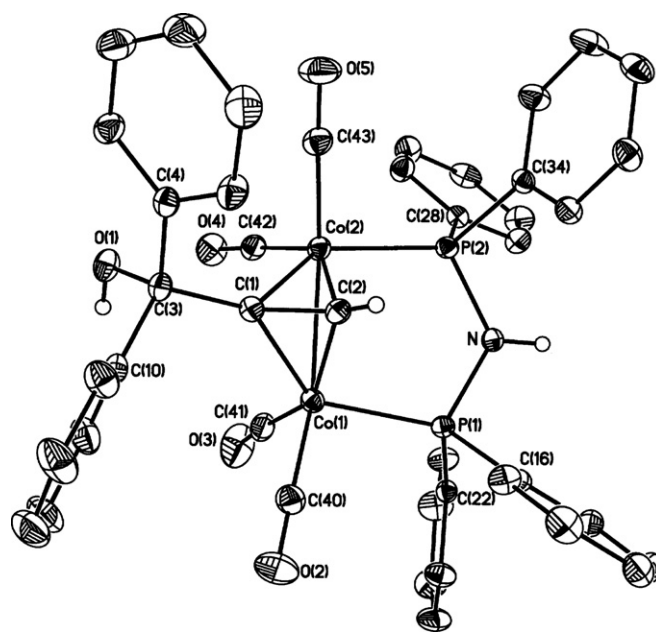
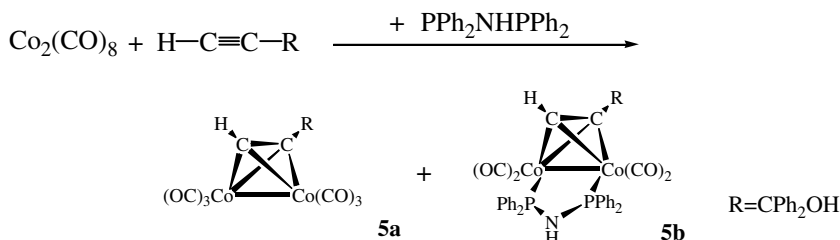


Fig. 5. ORTEP drawing of **5b**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles ( $^\circ$ ): Co(1)–Co(2) 2.4467(6); Co(1)–C(2) 1.932(3); Co(1)–C(1) 1.973(3); Co(1)–P(1) 2.2028(10); Co(2)–C(2) 1.956(3); Co(2)–C(1) 1.957(3); Co(2)–P(2) 2.1997(10); P(1)–N 1.687(3); P(2)–N 1.679(3); O(1)–C(3) 1.451(4); C(1)–C(2) 1.339(4); C(1)–C(3) 1.523(4); C(2)–Co(1)–C(1) 40.09(13); C(2)–Co(2)–C(1) 40.01(13); N–P(1)–Co(1) 111.64(10); N–P(2)–Co(2) 112.53(10); P(2)–N–P(1) 122.53(16); C(2)–C(1)–C(3) 141.8(3); Co(2)–C(1)–Co(1) 77.01(12); Co(1)–C(2)–Co(2) 77.99(13); O(1)–C(3)–C(1) 107.4(3).



Scheme 5.



