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Activation of unsaturated substrates by cobalt complexes. Crystal structure and reactivity of a complex of octacarbonyl dicobalt with *N*-methylbis(α,α-dimethylpropargyl)amine

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Abstract

A new complex of octacarbonyl dicobalt with *N*-methyl(α,α-dimethylpropargyl)-amine was prepared and characterized by spectroscopic and X-ray diffraction methods. Each triple bond is coordinated to a hexacarbonyldicobalt fragment and each metal shows a pseudo-octahedral geometry. The structure of the free ligand having NH in place of *N*-methyl has also been determined for comparison.

Thermal decomposition of the complex in toluene or in benzonitrile afforded a series of products, mainly resulting from the rearrangement of the original complex to a metallacyclic structure, able to incorporate either the acetylenic triple bond or carbon monoxide in the case of toluene and either the acetylenic or the nitrile triple bond in the case of benzonitrile. C–N bond cleavage of the starting amine was observed as a side reaction. Catalytic reactions leading to benzonitrile incorporation were also observed. A cross experiment with a 1/1 mixture of diynes, either with or without geminal methyl groups α to triple bonds showed that for conformation reasons the metallacycle moiety mainly comes from the substrate containing geminal groups, whilst for steric reasons the other substrate is preferentially incorporated into the metallacycle.

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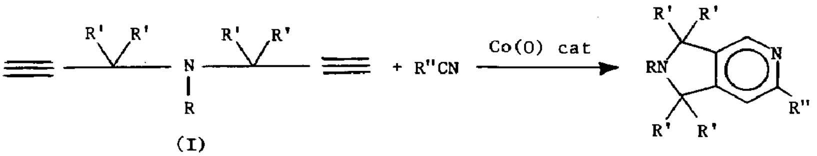
Introduction

In previous papers [1] we have reported the ability of cobalt(0) complexes to incorporate nitriles into diacetylenic substrates, containing α-alkyl substituents. In particular, amine I (R = H, R″ = alkyl) reacted with nitriles R″CN according to equation 1.



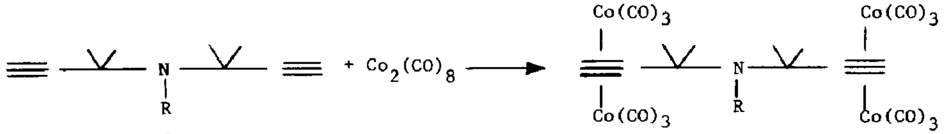
(I)

(1)

Interestingly, this reaction did not occur in significant yield when the geminal groups were absent. In an attempt to isolate intermediate complexes we treated octacarbonyldicobalt with the diacetylenic amine I and obtained complex II, the structure and reactivity of which are the subject of the present paper.

Results and discussion

Reaction of amine I (R = Me) (N-MeTMDPA) with $Co_2(CO)_8$ in n-hexane at room temperature proceeded according to eq. 2. Compound II (R = R′ = Me) was isolated as a crystalline solid and its structure was determined by X-ray diffraction. In equations and subsequently methyl groups are hereinafter indicated by single lines.



I II

(2)

For purposes of comparison, the X-ray structure of amine-I (R = H) HTMDPA was also determined.

X-ray structures

Complex II $[Co_2(CO)_6]_2$*N-MeTMDPA.* Fig. 1 shows a projection of the molecule of the complex. This consists of two hexacarbonyldicobalt fragments, each π-bonded to an ethynyl group of the amine having the C≡C direction perpendicular to a Co–Co bond with a "sawhorse" geometry. The two fragments are quite similar, and for each Co–Co–C–C tetrahedral group there is a non-crystallographic local pseudo mirror running through the alkyne carbons and the middle point of the Co–Co bond, and involving only the environment of the cobalt atoms.

The coordination geometry around each cobalt can be described in terms of a very distorted octahedron in which the coordination sites are occupied by three carbonyl groups at about 1.79 Å, an adjacent cobalt at 2.455(2) Å, and the two bridging acetylenic carbons at about 1.94 and 1.99 Å. Table 1 shows selected bond lengths and angles. In accord with observations on other molecules containing the acetylenedicobalt moiety, the two cobalt atoms are linked by a metal–metal single bond [2–6]; the two Co–Co distances turn out to be identical, and agree well with

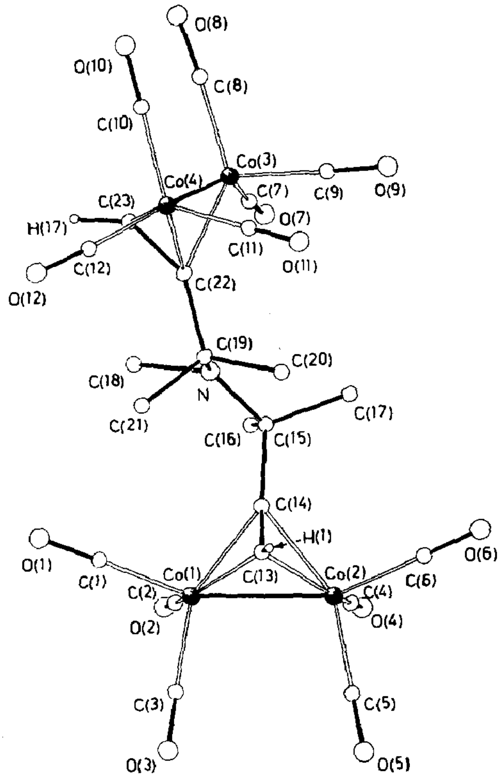


Fig. 1. Perspective view of the $[Co_2(CO)_6]_2$N-MeTMDPA molecule.

those found for the majority of other complexes having similar geometry [7–11]. The Co–C(carbonyl) bond distances are in the range 1.768(9)–1.831(12) Å, and the Co–C–O angles (range 176.2(9)–179.5(1.1)°) also agree well with those found in the quoted complexes described in ref. 7–11.

