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Preparation and characterization of tricobalt methylidyne clusters: X-ray crystal structures of $[Co_3(CO)_9(\mu_3\text{-}CR)]$ (R = CH_2CH_3, $CH_2C(=O)NH_2$, $CH_2C(=O)CH_3$) and $[Co_3(CO)_7(\mu\text{-}P,P\text{-}PPh_2CH_2PPh_2)(\mu_3\text{-}CCH_2C_6H_4NH_2)]$†

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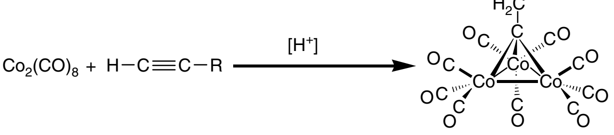
A small quantity of the tricobalt methylidyne cluster $[Co_3(CO)_9(\mu_3\text{-}CCH_2CH_3)]$ (2) was obtained, along with the major product, $[\{[Co_2(CO)_6(\mu\text{-}HC{\equiv}C\text{-})]\text{-}CH_2NH\}_2C{=}O]$ (1), from the reaction of $HC{\equiv}CCH_2NH_2$ with $Co_2(CO)_8$ in tetrahydrofuran at 45 °C for 5 h. The crystal structure of 2 showed that the amino group was unexpectedly detached from the propargylamine. The reactions of two related amines, $HC{\equiv}CC_6H_4NH_2$ and $HC{\equiv}CC(=O)NH_2$, with $Co_2(CO)_8$ gave two tricobalt methylidyne clusters, $[Co_3(CO)_9(\mu_3\text{-}CCH_2C_6H_4NH_2)]$ (5) and $[Co_3(CO)_9(\mu_3\text{-}CCH_2C(=O)NH_2)]$ (7), respectively. Further reaction of 5 with bis(diphenylphosphino)methane (DPPM) resulted in the formation of the DPPM-bridged tricobalt methylidyne cluster $[Co_3(CO)_7(\mu\text{-}P,P\text{-}PPh_2CH_2PPh_2)(\mu_3\text{-}CCH_2C_6H_4NH_2)]$ (6). Similar procedures were followed for the reaction of $HC{\equiv}C\text{-}C(=O)CH_3$ with $Co_2(CO)_8$; two compounds, $[Co_3(CO)_9(\mu_3\text{-}CCH_2C(=O)CH_3)]$ (8) and $[Co_2(CO)_6(\mu_2\text{-}\eta^2\text{-}HC{\equiv}CC(=O)CH_3)]$ (9), were obtained. All these compounds were characterized by spectroscopic means; the crystal structures of 2, 5, 6, and 7 were also determined. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: tricobalt methylidyne clusters; alkynamines; alkyne-bridged dicobalt complexes; bis(diphenylphosphino)methane

INTRODUCTION

Preparations of tricobalt methylidyne clusters with the formula $[Co_3(CO)_9(\mu_3\text{-}CCH_2R)]$ are performed by the reaction of the corresponding alkynes with $Co_2(CO)_8$ (Scheme 1).[1–5] It is generally accepted that the formation of this type of cluster by this method requires acidic reaction conditions, since the extra hydrogen has to come from protic sources.[6–9]



Scheme 1.

Our previous studies have demonstrated that unusual cobalt-mediated reactions of some primary amines might take place under mild reaction conditions[10,11] (Scheme 2). Compounds $\{[Co_2(CO)_6(\mu\text{-}HC{\equiv}C\text{-})]\text{-}CH_2NH\}_2C{=}O$ (**1**) and $\{[Co_2(CO)_6(\mu\text{-}HC{\equiv}CC_6H_4N{=}\}_2$ (**4**)) were obtained as the major products from the reactions of $HC{=}CCH_2NH_2$ and $HC{\equiv}CC_6H_4NH_2$ respectively with $Co_2(CO)_8$. These compounds can be regarded as two alkyne-bridged dicobalt fragments being linked either by a urea-based ligand in the former case or by a diazene-based ligand in the latter case. In addition to these coupled products, there were some more tricobalt

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†Dedicated to Professor Thomas P. Fehlner on the occasion of his 65th birthday, in recognition of his outstanding contributions to organometallic and inorganic chemistry.