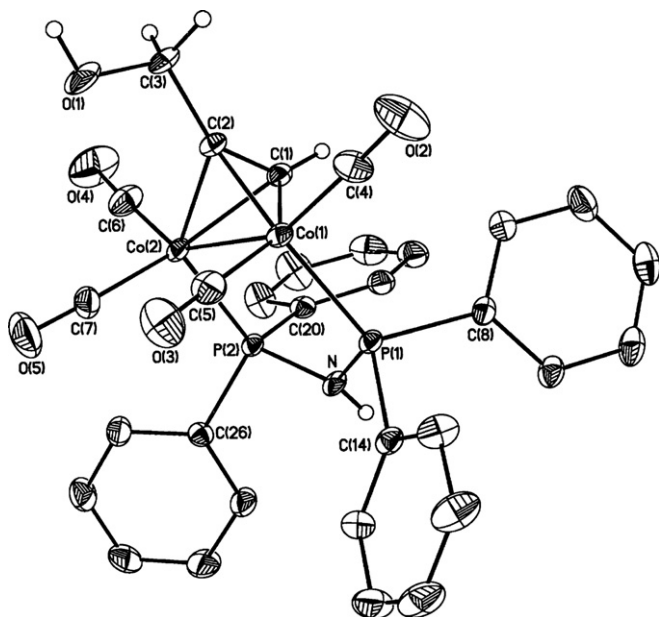


Fig. 6. ORTEP drawing of **6**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Co(1)–Co(2) 2.4675(7); Co(1)–C(2) 1.950(4); Co(1)–C(1) 1.960(4); Co(1)–P(1) 2.2018(9); Co(2)–C(2) 1.957(4); Co(2)–C(1) 1.966(4); Co(2)–P(2) 2.2045(9); P(1)–N 1.683(3); P(2)–N 1.687(3); O(1)–C(3) 1.411(5); C(1)–C(2) 1.341(5); C(2)–C(3) 1.489(4); C(2)–Co(1)–C(1) 40.10(14); C(2)–Co(2)–C(1) 39.96(14); N–P(1)–Co(1) 111.46(10); N–P(2)–Co(2) 111.76(10); P(1)–N–P(2) 123.19(17); Co(1)–C(1)–Co(2) 77.86(13); C(1)–C(2)–C(3) 141.8(4); Co(1)–C(2)–Co(2) 78.32(13); O(1)–C(3)–C(2) 110.0(3).

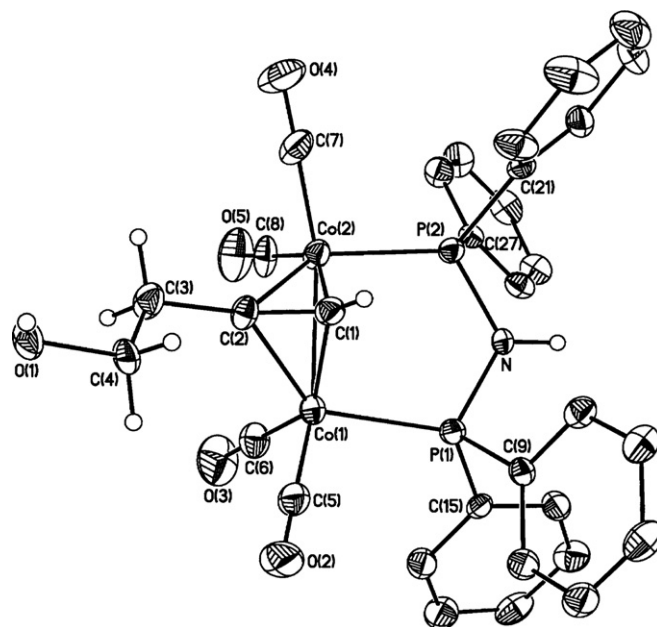
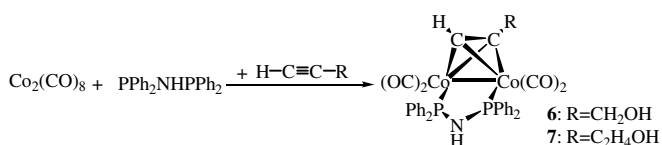


Fig. 7. ORTEP drawing of **7**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Co(1)–Co(2) 2.4701(10); Co(1)–C(1) 1.925(6); Co(1)–C(2) 1.965(6); Co(1)–P(1) 2.2017(15); Co(2)–C(2) 1.944(6); Co(2)–C(1) 1.947(6); Co(2)–P(2) 2.2023(16); O(1)–C(4) 1.445(5); P(1)–N 1.669(4); P(2)–N 1.687(4); C(1)–C(2) 1.313(7); C(2)–C(3) 1.505(7); C(3)–C(4) 1.458(7); C(2)–Co(2)–C(1) 39.5(2); C(1)–Co(1)–C(2) 39.4(2); N–P(1)–Co(1) 112.24(15); N–P(2)–Co(2) 110.88(15); P(1)–N–P(2) 123.3(2); Co(1)–C(1)–Co(2) 79.3(2); C(1)–C(2)–C(3) 140.1(6); Co(2)–C(2)–Co(1) 78.4(2); C(4)–C(3)–C(2) 113.1(5); O(1)–C(4)–C(3) 111.4(5).



