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The reaction of $Co_2(CO)_8$ and $Co_4(CO)_{12}$ with the dipropargylamine $[(HC{\equiv}CCMe_2)_2NMe]$. Synthesis and crystal structure of the complex $Co_4(CO)_{10}(\mu\text{-}CO)[H_2C{=}CC(Me)_2N(Me)C(Me_2)C(\mu_4\text{-}C)]$

Mirco Costa [a], Giuliana Gervasio [b,*], Domenica Marabello [b], Enrico Sappa [c,*]

[a] *Dipartimento di Chimica Organica e Industriale, Università di Parma, Parco Area delle Scienze 17A, I-43100 Parma, Italy*

[b] *Dipartimento di Chimica IFM, Università di Torino, Via P. Giuria 7, I-10125 Torino, Italy*

[c] *Dipartimento di Scienze e Tecnologie Avanzate, Università del Piemonte Orientale Amedeo Avogadro, C.so Borsalino 54, I-15100 Alessandria, Italy*

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Abstract

The reaction of $Co_4(CO)_{12}$ with the dipropargylamine $[(HC{\equiv}CCMe_2)_2NMe]$ (ligand **A**) leads to moderate yields of the title complex (complex **4**). An X-ray analysis has shown that this tetranuclear complex is a 'spiked' (or metallo-ligated) triangular cluster containing one molecule of ligand **A** partially cyclized and coordinated to all four metal atoms. Complex **4** is the first tetracobalt cluster showing this type of structure which was previously found only for two M_2Ni_2 (M = Fe, Ru) isopropenylacetylene derivatives. Reaction pathways leading to the formation of complex **4** are discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Cobalt carbonyls; Dipropargylamines; Heterocyclic organic molecules; Reaction intermediates; Template effect; Crystal structure

1. Introduction

Diacetylenic amines (or dipropargylamines) such as $[(HC{\equiv}CCMe_2)_2NMe]$ (ligand **A**) undergo co-cyclization reactions with alkynes (RC≡CH) or nitriles in the presence of $Co_2(CO)_8$ [1]. The mechanisms of these reactions have been evidenced. The first step of the reaction of $Co_2(CO)_8$ with ligand **A**, under very mild conditions, is the formation of $[Co_2(CO)_6]_2[(HC{\equiv}CCMe_2)_2NMe]$ (**1**) in which each terminal C≡C bond interacts with one $Co_2(CO)_6$ unit through two π-bonds forming a Co_2C_2 tetrahedral core [2]. The structure of **1** has been determined by an X-ray diffraction study [1]. A further step is the formation of metallacyclic intermediates: the mononuclear cobalt complex $(Cp)(PPh_3)Co[(HC{\equiv}CCMe_2)_2NMe]$ (**2**) was obtained and its structure confirmed by an X-ray study [3].

Starting from $Co_2(CO)_8$ and ligand **A**, under thermal conditions, we obtained the 'ferrole' complex $Co_2(CO)_5[(HC{\equiv}CCMe_2)_2NMe]$ (**3**) in good yields, together with three minor products (which were not investigated). Complex **3** reacts with terminal alkynes and nitriles to form the above mentioned condensed aromatic or heterocyclic products [4]. The structures of ligand **A** and of complexes **1**, **2**, **3** are shown in Plate 1.

We have now reacted ligand **A** with $Co_4(CO)_{12}$ with the aim at obtaining new tri- and tetra-nuclear cobalt–alkyne complexes, in particular tricobalt–methylidyne derivatives [5]. One of the main products obtained was complex **4** $Co_4(CO)_{10}(\mu\text{-}CO)[H_2C{=}CC(Me)_2N(Me)C(Me_2)C(\mu_4\text{-}C)]$ which-to our knowledge-is the first example of tetracobalt metallo–ligated (or 'spiked') triangular cluster containing an acetylide ligand. The structure of **4**, determined by an X-ray analysis, will be compared with that shown by the only two known heterometallic complexes containing similar metal–atom cores and a coordinated alkyne-derived ligand.

