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Observations on reaction pathways of dicobalt octacarbonyl with alkynyl amines

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Abstract

Treatments of a bis(diphenylphosphino)methylene (dppm) bridged dicobalt complex, $Co_2(CO)_6$(dppm) (**4**), with propargylamine and 4-ethynylaniline at 25 °C for 24 h gave [(dppm)$Co_2(CO)_4$(μ-HC≡CCH_2NH_2)] (**5**) and [(dppm)$Co_2(CO)_4$(μ-HC≡$CC_6H_4NH_2$)] (**6**), respectively. Interestingly, only alkynyl amines bridged dicobalt complexes were obtained rather than the previously observed coupling products. The results are in acceptance with the proposed mechanism which describes the formation of the coupling products {[$Co_2(CO)_6$(μ-HC≡C–)]–CH_2NH}$_2$C═O (**1**) and {[$Co_2(CO)_6$(μ-HC≡C–)]–C_6H_4N═}$_2$ (**2**) from the reaction of $Co_2(CO)_8$ with propargylamine and 4-ethynylaniline, respectively. Similar results were attained for the reactions of **4** with propioamide and 1-ethynylcyclohexylamine at 25 °C for 24 h which yielded [(dppm)$Co_2(CO)_4$(μ-HC≡CC(═O)NH_2)] (**7**) and [(dppm)$Co_2(CO)_4$(μ-HC≡$CC_6H_{10}NH_2$)] (**8**), respectively.

Reaction of 1-ethynylcyclohexylamine with one molar equivalent of $Co_2(CO)_8$ in THF at 25 °C for 15 min gave an alkyne bridged dicobalt complex, [$Co_2(CO)_6$(μ-HC≡$CC_6H_{10}NH_2$)] (**9**). Direct treatment of 3-ethynlaniline with one molar equivalent of $Co_2(CO)_8$ in THF at 25 °C for 1 h gave an alkyne bridged dicobalt complex, [$Co_2(CO)_6$(μ-HC≡$CC_6H_4NH_2$)] (**11**) and an azobenzene derivative, {[$Co_2(CO)_6$(μ-HC≡C)]C_6H_4N═}$_2$ (**10**).

Further treatments of **8**, **9**, and **11** with one molar equivalent of Sanger's reagent, 2,4-dinitrofluorobenzene, in THF at 25 °C for 48 h gave [(dppm)$Co_2(CO)_4$(μ-HC≡$CC_6H_{10}NHC_6H_3(NO_2)_2$)] (**13**), [$Co_2(CO)_6$(μ-HC≡$CC_6H_{10}NHC_6H_3(NO_2)_2$)] (**14**), and [$Co_2(CO)_6$(μ-HC≡$CC_6H_4NHC_6H_3(NO_2)_2$)] (**15**), respectively.

Keywords: Cobalt-mediated catalytic reaction; Carbonylation; Azobenzene; Sanger's reagent

1. Introduction

Reactions of alkynes with various metal complexes were extensively studied because of their diverse bonding modes and wide-ranged reactivities are interested to many chemists [1] In particular, the structures and reactivities of the alkyne bridged dicobalt complexes, $Co_2(CO)_6$(μ-alkyne), were well examined mainly due to key roles played in the Pauson–Khand reactions [2]. Generally, these type of complexes are prepared straightforward from the thermal reaction of $Co_2(CO)_8$ with designated alkynes [3]. The alkyne uses the both sets of filled π orbitals to bond with the dicobalt fragment. According to the Dewar–Chatt–Duncanson's model, the substituents on the bridged alkyne shall bend away from the metal center due to the metal to ligand π-electron backbonding mechanism [4].

Although catalytic carbonylation has been explored for many years, the subject remains of much interest to many researchers [5]. Normally, harsh reaction conditions including elevated temperature and high pressures are required for employing transition metals such as Mn

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[6], Co [7], Ni [8], Ru [9], Rh [10], W [11], Pd [12] as catalyst. As for main group elements such as S [13] or Se [14], large quantities of metals are generally required besides the severe reaction conditions. Our previous results had demonstrated that an unusual carbonylation of primary amine took place at room temperature utilizing $Co_2(CO)_8$ as catalyst (Scheme 1). Compound **1**, {[$Co_2(CO)_6$(μ-HC≡C–)]–CH_2NH}$_2$C=O, can be viewed as two deprotonated propargylamine bridged dicobalt fragments, [$Co_2(CO)_6$(μ-C≡CCH_2NH)]$^-$, being coupled by a carbonyl group through carbonylation [15]. We also reported a one-pot reaction of the formation for an azobenzene compound, {[$Co_2(CO)_6$(μ-HC≡C–)]–C_6H_4N=}$_2$ (**2**), a potential liquid crystal precursor [16], from 4-ethynylaniline through cobalt-assisted coupling reaction (Scheme 1) [17]. Interestingly, two divergent types of products, urea- and azobenzene-like derivatives, were observed from reactions started with close-related alkynyl amines.

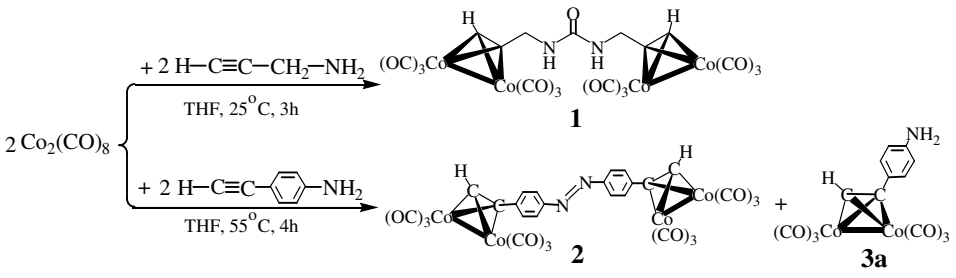
A reaction mechanism was proposed to account for the formation of **1** and **2** is presented in Figs. 1 and 2. It is apparent that the alkynyl amine plays dual roles here: first, as a metal-bridging moiety; second, as a coordinating ligand towards the dicobalt complex. It is generally accepted that in the first reaction step, the dicobalt hexacarbonyl fragment is bridged by the triple bond of the alkynyl amine and leads to the formation of NH_2[X] ([X]: $Co_2(CO)_6$(μ-HC≡C-Y-), **3a**: Y = C_6H_4; **3b**: Y = CH_2). Thereafter, the acidity of the amine protons of **3** is enhanced. It is followed by the coordination of **3** through its amine site to another molar equivalent of $Co_2(CO)_8$. After that, an oxidative addition of NH_2[X] towards $Co_2(CO)_8$ takes place and then it leads to the cleavage of the cobalt–cobalt bond. Presumably, an activated complex [$(CO)_4$Co–NH[X]] (**I**), having a direct Co–N covalent bond as well as a side product $HCo(CO)_4$, was formed [18]. The latter might be acting as a strong inorganic acid or convert disproportionately to $Co_2(CO)_8$ and H_2. Starting from (**I**), there are two distinct routes, *Route A* and *B*, each leads to the formation of **1**- or **2**-like products. For the *Route A*, there are two most probable reaction courses i.e. *Course 1* and *Course 2* are proposed and examined theoretically [19]. Elementary steps from (**II**) to (**X**) for both reaction pathways, including the amino group migration to the Co–CO bond, additional NH_2CH_3 molecule association, hydride migration of the coordinated amine proton to the cobalt center, and reductive elimination of –C(=O)$NHCH_3$ with –NH_2CH_3, are modeled and inspected. By contrast, for the *Route B*, the first step involves the release of a CO from (**I**), forming an activated complex (**XI**), which subsequently dimmerized to yield (**XII**). Then, consecutive processes including hydride migration, hydrogen elimination, and formation of N=N bond are attributed to the formation of intermediates (**XIII**), (**XIV**) and (**XV**), respectively. The processes are ended with the elimination of **2** from (**XV**). It is proposed that the formation of either **1**- or **2**-type compound depends on the characteristic of the activated complex [$(CO)_4$Co–NH[X]] (**I**).