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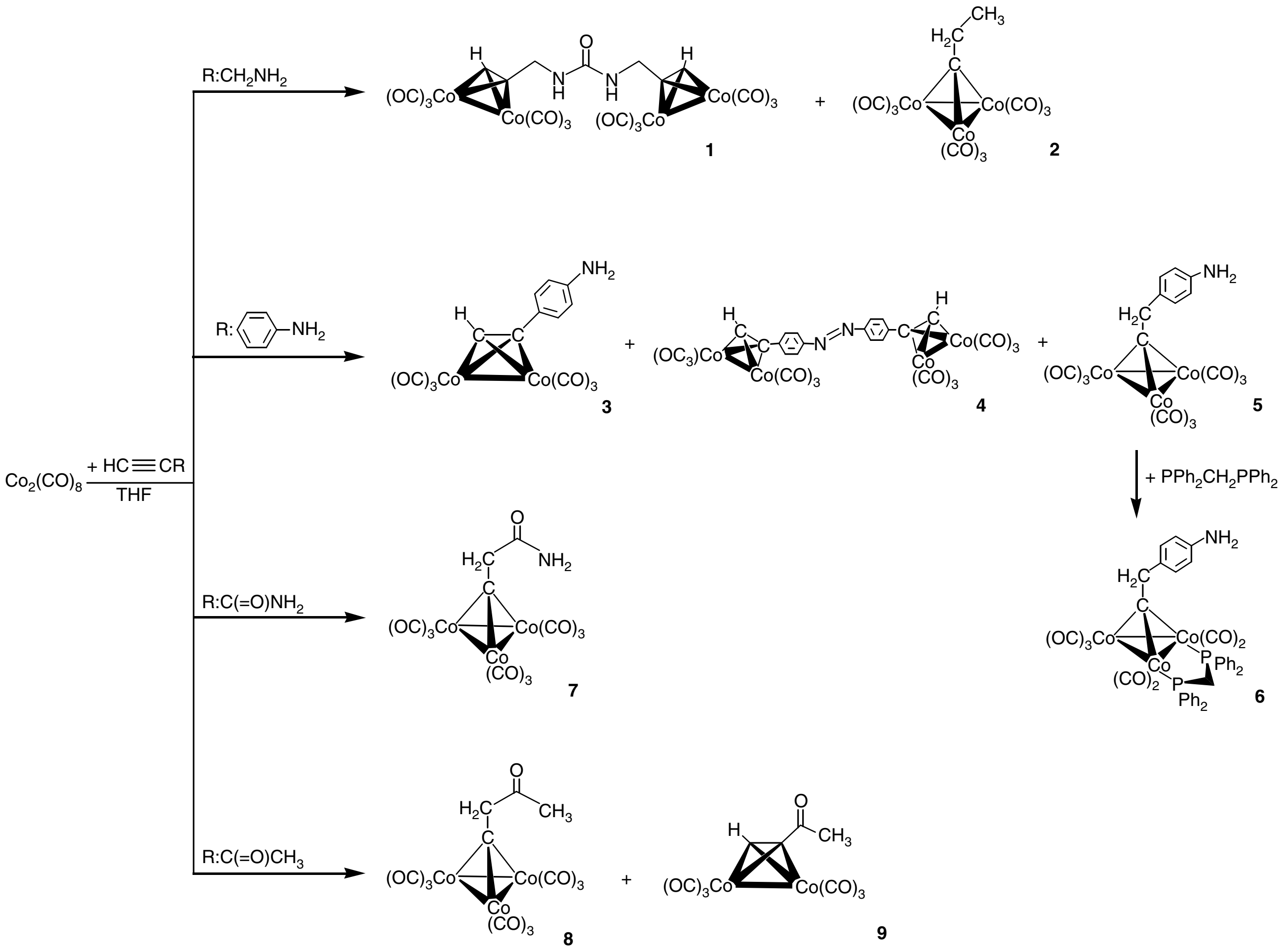


Scheme 2.

methylidyne clusters observed from the reactions. Herein, we report some interesting results from the preparation and characterization of several tricobalt methylidyne clusters from the reactions of $Co_2(CO)_8$ and the corresponding alkynes, some of which do not appear to be acidic at first glance.

RESULTS AND DISCUSSION

Reaction of $Co_2(CO)_8$ with $HC{\equiv}CCH_2NH_2$

Reaction of $Co_2(CO)_8$ with $HC{\equiv}CCH_2NH_2$ in tetrahydrofuran (THF) at 25 °C for 3 h gave the major product $\{[Co_2(CO)_6(\mu\text{-}HC{\equiv}C\text{-})]\text{-}CH_2NH\}_2C{=}O$ (**1**) (Scheme 2). The tricobalt methylidyne cluster $[Co_3(CO)_9(\mu_3\text{-}CCH_2CH_3)]$ (**2**) was observed from this reaction after 5 h only by raising the temperature to 45 °C;[12,13] the identify of **2** has been reported previously.[14] The yield of **2** could be moderately improved by more severe reaction conditions. Alternatively, compound **2** alone was obtained from the reaction of $Co_2(CO)_8$ with $HC{\equiv}CCH_2SPh$, instead of $HC{\equiv}CCH_2NH_2$, at 65 °C for 5 h. This cluster was characterized by spectroscopic means and by X-ray diffraction. A triplet and a quartet, in the ratio of 3 : 2, were observed in ^1H NMR spectrum for $-CH_3$ and $-CH_2-$. Meanwhile, the expected broad signal for the $-NH_2$ group could not be observed. Three signals, corresponding to methylidyne's three carbons atoms, were observed in ^{13}C NMR. Unfortunately, the carbon signals representing carbonyls could not observed even after long acquisition times. This might be due to the fluxional nature of carbonyl, as well as high nuclear spin value of their attached cobalt ($I = 7/2$).

