# Preparation and Characterization of a Cyclic Compound Consisting of Bis(diphenylphosphino)acetylene Joined Alkyne-Bridged Dicobalt Fragments

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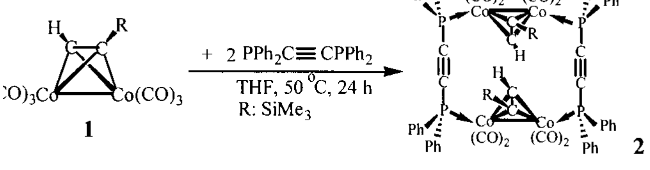
A cyclic compound, $[Co_2(CO)_4(\mu_2\text{-}HC\equiv CSiMe_3)(PPh_2C\equiv C\text{-}PPh_2)]_2$ **2**, was identified from the reaction of bis(diphenylphosphino)acetylene with an alkyne-bridged dicobalt complex, $(\mu_2\text{-}HC\equiv CSiMe_3)Co_2(CO)_6$ **1**. Crystal structure of **2** shows that it is a twelve-membered ring complex comprised of two DPPA coordinated pseudo-tetrahedral $Co_2C_2$ units. Further reaction of **2** with two equivalents of $Co_2(CO)_8$ resulted in the conversion of **2** into $[Co_2(CO)_6\{\mu\text{-P,P-}(\mu\text{-}PPh_2C\equiv CPPh_2)\}][Co_2(CO)_4(\mu\text{-}HC\equiv CSiMe_3)]$ **3**.

The phosphine ligands have played an important role ever since the discovery of the Wilkinson's catalyst, which probably is the most studied and well-documented soluble catalyst for olefin hydrogenation reaction.[1–5] Occasionally, some unpredicted marvelous results were reported from the reactions of multiple-functional phosphine ligands[6] such as alkynylphosphines $R_nP(C\equiv C\text{–}R')_{3-n}$ (n = 0–2), with transition metal compounds.[7,8] We report herein the synthesis and a detailed structural study of an unexpected twelve-membered ring complex from the reaction of a bi-functional ligand, bis(diphenylphosphino)-acetylene (DPPA), with **1**.[9]

Into a 100-$cm^3$ flask was placed dicobalt octacarbonyl, $Co_2(CO)_8$ (0.4 g, 1.17 mmol) and trimethylsilylacetylene (0.16 $cm^3$, 1.17 mmol) with 20 $cm^3$ of THF. The solution was stirred at room temperature for 3 h. Purification with centrifugal thin-layer chromatography was carried out from hexane. Quantitative yield was obtained for the alkyne-bridged dicobalt octacarbonyl complex, **1**. One equivalent of bis(diphenylphosphino)acetylene was added into a 100-$cm^3$ flask which contains **1** (0.449 g) with 20 $cm^3$ of THF. The solution was stirred at 50 °C for 24 h. There were three compounds being isolated by the similar purification procedure as shown above. The first band was identified as some unreacted **1**. The identity of the second band is unknown. The third band is **2** with the yield of 62%.



**Scheme 1.**

Compound **2** was characterized by spectroscopic means as well as crystal structure determination.[10] Crystals of **2** were obtained from the $CH_2Cl_2$ solution under 4 °C. The main structure of **2** is a twelve-membered ring complex comprised of two DPPA coordinated pseudo-tetrahedral $Co_2C_2$ units. Interestingly, the phosphorous atoms, instead of the more reactive alkyne, were coordinated to $Co_2C_2$ units in DPPA.[11–15] The twelve-membered ring is not coplanar, rather, it is more like a Möbius strip. Two bridged alkynes are inside the twelve-membered ring and point to each other. The distance between two acetylenic protons is 2.266 Å. Two DPPA ligands almost remain linear. The bond lengths of two triple bonds are the same, 1.189 Å. The acetylenic protons exhibit more downfield shift in $^1H$ NMR compared with regular alkyne-bridged, dicobalt-complex. Only one set of triplet acetylenic proton, caused by two coordinated, equivalent phosphorus atoms, was observed because of its symmetric conformation. For the same reason, only one signal was observed for four phosphorus atoms in $^{31}P$ NMR.

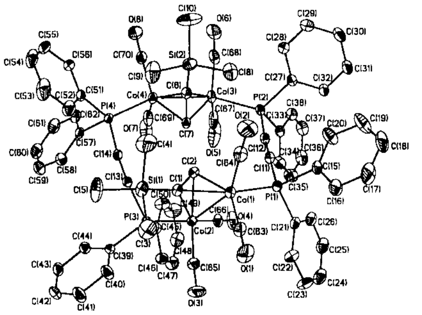
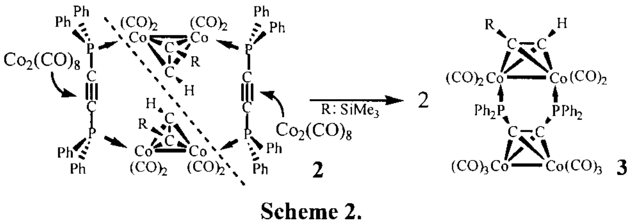


**Figure 1.** ORTEP drawing with the numbering scheme of **2**. Some atoms are omitted for clarity.

Two equivalents of $Co_2(CO)_8$ with **2** (0.375 g) were placed into a 100-$cm^3$ flask with 20 $cm^3$ of THF. The solution was stirred at 40 °C for 20 h. The reaction product **3** was isolated as the first band by the similar purification procedure as shown above. The second band is the unreacted **2** with some unidentified compounds. The yield of **3** is 18%. The conversion of **2** to **3** might take place through the attack of the triple bond of the DPPA ligand in **2** by $Co_2(CO)_8$. The coordination of dicobalt fragment to the triple bond of the DPPA ligand will cause the change of the geometry and the fragmentation follows. The release of one side of DPPA ligand will coordinate back to another cobalt center and yield **3**.



