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## Formation of metallacycles from terminal diynes with geminal methyl groups $\alpha$ to the triple bonds. Synthesis and crystal structure of $\text{Co}_2(\text{CO})_5[(\text{HC}\equiv\text{CCMe}_2)_2\text{NMe}]$ , an intermediate in cobalt-catalyzed organic syntheses

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### Abstract

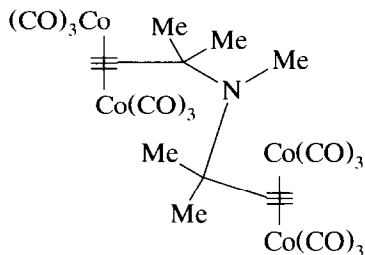
The title complex has been synthesized by refluxing a toluene solution of  $\text{Co}_2(\text{CO})_8$  and the diyne  $[(\text{HC}\equiv\text{CCMe}_2)_2\text{NMe}]$ . It has been characterized by IR and NMR spectroscopy and its structure determined by an X-ray diffraction study. The complex is one of the few examples of a crystallographically characterized cobaltacyclopentadiene derivative. It can be considered to be an intermediate in the cyclization reaction of acetylenic derivatives catalyzed by cobalt carbonyls, and a model for the intermediates in heterocycle formation from diynes and nitriles catalyzed by  $\text{Co}^0$  complexes.

### Introduction

Diacetylenic substrates containing  $\alpha$ -alkyl substituents, and in particular the amine  $[(\text{HC}\equiv\text{CCMe}_2)_2\text{NMe}]$  (tetramethyldipropargyl-*N*-methylamine, ligand **A**) incorporate  $\text{RC}\equiv\text{CH}$  alkynes or  $\text{RC}\equiv\text{N}$  nitriles in the presence of cobalt(0) complexes to give condensed aromatic or heterocyclic products, respectively [1].

It was recently found that  $\text{Co}_2(\text{CO})_8$  reacts with the amine **A** under mild conditions to give the complex  $[\text{Co}_2(\text{CO})_6]_2[(\text{HC}\equiv\text{CCMe}_2)_2\text{NMe}]$  (**1**), in which each terminal acetylenic carbon-carbon bond interacts with one  $\text{Co}_2(\text{CO})_6$  unit through

two  $\pi$  bonds; the structure of **1**, determined by an X-ray diffraction study [1], is shown schematically below:



(1)

When complex **1** was heated in the presence of  $\text{RC}\equiv\text{CH}$  or  $\text{RC}\equiv\text{N}$ , it gave benzene or pyridine derivatives, respectively, along with CO insertion products (cyclopentadienone derivatives) [1]. Thus, **1** is the first isolable intermediate in the  $\text{Co}_2(\text{CO})_8$  catalysed-diyne cyclization with alkynes or nitriles; the subsequent step in the reaction is assumed to be the formation of a cobaltacyclopentadiene, eventually stabilized by a second cobalt atom [1,2]. Compounds of this type, however, although suggested in several reaction schemes involving cobalt, have only rarely been isolated and characterized [3].

We report a simple synthesis of a cobaltacyclopentadiene derivative obtained from amine **A** and  $\text{Co}_2(\text{CO})_8$  under thermal conditions; the product,  $\text{Co}_2(\text{CO})_5\text{[(HC}\equiv\text{CCMe}_2)_2\text{NMe]}$  (**2**), has been characterized by spectroscopy and its structure determined by an X-ray study.

The isolation of complex **2** allowed us to present evidence for the intermediacy of the cobaltacyclopentadiene in the above mentioned cyclization reactions.

## Results and discussion

The reaction of  $\text{Co}_2(\text{CO})_8$  with amine **A** in hexane at room temperature gives complex **1** [1], which at higher temperatures gives the above-mentioned organic products. By contrast, the reaction of  $\text{Co}_2(\text{CO})_8$  with amine **A** in refluxing toluene for a short time affords complex **2**.

The synthesis of **2**, and its crystal structure are of interest for the following reasons:

(i) This is the first cobaltacyclopentadiene derivative obtained from a terminal diyne, the others having been obtained by coupling of cyclic alkynes [4] or by reaction of previously formed cobalt metallacycles with other metal fragments [5]. Comparable rhodium [6] and iridium species [7] have been reported, but, again, the syntheses were different.