The structural parameters in the Co–Co–C–C tetrahedral core have been correlated with the electronic properties of the substituents on the acetylenic group [8], and it was found that the metal to acetylenic ligand distances decrease with increasing electronegativity of the substituents, while the acetylenic C–C bond length increases, indicating a strengthening of the Co–C(acetylenic) bonds as a consequence of increased back donation.

The Co–C(acetylenic) bonds are significantly different: the terminal ones, 1.937(9) and 1.930(9) Å, are shorter than the others, 1.998(8), 1.971(7) Å. The latter compare favorably with those in $Co_2(CO)_6$ $(C_2Bu^t_2)$ [9], where the Co–C(acetylenic) distances are 1.982(2) and 1.988(2) Å, while the former are similar to those found for acetylenic compounds containing more electronegative substituents such as COOH or CF_3, for which the distances are 1.923(4)–1.946(4) Å and 1.925(5)–1.935(5) Å, respectively. In the present compound the most relevant influence is likely that of the interactions between the methyl groups of the ligand and the carbonyls in the molecule: the more hindered C(14) and C(22) form longer bonds, while C(13) and C(23), bearing hydrogens, show shorter bonds.

The C–C(acetylenic) bond lengths, 1.32(1) and 1.33(1) Å, are in the usual range,

Table 1

Selected bond distances (Å) and angles (°) for $[Co_2(CO)_6]_2$N-MeTMDPA

Co(1)–Co(2)	2.455(2)	Co(3)–Co(4)	2.455(2)
Co(1)–C(13)	1.937(9)	Co(3)–C(23)	1.930(9)
Co(1)–C(14)	1.998(8)	Co(3)–C(22)	1.971(7)
Co(2)–C(13)	1.948(8)	Co(4)–C(23)	1.938(10)
Co(2)–C(14)	2.010(7)	Co(4)–C(22)	1.976(8)
	Co–C(carbonyl)	1.794(5) av.	
	C–O(carbonyl)	1.123(4) av.	
C(13)–C(14)	1.32(1)	C(22)–C(23)	1.33(1)
C(14)–C(15)	1.51(1)	C(22)–C(19)	1.51(1)
C(15)–C(16)	1.54(1)	C(19)–C(20)	1.53(1)
C(15)–C(17)	1.55(1)	C(19)–C(21)	1.53(1)
N–C(15)	1.47(1)	N–C(18)	1.46(1)
N–C(19)	1.48(1)		
C(1)–Co(1)–Co(2)	153.7(7)	C(6)–Co(2)–Co(1)	150.1(3)
C(1)–Co(1)–C(13)	104.2(4)	C(6)–Co(2)–C(13)	101.1(4)
C(1)–Co(1)–C(14)	103.8(4)	C(6)–Co(2)–C(14)	101.0(4)
C(2)–Co(1)–Co(2)	98.9(3)	C(4)–Co(2)–Co(1)	99.4(3)
C(2)–Co(1)–C(13)	141.4(4)	C(4)–Co(2)–C(13)	141.7(4)
C(2)–Co(1)–C(14)	105.2(4)	C(4)–Co(2)–C(14)	105.7(4)
C(3)–Co(1)–Co(2)	98.4(4)	C(5)–Co(2)–Co(1)	100.0(3)
C(3)–Co(1)–C(13)	102.8(4)	C(5)–Co(2)–C(13)	104.3(5)
C(3)–Co(1)–C(14)	140.4(4)	C(5)–Co(2)–C(14)	141.7(4)
C(7)–Co(3)–Co(4)	149.2(3)	C(12)–Co(4)–Co(3)	148.8(4)
C(7)–Co(3)–C(23)	103.1(4)	C(12)–Co(4)–C(23)	98.5(5)
C(7)–Co(3)–C(22)	98.3(4)	C(12)–Co(4)–C(22)	104.1(4)
C(8)–Co(3)–Co(4)	101.7(3)	C(10)–Co(4)–Co(3)	95.3(4)
C(8)–Co(3)–C(22)	138.8(4)	C(10)–Co(4)–C(22)	140.8(5)
C(8)–Co(3)–C(23)	99.7(4)	C(10)–Co(4)–C(23)	105.2(5)
C(9)–Co(3)–Co(4)	97.2(3)	C(11)–Co(4)–Co(3)	102.9(3)
C(9)–Co(3)–C(22)	108.2(4)	C(11)–Co(4)–C(22)	102.7(4)
C(9)–Co(3)–C(23)	142.9(4)	C(11)–Co(4)–C(23)	141.1(4)
C(13)–C(14)–C(15)	146.0(8)	C(19)–C(22)–C(23)	143.2(7)
	C(15)–N–C(18)	115.6(6)	
	C(150–N–C(19)	125.3(6)	
	C(18)–N–C(19)	111.4(6)	

corresponding to a double bond. These distances, and the bending of the acetylenic group about the C–C bond, have been related to the extents of both the acetylene to metal σ-donation and the back donation from metal π-orbitals to the acetylene π*-orbitals, the bending increasing with the degree of π-back donation [9–11]. The C–C≡C angles, 143.2(7) and 146.0(8)°, agree with the values, 144.1(2) and 144.8(2)°, found for the t-butyl derivative [9], and the C≡C–H angles 139(5), 139(5)° with the value 138° reported for $(C_2H_2)Co_2(CO)_4[P(CH_3)_3]_2$ [11].