This work describes our efforts in comprehending the diversities of the catalytic reactions of dicobalt carbonyl complexes with some designated alkynyl amines by experimental means. The processes of labeling terminal amino group of the alkyne bridged dicobalt complexes by the Sanger's reagent are also reported.

2. Results and discussion

2.1. Reactions of $Co_2(CO)_6$(dppm) (4) with alkynyl amines

As presented in the proposed mechanism, more than one molar equivalent of $Co_2(CO)_8$ is required for the formation of (**I**), which thereafter leads to the formation of urea- or azobenzene-derivative product. A critical step is the oxidative addition process of **3** towards the second molar of $Co_2(CO)_8$, that leads to the cleavage of the metal–metal bond. In principle, it is unlikely to break the cobalt–cobalt bond of a dppm bridged dicobalt complex, $Co_2(CO)_6$(dppm) (**4**), at mild reaction conditions. According to the proposed mechanism, thereby, succeeding catalytic coupling reaction shall be halted and resulted in the commonly observed alkyne bridged dicobalt complex, [(dppm)$Co_2(CO)_4$(μ-alkyne)]. Compound **4** was prepared from direct thermal reaction of $Co_2(CO)_8$ with dppm [20]. Further reactions of **4** with



Scheme 1.

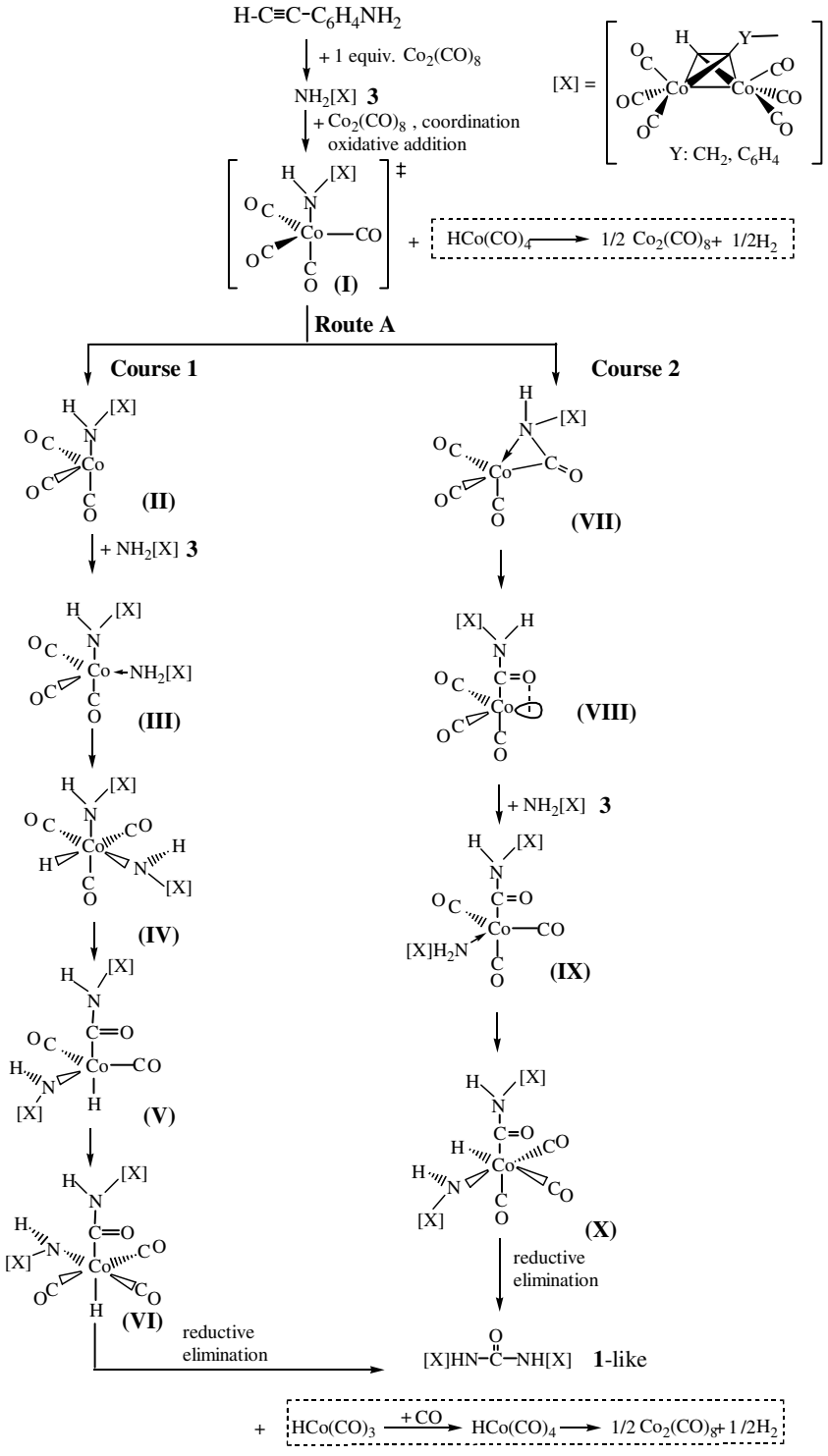


Fig. 1. Proposed mechanism for the formation of **1**.

propargylamine and 4-ethynylaniline at 25 °C for 24 h gave alkyne bridged dicobalt complexes, [(dppm)Co_2 $(CO)_4$(μ-HC≡CCH_2NH_2)] (**5**) and [(dppm)$Co_2(CO)_4$ (μ-HC≡$CC_6H_4NH_2$)] (**6**), respectively. (Scheme 2). Both **5** and **6** were characterized by spectroscopic means as well as X-ray structural determination.

As for the ^{1}H NMR spectrum of **6** in $CDCl_3$, it displays two sets of multiplet at 3.06 and 3.57 ppm which are assigned for the two methylene protons of the bridging dppm. In contrast, there is only one set of triplet signal at 3.50 ppm for the similar protons being observed for **5** in $CDCl_3$. While changing the d-solvent to CD_2Cl_2,