(ii) To our knowledge, the only previous X-ray structural characterization of a cobaltacyclopentadiene derivative is that of  $\text{Co}_2(\text{CO})_5(\text{C}_8\text{H}_{12})_2$  (complex **4**) [4] which is remarkable in view of the ease with which these complexes are formed during several cobalt-catalyzed organic syntheses [3]. Very recently the complex  $[(\text{Cp})_2\text{Co}_2(\text{ClC}\equiv\text{CCl})_2]$  (**5**) has been reported and characterized by X-ray diffraction and its intermediacy in the cyclo-oligomerization of alkynes discussed [8]. The

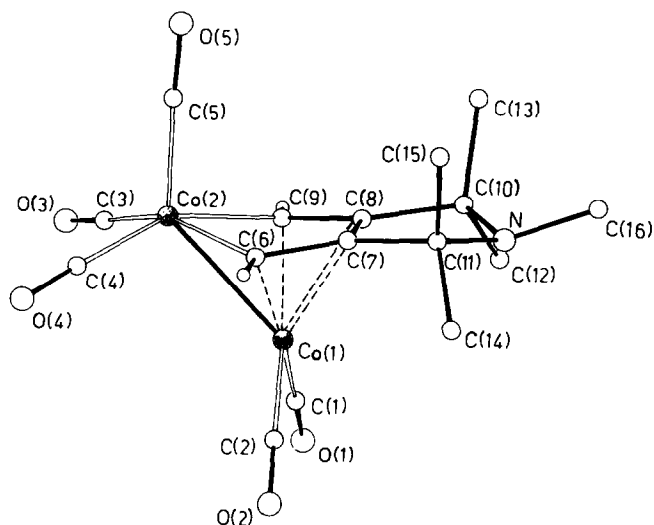
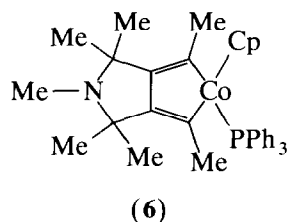


Fig. 1. The molecular structure of the complex  $\text{Co}_2(\text{CO})_5[(\text{HC}\equiv\text{CCMe}_2)_2\text{NMe}]\text{CMe}_2\text{C}\equiv\text{CH}$  (**2**) with the atomic labeling scheme.

mononuclear complex  $[\text{PPh}_3(\text{Cp})\text{Co}[(\text{MeC}\equiv\text{CCMe}_2)_2\text{NMe}]$  (**6**) has also been char-



acterized; it also represents a 'model' intermediate in the synthesis of the above-mentioned condensed heterocyclic derivatives [9]. The presence of cyclopentadienyl ligands instead of carbonyls in **5** and **6**, and its implication for the structure and reactivity are discussed further below.

#### *Description of the structure of $\text{Co}_2(\text{CO})_5[(\text{HC}\equiv\text{CCMe}_2)_2\text{NMe}]$ (**2**)*

The molecular structure of complex **2** is depicted in Fig. 1 together with the atom numbering scheme. Selected bond distances and angles are given in Table 1. The cyclized amine **A** interacts with the Co(2) atom through the terminal C(6) and C(9) carbon atoms with formation of a cobaltacyclopentadiene ring [the Co(2)–C(6) and Co(2)–C(9) bond lengths are 1.971(6) and 1.968(5) Å, respectively]. The electrons of the double bonds are delocalized over the four-atom system, as shown by the C(6)–C(7), C(7)–C(8) and C(8)–C(9) bond lengths, 1.403(7), 1.402(7) and 1.400(8) Å, respectively. The cobaltacyclopentadiene ring has an 'envelope' conformation, with the four carbon atoms strictly coplanar and the Co(2) atom deviating by 0.457(1) Å from the plane through the carbons. The C(6), C(7), C(8) and C(9) carbon system is involved in a  $\eta^4$ -interaction with the Co(1) atom, the Co–C distances being 2.007(5), 2.127(5), 2.121(5) and 2.006(5), respectively, with the Co(1) atom far from the plane containing the four carbon atoms of 1.552(1) Å and