The other structural parameters show no abnormal features, except that the bonds at the nitrogen atom show a significant flattening with respect to the tetrahedral distribution: nitrogen is out of the C(15) C(18) C(19) plane by 0.236(6) Å. This geometry is probably influenced also by the mutual repulsion between the methyl groups, the shortest contacts between their hydrogen atoms being: H(3)...H(8) 2.01(12) Å, H(4)...H(8) 2.01(12) Å and H(10)...H(15) 2.07(12) Å.

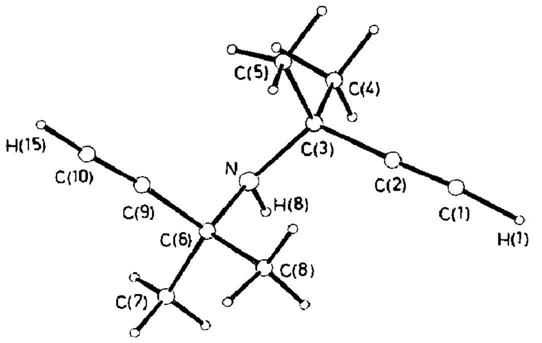


Fig. 2. Perspective view of the HTMDPA molecule.

The packing reflects Van der Waals contacts; one of these, involving an acetylenic group, could be regarded as a weak hydrogen bond [12]:

$$\mathrm{C(13)\text{–}H(1)},\ 0.94(9);\ \mathrm{C(13)\ldots O(2^{i})},\ 3.33(1);\ \mathrm{H(1)\ldots O(2^{i})},\ 2.64(9)\ \text{Å};$$

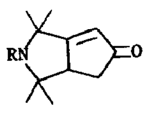
$$\mathrm{C(13)\text{–}H(1)\ldots O(2^{i})},\ 131(7)^{\circ}\ \left(i = x,\ \tfrac{1}{2} - y,\ z - \tfrac{1}{2}\right).$$

Amine I (R = H) HTMDPA. Figure 2 shows a perspective view of the molecule of I (R = H) in which the two alkyne groups are disposed on opposite sides of the plane through C(6), N, and C(3). The angle formed by the lines through the triple bonds is 48.3(2)°. This arrangement probably minimizes the steric repulsion between the methyl groups, whose crowding is clearly greater in the cobalt complex. This would be consistent with the opening of the C(3)–N–C(6) angle to 122.9(2)°, and with the narrowing of the angles involving the N–H(8) bond to 107(1) and 110(1)° owing to the different degree of crowding about the N atom in the two structures. The torsion angles around the C–N bonds show significant differences: C(14)–C(15)–N–C(19) 56.5(9)°, C(15)–N–C(19)–C(22) 144.8(7)° in the cobalt complex, C(2)–C(3)–N–C(6) 66.9(2)°, C(3)–N–C(6)–C(9) 80.4(2)° in HTMDPA.

Table 2

Selected bond distances (Å) and angles (°) for HTMDPA molecule

C(1)–C(2)	1.184(3)	N–C(6)	1.488(2)
C(2)–C(3)	1.492(3)	C(6)–C(7)	1.528(4)
C(3)–C(4)	1.540(3)	C(6)–C(8)	1.539(4)
C(3)–C(5)	1.531(3)	C(6)–C(9)	1.478(3)
C(3)–N	1.482(2)	C(9)–C(10)	1.186(5)
N–H(8)	0.84(2)		
H(1)–C(1)–C(2)	171(2)	C(6)–N–H(8)	107(1)
C(1)–C(2)–C(3)	178.4(2)	N–C(6)–C(7)	104.7(2)
C(2)–C(3)–N	113.9(1)	N–C(6)–C(8)	115.9(2)
C(2)–C(3)–C(5)	109.2(2)	N–C(6)–C(9)	109.6(1)
C(2)–C(3)–C(4)	107.7(2)	C(8)–C(6)–C(9)	109.0(2)
C(5)–C(3)–N	111.3(2)	C(7)–C(6)–C(9)	108.5(2)
C(4)–C(3)–N	105.1(2)	C(6)–C(9)–C(10)	174.6(3)
C(5)–C(3)–C(4)	109.5(2)	C(9)–C(10)–H(15)	174(2)
C(3)–N–C(6)	122.9(2)	C(3)–N–H(8)	110(1)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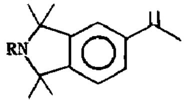
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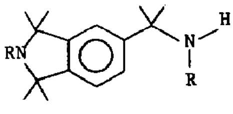
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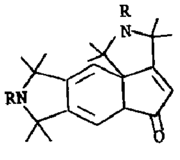
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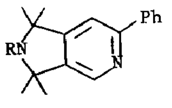

(VII)

Formule 3

The remaining bond distances and angles (Table 2) are normal, and comparable (apart from those for the alkyne groups, in which the triple bond has its normal value) with those found in the complex.

