

# Formation of heterocyclic compounds from reactions of dicobalt octa(xylyl isocyanide) with chloroacetone or methyl monochloroacetate<sup>1</sup>

Kazuyoshi Sugano, Tomoaki Tanase, Yasuhiro Yamamoto \*

Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba 274, Japan

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## Abstract

Reaction of xylyl isocyanide with chloroacetone in the presence of  $[\text{Co}_2(\text{XylNC})_8]$  ( $\text{Xyl} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$ ) gave the derivatives of azacyclopent-3-ene  $(\text{CH}_3\text{COCH}_2\text{XylNC})_4$  **1** and cobaltazacyclobutane  $\text{CoCl}(\text{CH}_3\text{COCH}_2\text{XylNC})_5$  **2**. Similar reaction with methyl monochloroacetate gave the analog of **1**  $(\text{CH}_3\text{COOMeXylNC})_4$  **4** and the 2,6-diaza-bicyclo[3.3.0]octa-1,7-diene derivative  $(\text{CHCOOMeXylNC})_5 \cdot \text{C}_6\text{H}_6$  **5**  $\cdot \text{C}_6\text{H}_6$ . Compounds **1** and **5**  $\cdot \text{C}_6\text{H}_6$  were confirmed by their X-ray analyses (**1** monoclinic, space group *Cc* (No. 9),  $a = 10.241(3)$ ,  $b = 19.474(6)$ ,  $c = 16.955(8)$  Å,  $\beta = 103.42(3)^\circ$ ,  $V = 3289(2)$  Å<sup>3</sup>,  $Z = 4$ , and  $R = 0.043$ ; **5**  $\cdot \text{C}_6\text{H}_6$  orthorhombic, space group *Pbcn* (No. 60),  $a = 21.642(5)$ ,  $b = 14.028(3)$ ,  $c = 30.449(8)$  Å,  $V = 9244(7)$  Å<sup>3</sup>,  $Z = 8$ , and  $R = 0.087$ ). A possible reaction route is discussed.

**Keywords:** Cobalt; Isocyanide; Metallacycle; Insertion

## 1. Introduction

Dicobalt octacarbonyl has played an important role in organometallic chemistry and metal-assisted organic synthesis [1]. Dicobalt octa(isocyanide) [2], which is isoelectronic with dicobalt octacarbonyl, also provides versatile reactivities. In fact,  $\text{Co}_2(\text{RNC})_8$  reacts with azobenzene in the presence of isocyanide to give heterocyclic compounds such as indazoline and diiminoindazole [3], and with diphenylacetylene to give 1,2-diphenyl-3,4,5-tri(N-2,6-xylylimino)cyclopent-1-ene [2c]. Treatment of  $\text{Co}_2(\text{RNC})_8$  with polyhalogen compounds forms organic compounds such as indolenine [4] or acetoamide derivatives [5]. Reaction with benzyl bromide leads to a successive insertion of isocyanide into a cobalt–carbon bond to give 1,6-diphenyl-2,3,4,5-tetra(N-2,6-xylylimino)hexane [4]. We have reported that the oligomerization and co-oligomerization of ac-

tive methylene compounds and aromatic isocyanides are catalyzed by zero valent cobalt isocyanide complex [6]. Recently, we also reported that the reaction of  $\text{Co}_2(\text{XylNC})_8$  with 2-bromoacetophenone leads to the multiple insertion of isocyanide molecules into a cobalt–carbon bond to give octahedral complexes and tetrahydrofuran derivatives [7,8].

In this paper we wish to describe the metal-assisted formation of heterocyclic compounds derived from  $\text{Co}_2(\text{RNC})_8$  and chloroacetone or methyl monochloroacetate.

## 2. Experimental

All solvents were distilled under calcium hydride. Isocyanide [9] and dicobalt octa(xylyl isocyanide) [2d] were prepared according to literature methods. The infrared and electronic absorption spectra were measured on FT/IR-5300 and U-best 30 spectrometers respectively. NMR spectroscopy was carried out on a Bruker AC250. <sup>1</sup>H chemical shifts were measured against Me<sub>4</sub>Si using solvent resonances as standard locks. Mass spectra were measured on a HITACHI M-80 model GC-MS spectrometer.

\* Corresponding author.

<sup>1</sup> Studies on Interaction of Isocyanide with Transition Metal Complexes. Part 45. For Part 44, see Y. Yamamoto and F. Arima, *J. Chem. Soc., Dalton Trans.*, (1996) 1815.