Scheme 6.

as a bridging ligand to stabilize the dicobalt complex as the dppm did in the case of compound **4**. This choice is due to the  $\text{PPh}_2\text{NHPPH}_2$  ability to function as an amine-like ligand, which dppm does not have. In addition to the characterization by spectroscopic means the molecular structures of **5a** and **5b** were determined by the single-crystal X-ray diffraction method. The structure of **5b** revealed that the –OH and –NH groups point at different directions. In  $\text{CDCl}_3$ , a hydroxyl proton is observed at 2.60 and 3.00 ppm for **5a** and **5b**, respectively, in  $^1\text{H}$  NMR. A broad signal at 3.62 ppm and a triplet signal at 5.75 ppm ( $J_{\text{PH}} = 9.0$  Hz) are assigned to the acetylenic proton and NH proton, respectively, of **5b** (see Figs. 5 and 6).

The reaction of  $\text{Co}_2(\text{CO})_8$  with  $\text{PPh}_2\text{NHPPH}_2$  in toluene at 65 °C produced  $[\text{Co}_2(\text{CO})_6(\mu-\eta-\text{PPh}_2\text{NHPPH}_2)]$  in 12 h. Further reaction of the latter compound with  $\text{HC}\equiv\text{CR}$  ( $\text{R} = \text{CH}_2\text{OH}$  or  $\text{C}_2\text{H}_4\text{OH}$ ) in toluene at 65 °C furnished  $[\text{Co}_2(\text{CO})_6(\mu-\eta-\text{HC}\equiv\text{CR})]$  (**6**:  $\text{R} = \text{CH}_2\text{OH}$ ; **7**:  $\text{R} = \text{C}_2\text{H}_4\text{OH}$ )

in 12 h (Scheme 6). Compounds **6** and **7** were characterized by spectroscopic means. Their molecular structures were determined by the single-crystal X-ray diffraction method. To the best of our knowledge, compounds **5b**, **6** and **7** are the first reported examples of  $\text{PPh}_2\text{NHPPH}_2$ -bridged dicobalt complexes. The crystal structures of **6** and **7** show that the –OH and –NH groups point at different directions as those in **5b** does (see Fig. 7).

Signals observed at 1.69 and 2.01 ppm in the  $^1\text{H}$  NMR spectra of **6** and **7**, respectively, in  $\text{CDCl}_3$  are assigned to the corresponding hydroxyl protons. Broad signals appearing at 3.60 ppm for **6** and 3.52 ppm for **7** are assigned to terminal acetylene protons. The triplet signals at 5.34 ppm for **6** and 5.30 ppm for **7** are assigned to the NH protons of the bridging  $\text{PPh}_2\text{NHPPH}_2$ .

### 2.3. Structural comparison of cobalt-containing diols and alcohols

Selected structural parameters of **1**, **2**, **3**, **5a**, **5b**, **6**, and **7** are given in Table 2 for the purpose of comparison. The atom numbering scheme of the framework of all these compounds is the same. As shown in Table 2, these frameworks are not very different. Again, it shows that the alkyne-bridging dicobalt framework ( $\text{Co}_2\text{C}_2$ ) is a rigid structure (Diagram 1).

Table 2  
Comparison of selected structural parameters of **1**, **2**, **3**, **5a**, **5b**, **6**, and **7**