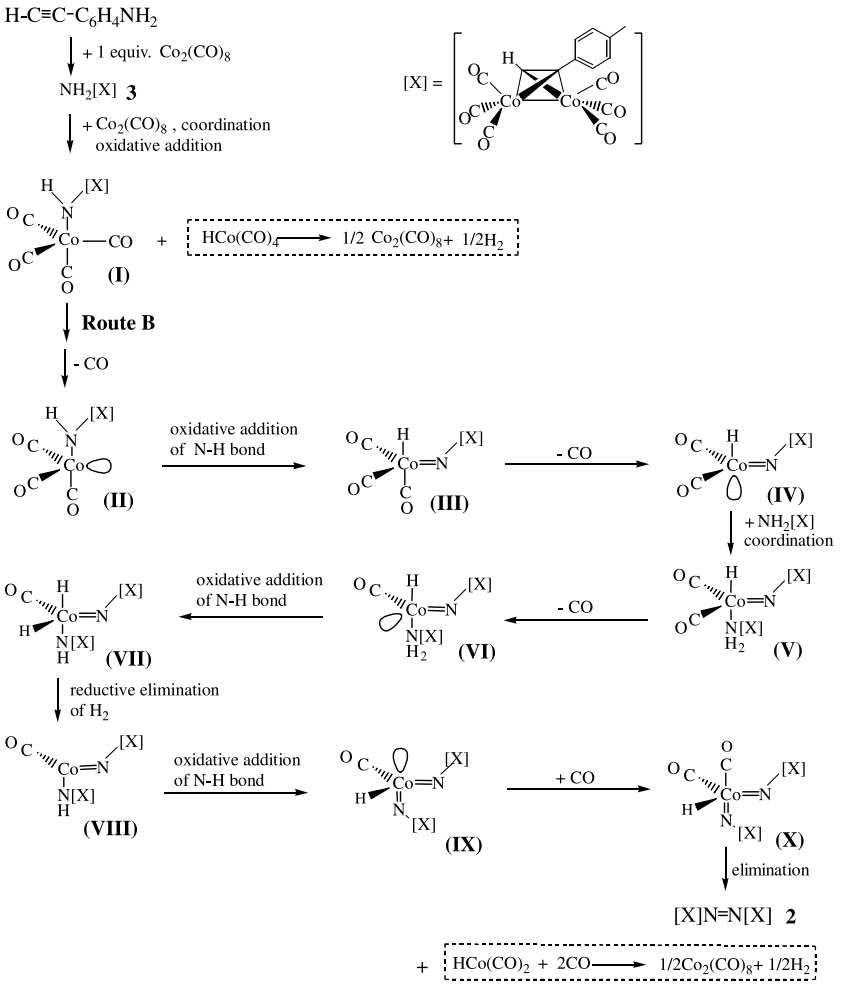
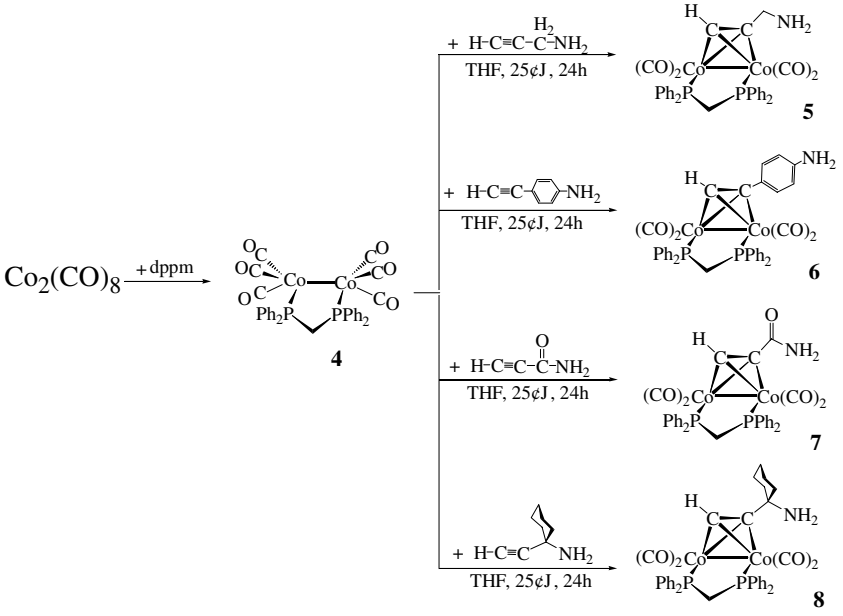


Fig. 2. Proposed mechanism for the formation of **2**.



Scheme 2.

two sets of multiplets showed at 3.39 and 3.57 ppm for **5**. These two sets of chemical shifts are separated away further when the spectrum is taken at lower temperature, i.e. at −60 °C. Surprisingly, the expected proton signals of the $-CH_2NH_2$ group do not appear in ^1H NMR. Previously, we observed a process of thermal rocking of the bridging dppm in a closely related compound [(dppm)$Co_2(CO)_4$\{μ-$PPh_2C{\equiv}CPPh_2$\}]. It was found that the two sets of multiplet of the methylene protons merged to one triplet while the rate of the back and forth motion of the dppm was fast enough. In the light of the previous observation, it is reasonable to state that the thermal motion of the bridging dppm is greater in **5** than that of **6**. In the ^{31}P NMR spectra, broad signals at 37.41 and 44.32 ppm are assigned for the phosphorous atoms of the bridging dppm of **5** and **6**, respectively. Suitable crystals of **5** and **6** were obtained from mixture solvent (CH_2Cl_2/hexanes = 1:1) at 4 °C. The structures of **5** and **6** were determined via X-ray diffraction methods and the ORTEP drawings are presented in Figs. 3 and 4. As expected, the structures of **5** and **6** show that only alkyne bridged dicobalt complexes rather than the previously observed coupling products. These results are in acceptance with the proposed mechanism which describes the formation of coupling products **1** and **2** from the reaction of $Co_2(CO)_8$ with propargylamine and 4-ethynylaniline, respectively. Further, the reaction of **6** with excess $Co_2(CO)_8$ at 25 °C for 24 h did not lead to the formation of azobenzene derivative. The bulkiness of the bridging dppm might be the key factor for hindering further coupling reaction.

Several selected structural parameters of **5** and **6** are presented in Table 2 for the comparison. As shown in Table 2, the major frameworks of these two compounds are quite similar. The bond angles of C(1)–C(2)–C(3) are 129.3(10)° and 143.9(7)° for **5** and **6**, respectively. It implies that the electronic back-bonding process from the dicobalt fragment to the bridged alkyne is greater for the latter than the former compound, thus causes the larger bending angle in **6** (see Diagram 1).

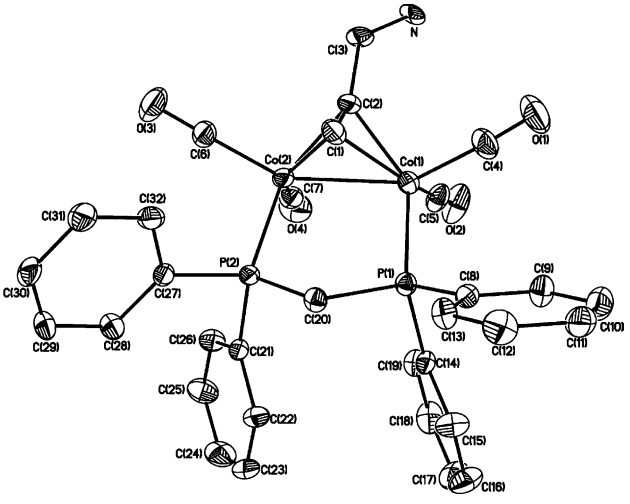


Fig. 3. ORTEP drawing of **5**. Hydrogen atoms are omitted for clarity.

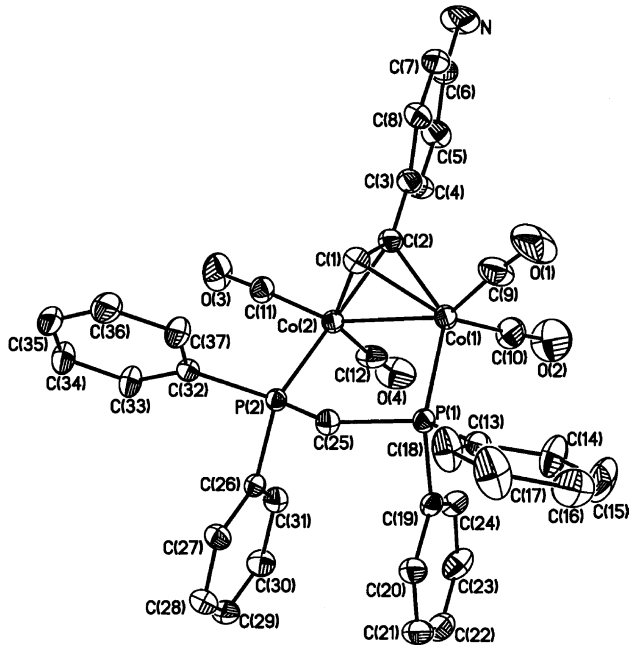


Fig. 4. ORTEP drawing of **6**. Hydrogen atoms are omitted for clarity.