For better understanding the reaction mechanisms leading to **4**, we decided to revisit also the reaction

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* Corresponding authors. Tel.: +39-011-670-7504; fax: +39-011-670-7855

E-mail address: giuliana.gervasio@unito.it (G. Gervasio).

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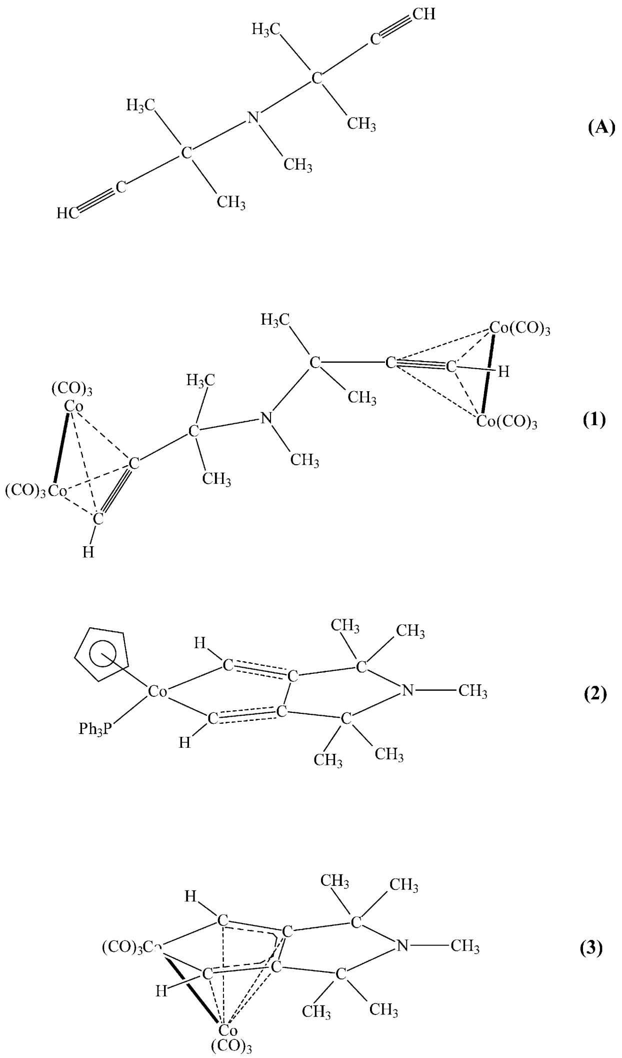


Plate 1.

leading to complex **3** and to the unidentified minor products mentioned above one of which was identified as complex **4**. On the grounds of chemical and spectroscopic evidence, two alternative pathways leading to complex **4** can be proposed; one of them requires the opening of the tetrahedral parent cluster; the other occurs through the template effect originated by the cyclization of ligand **A**.

2. Experimental

2.1. General details, materials, analysis of the products

Ligand **A** was obtained as previously reported [1,6]. The cobalt carbonyls, $Co_2(CO)_8$, $Co_4(CO)_{12}$ (Strem Chemicals) were used as received. Solvents, (hexane, heptane, toluene) were dehydrated over sodium. The reactions were performed under a dry nitrogen atmosphere in conventional three necked flasks equipped with gas inlet, cooler, mercury check valve and magnetic stirring.

The reaction mixtures were filtered under N_2, brought to small volume under reduced pressure and separated on T.L.C. plates (Merck Kieselgel PF, eluent mixtures of hexane and diethyl ether in variable v/v ratios depending on the reaction mixtures). Elemental analyses were performed in the laboratories of the DiSTA, Università del Piemonte Orientale. The IR spectra were obtained on a Bruker Equinox 55 IR spectrophotometer (KBr cells). The ^1H-NMR spectra were obtained on a JEOL JNM 270/89 instrument and the mass spectra with a Finnigan-Mat TSQ-700 mass spectrometer (Servizio di Spettrometria di Massa, Dipartimento di Scienza e Tecnologia del Farmaco, Università di Torino).