Suitable crystals of **2** were obtained from a solvent mixture (CH_2Cl_2–hexanes, 1 : 1) at 4 °C and its structure was determined. The ORTEP drawing for **2** is depicted in Fig. 1. The fact that the amino group was absent, judging from the crystal structure of **2**, is noteworthy the reaction of *N*,*N*-dimethylpropargylamine with $Co_2(CO)_8$ only resulted in the formation of simple alkyne-bridged dicobalt hexacarbonyl complex, $Co_2(CO)_6(\mu\text{-}\eta\text{-}HC{\equiv}CCH_2NMe_2)$.[15] This is in accord with the observation from ^1H NMR. Interestingly, the same compound **2** was obtained from the reaction of $Co_2(CO)_8$ with $HC{\equiv}CCH_2OH$ at 25 °C for 3 h. Structural similarities were confirmed by its crystallographic data.

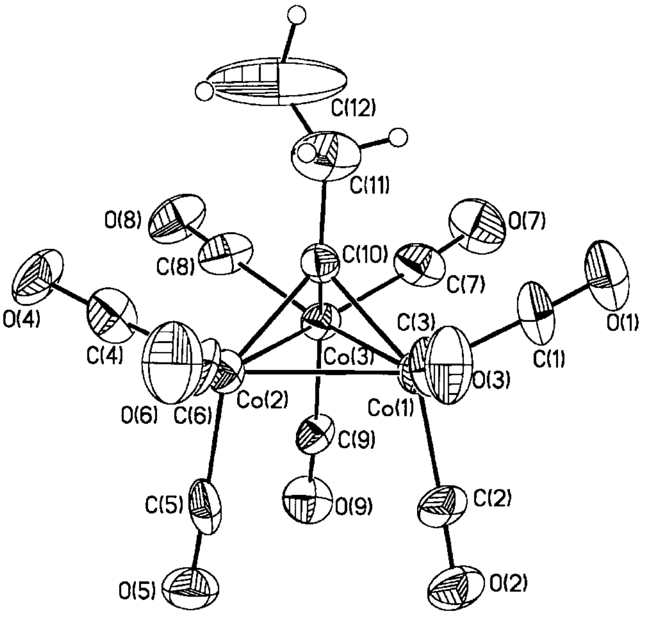
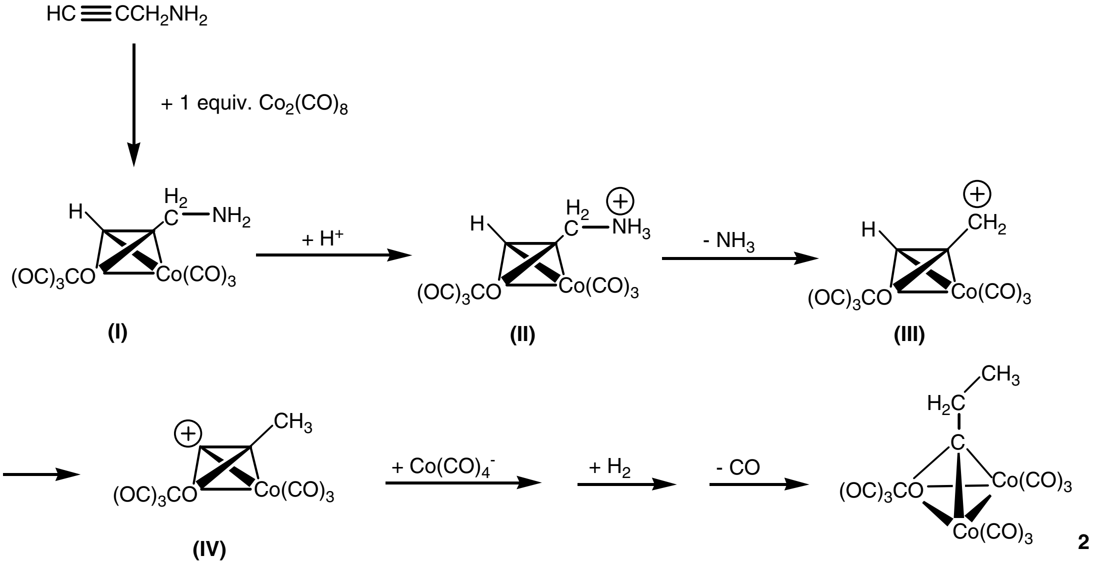


Figure 1. The molecular structure of $[Co_3(CO)_9(\mu_3\text{-}CCH_2CH_3)]$ (**2**). Selected bond lengths (Å) and bond angles (°) for **2**: Co(1)–C(10) 1.916(12), Co(2)–C(10) 1.892(13), Co(3)–C(10) 1.882(17), Co(1)–Co(3) 2.452(3), Co(1)–Co(2) 2.479(3), Co(2)–Co(3) 2.459(4), C(10)–C(11) 1.45(2), C(11)–C(12) 1.30(3); C(10)–Co(1)–Co(3) 49.2(5), C(10)–Co(2)–Co(3) 49.2(5), Co(3)–Co(1)–Co(2) 59.83(8), Co(3)–Co(2)–Co(1) 59.54(9), C(10)–Co(3)–Co(1) 50.4(3), Co(1)–Co(3)–Co(2) 60.63(9), O(1)–C(1)–Co(1) 173(2), O(2)–C(2)–Co(1) 178.2(19), O(3)–C(3)–Co(1) 172.0(17), C(12)–C(11)–C(10) 126(2).