Reaction of **4** with propioamide ($HC{\equiv}CC(=O)NH_2$) and 1-ethynylcyclohexylamine ($HC{\equiv}CC_6H_{10}NH_2$) at 25 °C for 24 h gave [(dppm)$Co_2(CO)_4$(μ-$HC{\equiv}CC(=O)NH_2$)] (**7**) and [(dppm)$Co_2(CO)_4$(μ-$HC{\equiv}CC_6H_{10}NH_2$)] (**8**), respectively. (Scheme 2). Both **7** and **8** were characterized spectroscopically. The ^1H NMR spectrum of **7** displays two sets of multiplet at 3.45 and 3.59 ppm and two sets of singlet at 5.51 and 5.95 ppm for the corresponding methylene protons and protons of amide group, respectively. For **8**, the ^1H NMR reveals two sets of multiplet at 3.21 and 3.77 ppm for the matching methylene protons. The signals of the corresponding cyclohexyl and amine protons are merged into a broad peak ranges from 1.31 to 2.09 ppm. Once again, only alkyne bridged dicobalt complexes were observed rather than the coupling products.

For comparison, similar procedure was employed for the reaction of propargylamine with bis-monodentate phosphine coordinated dicobalt complex, $(PPh_3)(CO)_3$-Co–Co$(CO)_3(PPh_3)$. A coupling reaction is expected from the above proposed mechanism since there no metals bridged ligand is present. Unfortunately, in contrast to the previous cases, the reaction was resulted into the formation of large amount of unidentified solid. Consequently, there is no way to find out the reaction route taken by these reactants. Repeatedly, we have found that the reaction of di-substituted dicobalt hexacarbonyl complexes, $Co_2(CO)_6L_2$ (L: PPh_3 or $P(OMe)_3$), with various alkynes always lead to insoluble precipitation.

Table 1
Crystal data of **5**, **6** and **14**

	5	**6**	**14**
Empirical formula	$C_{32}H_{22}Co_2NO_4P_2$	$C_{37}H_{29}Co_2NO_4P_2$	$C_{20}H_{15}Co_2N_3O_{10}$
Formula weight	669.38	731.44	575.21
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	P2(1)/c	P2(1)
a (Å)	35.109(4)	15.8596(16)	15.2107(14)
b (Å)	8.6187(10)	12.0939(11)	9.8627(9)
c (Å)	25.622(3)	19.578(2)	15.9711(14)
α (°)	–	–	–
β (°)	130.206(2)	111.178(2)	99.500(2)
γ (°)	–	–	–
V (Å^3)	5921.3(13)	3519.0(4)	2363.1(4)
Z	8	4	2
D_{calc} (Mg m^{-3})	1.49	1.387	1.617
λ (Mo Kα) (Å)	0.71073	0.71073	0.71073
μ (mm^{-1})	1.266	1.078	1.463
θ Range (°)	1.60–26.06	1.38–26.01	2.44–26.04
Observed reflections [$F > 4\sigma(F)$]	2938	3025	6458
Number of refined parameters	388	415	631
R_1[a] for significant reflections	0.0575	0.0604	0.0493
wR_2[b] for significant reflections	0.1559	0.1426	0.1409
Goodness-of-fit[c]	0.928	0.97	1.159

[a] $R_1 = |\sum(|F_o| - |F_c|)/|\sum F_o||$.
[b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\}^{1/2}$; $w = 0.1253, 0.0866$ and 0.0892 for **5**, **6** and **14**, respectively.
[c] Goodness-of-fit $= \sum[w(F_o^2 - F_c^2)^2/(N_{reflections} - N_{parameters})]^{1/2}$.

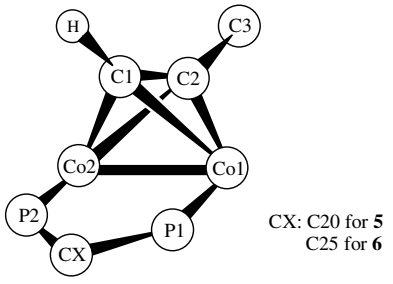
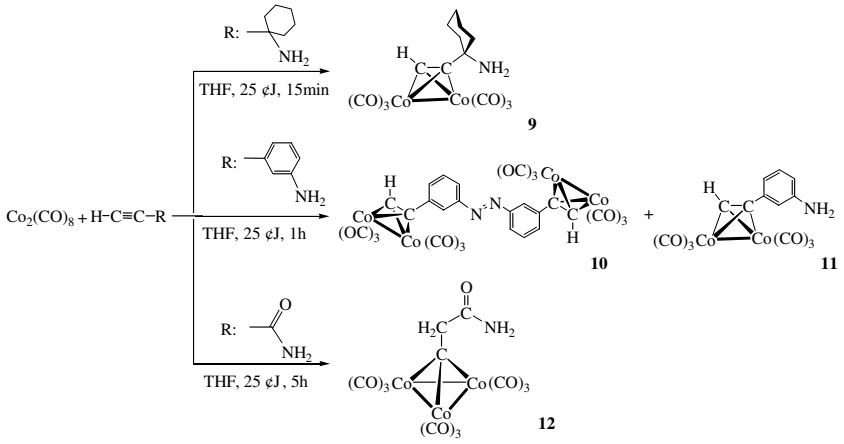


Diagram 1. Simplified structures for **5** and **6**.

2.2. Reactions of $Co_2(CO)_8$ with alkynyl amines

Direct treatment of 1-ethynylcyclohexylamine ($HC{\equiv}CC_6H_{10}NH_2$) with one molar equivalent of $Co_2(CO)_8$ in THF at 25 °C for 15 min gave an alkyne bridged dicobalt complex, [$Co_2(CO)_6$(μ-$HC{\equiv}CC_6H_{10}NH_2$)] (**9**) (Scheme 3). The ^{1}H NMR spectrum of **9** displays a group of broad peaks ranged from 1.40 to 1.64 ppm. They are assigned for the 10 protons of the cyclohexyl ring and for the two protons of the amine group. Further, the reaction of **9** with excess $Co_2(CO)_8$ at 65 °C for 1 h did not show any sign of coupling product formation. It is believed that the steric hindrance of



Scheme 3.