*2.2. Reaction of $Co_4(CO)_{12}$ with ligand A. Synthesis of complex **4***

In a typical reaction, 300 mg (0.52 mmol) of $Co_4(CO)_{12}$ was dissolved in toluene (20 ml) and added with 0.2 g (1.23 mmol ca.) of ligand **A.** The solution was heated under nitrogen to reflux for 2 min: T.L.C. purification showed the presence of unreacted parent carbonyl (10%), of complex **3** (10%) and of **4** (25% ca.), trace amounts of unidentified compounds and considerable decomposition.

*2.2.1. Complex **3***

For this complex (after crystallization from heptane–$CHCl_3$ or toluene at low temperatures, dark-orange crystals). Calc. C, 45.62; H, 4.07; N, 3.33. Found: C, 45.70; H, 4.1; N, 3.22%. IR (heptane): 2048 vs, 2027 vs, 2016 sh, 1978 cm^{-1}. ^1H-NMR (C_6D_6): 6.26 s (2H, C–H); 1.17 s (3H, N–Me); 0.82 s, 0.71 s (6,6H, 4 Me). (See [4]).

*2.2.2. Complex **4***

For this complex Calc.: C, 37.35; Co, 33.34; H, 2.24; N, 1.98. Found: C, 37.41; Co, 33.10; H, 2.26; N, 1.97%. IR (C_7H_{16}): 2089 s, 2048 vs, 2042 vs, 2032 vs, 2008 m–s, 1848 m–s, cm^{-1}. ^1H-NMR ($CDCl_3$): 3.35 s (1H, H_2C=); 2.48 s (3H, N–Me); 2.07 s (1H, H_2C); 1.72 s (3H), 1.43 s (3H), 1.39 s (3H), 1.09 s (3H) [Me].

2.3. Reaction of $Co_2(CO)_8$ with ligand A

The same reaction conditions leading to complex **3** were used [4]: $Co_2(CO)_8$ (1 g, 2.92 mmol) was reacted with an excess of ligand **A** (0.65 g, 4.0 mmol) in refluxing toluene (50 ml) for 2 min. After T.L.C. purification, yellow complex **3** (40% ca.) was collected; smaller amounts of a red (1% ca., complex **1**), a pale yellow (1%, unidentified) and a purple (5% ca., complex **4**) bands were also obtained together with considerable decomposition. The reaction was repeated in the same conditions, but for only 1 min reflux. Comparable results were obtained; the yields of **1** and **4** were slightly increased (3 and 10%, respectively).

2.4. *Thermal reactions of complex **1***

Complex **1** was obtained by reacting $Co_2(CO)_8$ with ligand **A** in hexane at room temperature (r.t.) for 24 h (deep red solution: direct crystallization at −20 °C, red crystals) [1]. A solution of **1** (50 mg,) in toluene (10 ml) was gently heated under nitrogen up to 80 °C and kept to this temperature for 20 min. T.L.C. purification showed the presence of unreacted **1** (20% ca.), complex **3** (10%), complex **4** (15% ca.) and of two minor products (yellow, red, trace amounts, unidentified) and considerable decomposition.

2.5. *Crystallography*

The data collection was made on a Siemens P4 diffractometer equipped with a Bruker APEX CCD detector using graphite-monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å). The complex **4** $Co_4(CO)_{10}(\mu\text{-}CO)[H_2C{=}CC(Me)_2N(Me)C(Me_2)C(\mu_4\text{-}C)]$ crystallizes in monoclinic $P2_1/c$ space group, with $a = 15.2935(14)$ Å, $b = 8.3942(7)$ Å, $c = 20.4461(19)$ Å, $\beta = 99.820(2)°$, $V = 2586.3(4)$ Å^3, $M = 704.06$, $Z = 4$, $D_{calc} = 1.808$ g cm^{-3}, $\mu = 2.580$ mm^{-1}. The black crystal used was prismatic of dimensions 0.06 × 0.18 × 0.28 mm. The θ range for measurement was 2.02–28.27°, 18 183 reflections were measured at 293 K and 6158 were unique ($R_{int} = 0.045$). The intensities were corrected semi-empirically for absorption, based on symmetry equivalent reflections. The refinement of 343 parameters was made using full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. Some of the hydrogen atoms were located on the last difference Fourier maps; it was preferred, however, to locate the methylic hydrogens in the calculated positions: they were all refined with a riding model and U_{iso}'s were set at 1.5 (for CH_3 groups) and at 1.2 (for CH_2 group) times U_{eq} of the corresponding C atom. The final parameters were: $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.0351$ for 'observed' reflections having $F_o^2 > 2\sigma(F_o^2)$, $R_w = [\Sigma(wF_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2} = 0.0627$, Goodness-of-fit $= [\Sigma w(F_o^2 - F_c^2)^2/(\text{no. of unique reflections} - \text{no. of parameters})]^{1/2} = 0.734$. Programs used were SHELXTL [7] for structure solution, refinement and molecular graphics, Bruker AXS SMART (control), SAINT (integration), and SADABS (absorption correction) [8].