Table 1

Important interatomic distances (Å) and angles (deg) for complex **2**

Co(1)–Co(2)	2.474(1)	C(7)–C(8)	1.402(7)
Co(1)–C(1)	1.751(7)	C(8)–C(9)	1.400(8)
Co(1)–C(2)	1.749(5)	C(8)–C(10)	1.514(8)
Co(1)–C(6)	2.007(5)	C(7)–C(11)	1.500(9)
Co(1)–C(7)	2.127(5)	N–C(10)	1.479(8)
Co(1)–C(8)	2.121(5)	N–C(11)	1.490(7)
Co(1)–C(9)	2.006(5)	N–C(16)	1.473(9)
Co(2)–C(3)	1.794(8)	C(1)–O(1)	1.133(9)
Co(2)–C(4)	1.792(6)	C(2)–O(2)	1.127(7)
Co(2)–C(5)	1.786(7)	C(3)–O(3)	1.125(11)
Co(2)–C(6)	1.971(6)	C(4)–O(4)	1.122(7)
Co(2)–C(9)	1.968(5)	C(5)–O(5)	1.122(10)
C(6)–C(7)	1.403(7)		
Co(2)–Co(1)–C(1)	120.1(2)	C(6)–Co(2)–C(9)	80.4(2)
Co(2)–Co(1)–C(2)	121.9(2)	C(10)–N–C(11)	112.2(5)
C(1)–Co(1)–C(2)	93.1(3)	C(10)–N–C(16)	115.6(5)
Co(2)–Co(1)–C(6)	50.9(1)	C(11)–N–C(16)	117.3(5)
Co(2)–Co(1)–C(7)	75.9(1)	Co(2)–C(6)–C(7)	113.8(4)
Co(2)–Co(1)–C(8)	75.7(1)	C(6)–C(7)–C(11)	135.4(5)
Co(2)–Co(1)–C(9)	50.8(1)	C(6)–C(7)–C(8)	113.6(5)
Co(1)–Co(2)–C(3)	105.4(2)	C(8)–C(7)–C(11)	110.9(4)
Co(1)–Co(2)–C(4)	103.5(2)	C(7)–C(8)–C(9)	114.4(5)
Co(1)–Co(2)–C(5)	133.9(2)	C(7)–C(8)–C(10)	110.3(4)
Co(1)–Co(2)–C(6)	52.2(1)	C(9)–C(8)–C(10)	135.2(5)
Co(1)–Co(2)–C(9)	52.2(2)	Co(2)–C(9)–C(8)	113.6(4)
C(3)–Co(2)–C(4)	93.5(3)	N–C(10)–C(8)	100.9(5)
C(3)–Co(2)–C(5)	106.2(3)	N–C(11)–C(7)	100.8(4)
C(3)–Co(2)–C(9)	88.2(3)	Co(1)–C(1)–O(1)	178.7(6)
C(4)–Co(2)–C(5)	107.1(3)	Co(1)–C(2)–O(2)	179.0(6)
C(4)–Co(2)–C(6)	88.8(3)	Co(2)–C(3)–O(3)	178.3(7)
C(5)–Co(2)–C(6)	94.7(3)	Co(2)–C(4)–O(4)	177.6(6)
C(5)–Co(2)–C(9)	96.5(3)	Co(2)–C(5)–O(5)	176.5(7)

on the opposite side with respect to the Co(2) atom. The separation between the two cobalt atoms [2.474(1) Å] is consistent with a metal–metal bond. The pentatomic heterocyclic ring, having the C(7)–C(8) bond in common with the cobaltacyclopentadiene ring, also has an ‘envelope’ conformation, with the C(10)–C(8)–C(7)–C(11) moiety strictly planar and the N atom deviating by 0.320 Å from the plane. This plane containing the four carbon atoms is tilted only by 0.9(3)° with respect to the C(6)–C(7)–C(8)–C(9) plane, so that all carbon atoms of the fused cobaltacyclopentadiene and heterocycle rings effectively lie in the same plane, with the Co and N atoms deviating on opposite sides of it. The structure of **2** as a whole displays an approximate  $C_s$  symmetry, with the mirror plane passing through the Co(1), Co(2), C(5), O(5), N and C(16) atoms.