Table 2
Comparison of selected structural parameters of **5** and **6**

	5	**6**
Bond length (Å)		
Co(1)–C(2)	1.932(8)	2.005(7)
Co(1)–C(1)	1.939(8)	2.013(8)
Co(1)–P(1)	2.222(2)	2.2269(19)
Co(1)–Co(2)	2.4947(13)	2.4623(12)
Co(2)–C(1)	1.942(9)	1.873(8)
Co(2)–C(2)	1.947(8)	1.934(7)
Co(2)–P(2)	2.2282(18)	2.2196(18)
P(1)–C(20)	1.815(6)	–
P(2)–C(20)	1.840(6)	–
P(1)–C(25)	–	1.822(6)
P(2)–C(25)	–	1.818(6)
C(1)–C(2)	1.341(13)	1.366(10)
C(2)–C(3)	1.357(14)	1.467(10)
N–C(3)	1.220(16)	–
N–C(6)	–	1.389(10)
Bond angle (°)		
C(2)–Co(1)–C(1)	40.5(4)	39.7(3)
C(2)–Co(1)–P(1)	137.1(3)	137.5(2)
C(1)–Co(1)–P(1)	99.0(3)	102.8(2)
C(2)–Co(1)–Co(2)	50.2(2)	50.0(2)
C(1)–Co(1)–Co(2)	50.1(3)	48.2(2)
P(1)–Co(1)–Co(2)	96.27(6)	92.10(6)
C(1)–Co(2)–C(2)	40.3(4)	42.0(3)
C(1)–Co(2)–P(2)	98.8(3)	93.5(2)
C(2)–Co(2)–P(2)	136.9(3)	134.8(2)
C(1)–Co(2)–Co(1)	49.9(2)	53.2(2)
C(2)–Co(2)–Co(1)	49.7(2)	52.63(19)
P(2)–Co(2)–Co(1)	97.28(6)	98.55(5)
C(20)–P(1)–Co(1)	109.7(2)	–
C(20)–P(2)–Co(2)	108.8(2)	–
C(25)–P(1)–Co(1)	–	108.2(2)
C(25)–P(2)–Co(2)	–	109.6(2)
C(2)–C(1)–Co(1)	69.4(5)	69.8(4)
C(2)–C(1)–Co(2)	70.0(6)	71.4(5)
Co(1)–C(1)–Co(2)	80.0(3)	78.6(3)
C(1)–C(2)–C(3)	129.3(10)	143.9(7)
C(1)–C(2)–Co(1)	70.0(5)	70.4(4)
C(3)–C(2)–Co(1)	135.1(8)	133.5(5)
C(1)–C(2)–Co(2)	69.6(5)	66.6(5)
C(3)–C(2)–Co(2)	141.6(9)	135.7(6)
Co(1)–C(2)–Co(2)	80.1(3)	77.4(3)
P(1)–C(20)–P(2)	111.4(3)	–
P(2)–C(25)–P(1)	–	108.3(3)
N–C(3)–C(2)	125.3(13)	–

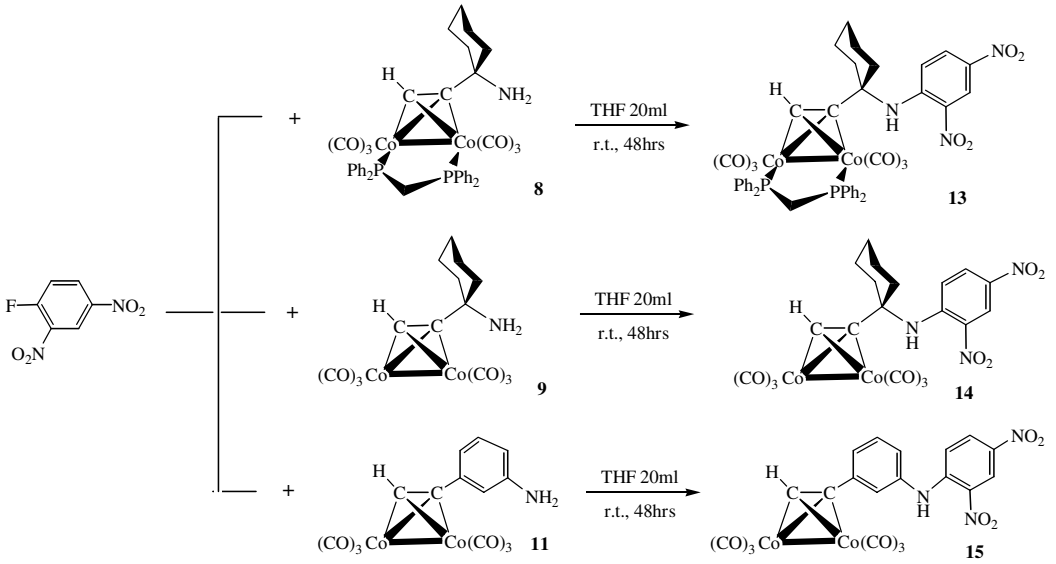
bulky substituent play an important role in preventing the formation of coupling products.

Reaction of 3-ethynlaniline, $HC{\equiv}CC_6H_4NH_2$, with one molar equivalent of $Co_2(CO)_8$ in THF at 25 °C for 1 h gave mostly alkyne bridged dicobalt complex, $[Co_2(CO)_6(\mu\text{-}HC{\equiv}CC_6H_4NH_2)]$ (**11**) [21] and small amount of azobenzene compound, $\{[Co_2(CO)_6(\mu\text{-}HC{\equiv}C)]C_6H_4N{=}\}_2$ (**10**) (Scheme 3). Both compounds were characterized by spectroscopic means. The corresponding signals of the amine protons are absent in ^{1}H NMR of **10** which is in acceptance with the chemical formula of the dimmerized product. The fact that both the azobenzene compound **10** and alkyne bridged dicobalt complex **11** are coexisted in the same batch of the reaction is noteworthy. Further, the reaction of **11** with $Co_2(CO)_8$ under high pressure of CO, 500 psi, at 25 °C for 30 h did not yield **10** or urea-like coupling product. In contrast, the reaction of **3a** under the same reaction conditions in fact yielded **2** even though no urea-like coupling product was observed. Our previous works had demonstrated the reaction of propiolamide, $HC{\equiv}CC(=O)NH_2$, with $Co_2(CO)_8$ gave a tricobalt methylidyne cluster, $[Co_3(CO)_9(\mu_3\text{–}CCH_2C(=O)NH_2)]$ **12** [22]. Interestingly, there was no alkyne bridged dicobalt complex being observed. It is generally accepted that the formation of this type of cluster via this route requires protonic reaction condition, providing the extra hydrogen comes from the acidic environs [23].

2.3. Reactions of *8*, *9*, *11* with 2,4-dinitrofluorobenzene

It is a frequent observation that the alkyne bridged dicobalt complexes are oily in nature; thereby, it makes the process of crystallization problematic. Besides, spectroscopic means such as the ^{1}H NMR may not always provide unambiguous evidence concerning the existence of an amino group in compounds. Sanger's reagent, 2,4-dinitrofluorobenzene, has been proved to be an effective agent for labeling terminal amino group [24]. It was employed here for examining the presence of a $–NH_2$ group in **8**, **9** and **11**. Reactions of **8**, **9** and **11** with one molar equivalent of 2,4-dinitrofluorobenzene in THF at 25 °C for 48 h gave $[(dppm)Co_2(CO)_4\text{-}(\mu\text{-}HC{\equiv}CC_6H_{10}NHC_6H_3(NO_2)_2)]$ (**13**), $[Co_2(CO)_6(\mu\text{-}HC{\equiv}CC_6H_{10}NHC_6H_3(NO_2)_2)]$ (**14**) and $[Co_2(CO)_6(\mu\text{-}HC{\equiv}CC_6H_4NHC_6H_3(NO_2)_2)]$ (**15**), respectively (Scheme 4). Another reagent isothiocyanatobenzene (Ph–N=C=S), that also has been proved to be an effective agent for spotting terminal amino group, was employed here to react with compound **9** and **11**. Unlike the previous works, the reactions were resulted in precipitated dark colored sulfidocobalt clusters.

All compounds were characterized by spectroscopic means. Suitable crystals of **14** were obtained from mixture solvent (CH_2Cl_2/hexanes = 1:1) at 4 °C and its structure was determined by an X-ray diffraction method. The structure of **14** reveals that the dinitrobenzene moiety is joined with the deprotonated **9** and the bond angle of C(3)–N(1)–C(9) is 130.0(3)° (Fig. 5). The hybridization of the centered nitrogen is close to sp^2 and indicates the presence of a N–H bond. It is also evidenced by the presence of corresponding signal appears at 9.16 ppm in the ^{1}H NMR spectrum. Although, some of the crystal structures of the products from Scheme 4 are not available, it is safe to state that only alkyne bridged dicobalt complexes were produced rather than the urea- or azobenzene-derivatives from the reaction as shown in Scheme 3.