3. Results and discussion

3.1. *Characterization of the complexes*

The already known complexes **1** and **3**,whose structures are shown in Plate 1, have been obtained following literature methods [2,4]; they have been characterized by elemental analyses and IR and ^{1}H spectroscopies.

The new complex **4**, whose structure is discussed below, has been obtained both by reacting ligand **A** with $Co_4(CO)_{12}$ or $Co_2(CO)_8$ and by thermally treating complex **1** in toluene. Elemental analysis, IR and ^{1}H-NMR of this complex accord with the structure as determined by X-rays.

We have also attempted the reactions of $Co_4(CO)_{12}$ and of $Co_2(CO)_8$ with isopropenyl–acetylene (IPA) [9] with the aim at obtaining the tetracobalt homologue of complexes **5** and **6**. From these reactions very small yields of a derivative were isolated, not fully characterized owing to its decomposition in the mass spectrometer and during attempts at obtaining crystals.

3.2. *X-ray structure of complex **4***

The structure of complex **4** is shown in Fig. 1 and relevant distances and angles are in Table 1.

The organic ligand, derived from the cyclization of $[(HC{\equiv}CCMe_2)_2NMe]$ with transfer of a hydrogen atom from C(1) to C(6), has a planar skeleton of carbon atoms C(1)–C(6) (mean deviation from planarity 0.028 Å), while N(1) is out of plane. Ligand **A** has undergone partial cyclization, using the acetylenic carbon atoms C(2) and C(5) to form a new C–C bond. The C(1) atom interacts with the four cobalt atoms, while C(2), C(5) and C(6) are bonded only to Co(1). The planarity of the C_6 moiety and the C–C bond values agree with a π delocalization on the C(1)C(2)C(5)C(6) fragment with a major double bond character on the C(5)–C(6) bond; the C(5)–C(6) bond corresponds to the former triple bond of ligand **A**. The Co(1)–C(1) distance is quite long,

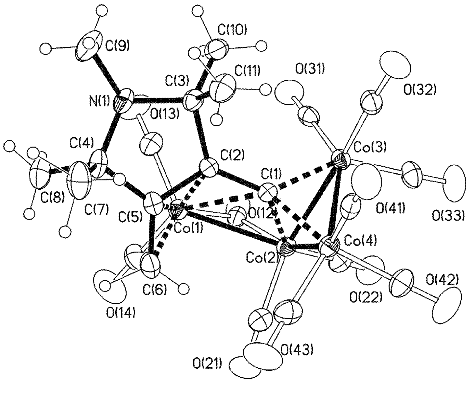


Fig. 1. ORTEP plot of complex **4** $Co_4(CO)_{10}(\mu\text{-}CO)[H_2C{=}CC(Me)_2N(Me)C(Me_2)C(\mu_4\text{-}C)]$, with thermal ellipsoids (30% probability) and atom labelling.