The nitrogen atom is out of the C(3), C(6), H(8) plane by 0.318(2) Å, so the flattening is less pronounced than in the cobalt complex, and the hydrogen atom is less precisely located.

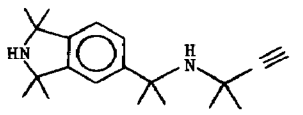
Contacts between hydrogen atoms and the weak interactions: C(1)–H(1), 1.18(4); C(1)...N^{ii}, 3.447(3); H(1)...N^{ii}, 2.32(4) Å; C(1)–H(1)...N^{ii} 158(2)° ($ii = x - 1$, y, z) are responsible for packing, which is loose enough to account for the high volatility of the compound.

Reactivity

Thermal decomposition of complex II (R = Me) in toluene at reflux gave metallic cobalt, and most of the organic product did not show up in GLC analysis. After partial CO evolution at lower temperature and with shorter time (100 °C, 2.5 h), products III [13], 1%, IV [1] and V [1] (in comparable amounts) together ca. 52%, VI, 29%, and a small amount of an unidentified isomer were obtained, where the yields are based on the amount of II used.

Under similar conditions, in benzonitrile as solvent, complex II gave products III [13], 53%, IV [1] and V [1], together ca. 14%, and VII [1], 33%.

To ascertain whether the reaction could be made catalytic, compound I (R = Me) and its analogue (I, R = H) were treated with $Co_2(CO)_8$ in a 36/1 molar ratio in benzonitrile. With R = H, products VII, 41%, VIII [1] and IX, 11%, VI, 3%, IV [1], 3%, X [1], 3% and XI, 14%, were obtained (95% conversion).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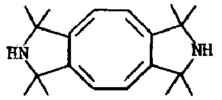
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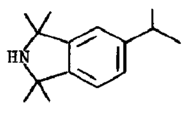
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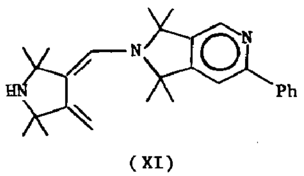
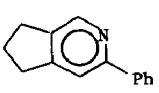

(XI)

Other diacetylenic substrates were treated similarly, but when there were no geminal substituents α to triple bonds poor results were obtained in terms of nitrile incorporation, reaction with the acetylenic triple bond being preferrred. Thus with



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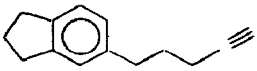

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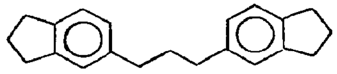
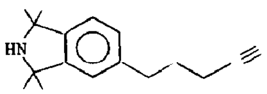


(XIV)

1,6-heptadiyne (HD) only 12% of the corresponding pyridine XII was formed. Compound XIII (18%) was the major product eluted by GLC, together with XIV (3%) (63% conversion).

Interestingly, when the amine I, R = H, and 1,6-heptadiyne were caused to react in 1/1 ratio in the presence of $Co_2(CO)_8$ (Co/HTMDPA/HD = 1/10/10) at 110 °C in toluene for 23 h, the following products were obtained: VI, 5%, VIII, 7%, XVI, 13%, XV, 20%, XVII, 5%, XVIII 6% (yields on substrate I), XIII, 20%, XIV, 7% (yields on heptadiyne). Of these compounds only VIII results from homodimerization of I, and XIII and XIV come from homodimerization of heptadiyne.



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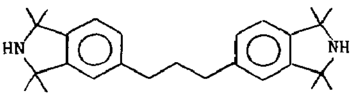

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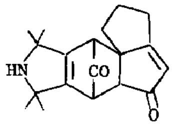

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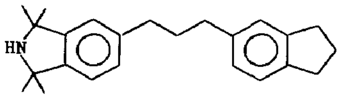
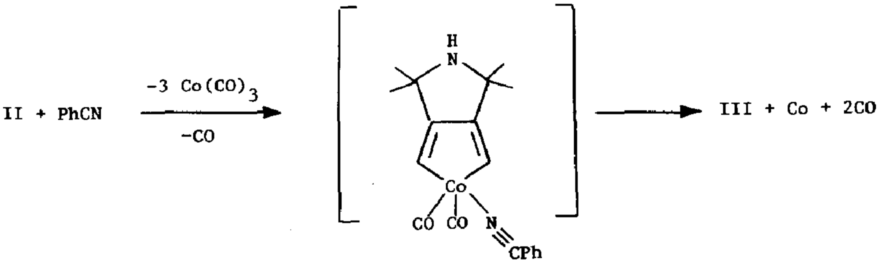


(XVIII)

Clear cut results were obtained when $CoCl_2$ and Mn powder were used as a source of cobalt(0): XV, 43%, XVI, 39%, VIII, 5%, and only 4% of XIII.

The results described allow us to draw some conclusions about the catalytic intermediate in the cobalt(0)-catalyzed ring formation reactions. Although the substrate is not bonded to cobalt in the expected cobaltacyclopentadiene form, the products formed require such an intermediate. Fragmentation of the complex and rearrangement of the substrate must occur, possibly via the pathway shown in eq. 3 (for formation of the main product from benzonitrile).



(3)

However, intermediate dimeric cobalt complex, containing a cobaltacyclopentadiene ring of the type reported in the literature for cyclooctyne [14*], cannot be excluded.