Scheme 4.

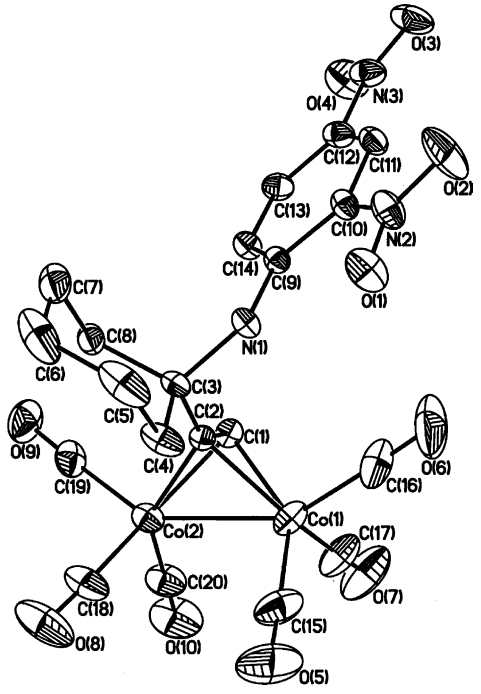


Fig. 5. ORTEP drawing of 14. Selected bond lengths (Å) and bond angles (°): Co(1)–C(1) 1.939(8), Co(1)–C(2) 1.993(7), Co(1)–Co(2) 2.477(2), Co(2)–C(1) 1.938(9), N(1)–C(9) 1.370(10), N(1)–C(3) 1.479(12), C(1)–C(2) 1.302(9), C(2)–C(3) 1.494(10), C(9)–N(1)–C(3) 130.8(7), Co(1)–C(1)–Co(2) 79.4(3), C(1)–C(2)–C(3) 143.8(7), N(1)–C(3)–C(2) 109.8(7).

3. Summary

In this work, reactions of $Co_2(CO)_8$ or $Co_2(CO)_6$(dppm) (**4**) with several selected alkynyl amines were pursued. The experimental results are consistent with the proposed reaction mechanism. It is observed that the breaking of the Co–Co bond in $Co_2(CO)_8$ is essential for the catalytic coupling reactions during the formation of **1** or **2**. In the cases of using **4** as dicobalt source, only alkyne bridged dicobalt complexes were observed. The steric hindrance of bulky substituent, as in the case of 1-ethynylcyclohexylamine, might be blocking the plausible coupling process. The preparation of another azobenzene derivative, **10**, from two primary amines through a cobalt-mediated reaction was proved successfully. The presence of amino groups in the products **8**, **9** and **11** were verified by reacting with the Sanger's reagent.

4. Experimental

4.1. General procedures

All operations were performed in a nitrogen flushed glove box or in a vacuum system using freshly distilled solvents. Separations of the products were performed by Centrifugal Thin Layer Chromatography (CTLC, Chromatotron, Harrison model 8924). ^{1}HNMR spectra were recorded (Varian VXR-300S spectrometer) at 300.00 MHz and chemical shifts were reported in ppm relative to internal $CHCl_3$ or CH_2Cl_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 on the same instrument. 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 JOEL

JMS-SX/SX 102A GC/MS/MS spectrometer. Elemental analyses were recorded on Heraeus CHN-O-S-Rapid. Accurate elemental analyses were precluded for the following compounds probably due to their chemical labilities.

4.1.1. Reaction of **4** with propargylamine

The preparative procedure of $[Co_2(CO)_6(dppm)]$ (**4**) was described elsewhere. Compound **4** (0.676 g, 1.008 mmol) and propargylamine (0.069 ml, 1.008 mmol) with 20 ml of THF were taken into a 100 cm^3 flask. The solution was stirred at 25 °C for 24 h. Subsequently, the resulting dark red solution was filtered through a small amount of silica gel. Purification was carried out with centrifugal thin-layer chromatography (CTLC). The first band (red in color), $[(dppm)Co_2(CO)_4(\mu\text{-}HC{\equiv}CCH_2NH_2)]$ (**5**), was eluted by CH_2Cl_2 and the yield is 33% (0.226 g, 0.337 mmol).

4.1.2. Characterization of **5**

^1H NMR ($CDCl_3$, δ/ppm): 3.5(t, J_{P-H} = 10.20 Hz, 2H, –CH_2 of dppm), 6.11(s, 1H, HC≡), 7.13–7.44(m, 20H, arene). ^{13}C NMR ($CDCl_3$, δ/ppm): 39.81(t, J_{P-C} = 21.12 Hz, 1C, –CH_2 of dppm), 53.41(1C, CH_2NH_2), 78.33(1C, HC≡), 87.49(1C, C≡CH), 128.34(d, J_{P-C} = 23.54 Hz, 2C, arene), 129.82(d, J_{P-H} = 25.04 Hz, 2C, arene), 131.00(t, J_{P-C} = 5.85 Hz, 2C, arene), 136.98(t, J_{P-C} = 23.08 Hz, 1C, arene), 194.82(2C, CO), 203.09(1C, CO), 203.76(1C, CO). ^{31}P NMR ($CDCl_3$, δ/ppm): 37.4(2P, dppm). IR (KBr/cm^{-1}): ν_{NH_2} 1646(m), ν_{CO} 1976(s), 2005(s), 2025(s). Anal. Calc. for **5**: N, 2.09; C, 57.42; H, 4.07. Found: N, 2.43; C, 55.72; H, 6.87%. M.S. (*m*/*z*): 669(M^+); m.p.: 186 °C (dec. temp.).

4.1.3. Reaction of **4** with 4-ethynylaniline

Following the similar procedure as shown above, **4** (1.176 g, 1.755 mmol) and 4-ethynlaniline (0.206 g, 1.755 mmol) with 20 ml of THF were placed into a 100 cm^3 flask. The solution was stirred at 25 °C for 24 h and followed similar purification processes. The first band (purple in color), $[(dppm)Co_2(CO)_4(\mu\text{-}HC{\equiv}CC_6H_4NH_2)]$ (**6**), was eluted by CH_2Cl_2 and the yield is 41% (0.521 g, 0.712 mmol).

4.1.4. Characterization of **6**

^1H NMR ($CDCl_3$, δ/ppm): 3.06(m, 1H, –CH_2 of dppm), 3.57(m, 1H, –CH_2 of dppm), 5.68(t, J_{P-H} = 7.61 Hz, 1H, HC≡), 6.49(broad, 2H, NH_2), 7.19–7.43(m, 20H, arene, 2H, C_6H_4), 7.58(d, J_{H-H} = 5.01 Hz, 2H, C_6H_4). ^{13}C NMR ($CDCl_3$, δ/ppm): 40.87(t, J_{P-C} = 20.37 Hz, 1C, –CH_2 of dppm), 72.85 (1C, HC≡), 128.10–128.3(m, 10C, arene), 129.35(2C, arene), 129.45(2C, arene), 136.47(1C, *ipso* of C_6H_4), 136.62(1C, *ipso* of arene), 136.73(1C, *ipso* of arene), 136.86(1C, *ipso* of arene), 136.99(1C, *ipso* of arene), 137.12(1C, *ipso* of C_6H_4), 203.28(2C, CO), 207.32(2C, CO). ^{31}P NMR ($CDCl_3$, δ/ppm): 44.3(2P, dppm); IR (KBr/cm^{-1}): ν_{NH2} 1613(m), ν_{CO} 1985(s). Anal. Calc. for **6**: N, 1.91; C, 60.76; H, 4.00. Found: N, 1.38; C, 60.26; H, 3.88%. M.S. (*m*/*z*): 731(M^+); m.p.: 89 °C.