A reaction mechanism was proposed to account for the formation of **2** (Scheme 3). First, the triple bond of the propargylamine is bridged by a dicobalt hexacarbonyl fragment and forms an alkyne-bridged dicobalt complex, $Co_2(CO)_6(\mu\text{-}\eta\text{-}HC{\equiv}CCH_2NH_2)$ (**I**).[16–18] This is then followed by picking up of a proton from solution, which is believed to be expelled during the process of forming **1**, and the formation of **II**. Subsequently, **III** is formed after the release of one NH_3 from **II**. Presumably, an acetylenic proton shift process takes place and forms **IV**. Eventually, **2** is formed after the sequential steps of incorporation of $Co(CO)_4^-$, H_2 and release of a CO.[19,20] A similar mechanism could be given in the case of propargylalcohol. The hydroxyl site of the dicobalt-bridged propargylalcohol complex might be protonated and followed by the release of an H_2O molecule and the formation **III**. Then, the same cycles continue to the formation of product, **2**.

Reaction of $Co_2(CO)_8$ with $HC{\equiv}CC_6H_4NH_2$

Treatment of $Co_2(CO)_8$ with $HC{\equiv}CC_6H_4NH_2$ in THF at 55 °C for 4 h gave the major product $\{[Co_2(CO)_6(\mu\text{-}HC{\equiv}CC_6H_4N{=}\}_2$ (**4**) and two minor products, *viz* the alkyne-bridged dicobalt hexacarbonyl complex $[Co_2(CO)_6(\mu\text{-}\eta\text{-}HC{\equiv}CCH_2C_6H_4NH_2)]$ (**3**) and the tricobalt methylidyne cluster $[Co_3(CO)_9(\mu_3\text{-}CCH_2C_6H_4NH_2)]$ (**5**; Scheme 2). Compound **5** was characterized by spectroscopic means. Four sets of signals in the ratio of 2 : 2 : 2 : 2 were observed for the corresponding protons, including the $-NH_2$ group, in ^1H NMR. Unfortunately, owing to oily nature of **5**, the crystallization was not successful. Further reaction of **5** with DPPM resulted in the formation of the DPPM-bridged tricobalt methylidyne cluster $[Co_3(CO)_7(\mu\text{-}P,P\text{-}PPh_2CH_2PPh_2)(\mu_3\text{-}CCH_2C_6H_4NH_2)]$ (**6**). Compound **6** was characterized by spectroscopic means. Besides the alkylidyne peaks, two distinct signals in the ratio of 1 : 1 were observed for the methylene protons in ^1H NMR for **6**. Fortunately, suitable crystals of **6** were obtained and its



Scheme 3. Proposed mechanism for the formation of tricobalt methylidyne cluster 2.