The cobaltacyclopentadiene complex can incorporate a carbonyl group, giving rise to III or VI (the latter arising by dimerization and decarbonylation of an intermediate cyclopentadienone [13]) or XVII, depending on the conditions. In catalytic reactions the carbonyl group is not readily available, and the main competition occurs between the acetylenic (compounds IV, VIII, IX, X) and nitrile (compound VII) triple bonds.

Incorporation of the acetylenic triple bond is the preferred pathway in the absence of geminal groups. The change in chemoselectivity from reactions at the acetylenic to that at the nitrile triple bond is clearly due to conformational as well as to steric hindrance effects. These effects were clearly observed in the cross experiment in which amine and 1,6-heptadiyne were brought into reaction in 1/1 ratio. The mixed products result from cobaltacycle formation from I (conformational effect of the geminal groups) and incorporation of the heptadiyne triple bond (steric hindrance on the acetylenic amine favors incorporation of the less hindered heptadiyne triple bond.)

Formation of compounds IV and V deserves comment. Activation of the carbon–nitrogen bond of the coordinated dialkyne has apparently occurred under the action of a cobalt center, possibly via nitrogen coordination. The two fragments thus formed both react with a molecule of I. This behaviour is a further illustration of the remarkable ability of cobalt(0) to activate a variety of bonds.

Experimental

All the organic materials and $Co_2(CO)_8$ were pure commercial products, except for tetramethyl-substituted dipropargylamines (HTMDPA) [15] I (R = H) and N-MeTMDPA [16] I (R = Me), which were prepared by published procedures.

The organic products were isolated by conventional methods and identified by their ^1H and ^{13}C NMR, mass, and IR spectra. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AC100 or CXP200 instrument with $CDCl_3$ as solvent and TMS as internal standard. The ^{59}Co spectra were recorded on a Bruker CXP200 spectrometer operating at 47.4 MHz. Benzene-d_6 was used as solvent; chemical shifts are given relative to external $K_3Co(CN)_6$(aq.). 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.

Intensity measurements

The crystals of both compounds were mounted in a random orientation on a Siemens AED automated diffractometer. The crystal of HTMDPA, which readily sublimes, was sealed in a glass capillary. Crystal data and details of data collections and refinements are quoted in Table 3. For HTMPDA the intensity of the standard

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* Reference number with asterisk indicates a note in the list of references.

Table 3

Experimental data for the crystallographic analyses

Formula		$C_{23}H_{17}Co_4O_{12}N$	$C_{10}H_{15}N$
M.W.		735.12	149.23
Space group		$P2_1/c$	$P2_1/c$
a, Å		13.427(3)	6.7837(8)
b, Å		15.126(8)	20.568(5)
c, Å		14.114(6)	7.6488(4)
β, deg		101.96(2)	110.31(1)
V, Å^3		2804(2)	1000.8(3)
Z		4	4
Dc, g cm^{-3}		1.741	0.99
Dm, g cm^{-3}		1.76	1.03
Reflection for lattice parameters	number	14	16
	θ range, deg	20.4–24.7	52.9–59.9
Radiation		Mo-K_α	Cu-K_α
$F(000)$		1464	328
Temperature, K		293	293
Crystal size, mm^3		$0.82 \times 0.46 \times 0.20$	$0.75 \times 0.59 \times 0.65$
Diffractometer		Siemens AED	Siemens AED
μ, cm^{-1}		23.81	4.07
Scan speed, deg min^{-1}		3.0	6.0
Scan width, deg		$1.2 + 0.35$ tg θ	1.2 ± 0.35 tg θ
θ range, deg		3–25	6–60
h range		± 15	± 8
k range		0, 18	0, 25
l range		0, 15	0, 7
Standard reflection		0 8 0	2 −6 0
Max. intensity variation		4.7%	43%
Scan mode		$\omega - 2\theta$	$\omega - 2\theta$
No. of measured reflections		5282	1771
Condition for observed reflections		$I > 2\sigma(I)$	$I > 2\sigma(I)$
No. of reflections used in the refinements		2589	1357
$(\Delta/\sigma)_{mean}$		0.87	0.41
Min. max. height in final $\Delta\rho$, eÅ^{-3}		−0.29, 0.40	−0.14, 0.10
No. of refined parameters		411	156
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_0\rvert$		0.0456	0.0636
$R_w = [\Sigma w(\Delta F)^2/\Sigma w F_0^2]^{1/2}$		0.0468	0.0749
$S = [\Sigma w(\Delta F)^2/(N-P)]^{1/2}$		0.352	1.051
$k, g\ (w = k/[\sigma^2(F_0) + gF_0^2])$		$0.35, 6.58 \times 10^{-3}$	$1.0, 9.18 \times 10^{-3}$

reflection at the end of the collection had fallen to 43% of its initial value, and the data were corrected accordingly. Corrections were made for Lorentz and polarization effects, but not for absorption.