4.1.5. Reaction of **4** with propioamide

Dicobalt octacarbonyl $Co_2(CO)_8$ (0.358 g, 1.047 mmol) and dppm (0.405 g, 1.052 mmol) with 10 ml of THF were taken into a 100 cm^3 round bottomed flask charged with magnetic stirrer. The solution was stirred at 65 °C for 6 h and compound **4** was obtained. Without further separation, a solution containing propioamide (0.077g, 1.115 mmol) and 5 ml of THF was transferred into the flask. The mixture was stirred at 25 °C for 8 h and followed the similar purification processes. The third band (red in color), $[(dppm)Co_2(CO)_4(\mu\text{-}HC{\equiv}CC(=O)NH_2)]$ (**7**), was eluted by CH_2Cl_2 and the yield is 56% (0.388 g, 0.568 mmol).

4.1.6. Characterization of **7**

^1H NMR ($CDCl_3$, δ/ppm): 3.45(m, 1H, –CH_2 of dppm), 3.59(m, 1H, –CH_2 of dppm), 5.51(s, 1H, NH_2), 5.87(t, J_{P-H} = 4.02 Hz, 1H, HC≡), 5.95(s, 1H, NH_2), 7.12–7.41(m, 20H, arene). ^{13}C NMR ($CDCl_3$, δ/ppm): 40.8(s, 1C, –CH_2 of dppm), 67.0(1C, H*C*≡C), 128.2–132.5(24C, arene). IR (KBr/cm^{-1}): ν_{CO} 2062(s), 2033(s), 2004(s), 1969(s), 1648(C=O). Anal. Calc. for **7**: N, 2.05; C, 56.24; H, 3.69. Found: N, 2.11; C, 55.98; H, 3.74%. M.S. (*m*/*z*): 655 $(M - CO)^+$.

4.1.7. Reaction of **4** with 1-ethynylcyclohexylamine

The similar reaction procedure was followed as shown above. Dicobalt octacarbonyl $Co_2(CO)_8$ (0.347 g, 1.017 mmol) and dppm (0.389 g, 1.011 mmol) with 10 ml of THF were taken in a 100 ml round bottomed flask charged with magnetic stirrer. The solution was stirred at 65 °C for 6 h and compound **4** was yielded. Without further separation, a solution containing 1-ethynyl–cyclohexylamine (0.134 g, 1.087 mmol) and 5 ml of THF was transferred into the flask. The mixture was stirred at 25 °C for 8 h and followed similar purification processes. The third band (red in color), $[(dppm)Co_2(CO)_4(\mu\text{-}HC{\equiv}CC_6H_{10}NH_2)]$ (**8**), was eluted by CH_2Cl_2 and the yield is 61% (0.4525 g, 0.614 mmol).

4.1.8. Characterization of **8**

^1H NMR ($CDCl_3$, δ/ppm): 1.31–2.09(m, 12H, C_6H_{10} and NH_2), 3.21(m, 1H, –CH_2 of dppm), 3.75(m, 1H, –CH_2 of dppm), 5.72(s, 1H, HC≡C), 7.23–7.47(m, 20H, arene). ^{13}C NMR ($CDCl_3$, δ/ppm): 22.55(2C, C_6H_{10}), 25.90(2C, C_6H_{10}), 41.35(1C, C_6H_{10}), 55.84(1C, C_6H_{10}), 42.32(1C, dppm), 74.36(1C, H*C*≡C), 117.61(1C, HC≡*C*), 128.17–136.99(24C, arene), 203.93(2C, CO), 207.96(2C, CO). ^{31}P NMR ($CDCl_3$, δ/ppm): 42.3. IR (KBr/cm^{-1}): ν_{CO} 1956(s), 1987(s), 2014(s). Anal. Calc. for **8**: N 1.90, C 60.24, H 4.78%.

Found: N 2.06, C 60.68, H 5.23%; M.S. (*m*/*z*): 721 $(M - NH_2)^+$.

4.1.9. Reaction of $Co_2(CO)_8$ with $HC{\equiv}CC_6H_{10}NH_2$

Similar reaction procedures were employed as mentioned above. $Co_2(CO)_8$ (0.600 g, 1.755 mmol) and 1-ethynylcyclohexylamine (0.237 ml, 1.755 mmol) with 20 ml of THF were placed into a 100 cm^3 flask. The solution was stirred at 25 °C for 15 min and followed the similar purification processes. The first band (red-brown in color) is $[Co_2(CO)_6(\mu\text{-}HC{\equiv}CC_6H_{10}NH_2)]$ (**9**) and the yield is 84% (0.607 g, 1.483 mmol).

*4.1.10. Characterization of **9***

^1H NMR ($CDCl_3$, δ/ppm): 1.40–1.64(m, 12H, C_6H_{10} and NH_2), 6.12(s, 1H, ≡CH). ^{13}C NMR ($CDCl_3$, δ/ppm): 22.40(2C, C_6H_{10}), 25.56(2C, C_6H_{10}), 42.41(1C, C_6H_{10}), 55.27(1C, C_6H_{10}), 73.61(1C, H*C*≡C), 110.20(1C, *C*≡CH), 200.08(6C, CO). IR (KBr/cm^{-1}): ν_{CO} 2017(s), 2051(s), 2093(s). Anal. Calc. for **9**: N, 3.42; C, 41.10; H, 3.20%. Found: N, 2.96; C, 40.84; H, 3.73%. M.S. (*m*/*z*): 410 $(M + 1)^+$.

4.1.11. Reaction of $Co_2(CO)_8$ with 3-ethynlaniline

$Co_2(CO)_8$ (0.600 g, 1.755 mmol) and 3-ethynlaniline (0.184 ml, 1.755 mmol) with THF 20 ml were placed into a 100 cm^3 flask. The solution was stirred at 25 °C for 1 h and followed the similar purification processes. The first band (brown in color), $\{[Co_2(CO)_6(\mu\text{-}HC{\equiv}C)]C_6H_4N{=}\}_2$ (**10**) was eluted by mixture solvent (CH_2Cl_2:hexane = 1:1) and the yield is 20% (0.139 g, 0.174 mmol, based on $Co_2(CO)_8$) and the second band (purple in color), $Co_2(CO)_6(\mu\text{-}HC{\equiv}C)C_6H_4NH_2$ (**11**) was eluted by CH_2Cl_2, in the yield of 46% (0.324 g, 0.805 mmol).

*4.1.12. Characterization of **10***

^1H NMR($CDCl_3$, δ/ppm): 6.45(s, 1H, HC≡), 7.51(t, J_{H-H} = 7.80 Hz, 1H, arene), 7.66(d, J_{H-H} = 7.50 Hz, 1H, arene), 7.88(d, J_{H-H} = 8.10 Hz 1H, arene), 8.07(s, 1H, arene). ^{13}C NMR($CDCl_3$, δ/ppm): 72.66(s, 1C, H*C*≡C), 88.75(s, 1C, *C*≡CH), 122.13(s, 1C, arene), 124.69(s, 1C, arene), 129.70(s, 1C, arene), 132.88(s, 1C, arene), 138.92(s, 1C, *ipso*-arene), 152.85(s, 1C, *ipso*-arene), 199.26(s, 6C, COs). IR (KBr/cm^{-1}): ν_{CO} 2022(s), 2057(s), 2096(s). Anal. Calc. for **10**: N, 3.49; C, 41.93; H, 1.26. Found: N, 3.23; C, 40.28; H, 3.59%. MS (FAB): 803 $(M + 1)^+$.