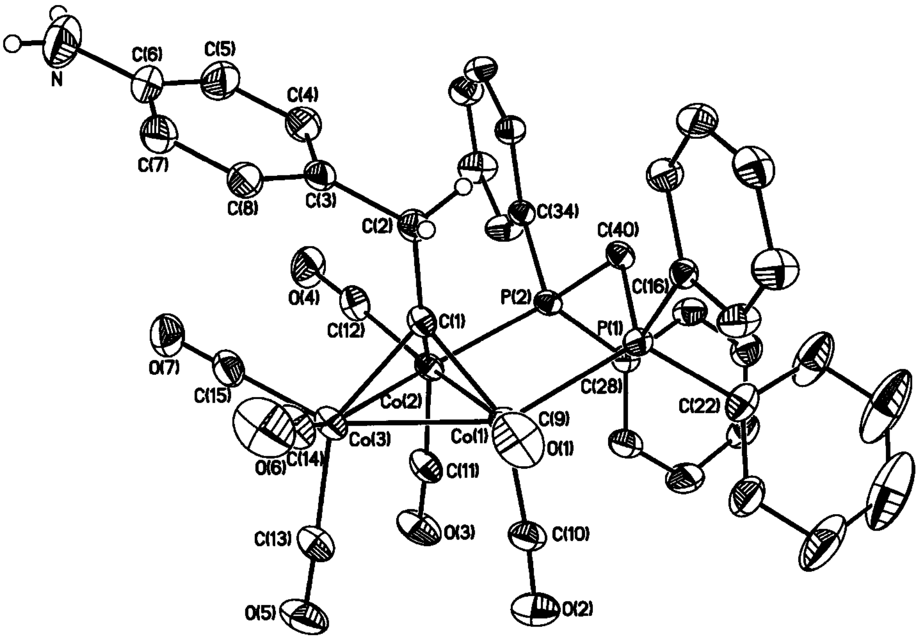


Figure 2. The molecular structure of $[Co_3(CO)_7(\mu\text{-}P,P\text{-}PPh_2CH_2PPh_2)(\mu_3\text{-}CCH_2C_6H_4NH_2)]$ **6**. Some hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°) for **6**: Co(1)–C(1) 1.886(4), Co(1)–P(1) 2.2058(12), Co(1)–Co(2) 2.4725(8), Co(1)–Co(3) 2.4792(8), Co(2)–C(1) 1.902(4), Co(2)–P(2) 2.1920(11), Co(2)–Co(3) 2.4694(8), Co(3)–C(1) 1.943(4), P(1)–C(40) 1.828(4), P(2)–C(40) 1.833(4), C(1)–C(2) 1.510(6); P(1)–Co(1)–Co(2) 98.44(4), P(2)–Co(2)–Co(1) 93.87(4), Co(2)–Co(3)–Co(1) 59.95(2), Co(2)–Co(1)–Co(3) 59.83(2), Co(3)–Co(2)–Co(1) 60.22(2), C(1)–C(2)–C(3) 116.9(4), P(1)–C(40)–P(2) 108.23(19).

structure was determined by X-ray diffraction. The ORTEP drawing of **6** is shown in Fig. 2. The bridging μ-*P*,*P*-DPPM takes the equatorial position in the cluster.[21–23] The aniline fragment keeps away from the bridging DPPM ligand to avoid the steric hindrance. The crystal structure reveals that compound **6** has an amino group, which is consistent with the ^1H NMR observation. In contrast to **2**, that the amino group remains intact in **6** may be due to the instability of forming the cationic phenyl derivative after the removal of the NH_3 moiety from a protonated **3**. Reaction of **3** with excess $Co_2(CO)_8$ in THF at 55 °C for 4 h produced **4**, **5** and a large amount of unreacted **3**. The ratio of products varies with the reaction conditions. (The yields of **4** and **5** range from 5 to 10% and 20 to 25% respectively.) This indicates that the tricobalt methylidyne clusters were converted from their precursors, alkyne-bridged dicobalt complexes, as generally believed.[6] Further reaction of **5** with excess $Co_2(CO)_8$ in THF at 55 °C for a long time did not produce any **4**-like derivative.

Reaction of $Co_2(CO)_8$ with $HC{\equiv}C{-}C({=}O)NH_2$

A related case was studied with a different amine derivative, $HC{\equiv}C{-}C({=}O)NH_2$. This was reacted with $Co_2(CO)_8$ in THF at 25 °C for 5 h and yielded the tricobalt methylidyne cluster $[Co_3(CO)_9(\mu_3\text{-}CCH_2C({=}O)NH_2)]$ (**7**; Scheme 2). The identity of **7** was confirmed by spectroscopic means and by X-ray diffraction. The ORTEP drawing of **7**, shown in Fig. 3, reveals that the amino group remains. This is consistent with the observed two distinct signals of the amino protons in the ^1H

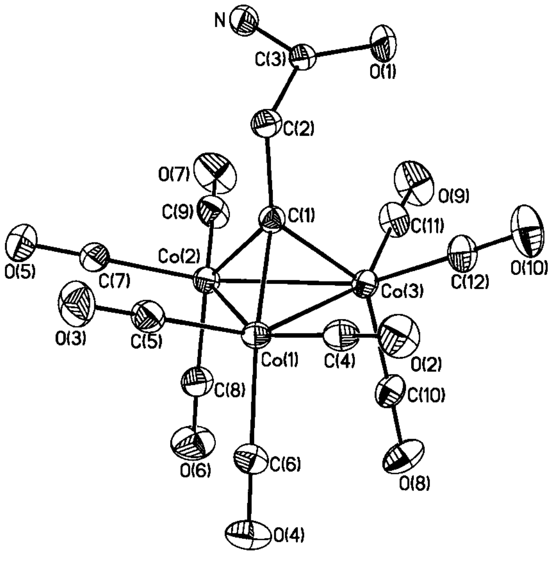


Figure 3. The molecular structure of $[Co_3(CO)_9(\mu_3\text{-}CCH_2C({=}O)NH_2)]$ **7**. Some hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°) for **7**: Co(1)–C(1) 1.909(3), Co(1)–Co(3) 2.4644(6), Co(1)–Co(2) 2.4697(6), Co(2)–C(1) 1.910(3), Co(2)–Co(3) 2.4688(6), Co(3)–C(1) 1.898(3), C(1)–C(2) 1.497(4), C(2)–C(3) 1.518(5), N–C(3) 1.320(5), O(1)–C(3) 1.221(4); Co(3)–Co(1)–Co(2) 60.048(17), Co(3)–Co(2)–Co(1) 59.871(17), Co(1)–Co(3)–Co(2) 60.082(17), C(1)–C(2)–C(3) 112.3(3), O(1)–C(3)–N 122.6(4), O(1)–C(3)–C(2) 120.3(4), N–C(3)–C(2) 117.1(3).

NMR spectrum. The same reasoning for the presence of the amino group in **7**, as in the case of **6**, is presumably valid here.