	<b>1</b>	<b>2</b>	<b>3</b>	<b>5a</b>	<b>5b</b>	<b>6</b>	<b>7</b>
<i>Bond length (Å)</i>							
Co(1)–Co(2)	2.4720(8)	2.4639(5)	2.4472(6)	2.4729(8)	2.4467(6)	2.4675(7)	2.4701(10)
C(1)–C(2)	1.341(5)	1.324(3)	1.346(4)	1.340(5)	1.339(4)	1.341(5)	1.313(7)
C(1)–Co(1)	1.965(4)	1.965(2)	1.972(3)	1.986(4)	1.973(3)	1.960(4)	1.925(6)
C(1)–Co(2)	1.968(4)	1.972(2)	1.952(3)	1.977(4)	1.957(3)	1.966(4)	1.947(6)
C(2)–Co(1)	1.965(4)	1.971(2)	1.978(3)	1.969(4)	1.932(3)	1.950(4)	1.965(6)
C(2)–Co(2)	1.969(4)	1.951(3)	1.985(3)	1.951(4)	1.956(3)	1.957(4)	1.944(6)
C(1)–C(A)	1.497(5)	1.522(4)	1.521(4)	1.499(5)	1.523(4)		
C(2)–C(B)	1.508(5)	1.526(4)	1.536(4)			1.489(4)	
C(A)–O(1)	1.444(5)	1.445(3)	1.445(4)	1.436(4)	1.451(4)	1.411(5)	
C(B)–O(2)	1.438(5)	1.434(3)	1.435(3)				
Co(1)–P(1)					2.2028(10)	2.2018(9)	2.2017(15)
Co(2)–P(2)					2.1997(10)	2.2045(9)	2.2023(16)
P(1)–X					1.687(3)	1.683(3)	1.669(4)
P(2)–X					1.679(3)	1.687(3)	1.687(4)
<i>Distance (Å)</i>							
O(2)–H(1)	2.052	3.303	1.934				
O(1)–O(2)	2.847	2.637	2.709				
<i>Angle (°)</i>							
C(A)–C(1)–C(2)	139.6(3)	137.5(2)	140.4(3)	146.5(4)	141.8(3)		140.1(6)
C(B)–C(2)–C(1)	138.6(4)	136.9(2)	138.2(3)			141.8(4)	
Co(1)–C(1)–Co(2)	77.87(14)	77.49(9)	77.15(10)	77.22(13)	77.01(12)	77.86(13)	79.3(2)
Co(1)–C(2)–Co(2)	77.87(14)	77.86(9)	76.28(10)	78.21(15)	77.99(13)	78.32(13)	78.4(2)
C(1)–Co(1)–C(2)	39.89(15)	39.30(10)	39.84(11)	39.60(15)	40.09(13)	40.10(14)	39.4(2)
C(1)–Co(2)–C(2)	39.81(15)	39.44(10)	39.98(11)	39.88(15)	40.01(13)	39.96(14)	39.5(2)
P(1)–X–P(2)					122.53(16)	123.19(17)	123.3(2)
Co(1)–P(1)–X					111.64(10)	111.46(10)	112.24(15)
Co(2)–P(2)–X					112.53(10)	111.76(10)	110.88(15)
C(1)–C(A)–O(1)	105.7(3)	106.4(2)	102.8(2)	109.3(3)	107.4(3)		
C(2)–C(B)–O(2)	106.5(3)	103.4(2)	106.9(2)			110.0(3)	

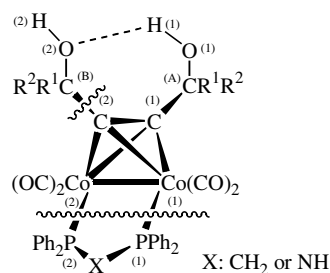


Diagram 1. A generalized structure for **1**, **2**, **3**, **5a**, **5b**, **6**, and **7**.

## 2.4. Summary

Several cobalt-containing alcohols and diols were prepared and characterized by NMR spectroscopic and single-crystal X-ray diffraction. Their molecular structures were compared. Unfortunately, reactions of the metal-containing diol ligands with aluminum complexes such as  $\text{AlEt}_3$  or  $\text{AlMe}_3$  resulted in a number of unidentified products.

## 3. Experimental

*General information:* All manipulations were carried out under a dry nitrogen atmosphere. Solvents including deu-

terated solvents were purified before use. Most of separations were performed by Centrifugal Thin Layer Chromatography (CTLC, Chromatotron, Harrison model 8924). The  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra were recorded on a Varian-400 spectrometer at 400.44 and 162.10 MHz, respectively;  $^{13}\text{C}$  NMR spectra were recorded on a Varian VXR-300 S spectrometer at 75.43 MHz. Chemical shifts are reported in ppm relative to the residual proton signals of deuterated  $\text{CHCl}_3$  or  $\text{CH}_2\text{Cl}_2$ . Mass spectra were recorded on a JOEL JMS-SX/SX 102A GC/MS/MS spectrometer. Elemental analyses were obtained on a Heraeus CHN-O-S-Rapid instrument.