Table 1
Relevant bond lengths (Å) and angles (°) for complex **4**

Bond lengths	
Co(1)–C(5)	2.064(3)
Co(1)–C(6)	2.136(3)
Co(1)–C(2)	2.144(3)
Co(1)–C(1)	2.502(3)
Co(1)–Co(2)	2.6137(7)
Co(2)–C(1)	1.968(3)
Co(2)–Co(3)	2.4405(7)
Co(2)–Co(4)	2.4957(6)
Co(3)–C(1)	1.925(3)
Co(3)–Co(4)	2.4672(7)
Co(4)–C(1)	1.927(3)
C(1)–C(2)	1.423(4)
C(2)–C(5)	1.438(4)
C(2)–C(3)	1.556(4)
C(5)–C(6)	1.384(4)
Bond angles	
C(1)–Co(2)–Co(1)	64.40(9)
Co(3)–Co(2)–Co(1)	101.06(2)
Co(4)–Co(2)–Co(1)	106.77(2)
C(4)–N(1)–C(3)	112.1(3)
C(1)–C(2)–C(5)	124.4(3)
C(1)–C(2)–C(3)	127.7(3)
C(5)–C(2)–C(3)	106.6(3)
C(6)–C(5)–C(2)	122.3(3)
C(6)–C(5)–C(4)	126.1(3)
C(2)–C(5)–C(4)	111.4(3)

thus indicating weak interaction; it is, however, shorter than the sum of van der Waals radii.

The metal core of the complex is a ‘spiked triangular’ or metallo–ligated triangle of four cobalt atoms. The Co(1)–Co(2) bond forms an angle of 107° with the plane of the Co_3 cluster and is bridged by a slightly asymmetric carbonyl. Assuming the 64 e^- count required by this type of clusters, the ligand should act as a 6 e^- donor.

The metal cluster core of complex **4** is—to our knowledge—the first example of a tetracobalt triangular metallo–ligated cluster containing an *acetylide*-ligand. Tetracobalt complexes containing *alkynes* generally prefer the butterfly arrangement of metal atoms [10].

This type of interaction between a spiked triangular cluster and an acetylide ligand has been found for only two other heterometallic complexes, that is the isopropenylacetylide derivatives $(Cp)_2Ni_2M_2(CO)_5(\mu_3\text{-}CO)[C_2(H)C(=CH_2)CH_3]$ (M = Fe, complex **5** [11]; M = Ru, complex **6** [12]).

A comparison between the relevant bonding distances and angles of complexes **4**, **5**, **6** is shown in Table 2.

Complexes **4**, **5** and **6** show a similar skeleton formed by the four metal atoms and by C(1), C(2), C(5) and C(6).

Complex **5**, showing a metal–atom core *isoelectronic* with that of **4**, has a very asymmetric triply bridging CO on the metal triangle whereas **4** contains a bridging carbonyl on the ‘spike’; complex **6** has all terminal carbonyl ligands. A difference is shown by the C(1)–M(1) distance ranging from 2.27 (M(1)=Fe) to 2.45 (M(1)=Ru) to 2.50 (M(1)=Co); the difference is not related to the dimensions of the metal, so a major or minor interaction of the C(1)–C(2) bond with the metal must be invoked. These differences should be correlated to the C–C bond values involved in the interaction; unfortunately the high Estimated standard deviations of some bond lengths do not allow such correlation. The great hindrance of the pentaatomic ring may contribute to the elongation of the Co(1)–C(1) distance.

The M(1)–M(2) distance is always longer than the other metal–metal distances, and more or less perpendicular to the M(2)M(3)M(4) plane.

As previously pointed out C(1) interacts with all the four metal atoms and with C(2). The ‘pentacoordination’ of a carbon atom to four metals and another carbon is not uncommon in homo- and hetero-metallic clusters containing *acetylide* ligands. It has been observed not only in clusters **4**–**6** but also in a number of metallo–ligated triangular clusters substituted with *parallel* [13] or *quasi-parallel* [14] acetylides. It has also been found in penta-iron bis-acetylido derivatives showing *bow-tie* structures [15]. Complexes **7** $[Fe_2(NiCp)_2(CO)_5PPh_2(CCPh)]$ [13d] and **8** $[Fe_5(CO)_{14}(CCR)_2]$ [15] of Plate 2 are examples of these two kinds of structures: the metal–C distances around the pentacoordinated carbon atom are in the range 1.866(7)–2.313(7) Å, and in the range 1.920(5)–2.073(6) Å for complexes **7** and for complex **8**, respectively. In particular, complex **7** was obtained by reacting $[CpNi(CO)]_2$ with $Ph_2P–C\equiv CPh$ and $Fe_3(CO)_{12}$ in a reaction similar to those leading to clusters **5** and **6** and involving metal fragment condensation.