Reaction of $Co_2(CO)_8$ with $HC{\equiv}C{-}C({=}O)CH_3$

For the purpose of comparison, the reaction of a non-amino group substituted alkyne, $HC{\equiv}C{-}C({=}O)CH_3$, with $Co_2(CO)_8$ was carried out in THF at 40 °C for 6 h. The tricobalt methylidyne cluster $[Co_3(CO)_9(\mu_3\text{-}CCH_2C({=}O)CH_3)]$ (**8**) and the alkyne-bridged dicobalt hexacarbonyl complex $[Co_2(CO)_6(\mu_2\text{-}\eta^2\text{-}HCCH_2C({=}O)CH_3)]$(**9**) were obtained from the reaction (Scheme 2). Only **8** was obtained when the reaction temperature was raised to 60 °C and reacted for 6 h.

Both **8** and **9** were characterized by spectroscopic means; **8** was also studied by X-ray diffraction. The ORTEP drawing of **8** is shown in Fig. 4. One finds that the functional group of the alkyne remains.

Selected structural parameters of **2**, **6**, **7** and **8** are shown in Table 2 for comparison. As shown in Table 2, the main frameworks for these compounds are not much different.

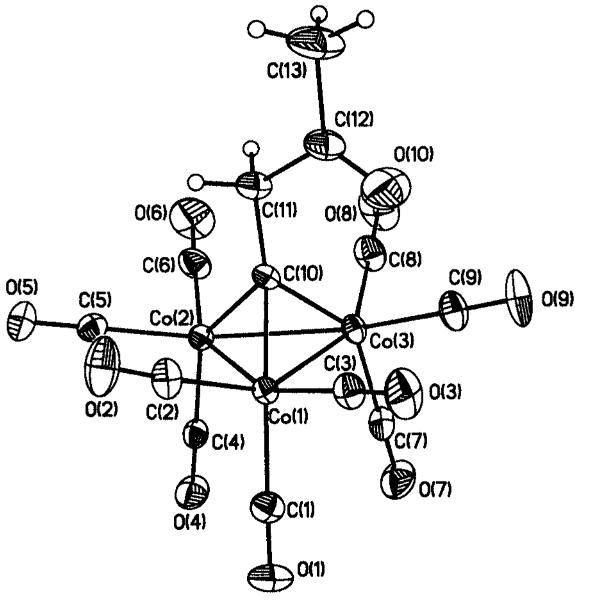


Figure 4. The molecular structure of $[Co_3(CO)_9(\mu_3\text{-}CCH_2C({=}O)CH_3)]$ **8**. Some hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°) for 8: Co(1)–C(10) 1.901(4), Co(1)–Co(2) 2.4664(7), Co(1)–Co(3) 2.4711(8), Co(2)–C(10) 1.905(4), Co(2)–Co(3) 2.4715(8), Co(3)–C(10) 1.906(4), O(10)–C(12) 1.210(8), C(10)–C(11) 1.496(6), C(11)–C(12) 1.517(8), C(12)–C(13) 1.486(8); Co(2)–Co(1)–Co(3) 60.07(2), Co(1)–Co(2)–Co(3) 60.06(2), Co(1)–Co(3)–Co(2) 59.87(2), C(10)–C(11)–C(12) 118.1(4), O(10)–C(12)–C(13) 120.5(6), O(10)–C(12)–C(11) 124.4(5), C(13)–C(12)–C(11) 115.1(6).

Summary

Four tricobalt methylidyne clusters, **2**, **6**, **7** and **8**, were prepared from the reactions of $Co_2(CO)_8$ with the corresponding alkynes. They were all characterized by spectroscopic means and by X-ray diffraction. A mechanism for the formation of **2** was proposed to account for the detachment of the amino group from the starting material, i.e. propargylamine. It was also demonstrated that the tricobalt methylidyne clusters were converted from the reaction of $Co_2(CO)_8$ with their precursors, alkyne-bridged dicobalt complexes.

EXPERIMENTAL

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). ^1H NMR spectra were recorded (Varian VXR-300S spectrometer) at 300.00 MHz; chemical shifts are reported in ppm relative to internal tetramethylsilane. ^{31}P and ^{13}C NMR spectra were recorded at 121.44 MH$_3$ and 75.46 MHz respectively. Some other ^1H NMR spectra were recorded using a Gemini-200 spectrometer at 200.00 MHz or a 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 a JOEL JMS-SX/SX 102A GC/MS/MS spectrometer. Elemental analyses were recorded a Heraeus CHN-O-S-Rapid instrument. Accurate elemental analyses were precluded for some of the following compounds, probably due to their chemical labilities.

The preparation of $[Co_3(CO)_9(\mu_3\text{-}CCH_2CH_3)]$ *(2)*

$Co_2(CO)_8$ (0.600 g, 1.750 mmol) and propargylamine (0.120 mml, 1.750 mmol) along with 20 ml of THF was placed in a 100 cm^3 flask. The solution was stirred at 45 °C for 5 h. Subsequently, the resulting reddish orange solution was filtered through a small silica gel column. Purification with CTLC was carried out. The first band (purple in color), **2** (0.124 g, 0.264 mmol), was eluted out by hexanes. The yield of **2** was 15.0%. The second band (reddish brown in color), **1** (0.257 g, 0.363 mmol), was eluted out by CH_2Cl_2. The yield of **1** was 21.0%

^1H NMR ($CDCl_3$, δ/ppm): 3.75 (q, 2H, $J_{H-H} = 6.80$ H$_3$, CH_2), 1.52 (t, 3H, $J_{H-H} = 7.20$ H$_3$, CH_3). ^{13}C NMR ($CDCl_3$): 1.015 (1C, μ_3-C), 20.62 (1C, CH_3), 51.94 (1C, CH_2). Elemental analysis: Found, C, 30.36, H, 1.52. Calc., C, 30.67; H, 1.07%. IR (CH_2Cl_2, cm^{-1}): $\nu_{(CO)}$ = 1999(m), 2035(s), 2103(w).