The structural parameters of the  $\text{Co}_2(\text{CO})_5(-\text{C}=\text{CR}-\text{CR}=\text{C}-)$  moiety of complex **2** are closely comparable to those for the same moiety in **4** [4], in which the organic moiety has been formed from two molecules of cyclooctyne. The dimetal–ligand interaction, as well as the stereochemistry of the COs (and of the phosphines when present) around the cobalt atoms, are comparable for complexes with known

structure [4,6,7], regardless of the nature of the (cobalt triad) coordinating metal. This indicates a rather rigid structure, at least in the solid state. The experimental data indicate, however, that in complex **2** there is delocalized scrambling of carbonyls in solution at room temperature.

It is of interest to compare the cobaltacyclopentadiene ring in **2** with the methyl-substituted one in the mononuclear **6**, obtained from the  $(\text{MeC}\equiv\text{CCMe}_2)_2\text{NMe}$  amine. The Co–C  $\sigma$ -bonds in **6** are practically equal (1.975(9) and 1.987(16) Å) in spite of the presence of the moderately bulky methyl groups, with the Co atom deviating by 0.37 Å from the planar four carbon atom skeleton, in which the two double bonds seem to be localized, as shown by the lengths of the C–C bonds, 1.34(2), 1.46(2) and 1.38(2) Å. As regards the fused cobaltacyclopentadiene and heterocycle rings, the six carbon atoms are coplanar as in **2** with the Co and N atoms deviating on opposite sides (the N atom by 0.30(1) Å).

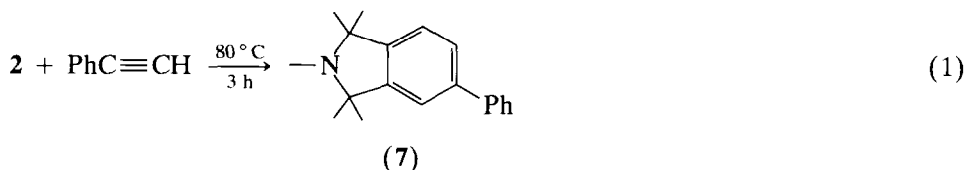
The metal–alkyne interaction found in complex **2** is quite rare for cobalt but is commonly found for iron, in the ‘ferrole’  $\text{Fe}_2(\text{CO})_6(\text{RC}\equiv\text{CR}')_2$  complexes [10]. It is noteworthy that the iron derivatives can exist in two closely related (on the energy profile) forms, ‘non-sawhorse’ and ‘sawhorse’, respectively, with or without semi-bridging COs [11], the former arrangement being most frequently found [12]. By contrast, the cobalt triad complexes mentioned in this paper show no tendency to give semibridging systems, and the ‘sawhorse’ geometry seems to be preferred.

Complexes **5** and **6** merit further discussion in view of the role of cobalt complexes as intermediates. In the dinuclear **5**, two Cp take the place of five CO ligands in the ‘ferrole’ structure. Noteworthy is that one five-electron donor Cp group is bound to each cobalt, whereas in **2** three COs, contributing 6 electrons, are bound to Co(2) and two COs, contributing 4 electrons, are on Co(1); in spite of this different ‘charge distribution’, the metal–carbon interactions in the two complexes are comparable, and moreover no semibridging COs are found in **2**. In the case of **6**, it is evident that the 18 electron count for cobalt is ensured by the presence of one Cp and one  $\text{PPh}_3$  on the metal, contributing a total of 7 electrons (5 + 2); this possibility is precluded when only CO ligands are present on the starting cobalt complex. This may be the reason why mononuclear intermediates have not been isolated in the reactions reported here.

*Considerations on the reactivity of  $\text{Co}_2(\text{CO})_5[(\text{HC}\equiv\text{CCMe}_2)_2\text{NMe}]$  (**2**)*

As suggested previously, complex **2** is to be regarded as the intermediate in the reaction of complex **1** with alkynes [1,2]. The formation of a metallacycle system starting from the amine **A**, which has a ‘linear’ structure, involves a considerable structural rearrangement, which is favourably assisted by conformational effects of the four methyl groups  $\alpha$  to the triple bonds. Moreover, the steric effect caused by these groups prevents further insertion of an acetylene of the same amine.