Shift of a terminal alkynic hydrogen occurs during the formation of **5** and **6** (through an unknown mechanism, presumably mediated by metals), as in the formation of complex **4**.

Cyclization reactions of ligand **A** in the presence of cobalt carbonyls have been previously discussed [1,3,4]. Formation of ‘ferrole’ [16] metallacyclic complexes such as **3** has been observed: the ferrole ring is formed by the two propargylic ‘arms’ of ligand **A.** In the formation of cluster **4** ligand **A** undergoes, once again, cyclization to form a heterocyclic ring. However, ligand **A** forms a more complex structure that is a four-carbon atom system interacting with all the cluster metals. Partial cyclization of ligand **A** was also observed on $Ru_3(CO)_{12}$ and reaction mechanisms were proposed to explain the formation of a complex containing an organic moiety obtained by condensation of (cyclized) **A** with hydrocarbyl fragments [17].

Table 2
Comparison of relevant bond distances (Å) and angles (°) in clusters **4**, **5**, **6**

Complexes	**4**, M(1)=M(2)=M(3)=M(4)=Co	**5**, M(1)=M(2)=Fe, M(3)=M(4)=Ni	**6**, M(1)=M(2)=Ru, M(3)=M(4)=Ni
M(1)–M(2)	2.6197(7)	2.755(3)	2.960(6–8)
M(2)–M(4)	2.4957(6)	2.384(2)	2.515
M(2)–M(3)	2.4405(7)	2.384(2)	
M(3)–M(4)	2.4672(7)	2.337(3)	2.368
M(1)–M(2)–M(4)	106.77(2)	93.7(1)	91.4(1–2)
M(1)–M(2)–M(3)	101.06(2)	100.1(1)	94.7
M(1)–C(1)	2.5018(30)	2.266(8)	2.45(2–3)
M(2)–C(1)	1.9675(30)	1.905(8)	2.06
M(3)–C(1)	1.9250(30)	1.931(7)	1.85
M(4)–C(1)	1.9272(31)	1.868(8)	1.83
M(1)–C(2)	2.1441(29)	2.066(9)	2.17
M(1)–C(5)	2.0643(31)	2.072(10)	2.25
M(1)–C(6)	2.1356(32)	2.128(10)	2.26
C(1)–C(2)	1.423(4)	1.410(12)	1.45(4)
C(2)–C(5)	1.438(4)	1.427(12)	1.44(4)
C(5)–C(6)	1.384(4)	1.407(12)	1.45(4)

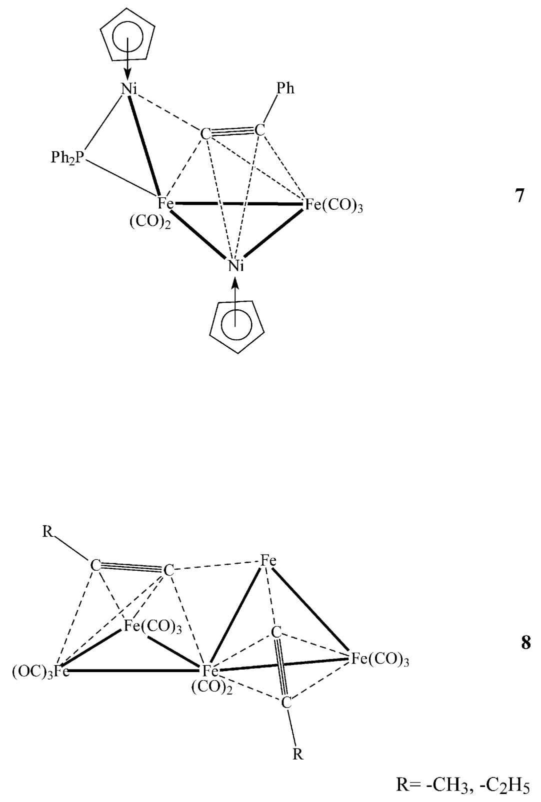


Plate 2.