### 3.1. Synthesis of **1** and **2**

$\text{Co}_2(\text{CO})_8$  (0.342 g, 1.000 mmol), 3,6-dimethyl-4-octyn-3,6-diol (0.170 g, 1.000 mmol) and 10 mL of THF were placed in a 100 mL round-bottomed flask charged with a magnetic stirrer. The solution was stirred at 25 °C for 4 h. Then the solvent was removed under reduced pressure, and the resulted dark-red residue was separated by CTLC. A red band was eluted out using a mixed solvent system ( $\text{CH}_2\text{Cl}_2/\text{EA} = 1:1$ ). The product was identified as **1** (0.437 g, 0.96 mmol, 96%). A similar procedure was used for the preparation of **2**.  $\text{Co}_2(\text{CO})_8$  (0.342 g, 1.000 mmol), 4,7-dimethyl-5-decyn-4,7-diol (0.198 g, 1.000 mmol) and

10 mL of THF were placed in 100 mL round-bottomed flask charged with a magnetic stirrer. The solution was stirred at 25 °C for 4 h followed by workup. A dark-red band was eluted out using a mixed solvent system (EA:CH<sub>2</sub>Cl<sub>2</sub> = 1:1). The product was identified as **2** (0.460 g, 0.95 mmol, 95%).

**1**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ/ppm): 1.09(br., 6H, C–CH<sub>2</sub>–CH<sub>3</sub>), 1.54(br., 6H, C–CH<sub>3</sub>), 1.83(br., 4H, C–CH<sub>2</sub>), 2.99(br., 2H, OH); <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ/ppm): 8.76(s, C–CH<sub>2</sub>–CH<sub>3</sub>), 28.79(s, C–CH<sub>2</sub>), 37.90(s, C–CH<sub>3</sub>), 75.15(s, C≡C), 106.89(s, C–OH), 199.83(s, CO); *Anal. Calc.* for **1**: C, 42.13; H, 3.98. *Found*: C, 41.17, H, 3.84%. IR(KBr/cm<sup>−1</sup>): 2017.7(s), 2052.5(s), 2093.0(s), 3332.0(br.); color: red (solid state).

**2**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ/ppm): 0.99(br., 6H, C–CH<sub>2</sub>–CH<sub>3</sub>), 1.56(br., 10 H, C–CH<sub>2</sub>, C–CH<sub>3</sub>), 1.77(br., 4H, C–CH<sub>2</sub>), 2.98(br., 2H, OH); <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ/ppm): 14.40(s, C–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>3</sub>), 17.70(s, C–CH<sub>2</sub>–CH<sub>3</sub>), 29.48, 29.66(d, C–CH<sub>2</sub>), 47.77(s, C–CH<sub>3</sub>), 75.13(s, C≡C), 106.96(s, C–OH), 199.8(s, CO); *Anal. Calc.* for **2**: C, 44.65; H, 4.58. *Found*: C, 44.48, H, 4.70%; IR(KBr/cm<sup>−1</sup>): 2022.6(s), 2053.5(s), 2091.7(s), 3257.9(br.); color: red (solid state).

### 3.2. Synthesis of **3**

A 100 cm<sup>3</sup> flask was charged with dicobalt octacarbonyl, Co<sub>2</sub>(CO)<sub>8</sub> (0.171 g, 0.500 mmol) and 1,1,4,4-tetraphenyl-2-butyne-1,4-diol (0.195 g, 0.500 mmol) in 5 mL of THF. The mixture was stirred at 60 °C for 3 h resulting in a red solution. The solvent was removed under reduced pressure, and the resulting residue was chromatography by CTLC. A red band was eluted out using a mixed solvent system (CH<sub>2</sub>Cl<sub>2</sub>/hexane = 1:1). The product was identified as **3** (0.316 g, 0.467 mmol, 93.4%).

**3**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ/ppm): 4.31(s, 2H, OH), 7.28(br., 12H, Ph), 7.61(br., 8H, Ph); <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ/ppm): 80.62(s, C≡C), 108.23(s, C–(OH)Ph<sub>2</sub>), 126.93(s, arene), 127.67(s, arene), 128.03(s, Ph), 146.12(s, *ipso* of arene), 198.46(br., COs); *Anal. Calc.* for **3**: C, 60.37, H, 3.28. *Found*: C, 59.60; H, 3.62%; color: red (solid state).

### 3.3. Synthesis of **4**

A 100 cm<sup>3</sup> flask was charged with complex **3** (0.344 g, 0.509 mmol) and dppm (0.196 g, 0.509 mmol) in 5 mL of toluene. The mixture was stirred at 100 °C for 16 h yielding a dark-brown solution. The solvent was removed under reduced pressure, and the resulting residue was chromatography by CTLC. The first band was eluted out using a mixed solvent system (CH<sub>2</sub>Cl<sub>2</sub>/hexane = 2:1). The product was identified as the title compound **4** (0.501 g, 0.499 mmol, 97.9%).