### 2.1. Reaction of $\text{Co}_2(\text{XylNC})_8$ and xylyl isocyanide with chloroacetone

A mixture of xylyl isocyanide (0.35 g, 2.68 mmol),  $\text{Co}_2(\text{XylNC})_8$  (0.36 g, 0.31 mmol) and chloroacetone (0.073 g, 0.79 mmol) was refluxed in benzene (20 ml) for 3 h. The solvent was removed in vacuo and the residue chromatographed on deactivated alumina (containing 10%  $\text{H}_2\text{O}$ ), using benzene and methanol as eluants. An elution with benzene gave a violet solution. The solvent was removed under reduced pressure and crystallization of the residue from benzene/hexane gave  $(\text{CH}_3\text{COCH}_2)(\text{XylNC})_4$  **1** (0.056 g, 16%) as violet crystals. An elution with methanol gave the violet compound  $\text{CoCl}(\text{CH}_3\text{COCH})(\text{XylNC})_5$  **2** (0.125 g, 25%), followed by crystallization from acetone/ether/hexane. **1** (16%) mass ( $m/z$ ): 582 (582). IR (Nujol): 3415 (NH), 1648, 1618, 1579 (C=C, C=N)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.74, 2.06, 2.17, 2.32 (s, o-Me, 6H), 2.11 (s, MeCO, 3H), 4.31 (s, NH, 1H), 5.19 (s, C=CH, 1H), 9.87 (s, NH, 1H) ppm. UV-vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  518 (log  $\epsilon$  3.56), 339 (4.41), 276 (4.20) nm. Anal. Found: C, 80.15; H, 7.26; N, 9.47.  $\text{C}_{39}\text{H}_{42}\text{N}_4\text{O}$  Calc.: C, 80.52; H, 7.10; N, 9.63%. **2** (12%) IR (Nujol): 2138, 2108 ( $\text{N}\equiv\text{C}$ ), 1629, 1580 (C=O, C=N)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.74 (s, o-Me, 12H), 1.79 (s, o-Me, 6H), 1.93 (s, MeCO, 3H), 2.22, 2.26 (s, o-Me, 6H), 5.14 (s, C=CH, 1H), ca. 7.0 (m, Ph) ppm. UV-vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  868 (2.42), 551 (3.86), 370sh (2.42) nm. Anal. Found: C, 66.29; H, 5.85; N, 7.87.  $\text{C}_{48}\text{H}_{40}\text{N}_5\text{OClCo}$  Calc.: C, 66.03; H, 5.76; N, 7.86%.

### 2.2. Reaction of $\text{Co}_2(\text{XylNC})_8$ and xylyl isocyanide with methyl monochloroacetate

A mixture of xylyl isocyanide (0.357 g, 2.72 mmol),  $\text{Co}_2(\text{XylNC})_8$  (0.286 g, 0.245 mmol) and  $\text{ClCH}_2\text{COOMe}$  (0.079 g, 0.73 mmol) was refluxed in benzene (20 ml). After 3 h, the mixture was chromatographed on silica gel, using benzene/hexane (1:1) as eluant. Two red bands were observed; the first band gave  $(\text{CH}_3\text{COOMe})(\text{XylNC})_4$  **4** (0.527 g, 18%) as red crystals, and the second band gave the red compound  $(\text{CHCOOMe})(\text{XylNC})_5 \cdot \text{C}_6\text{H}_6$  **5** ( $\text{C}_6\text{H}_6$  (3%), 4 mass ( $m/z$ ): 598 (598). IR (Nujol): 3400 (NH), 1678, 1656, 1602, 1585 (C=O, C=N, C=C)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.75, 2.05, 2.18, 2.32 (s, Me, 3H), 3.60 (s, MeO, 3H), 4.31 (s, NH, 1H), 4.81 (s, C=CH, 1H), ca. 7.0 (m, Ph), 9.2 (s, NH, 1H) ppm. UV-vis ( $\text{C}_6\text{H}_6$ ):  $\lambda_{\text{max}}$  500 (3.57), 337 (4.39), 284 (4.21) nm. Anal. Found: C, 77.03; H, 7.29; N, 8.98.  $\text{C}_{39}\text{H}_{42}\text{N}_4\text{O}_2$  Calc.: C, 77.23; H, 7.07; N, 8.98%. **5** ( $\text{C}_6\text{H}_6$  mass ( $m/z$ ): 727 (727). IR (Nujol): 3346 (NH), 1664, 1626, 1585, 1557 (C=O, C=N, C=C)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.62, 1.89, 2.01, 2.05, 2.24 (s, Me, 3H), 3.44 (s, MeO, 3H), ca. 6.8 (m, Ph), 7.36 (s, NH, 1H) ppm. UV-vis ( $\text{C}_6\text{H}_6$ ):  $\lambda_{\text{max}}$  497 (2.59), 390 (2.76), 339 (3.02) nm. Anal. Found: C, 79.19; H, 6.91; N, 9.59.  $\text{C}_{48}\text{H}_{49}\text{N}_5\text{O}_2$  Calc.: C, 79.20; H, 6.79; N, 9.62%.