The preparations of $[Co_3(CO)_9(\mu_3\text{-}CCH_2C_6H_4NH_2)]$ *(5) and* $[Co_3(CO)_7(\mu\text{-}P,P\text{-}PPh_2CH_2PPh_2)(\mu_3\text{-}CCH_2C_6H_4NH_2)]$ *(6)*

Similar reaction procedures as in the preparation of the above compound were followed. Into a 100 cm^3 flask was placed cobalt carbonyl ($Co_2(CO)_8$, 0.600 g, 1.750 mmol) and 4-ethynylaniline (0.210 g, 1.790 mmol) with 20 ml of THF. The solution was stirred at 55 °C for 4 h, and gave a purple solution. Purification with CTLC was carried out. The first and second bands were identified as **4** and **3** respectively. The third band (purple in color), **5** (0.390 g 0.446 mmol), was eluted by CH_2Cl_2. The yield of **5** was 25.5%.

Compound **5** (0.546 g, 1.009 mmol) and DPPM (0.3850 g, 1.002 mmol) were placed in a 100 cm^3 flask with 20 ml of THF. The solution was stirred at 65 °C for 12 h, and this resulted in a black solution. Purification was performed by CTLC. The first band (black in color), **6** (0.737 g, 0.796 mmol), was eluted by CH_2Cl_2. The yield of **6** was 79.6%.

Complex **5**, purple. ^1H NMR ($CDCl_3$, δ/ppm): 4.84 (d, 2H, CH_2), 7.09 (d, 2H, Ph), 7.41 (d, 2H, Ph), 7.66 (s, 2H, NH_2); ^{13}C NMR ($CDCl_3$): 62.09 (s, 1C, CH_2), 118.39–130.27(6C, Arene). IR (KBr, cm^{-1}): $\nu_{(CO)} = 2068$(s), $\nu_{(NH)} = 3485$(s).

Complex **6**, black. ^1H NMR ($CDCl_3$, δ/ppm): 3.65 (m, 1H, CH_2), 4.92 (m, 1H, CH_2), 4.989 (s, 1H, CH_2), 6.75 (s, 2H, NH_2), 7.09–7.49 (24H, Arene). ^{13}C NMR ($CDCl_3$): 41.94 (s, 1C, CH_2–Ph), 128.18–132.14 (20C, Arene), 134.90 (d, $J_{P-C} = 126.28$ Hz, 1C, *ipso*-Arene), 135.11 (d, $J_{P-C} = 164.98$ Hz, 1C, *ipso*-Arene), 137.00 (d, $J_{P-C} = 99.29$ H_3, 1C, *ipso*-Arene), 137.24 (d, $J_{P-C} = 140.68$ Hz, 1C, *ipso*-Arene), 204.88 (m, 7C, CO). ^{31}P NMR ($CDCl_3$): 33.75 (s, 2P, DPPM). M. pt: 195 °C.

The preparation of [$Co_3(CO)_9(\mu_3$-$CCH_2C(=O)NH_2)$] (7)

The preparative procedure of forming propioamide has been described elsewhere.[24] Following the same processes, $Co_2(CO)_8$ (0.600 g, 1.755 mmol) with a molar equivalent of propioamide (0.121 g, 1.755 mmol) were dissolved in 20 cm^3 THF, then transferred into a 100 cm^3 flask. The solution was stirred at 25 °C for 5 h. Subsequently, the resulting reddish orange solution was filtered through a small amount of silica gel. Purification with CTLC was carried out. The first band (reddish orange in color), **7** (0.2045 g, 0.4099 mmol), was eluted out by CH_2Cl_2. The yield of **7** was 35.0% based on $Co_2(CO)_8$.

^1H NMR ($CDCl_3$, δ/ppm): 5.68 (s, 1H, NH_2), 6.16 (s, 2H, CH_2), 6.71 (s, 1H, NH_2). ^{13}C NMR ($CDCl_3$): 74.83 (1C, CH_2), 103.14 (1C, CCH_2), 186.21 (1C, C=O), 198.35 (9C, CO). Elemental analysis: found, C, 29.03; H, 0.97; N, 3.81; Calc., C, 28.89; H, 0.81; N, 2.81. M. pt: 61 °C. MS (FAB): 499(M^+).