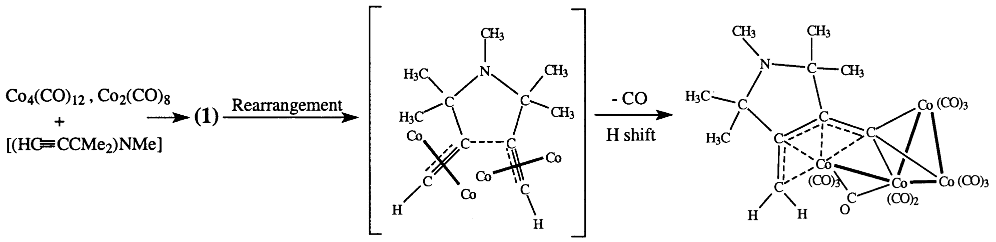
3.3. Formation pathways for cluster 4

There are at least two possible mechanisms leading to cluster **4**. It is obtained from $Co_4(CO)_{12}$ in moderate yields (and in minor amounts in the other reactions described); thus the main reaction pathway would be the opening of the tetrahedral (60 electrons) $Co_4(CO)_{12}$ cluster and the cyclization of ligand **A** to give the (64 electron) complex **4** in one or more reaction steps, for example through the intermediacy of a butterfly (alkynic) complex. When discussing the formation pathways of complex **5** we considered the possibility that opening of tetrahedral clusters induced by alkynes, will result in formation of lozenge and/or spiked triangular structures [11].

However, cluster **4** is formed also (albeit in lesser yields) both by reacting $Co_2(CO)_8$ with ligand **A** and by complex **1** under mild thermal treatment; therefore, another possibility should also be considered. This would require a *template effect* of ligand **A** and the intermediacy of complex **1**. The cyclization of ligand **A** to give complexes **2** and **3** requires conformational changes. To form metallacyclic rings, indeed, the 'arms' of ligand **A** must rearrange from the original position to a nearly parallel position. A tempting hypothesis could be that in complex **1** also, rotation of the substituted 'arms' would bring the two $Co_2(CO)_6$ 'fragments' close each to the other and in favorable position (e.g. perpendicular each to the other) to form the metal core of **4** through a metal fragment condensation process [18]. This is shown in Scheme 1.

This hypothesis is supported by the formation of complexes **5** and **6** which are obtained by reacting $(Cp)_2Ni_2[HC_2C(=CH_2)CH_3]$ with $M_3(CO)_{12}$ (M = Fe, Ru) carbonyls. Metal fragment condensation occurs during these reactions and, in addition, the dinickel and diiron or diruthenium fragments (the latter originated upon cluster cleavage) are disposed in perpendicular way each with respect to the other in the final product.

In the above reactions, therefore, ligand **A,** its metal-substituted derivative **1** (and IPA) would act as tem-



Scheme 1. Hypothesis of formation pathway for cluster **4**.

plates for the formation of the tetrametallic cores of clusters **4**–**6**. Interestingly, one usually thinks that *template effect* occurs when the *metal core* of an organometallic complex coordinates and orients the organic *ligands* in positions favorable to react and form new products [19]. In this case, however, the opposite occurs and the ligand induces the condensation of metal fragments.

An attempt at better clarifying the proposed pathways was made; the reactions of $Co_2(CO)_8$ and $Co_4(CO)_{12}$ with IPA gave very small amounts of a purple product **4b** which, unfortunately, did not afford crystals suitable for X-ray analysis. Partial decomposition in the mass spectrometer did not allow to characterize unequivocally the complex. It could be both a butterfly acetylenic cluster or the spiked acetylide homologue of **4**–**6**.

The reactions reported in this work and the structure of **4** show that, although the reactions of cobalt carbonyls with alkynes derivatives are one of the oldest branch of cluster chemistry, this field is far from being fully explored and new structures and reaction mechanisms can be still evidenced.

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