Solution of the structures and refinements

Both structures were solved by direct and Fourier methods and refined by least-squares by use of the SHELX76 system of programs [17]. The hydrogen atoms were placed at the calculated positions, and refined isotropically in the last cycle of the refinement. The atomic scattering factors and the anomalous scattering coefficients are taken from ref. 18. Final atomic coordinates for the two structures are

Table 4

Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($Å^2 \times 10^4$) with e.s.d.'s in parentheses. $U_{eq} = \frac{1}{3}$ trace of the diagonalized U_{ij} tensor

Atom	x/a	y/b	z/c	U_{eq}
$[Co_2(CO)_6]_2$N-MeTMDPA				
Co(1)	5055.7(8)	3386.4(7)	4259.6(8)	435(4)
Co(2)	5918.9(8)	1978.3(7)	4110.2(8)	476(4)
Co(3)	258.0(8)	747.8(7)	2856.6(8)	446(4)
Co(4)	−100.7(8)	1682.1(7)	1403.5(9)	522(4)
O(1)	3366(6)	4616(5)	3833(6)	1029(38)
O(2)	5441(8)	3519(6)	6361(5)	1089(43)
O(3)	6522(7)	4554(6)	3620(7)	1246(46)
O(4)	6649(7)	1565(6)	6148(6)	1193(42)
O(5)	7734(6)	2621(6)	3467(9)	1386(54)
O(6)	5909(5)	221(5)	3248(6)	817(31)
O(7)	1329(6)	433(6)	4837(5)	903(33)
O(8)	−1810(6)	338(6)	3101(6)	1067(38)
O(9)	958(8)	−797(5)	1954(7)	1104(43)
O(10)	−2260(6)	1245(7)	877(8)	1459(50)
O(11)	870(7)	698(5)	51(6)	983(38)
O(12)	−323(8)	3450(6)	570(7)	1208(44)
N	2536(4)	1969(4)	3780(4)	368(20)
C(1)	4017(7)	4127(6)	3989(7)	598(36)
C(2)	5296(8)	3462(6)	5557(7)	603(35)
C(3)	5963(8)	4115(6)	3888(8)	724(41)
C(4)	6364(8)	1727(6)	5373(8)	681(40)
C(5)	7051(8)	2382(7)	3712(10)	850(49)
C(6)	5919(7)	896(6)	3592(7)	569(35)
C(7)	917(7)	585(6)	4073(8)	595(37)
C(8)	−1010(7)	470(6)	3002(7)	669(35)
C(9)	703(8)	−199(6)	2308(7)	650(40)
C(10)	−1429(9)	1405(7)	1077(9)	857(48)
C(11)	496(8)	1074(7)	552(7)	647(39)
C(12)	−205(8)	2753(7)	890(8)	746(42)
C(13)	4786(6)	2528(5)	3219(7)	415(28)
C(14)	4417(5)	2201(5)	3944(6)	357(25)
C(15)	3571(6)	1676(5)	4231(5)	370(25)
C(16)	3712(9)	1723(8)	5341(6)	544(37)
C(17)	3713(7)	681(5)	4018(8)	568(38)
C(18)	2093(7)	2640(6)	4318(6)	520(32)
C(19)	2127(5)	2040(5)	2728(5)	345(24)
C(20)	2649(7)	1420(6)	2123(7)	443(33)
C(21)	2199(6)	2979(5)	2338(6)	448(30)
C(22)	1017(6)	1790(4)	2554(6)	369(26)
C(23)	131(7)	2017(6)	2757(7)	535(32)
HTMDPA				
N	7590(2)	4148(1)	5282(2)	349(6)
C(1)	2037(3)	4104(1)	4080(3)	527(9)
C(2)	3692(3)	4044(1)	3900(3)	411(7)
C(3)	5752(3)	3977(1)	3619(2)	370(7)
C(4)	5782(4)	4470(1)	2113(3)	540(9)
C(5)	5949(4)	3287(1)	2946(3)	549(9)
C(6)	8239(3)	3760(1)	7033(2)	418(7)
C(7)	9713(6)	4208(2)	8505(4)	711(12)
C(8)	6451(4)	3538(1)	7699(3)	542(9)
C(9)	9443(4)	3184(1)	6827(3)	539(9)
C(10)	10465(5)	2717(2)	6818(5)	858(14)

given in Table 4. Calculations were carried out on the CRAY X/MP computer of the Consorzio per la Gestione del Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale (CINECA, Casalecchio, Bologna) with the financial support of the University of Parma and on the Gould 32/77 Computer of the Centro di Studio per la Strutturistica Diffrattometrica del CNR (Parma). In addition to the quoted programs, LQPARM, [19] PARST [20] programs were used.

Preparation of complex II $[Co_2(CO)_6]_2N$*-MeTMDPA*

Compound I (0.26 g, 1.56 mmol) was added to a stirred solution of $Co_2(CO)_8$ (1.07 g, 3.13 mmol) in degassed n-hexane (30 ml) under N_2, at room temperature. After 24 h stirring the deep red solution was concentrated under vacuum and the residual mixture was kept at −20 °C. Deep red crystals separated, and these were filtered off and washed with cold hexane to give complex II in a 58% yield (0.74 g, 1.09 mmol); MW 735.12. Elemental analysis C, 37.55; H, 2.31; N, 1.90. $Co_4C_{23}H_{17}NO_{12}$ calcd.: C, 37.58; H, 2.33; N, 1.91%. The crystals are fairly stable in air and soluble in n-hexane. IR spectrum (KBr) cm^{-1}: 2960, 2095 (CO), 2010 (CO), 1500, 1375, 1350, 1225, 1140, 960, 865, 775, 595, 520, 495, 450.

II ^1H NMR, δ: 1.70, brs, 12H, 4Me; 2.75, brs, 3H, N–Me; 6.18, brs, 2H, 2 C–H. Uncomplexed I (R = Me) gave: 1.5, s, 12H, 4Me; 2.28, s, 2H, 2 CH; 2.38, s, 3H, NMe.