**Scheme 2.**

Crystals of **3** were obtained from the $CH_2Cl_2$ solution under 4 °C and the structure was determined.[16] The bond lengths of bridged alkynes are 1.337 Å and 1.358 Å; they are within the double bond range. Two sets of Co–Co bond distances are 2.541 Å and 2.459 Å. All carbonyls are terminal. The bulky group, $-SiMe_3$, points away from the center of molecule. Only one signal was observed for two equivalent phosphorus atoms in $^{31}P$ NMR. There is one set of triplet acetylenic proton, caused by two coordinated, equivalent phosphorus atoms, was observed due to its symmetric nature.

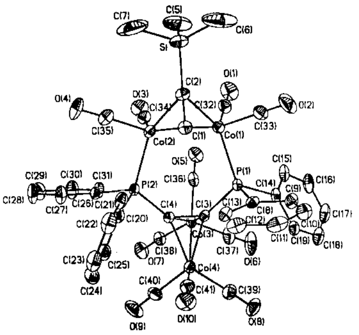


**Figure 2.** ORTEP drawing with the numbering scheme of **3**. Some atoms are omitted for clarity.

In this work, an unusual twelve-membered ring compound, **2**, which is comprised of two DPPA coordinated pseudo-tetrahedral $Co_2C_2$ units, was characterized. The fragmentation of **2** occurs and forms **3** while two equivalents of $Co_2(CO)_8$ was added.

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## References and Notes

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10 Crystal data for **2**: $C_{71}H_{60}Cl_2Co_4O_8P_4Si_2$, $M_r$ = 1527.87, triclinic, space group $P2(1)/c$, $a$ = 13.1393(13) Å, $b$ = 13.5047(13) Å, $c$ = 23.903(3) Å, $\alpha$ = 95.769(2)°, $\beta$ = 100.752(2)°, $\gamma$ = 114.872(2)°, $V$ = 3703.4(6) Å$^3$, $Z$ = 2 , $D_c$ = 1.370 Mg/m$^3$, $R_1$ = 0.0487. Selected spectroscopic data for **2**: Brown solid; $^1H$ NMR ($CDCl_3$, $\delta$) –0.05 (s, 18H, $-SiMe_3$), 6.52 (t, $J_{P\text{-}H}$ = 6.2Hz, 2H, CH), 7.22–7.84 (m, 40H, arene); $^{13}C$ NMR ($CDCl_3$, $\delta$): 1.16(s, 6C, –Me); 74.26, 87.33 (s, 2C, C≡C); 110.6 (b, 2C, C≡C); 132.92 (d, $J_{P\text{-}C}$ = 20Hz, 1C, arene); 131.57 (d, $J_{P\text{-}C}$ = 13Hz, 1C, arene); 130.30 (d, $J_{P\text{-}C}$ = 9Hz, 1C, arene); 129.61 (s, 1C, arene); 132.58 (d, $J_{P\text{-}C}$ = 24Hz, 1C, arene); 131.20 (d, $J_{P\text{-}C}$ = 13Hz, 1C, arene); 128.86 (s, 1C, arene); 128.61 (d, $J_{P\text{-}C}$ = 9Hz, 1C, arene); 201.783(m, CO); 204.774(m, CO); $^{31}P$ NMR ($CDCl_3$, $\delta$): 29.294(s, 4P); Anal. Calcd. for $C_{71}H_{60}Cl_2Co_4O_8P_4Si_2$: C 58.18, H 4.18. Found C 59.77, H 4.76; MS(FAB): $m/z$ 1332(M$^+$ – 4CO); IR($CH_2Cl_2$, $\nu_{CO}$, cm$^{-1}$) 2057(m), 2020(s), 1993(s), 1965(s).
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16 Crystal data for **3**: $C_{41}H_{30}Co_4O_{10}P_2Si$, $M_r$ = 1008.40, triclinic, space group $P1$, $a$ =11.7995(8) Å, $b$ = 13..0453(9) Å, $c$ = 15.5864(11) Å, $\alpha$ = 95.734(2)°, $\beta$ = 100.2760(10)°, $\gamma$ = 111.1890(10)°, $V$ =2165.5(3) Å$^3$, $Z$ = 2 , $D_c$=1.547 Mg/m$^3$, $R_1$ = 0.0439. Selected spectroscopic data for **3**: Brown solid; $^1H$ NMR ($CDCl_3$, $\delta$) 0.28 (s, 9H, $-SiMe_3$), 5.76 (t, $J_{P\text{-}H}$ = 7.8Hz, 1H, CH), 7.32–7.97 (m, 20H, arene); $^{31}P$ NMR ($CDCl_3$, $\delta$): 56.41 (s, 2P); MS(FAB): $m/z$ 1011(M$^+$+1); IR($CH_2Cl_2$, $\nu_{CO}$, cm$^{-1}$) 2056(m), 1991(w), 1958(w).