**4**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ/ppm): 2.51(s, 2H, OH), 3.69(t, *J*<sub>PH</sub> = 10.5 Hz, 2H, CH<sub>2</sub>), 7.15–7.46(br. 40 H, arene); <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ/ppm): 36.28(t, *J*<sub>PC</sub> = 82.5 Hz, CH<sub>2</sub>), 81.09(s, C≡C), 109.81(s, C–(OH)Ph<sub>2</sub>), 126.95–131.52(br.,

arene), 146.72(s, *ipso* of arene), 204.68(br., COs); <sup>31</sup>P NMR (CDCl<sub>3</sub>, δ/ppm): 35.8(s, dppm); *Anal. Calc.* for **4**: C, 68.14; H, 4.14. *Found*: C, 64.64; H, 4.55%; IR(KBr/cm<sup>−1</sup>): 1966.5(s), 1992.7(s), 2022.8(s); MS (*m/z*): 977(M<sup>+</sup>–CO). color: brown (solid state).

### 3.4. Synthesis of **5a** and **5b**

Co<sub>2</sub>(CO)<sub>8</sub> (0.171 g, 0.500 mmol), 1,1-diphenyl-2-propyn-1-ol (0.104 g, 0.500 mmol) and 5 mL of toluene were placed in a 100 mL round-bottomed flask charged with a magnetic stirrer. The red colored solution was stirred at 60 °C for 2 h. To the mixture was then added *N,N*-bis(diphenylphosphino)amine (0.192 g, 0.500 mmol) with 5 cm<sup>3</sup> of toluene followed by stirring at 80 °C for additional 16 h. The solvent was removed under reduced pressure, and the resulting residue was chromatography by CTLC. Complex **5a** was obtained from the first red band eluted by hexane, while complex **5b** from the second red-pink band by CH<sub>2</sub>Cl<sub>2</sub>/hexane (1/1) solution. The yields for **5a** and **5b** were 33.9% (0.084 g, 0.170 mmol) and 39.1% (0.161 g, 0.196 mmol), respectively.

**5a**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ/ppm): 2.60(s, 1H, OH), 6.52(s, 1H, CH), 7.23–7.25(br., 2H, arene), 7.30–7.32(br., 4H, arene), 7.69–7.71(br., 4H, arene); <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ/ppm): 73.06, 80.08(s, C≡C), 105.80(s, C–(OH)Ph<sub>2</sub>), 125.71(s, arene), 127.48(s, arene), 128.26(s, Ph), 146.71(s, *ipso* of arene), 198.88(br., COs); *Anal. Calc.* for **5a**: C, 51.04; H, 2.45. *Found*: C, 50.07; H, 2.99%; IR(KBr/cm<sup>−1</sup>): 1977.7(w), 2002.7(s), 2027.8(s), 2051.8(s), 2093.9(m); MS (*m/z*): 466 (M<sup>+</sup>–CO); color: red (solid state).

**5b**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ/ppm): 3.00(s, 1H, OH), 3.61(br. 2 H, CH<sub>2</sub> or NH), 5.75(t, *J*<sub>PH</sub> = 9.0 Hz, 1H, CH), 7.15–7.78(br., 30 H, arene); <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ/ppm): 73.12(s, C≡CH), 80.61(s, C≡C(OH)Ph<sub>2</sub>), 126.31–130.90(br., arene), 147.92(s, *ipso* of arene), 201.20(br., COs), 206.24(br., COs); <sup>31</sup>P NMR(CDCl<sub>3</sub>, δ/ppm): 98.6(s, 2 P, dppm); *Anal. Calc.* for **5b**: N, 1.70; C, 62.71; H, 4.04. *Found*: N, 2.89; C, 61.85; H, 4.21%; IR(KBr/cm<sup>−1</sup>): 1977.0(s), 2003.0(s), 2027.7(s); MS (*m/z*): 823 (M<sup>+</sup>); color: red (solid state).