It has been recently shown [9] that complex **2** reacts with an excess of  $\text{PhC}\equiv\text{CH}$  during 3 h at 80 °C in toluene to give product **7** in 95% yield (eq. 1), along with a large quantity of phenylacetylene trimers:





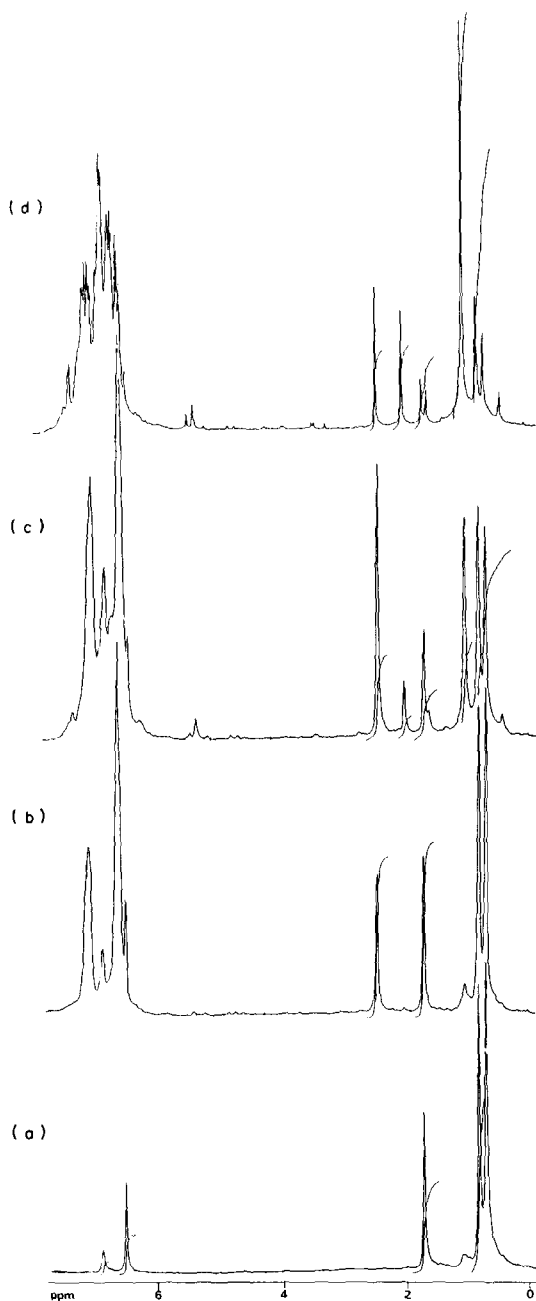


Fig. 2.  $^1\text{H}$  NMR spectra in  $\text{C}_6\text{D}_6$  at  $35^\circ\text{C}$  of complex **2** +  $\text{PhC}\equiv\text{CH}$ . (a) Complex **2**; (b) complex **2** +  $\text{PhC}\equiv\text{CH}$  at the beginning; (c) complex **2** +  $\text{PhC}\equiv\text{CH}$  after 10 h; (d) complex **2** +  $\text{PhC}\equiv\text{CH}$  after 22 h.

prepared by published procedures [14]. Products were isolated by conventional methods and identified by their  $^1\text{H}$  and  $^{13}\text{C}$  NMR, mass and IR spectra. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AC100 or CXP200 instrument in  $\text{C}_6\text{D}_6$  or  $\text{CDCl}_3$  as solvents and TMS as internal standard. Mass spectra were

obtained with a Finnigan 1020 mass spectrometer at 70 eV ionizing voltage, and IR spectra were recorded on a Perkin-Elmer 283B Infrared Spectrometer. Analytical GLC was carried out with a Dani 3900 chromatograph fitted with a methylsilicone (OV101) coated capillary column.

#### *Preparation of complex 2*

Treatment of a solution of  $\text{Co}_2(\text{CO})_8$  (1 g, 2.92 mmol) in toluene (100 ml), saturated with dry nitrogen, with an excess of amine **A** (0.65 g, 4.0 mmol) caused an immediate change of colour to very dark brown: the solution was slowly heated to reflux and refluxed for 1 min. No further change in colour was observed. The mixture was then filtered under nitrogen and concentrated to small volume under reduced pressure; purification by preparative TLC (Kieselgel P.F. Merck; eluant, a mixture of light petroleum and diethyl ether, 80:20 by volume) yielded five derivatives, three of them in trace amounts. The main product (yield ca. 40% based on cobalt) was the yellow complex **2**.