The ^{59}Co NMR spectrum of the complex in benzene shows a broad resonance ($W_{1/2}$ 22.800 Hz) centered at −1986 ppm. Under the same condition $Co_2(CO)_8$ gives a resonance at −2120 ppm.

Thermal decomposition of complex II

Complex II (0.15 g, 0.2 mmol) in toluene (10 ml) was refluxed under N_2 for 16 h. A dark paramagnetic solid was recovered (0.05 g) that did not show carbonyl bands in the IR. No organic compounds were observable by GLC. Similar results were obtained upon decomposition of complex II in benzonitrile at 120 °C for 24 h.

Complex II (0.15 g, 0.2 mmol) in toluene (10 ml) was heated under N_2 at 100 °C. The flask was connected to a graduated cylinder and after evolution of CO corresponding to 0.2 mmol (2.5 h) the mixture was cooled to room temperature. A brown solid (0.09 g) was recovered, showing carbonyl absorptions at 2000 and 1800 cm^{-1}. The organic compounds III–VI were identified and quantitatively determined by GLC.

Complex II (0.14 g, 0.19 mmol) in benzonitrile (10 ml) was heated for 3.0 h under N_2 until 0.3 mmol of CO had been evolved. The mixture of products III–V and VIII was treated and analyzed as above.

Catalytic reaction of I (R = H) with PhCN in presence of $Co_2(CO)_8$

The reaction was carried out in a flask with a side arm for introduction of N_2 and a reflux condenser connected to a trap at −78 °C to allow trapping of any amine I which escaped. Amine I (R = H) (0.68 g, 4.53 mmol) was added to the solution of $Co_2(CO)_8$ (0.04 g, 0.12 mmol) in freshly distilled PhCN (10 mmol) under N_2. The mixture was heated at 120 °C for 24 h under a slight flow of N_2 to drive off the CO evolved from the catalyst. Lower yields were obtained when the CO was not removed. Yields of the products IV, VI–XI were determined by GLC by the use of internal standards.

Catalytic reaction of 1,7-heptadiyne (HD) with PhCN in the presence of $Co_2(CO)_8$

HD (0.99 g, 10.64 mmol) was added to the solution of $Co_2(CO)_8$ (0.06 g, 0.18 mmol) in PhCN (7.0 ml). After 24 h at 100 °C the reaction was stopped and products XII–XIV were quantitatively determined by GLC.

Cross reactions of I (R = H) with HD

(a) HTMDPA (0.79 g, 5.30 mmol) and HD (0.49 g, 5.33 mmol) were added to the solution of $Co_2(CO)_8$ (0.09 g, 0.27 mmol) in toluene (10 ml). After 23 h at 110 °C the reaction was stopped and products VI, VIII, XIII–XVIII were quantitatively determined by GLC.

(b) HTMDPA (0.50 g, 3.36 mmol) and HD (0.31 g, 3.33 mmol) were added to the solution of $CoCl_2$ (0.04 g, 0.33 mmol) in dimethylformamide (10 ml). Powdered manganese (0.09 g, 1.67 mmol) was added to the mixture. After 23 h at 110 °C the reaction was stopped and products XIII, XV, XVI and VIII were determined as described under (a).

Spectroscopic data of new compounds

VI (R = Me). Pale yellow-green solid m.p. 127–128 °C.

MS (m/e): 354 (M^+) 339 ($M-$ Me), 311, 283, 268(100), 253, 56. IR (KBr) cm^{-1} 2985, 2940, 1720, 1650, 1630, 1460, 1450, 1380, 1365, 1045, 965, 855, 810, 700.

^1H NMR δ: 0.80, s, 3H, Me; 1.04, s, 3H, Me; 1.07, s, 3H, Me; 1.17, s, 6H, 2Me; 1.23, s, 3H, Me; 1.26, s, 3H, Me; 1.37, s, 3H, Me; 2.26, s, 6H, 2NMe; 3.20, d, 1H, CH, J 6.0 Hz; 5.67, dd, 1H, =CH, J 6.0, J 1.0 Hz; 5.77, d, 1H, =CH, J 1.0 Hz; 6.03, s, 1H, =CH.

^{13}C NMR δ: 23.29, 25.18, 26.00, 26.10, 26.14, 26.28 (2C), 26.58, 27.00, 27.80, 10 Me; 51.20, CH; 59.32, 61.45, 61.62, 61.69, 65.28, sat. q. C. 112.01, 118.97, 124.16, 3C, 3=CH; 144.31, 146.21 196.91, 3 ins. q. C, 211.66, 1C, CO.

VII (R = Me). MS (m/e): 266, 251 (100), 236, 235, 220, 118, 105, 77, 56.

^1H NMR δ: 1.31, s, 6H, 2Me; 1.37, s, 6H, 2Me; 2.37, s, 3H, NMe; 7.0, s, 1H, pyr. H; 7.21–7.57, m, 5H, Ph, 8.40, s, 1H, pyr. H.

XI (R = H). MS (m/e): 401 (M^+), 386 (100) ($M-$ Me), 371, 370, 356, 341, 234, 186, 178, 171, 58.

IR (liq. film) cm^{-1}: 3310, 2970, 2925, 1605, 1460, 1380, 1170, 995, 900.