The preparation of [$Co_3(CO)_9(\mu_3$-$CCH_2C(=O)CH_3)$] (8)

Following the same processes, 1.5 mmol of $Co_2(CO)_8$ (0.512 g, 1.500 mmol) with 1 mmol of 3-butyne-2-one (0.080 ml, 1.000 mmol) were placed in a 100 cal^3 flask in 10 cm^3 THF. The solution was stirred at 60 °C for 7 h. Subsequently, the resulting dark-brown solution was purified with CTLC. A

Table 1. Crystal data for **2**, **6**, **7** and **8**

Compound	**2**	**6**	**7**	**8**
Formula	$C_{12}H_5Co_3O_9$	$C_{40}H_{30}Co_3NO_7P_2$	$C_{12}H_4Co_3NO_{10}$	$C_{13}H_5Co_3O_{10}$
Formula weight	469.95	875.38	498.95	497.96
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P\overline{1}$
a (Å)	7.973(5)	15.8399(10)	9.2532(7)	8.0528(8)
b (Å)	25.880(17)	12.4201(8)	9.4801(7)	8.5897(8)
c (Å)	8.781(6)	20.7657(13)	19.2931(14)	14.2280(14)
α (°)	—	—	—	76.188(2)
β (°)	112.196(13)	110.2650(10)	92.329(2)	78.672(2)
γ (°)	—	—	—	68.376(2)
V (Å^3)	1677.7(19)	3832.4(4)	1691.0(2)	882.01(15)
Z	4	4	4	2
D_c(Mg m^{-3})	1.861	1.517	1.960	1.875
λ (Mo Kα) Å	0.710 73	0.710 73	0.710 73	0.710 73
μ (mm^{-1})	2.972	1.417	2.960	2.836
2θ range (°)	2.63 to 26.16	1.99 to 26.06	2.20 to 26.04	2.59 to 26.02
Observed reflections ($F > 4\sigma(F)$)	1255	4509	4004	2850
No. of refined parameters	217	478	235	235
R_1 for significant reflections[a]	0.1060	0.0449	0.0295	0.0479
wR_2 for significant reflections[b]	0.2354	0.1016	0.0652	0.1351
GoF[c]	0.925	0.922	1.005	1.029

[a] $R1 = |\Sigma(|F_o| - |F_c|)/|\Sigma F_o||$.
[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 0.1352$, 0.0609, 0.0376 and 0.1049 for **2**, **6**, **7** and **8** respectively.
[c] $\text{GoF} = [\Sigma w(F_o^2 - F_c^2)^2/(N_{\text{rflns}} - N_{\text{params}})]^{1/2}$.

Table 2. Comparison of selected structural parameters of **2**, **6**, **7** and **8**[a]

	2	8	7	6
Bond length (Å)				
$r_{Co-Co(av)}$,	2.46	2.47	2.47	2.47
$r_{Co-C(av)}$,	1.90	1.90	1.91	1.91
r_1,	1.45(2)	1.496(6)	1.497(4)	1.510(6)
r_2,	1.30(3)	1.517(8)	1.518(5)	1.513(6)
Angle (°)				
∠Co-C-Co,	81.0	80.9	80.7	80.7
∠C-C-R,	126.0(2)	118.1(4)	112.3(3)	116.9(4)

[a]

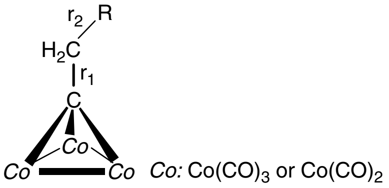


Diagram 1. A generalized structure for **2**, **6**, **7** and **8**.

purple band of **8** (0.7958 g, 0.3932 mmol) was eluted out by CH_2Cl_2/Hexane (1 : 1). The yield of **8** was 26.2% based on $Co_2(CO)_8$.

^1H NMR ($CDCl_3$, δ/ppm): 2.35 (s, 3H, CH_3), 4.82 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$): 30.56 (1C, CH_3), 67.15 (1C, CH_2), 199.77 (CO of Co), 203.01 (1C, C=O). Elemental analysis: found, C, 31.95; H, 1.82; calc., C, 31.35; H, 1.01%; IR (CH_2Cl_2, cm^{-1}): $\nu_{(C=O)} = 1602$(w), 2036(m), 2054(s); MS (FAB): m/z 499 ($M^+ + 1$).

X-RAY CRYSTALLOGRAPHIC STUDIES

Suitable crystals of **2**, **6**, **7** and **8** were sealed in thin-walled glass capillaries under nitrogen atmosphere and were mounted on a Siemens Smart CCD diffractometer. The crystallographic data were collected using a $\theta - 2\theta$ scan mode with Mo K_α radiation. The space group determination was based on a check of the Laue symmetry and systematic absences, and was confirmed by the structure solution. The structure was solved by direct methods using the Siemens SHELXTL PLUS package.[25] All the non-hydrogen atoms were located from successive Fourier maps. Anisotropic thermal parameters were used for all non-hydrogen atoms and fixed isotropic for hydrogen atoms that were refined using the riding model. Hydrogen atoms were riding on carbon or oxygen atoms in their idealized positions and held fixed with C–H distances of 0.96 Å. Crystallographic data for **2**, **6**, **7** and **8** are summarized in Table 1.

SUPPLEMENTARY MATERIAL

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 173696 for compound **2**, CCDC no. 197590 for compound **6**, CCDC no. 197591 for compound **7**, CCDC no. 197592 for compound **8**. 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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