Complex **2** was recrystallized from heptane/chloroform (80:20, by volume) or from toluene under nitrogen at 253 K during some days to give dark orange crystals suitable for the X-ray analysis. Attempts to crystallize complex **3** from various solvents or mixtures (toluene, cyclohexane, heptane/chloroform) under the same conditions as above and also for shorter time (hours) always resulted in the deposition of crystals showing the same unit cell as complex **2**. Complex **2**: Anal. Found: C, 45.58; H, 4.06; Co, 28.03; N, 3.20.  $\text{C}_{16}\text{H}_{17}\text{Co}_2\text{NO}_5$  calc.: C, 45.62; H, 4.07; Co, 27.99; N, 3.33%. IR ( $\nu(\text{CO})$ , heptane solution): 2048vs, 2027vs, 2016sh, 1978vs  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\delta$ ,  $\text{C}_6\text{D}_6$  solution, TMS internal standard): 6.52 (s, 2H, C=CH), 1.71 (s, 3H, N-Me), 0.82 (s, 6H, 2Me), 0.71 ppm (s, 6H, 2Me).  $^{13}\text{C}$  NMR ( $\delta$ ,  $\text{C}_6\text{D}_6$  solution, TMS internal standard): 200 (broad, COs), 153.45 ( $\text{C}_6$ ,  $\text{C}_9$ ), 140.35 ( $\text{C}_7$ ,  $\text{C}_8$ ), 60.34 ( $\text{C}_{10}$ ,  $\text{C}_{11}$ ), 29.30 ( $\text{C}_{16}$ ), 26.72, 23.16 ( $\text{C}_{12}$ - $\text{C}_{15}$ ). Mass spectrum (EI, 70 eV, Kratos Ms-50);  $M^+ = 421 m/e$ , loss of 3 COs, then loss of the remaining two COs in competition with loss of  $\text{H}_2$  and of one cobalt atom, followed by complete fragmentation of the organic moiety.

#### *Reaction of complex 2*

Acetonitrile (1.0 ml) was added to a solution of complex **2** (0.335 g, 0.8 mmol) in toluene (15 ml) under nitrogen and the mixture was heated at 80 °C for 24 h. A weak flow of nitrogen was used to remove the evolved CO. Product **8** (0.013 g, 0.06 mmol), 8% yield, and the previously reported product **9** [1] (0.052 g, 0.27 mmol), 34% yield, were identified by GLC. They were isolated by TLC on silica gel with hexane/acetone (7:3) as eluent. **8**: white solid, m.p. 73–74 °C. MS,  $m/e$ : 204 ( $M^+$ ), 190, 189(100), 188, 175, 174, 173, 159, 87, 77, 56.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ): 8.20, 6.40 (2 br s, 2H, 2C=CH); 2.28 (s, 3H,  $\text{CH}_3$ ); 1.70 (s, 3H,  $\text{NCH}_3$ ); 0.91, 0.89 (2s, 12H, 4 $\text{CH}_3$ ).

A reaction in a 5-mm NMR tube was carried out in a Bruker AC 100 instrument equipped with a temperature controller. Complex **2** (0.04 g, 0.1 mmol) was dissolved in  $\text{C}_6\text{D}_6$  inside the tube and  $\text{PhC}\equiv\text{CH}$  (0.03g, 0.03 mmol) was added at room temperature under nitrogen; the mixture was kept at 35 °C in the probe and  $^1\text{H}$  NMR spectra were recorded during more than 24 h.



Table 2

Summary of crystallographic data for complex 2

Formula	C <sub>16</sub> H <sub>17</sub> Co <sub>2</sub> NO <sub>5</sub>
Mol. wt.	421.18
Crystallographic system	triclinic
Space group	$P\bar{1}$
Radiation ( $\lambda$ , Å)	niobium-filtered Mo- $K_{\alpha}$ (0.71073)
$a$ (Å)	9.145(5)
$b$ (Å)	12.679(6)
$c$ (Å)	8.225(5)
$\alpha$ (deg)	91.31(2)
$\beta$ (deg)	97.70(2)
$\gamma$ (deg)	104.63(2)
$V$ (Å <sup>3</sup> )	912.8(9)
$Z$	2
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	1.532
$F(000)$	428
Crystal size (mm)	0.15 × 0.20 × 0.26
$\mu(\text{Mo-}K_{\alpha})$ (cm <sup>-1</sup> )	18.36
Diffractometer	Siemens AED
$2\theta$ range (deg)	6–54
Reflectns measured	$\pm h, \pm k, l$
Unique total data	4029
Unique observed data [ $I > 2\sigma(I)$ ]	2719
$R$	0.0429
$R_w$	0.0611