^1H NMR δ: 1.21, s, 6H, 2Me; 1.34, s, 6H, 2Me; 1.45, s, 6H, 2Me; 1.53, s, 6H, 2Me; 2.97, br s, 1H, NH; 4.80, s, 1H, =CH; 4.86, s, 1H, =CH, 6.46, s, 1H, N–CH=; 7.19, d, 1H, pyr. H, J 1.0 Hz; 7.34–7.62, m, 5H, Ph; 8.45, d, 1H, pyr. H, J 1.0 Hz.

^{13}C NMR δ: 29.72, 30.55, 31.17, 31.70, 8C, 8Me; 61.43, 61.72, 62.15, 62.97, 4 sat. q. C; 109.41, 1C, $=CH_2$; 116.94, 1C, =CH–N, 123.68, 1C, pyr. CH; 127.46, 128.29, 129.16, 129.99, 5C, aromatic CH; 135.47, 139.63, 142.64, 3 ins. C; 143.07, 1C, pyr. CH; 145.98, 151.89, 157.52, 3 ins. q. C.

XI, hydrogenated with Pd/C, gave a semihydrogenated product, containing the residual double bond in the 3–4 position of the dihydropyrrole ring.

MS (m/e): 403 (M^+), 388 (100) ($M-$ Me), 372, 358, 265, 250, 235, 220, 187, 172, 122, 108, 91, 58.

^1H NMR δ: 1.49, 1.50, 1.56, 1.64, 1.99, 2.05, 6s, 27H, 9Me; 3.59, brs, 2H, NCH_2; 7.20, s, 1H, pyr. H, 7.26–7.32 m, 5H, Ph; 8.54, s, 1H, pyr. H; 9.60, brs, 1H, NH.

XII. MS (m/e): 195 (M^+), 194 (100), 167, 165, 152, 139, 116, 91, 63, IR (liq. film) cm^{-1}: 3060, 2970, 2860, 1605, 1550, 1475, 1450, 1380, 1305, 1025, 880, 780, 740, 705, 590, 455, 410.

^{1}H NMR δ: 1.91–2.20, m, 2H, CH$_2$; 2.88, (pseudo t), 4H, 2 benzylic CH$_2$; *J* 7.1–7.2 Hz; 7.35–7.54, m, 4H, 1 pyr. H and 3 aromatic H; 7.87–7.98, m, 2H, 2 aromatic H; 8.50, s, 1H, 1 pyr. H.

XIII. MS (m/e): 184 (M^+), 169, 156, 144, 131, 117, 91, 77. IR (liq. film) cm^{-1}: 3295, 3000, 2940, 2120, 1480, 1440, 820, 630.

^{1}H NMR δ: 1.82–2.29 m, 7H, 3CH$_2$ and 1 CH; 2.62, t, 2H, benzylic CH$_2$ (exocyclic), *J* 7.5 Hz; 2.88, t, 4H, 2 benzylic CH$_2$ (endocyclic), *J* 7.1 Hz.

XIV. MS (m/e) 276, 158, 145, 132 (100), 117, 91, 77.

^{1}H NMR δ: 1.62–2.19, m, 6H, 1CH$_2$, 2 cyclic CH$_2$; 2.62, t, 4H, 2 benzylic CH$_2$ (exocyclic), *J* 7.2 Hz; 2.86, pseudo t, 8H, 4 benzylic CH$_2$ (endocyclic); *J* 7.1–7.3 Hz; 6.70–7.15, m, 6H, aromatics.

XV (R = H). MS (m/e): 241, 226 (100), 211, 186, 158, 115, 91.

IR (liq. film) cm^{-1}: 3305, 2990, 2960, 2860, 2120, 1610, 1490, 1460, 1365, 995, 890, 820, 630.

^{1}H NMR δ: 1.45, s, 12H, 4Me; 1.77–2.00, m, 2H, CH$_2$; 2.14–2.33, m, 3H, CH and CH$_2$; 2.74, t, 2H, benzylic CH, *J* 7.1 Hz; 3.7, brs, 1H, NH; 6.93, s, 1 aromatic H; 7.05, s, 2H, aromatics.

XVI (R = H). Pale yellow solid m.p. 98 ° C.

MS (m/e): 390, 376 (100), 360, 346, 180, 173, 158, 58.

IR (KBr) cm^{-1}: 3320, 2960, 2860, 1610, 1480, 1415, 1385, 1165, 1125, 990, 880, 815, 530.

^{1}H NMR δ: 1.65, s, 24H, 8Me; 1.97–2.20, m, 2H, CH$_2$; 2.71, t, 4H, 2 benzylic CH$_2$, *J* 7.5 Hz; 5.79, brs, 2H, 2NH; 6.94–7.10, m, 6 aromatic H.

XVII (R = H). Tentatively assigned structure, on the basis of MS only.

MS (m/e): 269 (M^+), 254 (100) (M – Me), 239, 238, 210, 91, 58.

XVIII (R = H). MS (m/e): 333 (M^+), 319 (100), 303, 158, 115, 91.

^{1}H NMR δ: 1.54, s, 12H, 4Me; 1.82–2.19, m, 4H, 2CH$_2$; 2.55–2.78, m, 4H, benzylic CH$_2$; 2.87, t, 4H, 2 benzylic CH$_2$ (endocyclic), *J* 7.3 Hz; 3.81, br s, 1H, NH; 6.81–7.14, m, 6 aromatic H.

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