*4.1.13. Characterization of **11***

^1H NMR($CDCl_3$, δ/ppm): 3.69(s, 2H, NH_2), 6.34(s, 1H, HC≡), 6.63(d, J_{H-H} = 6.60 Hz, 1H, arene), 6.85(s, 1H, arene), 6.95(d, J_{H-H} = 7.20 Hz, 1H, arene), 7.12(t, J_{H-H} = 7.50 Hz, 1H, arene). ^{13}C NMR($CDCl_3$, δ/ppm): 72.58(s, 1C, H*C*≡C), 90.50(s, 1C, *C*≡CH), 115.19(s, 1C, arene), 116.54(s, 1C, arene), 120.90(s, 1C, arene), 129.57(s, 1C, arene), 138.20(s, 1C, *ipso*-arene), 146.50(s, 1C, *ipso*-arene), 199.44 (s, 6C, COs). IR (KBr/cm^{-1}): ν_{NH_2} 1621(w), ν_{CO} 2023(s), 2055(s), 2093(s). Anal. Calc. for **11**: N, 3.47; C, 41.72; H, 1.75. Found: N, 3.49; C, 41.15; H, 1.74%. MS (FAB): 403(M^+).

*4.1.14. Reaction of **8** with 2,4-dinitrofluorobenzene*

Compound **8** (0.453 g, 0.614 mmol) and 2,4-dinitrofluorobenzene (0.116 g, 0.624 mmol) with THF 20 ml were placed into a 100 cm^3 flask. The solution was stirred at room temperature for 46 h. Purification was carried out by using CTLC. The first band eluted was the unreacted **8**. The second band, $(dppm)Co_2(CO)_4[\mu\text{-}HC{\equiv}CC_6H_{10}NH\text{–}C_6H_3(NO_2)_2]$ (**13**), was eluted with mixed solvent (CH_2Cl_2:EA = 1:1) in the yield of 21% (0.194 g, 0.215 mmol).

*4.1.15. Characterization of **13***

^1H NMR ($CDCl_3$, δ/ppm): 1.28–2.12, 2.61–2.64(m, 10H, C_6H_{10}), 3.05–3.14(m, 1H, –CH_2 of dppm), 3.55–3.64(m, 1H, –CH_2 of dppm), 5.49(s, 1H, HC≡), 7.18–7.37(m, 20H, arene), 7.78(d, J_{H-H} = 10.0 Hz, 1H, arene), 8.27(dd, J_{H-H} = 9.61 Hz, J_{H-H} = 2.40 Hz, 1H, arene), 9.17(t, J_{H-H} = 2.80 Hz, 1H, NH). ^{13}C NMR ($CDCl_3$, δ/ppm): 22.4(2C, C_6H_{10}), 25.3(2C, C_6H_{10}), 40.1(1C, C_6H_{10}), 61.8(1C, C_6H_{10}), 73.8(1C, H*C*≡C), 117.3 (1C, HC≡*C*), 123.8(1C, arene), 124.7(1C, arene), 126.7(1C, arene), 132.6(1C, arene), 138.1(1C, arene), 148.2(1C, arene), 128.3–131.5, 135.4–137.2(20C, arene) 203.1, 206.9(4C, CO). IR (KBr/cm^{-1}): ν_{NO_2} 1332(s), ν_{CO} 1960(s), 1987(s), 2020(s). Anal. Calc. for **13**: N, 4.65; C, 57.16; H, 4.13. Found: N, 4.21; C, 54.31; H, 4.74%. M.S. (*m*/*z*): 903 (M^+).

*4.1.16. Reaction of **9** with 2,4-dinitrofluorobenzene*

Compound **9** (0.784 g, 1.916 mmol) and 2,4-dinitrofluorobenzene (0.357 g, 1.916 mmol) with THF 20ml were placed into a 100 cm^3 flask. The solution was stirred at 25 °C for 48 h. Purification was carried out by using CTLC and then washed with pure water. The first band (dark red in color) $Co_2(CO)_6[\mu\text{-}HC{\equiv}CC_6H_{10}NH\text{-}C_6H_3(NO_2)_2]$ (**14**), in the yield of 43% (0.479 g, 0.833 mmol).

*4.1.17. Characterization of **14***

^1H NMR ($CDCl_3$, δ/ppm): 1.33–1.89, 2.47–2.51(m, 10H, C_6H_{10}), 6.20(s, 1H, HC≡C), 7.42(d, J_{H-H} = 9.30 Hz, 1H, arene), 8.30(dd, J_{H-H} = 9.45 Hz, J_{H-H} = 2.10 Hz, 1H, arene), 9.01(s, 1H, arene), 9.16(d, J_{H-H} = 2.40 Hz, 1H, NH). ^{13}C NMR ($CDCl_3$, δ/ppm): 21.97(2C, C_6H_{10}), 24.95(2C, C_6H_{10}), 39.99(1C, C_6H_{10}), 59.97(1C, C_6H_{10}), 73.61(1C, HC≡C), 100.00(1C, C≡CH), 116.13(1C, arene), 124.70(1C, arene), 129.19(1C, arene), 131.46(1C, arene), 136.24(1C, arene), 147.04(1C, arene), 199.05(6C, CO). IR (KBr/cm^{-1}): ν_{NO_2} 1337(s), 1517(s),

ν_{CO} 2054(s), 2097(s). Anal. Calc. for **14**: N, 7.31; C, 41.76; H, 2.63. Found: N, 7.52; C, 42.16; H, 3.08%; m.p. = 142 °C (dec. temp.).

4.1.18. Reaction of *10* with 2,4-dinitrofluorobenzene

Compound **10** (0.248 g, 0.616 mmol) and 2,4-dinitrofluorobenzene (0.115 g, 0.616 mmol) with THF 20ml were placed into a 100 cm^3 flask. The solution was stirred at 25 °C for 48 h. Purification was carried out by using CTLC and then washed with pure water. The first band (dark red in color) $Co_2(CO)_6[(\mu\text{-}HC{\equiv}C)C_6H_4NHC_6H_3(NO_2)_2]$ (**15**), in the yield of 46% (0.0.161 g, 0.283 mmol).

4.1.19. Characterization of *15*

^1H NMR ($CDCl_3$, δ/ppm): 6.40(s, 1H, HC≡C), 7.22–7.26(m, 2H, arene), 7.45–7.51(m, 3H, arene), 8.17(d, J_{H-H} = 9.00 Hz, 1H, arene), 9.19(s, 1H, NH), 10.00(s, 1H, arene). ^{13}C NMR ($CDCl_3$, δ/ppm): 72.61(1C, HC≡C), 87.66(1C, C≡CH), 116.01(1C, arene), 124.12(1C, arene), 124.70(1C, arene), 126.25(1C, arene), 129.19(1C, arene), 129.95(1C, arene), 130.82(1C, arene), 131.42(1C, arene), 137.28(1C, arene), 137.71(1C, arene), 140.40(1C, arene), 146.72(1C, arene), 198.94(6C, CO). IR (KBr/cm^{-1}): ν_{NO_2} 1331(s), 1512(s), ν_{CO} 2031(s), 2094(s). Anal. Calc. for **15**: N, 7.38; C, 42.20; H, 1.59. Found: N, 6.89; C, 42.66; H, 1.90%; m.p.: 94 °C (dec. temp.).

5. X-ray crystallographic study

Suitable crystals of **5**, **6** and **14** 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 (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. 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. Crystallographic data of **5**, **6** and **14** are summarized in Table 1.

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Appendix A. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 223184, 223185 and 223186 for **5**, **6** and **14**, 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). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2004.07.047.

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