*X-ray data collection, structure determination and refinement for Co<sub>2</sub>(CO)<sub>5</sub>[(HC≡CMe<sub>2</sub>)<sub>2</sub>NMe]CMe<sub>2</sub>C≡CH] (2)*

The crystallographic data are summarized in Table 2. Unit cell parameters were determined from the  $\theta$  values of 30 carefully centered reflections, having  $13.1 < \theta < 19.6^\circ$ . Data were collected at room temperature (22 °C) on a Siemens AED diffractometer, using the niobium-filtered Mo- $K_{\alpha}$  radiation and the  $\theta/2\theta$  scan mode. The reflections were collected with a variable scan speed of 3–12 ° deg min<sup>-1</sup> and a scan width from  $(\theta - 0.65)^\circ$  to  $(\theta + 0.65 + 0.346 \tan \theta)^\circ$ . One standard reflection was monitored every 50 measurements; no significant decay was noticed during the data collection. The individual profiles were analyzed as described by Lehmann and Larsen [15]. Intensities were corrected for Lorentz and polarization effects; no correction for absorption was necessary. Only 'observed' reflections (see Table 2) were used in the structure solution and refinement.

The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares first with isotropic thermal parameters and then with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms, except those of the methyl group on the nitrogen atom, were clearly located in the final  $\Delta F$  map, but those of the methyl group at the nitrogen atom were placed at calculated positions. All were introduced in the final structure factor calculations, with fixed isotropic thermal parameters, but not refined. The final cycles of refinement were carried out on the basis of 217 variables; after the last cycles, no parameters shifted by more than 0.82 esd. The largest remaining peak in the final

Table 3

Fractional atomic coordinates ( $\times 10^4$ ) with esd's in parentheses for the non-hydrogen atoms of complex 2

	x	y	z
Co(1)	4199(1)	2956(1)	1635(1)
Co(2)	4159(1)	1444(1)	3492(1)
O(1)	4940(8)	2747(5)	-1635(6)
O(2)	6324(5)	5065(4)	2345(8)
O(3)	5315(8)	-143(5)	1769(7)
O(4)	6961(5)	2265(5)	5790(7)
O(5)	1841(6)	212(6)	5309(10)
N	422(5)	3456(4)	1262(6)
C(1)	4666(7)	2836(5)	-345(8)
C(2)	5493(7)	4236(5)	2080(8)
C(3)	4891(8)	478(5)	2441(9)
C(4)	5884(7)	1927(5)	4910(7)
C(5)	2758(7)	663(6)	4613(9)
C(6)	3652(6)	2837(4)	3919(6)
C(7)	2333(5)	2949(4)	2928(6)
C(8)	1844(5)	2188(4)	1577(6)
C(9)	2757(6)	1462(4)	1463(7)
C(10)	437(6)	2375(5)	556(8)
C(11)	1305(6)	3701(5)	2946(7)
C(12)	581(9)	2438(7)	-1305(8)
C(13)	-963(7)	1432(6)	842(12)
C(14)	2206(8)	4923(5)	3124(9)
C(15)	347(9)	3407(7)	4376(10)
C(16)	-1056(8)	3735(7)	975(11)

difference maps was equivalent to about  $0.57 \text{ e } \text{\AA}^{-3}$ . In the final cycles of refinement a weighting scheme,  $w = [\sigma^2(F_o) + gF_o^2]^{-1}$  was used; at convergence, the  $g$  value was 0.0054. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, were taken from ref. 16. All calculations were carried out on the CRAY X-MP/12 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale (CINECA, Casalecchio Bologna) and on the Gould Povernode 6040 of the Centro di Studio per la Strutturistica Diffraattometrica del C.N.R., Parma, using the SHELX-76 and SHELXS-86 systems of crystallographic computer programs [17]. The final atomic coordinates for the non-hydrogen atoms are given in Table 3. Tables of hydrogen atom coordinates thermal parameters, and structural factors are available from the authors.

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