### 3.5. Synthesis of **6** and **7**

A 100 cm<sup>3</sup> round flask was charged with Co<sub>2</sub>(CO)<sub>8</sub> (0.342 g, 1.000 mmol) and *N,N*-bis(diphenylphosphino)amine (0.385 g, 1.000 mmol) with 15 cm<sup>3</sup> of THF. The mixture was warmed up to 65 °C and stirred for 12 h. Then, one molar equivalent of 2-propyn-1-ol (0.056 g, 1.000 mmol) was added. The mixture was stirred at 65 °C for another 12 h. The resulting green solution was purified by centrifugal thin-layer chromatography (CTLC). The second red-colored band was eluted out with CH<sub>2</sub>Cl<sub>2</sub>. The solvent was removed in vacuo, and the resulting solid was identified as **6** (0.618 g, 0.920 mmol, 92% yield). A similar procedure was used for the preparation



of **7**.  $\text{Co}_2(\text{CO})_8$  (0.342 g, 1.000 mmol), *N,N*-bis(diphenylphosphino)amine (0.385 g, 1.000 mmol) and 15 mL of THF were placed in a 100 mL round-bottomed flask equipped with a magnetic stirrer. The solution was stirred at 65 °C for 12 h. Then, one molar equivalent of 3-butyne-1-ol (0.070 g, 1.000 mmol) was added. The solution was stirred at 65 °C for another 12 h. The resulting green solution was purified by centrifugal thin-layer chromatography (CTLC). The second red-colored band was eluted out with  $\text{CH}_2\text{Cl}_2$ . The solvent was removed in vacuo, and the residual solid was identified as **7** (0.589 g, 0.86 mmol, 86% yield).

**6**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 1.69(s, 1H, OH), 3.60(s, 1H, NH), 4.76(d,  $J_{\text{H-H}} = 6.0$  Hz, 2H,  $\text{CH}_2$ ), 5.34(t, 1H,  $\equiv\text{CH}$ ), 7.38–7.46(br., 10H, arene);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 65.10(s,  $\text{CH}_2\text{-OH}$ ), 71.10(s,  $\text{C-CH}_2\text{-OH}$ ), 101.84(s,  $\equiv\text{CH}$ ), 128.47–130.41(arene), 140.10(d,  $J_{\text{p-c}} = 36.6$  Hz, *ipso*-arene), 202.6 (br, COs), 206.3 (br, COs);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 33.7(s, PNP); *Anal.* Calc. for **6**: C, 55.46, H, 3.75, N, 2.09%. Found: C, 54.54, H, 3.90, N, 2.71%; M.S.(FAB): 643( $\text{M}^+ - \text{CO}$ ); color: red (solid state).

**7**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 2.01(s, 1H, OH), 3.12(d,  $J_{\text{H-H}} = 6.0$  Hz, 2H,  $\text{CH}_2\text{-OH}$ ), 3.52(s, 1H, NH), 3.98(d,  $J_{\text{H-H}} = 6.0$  Hz, 2H,  $\text{CH}_2\text{-CH}_2$ ), 5.30(t, 1H,  $\equiv\text{CH}$ ), 7.37–7.44(br., 10H, arene);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 38.32(s,  $\text{CH}_2\text{-CH}_2\text{-OH}$ ), 64.44(s,  $\text{CH}_2\text{-OH}$ ), 71.10(s,  $\text{C-CH}_2\text{-CH}_2\text{-OH}$ ), 98.61(s,  $\equiv\text{CH}$ ), 128.65–130.87(arene), 140.64(d,  $J_{\text{p-c}} = 73.9$  Hz, *ipso*-arene), 203.4(s, CO), 206.7 (s, CO);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 33.8(s, PNP); *Anal.* Calc. for **7**: C, 56.08; H, 3.97; N, 2.04%; Found: C, 56.36; H, 4.12; N, 2.25%; M.S.(FAB): 685( $\text{M}^+ + 1$ ); color: red (solid state).

### 3.6. X-ray crystallographic studies

Suitable crystals of **1**, **2**, **4**, **5a**, **5b**, **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  $\omega$  (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<sup>1</sup>. Crystallographic data for compounds **1**, **2**, **3**, **5a**, **5b**, **6**, and **7** are summarized in Table 1.

### Acknowledgement

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### Appendix A. Supplementary material

CCDC 616907, 616908, 616909, 616910, 616911, 616912 and 616913 contain the supplementary crystallographic data for compounds **1**, **2**, **3**, **5a**, **5b**, **6**, and **7**. These data can be obtained free of charge via <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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.01.037.

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