### 2.3. Data collection

Complexes **1** and **5** were recrystallized from benzene/hexane. Complex **5** was analyzed as the molecule

Table 1  
Crystal data for **1** and **5**  $\cdot$   $\text{C}_6\text{H}_6$

Compound	<b>1</b>	<b>5</b> $\cdot$ $\text{C}_6\text{H}_6$
Formula	$\text{C}_{39}\text{H}_{42}\text{N}_4\text{O}$	$\text{C}_{54}\text{H}_{53}\text{N}_5\text{O}_2$
Molecular weight	582.79	806.06
Color	violet	red
Crystal dimensions ( $\text{mm}^3$ )	0.50 $\times$ 0.40 $\times$ 0.20	0.65 $\times$ 0.65 $\times$ 0.40
Crystal system	monoclinic	orthorhombic
Space group	$\text{C}c$ (No. 9)	$\text{Pbcn}$ (No. 60)
Lattice parameters		
$a$ ( $\text{\AA}$ )	10.241(3)	21.642(5)
$b$ ( $\text{\AA}$ )	19.474(6)	14.028(3)
$c$ ( $\text{\AA}$ )	16.955(8)	30.449(8)
$\alpha$ ( $^\circ$ )	90.0	90.0
$\beta$ ( $^\circ$ )	103.42(3)	90.0
$\gamma$ ( $^\circ$ )	90.0	90.0
$V$ ( $\text{\AA}^3$ )	3289(2)	9244(7)
$Z$	4	8
$D_{\text{calc}}$ ( $\text{g cm}^{-3}$ )	1.177	1.158
$\mu$ ( $\text{cm}^{-1}$ )	0.66	0.66
No. of unique data	2932	7582
No. of variables	563	550
$F(000)$	1248	3440
$R$ ; $R_w$ <sup>a</sup>	0.043; 0.030	0.087; 0.079

<sup>a</sup>  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$  and  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$  ( $w = 1/\sigma^2(F_o)$ ).

$5 \cdot C_6H_6$  containing one benzene. Cell constants were determined on a Rigaku AFC5S four-circle automated diffractometer from the setting angles of 20–25 reflections. The crystal parameters along with data collection details are summarized in Table 1. Data collection was carried out on a Rigaku AFC5S diffractometer. Intensities were measured by the  $2\theta$ – $\omega$  scan method using Mo K $\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ). A scan rate of  $8^\circ \text{ min}^{-1}$  was used. Throughout the data collection the intensities of the three standard reflections were measured every 150 reflections as a check on the stability of the crystals, and no decay was observed. A total of 2932 independent intensities ( $2\theta < 50^\circ$ ) was measured for **1**, and 7582 ( $2\theta < 50^\circ$ ) for  $5 \cdot C_6H_6$ . Of these, there are respectively 1751 unique reflections with  $I > 3.0\sigma(I)$  and 2583 with  $I > 2.0\sigma(I)$  which were used in the solutions and refinements of the structures. Intensities were corrected for Lorentz and polarization effects and for absorption. Atomic scattering factors [10] and anomalous dispersion effects  $\Delta f'$  and  $\Delta f''$  [11] were taken from the usual tabulation. All calculations were performed on a Digital VAX Station 3100 M38 computer using the TEXSAN-TEXRAY program system [12]. The positional parameters of **1** and  $5 \cdot C_6H_6$  are listed in Tables 2 and 3.

#### 2.4. Determination of the structures

The structures were solved by direct methods with MITHRIL. All non-hydrogen atoms were located in the initial  $E$  map, and subsequent Fourier syntheses gave the positions of other non-hydrogen atoms. For **1**, hydrogen atoms were located by difference Fourier syntheses. For  $5 \cdot C_6H_6$ , hydrogen atoms were calculated at the ideal positions with C–H distance 0.95 Å and were not refined. The non-hydrogen atoms were refined with anisotropic thermal parameters using full-matrix least-squares methods. The final refinement converged to  $R = 0.043$  and  $R_w = 0.030$  for **1**, 0.087 and 0.079 for  $5 \cdot C_6H_6$ . Selected bond lengths and angles are listed in Tables 4 and 5.

### 3. Results and discussion

#### 3.1. Reaction of $Co_2(XylNC)_8$ ( $Xyl = 2,6-Me_2C_6H_3$ ) with chloroacetone

A mixture of chloroacetone,  $Co_2(XylNC)_8$  and xylyl isocyanide was refluxed in benzene, and two violet compounds were obtained, formulated as  $(CH_3CO-CH_2)(XylNC)_4H$  **1** and  $CoCl(CH_3COCH)(XylNC)_5$  **2** from elemental analyses and mass spectra. The mass spectrum of **1** showed a fragment ion  $[M-COCH_3]^+$ , suggesting the presence of an acetyl group. The infrared spectrum showed the presence of the N–H bond (3415

Table 2  
Positional parameters for **1**

Atom	x	y	z	$B_{eq}^a$
O(1)	0.2285	0.1500	0.3520	5.6
N(1)	0.2217(6)	−0.0568(2)	0.4572(4)	3.1(2)
N(2)	0.4126(7)	0.0993(3)	0.4781(4)	4.0(2)
N(3)	0.5690(7)	−0.0307(3)	0.5566(4)	3.9(2)
N(4)	0.3524(6)	−0.1446(2)	0.5269(4)	3.6(2)
C(1)	0.2357(7)	0.0110(3)	0.4350(5)	3.3(3)
C(2)	0.3716(6)	0.0319(3)	0.4779(4)	3.0(3)
C(3)	0.4373(7)	−0.0244(3)	0.5139(4)	3.0(3)
C(4)	0.3418(7)	−0.0821(3)	0.5039(5)	3.1(3)
C(5)	0.1326(7)	0.0448(3)	0.3845(4)	3.7(3)
C(6)	0.1318(6)	0.1111(3)	0.3457(5)	4.1(3)
C(7)	0.0012(8)	0.1322(4)	0.2890(6)	5.7(4)
C(11)	0.1028(7)	−0.0976(3)	0.4301(5)	3.3(3)
C(12)	0.0177(7)	−0.1076(3)	0.4820(5)	4.0(3)
C(13)	−0.1028(8)	−0.1440(4)	0.4504(7)	5.5(4)
C(14)	−0.1321(9)	−0.1691(4)	0.3743(6)	5.7(4)
C(15)	−0.0459(8)	−0.1609(3)	0.3245(5)	5.0(3)
C(16)	0.0753(7)	−0.1246(3)	0.3521(5)	4.0(3)
C(17)	0.172(1)	−0.1158(5)	0.2985(6)	5.8(4)
C(18)	0.051(1)	−0.0826(5)	0.5679(6)	5.9(4)
C(21)	0.4881(7)	0.1354(3)	0.5449(5)	3.3(3)
C(22)	0.5783(7)	0.1851(3)	0.5281(5)	3.8(3)
C(23)	0.6513(9)	0.2246(4)	0.5901(6)	5.2(4)
C(24)	0.6360(9)	0.2165(4)	0.6679(7)	6.0(4)
C(25)	0.546(1)	0.1691(4)	0.6858(6)	5.5(4)
C(26)	0.4687(7)	0.1284(3)	0.6234(5)	4.3(3)
C(27)	0.361(1)	0.0831(4)	0.6406(7)	6.0(4)
C(28)	0.595(1)	0.1964(4)	0.4434(6)	6.1(4)
C(31)	0.6789(7)	0.0079(3)	0.5444(5)	3.5(3)
C(32)	0.7008(8)	0.0184(3)	0.6680(6)	4.9(4)
C(33)	0.811(1)	0.0579(5)	0.6608(8)	7.2(5)
C(34)	0.896(1)	0.0846(5)	0.528(1)	8.4(6)
C(35)	0.8799(9)	0.0719(4)	0.6037(8)	6.5(4)
C(36)	0.7711(7)	0.0322(3)	0.6142(5)	4.2(3)
C(37)	0.750(1)	0.0169(5)	0.6965(6)	6.2(5)
C(38)	0.611(1)	−0.0146(5)	0.3926(6)	6.5(4)
C(41)	0.4758(7)	−0.1724(3)	0.5725(5)	3.9(3)
C(42)	0.5095(8)	−0.1662(3)	0.6574(5)	4.4(3)
C(43)	0.6282(9)	−0.1971(4)	0.7004(6)	6.2(4)
C(44)	0.711(1)	−0.2330(4)	0.6583(8)	7.5(5)
C(45)	0.6729(9)	−0.2413(4)	0.5753(4)	6.0(4)
C(46)	0.5548(8)	−0.2113(3)	0.5329(6)	4.8(4)
C(47)	0.514(1)	−0.2199(5)	0.4424(7)	7.1(5)
C(48)	0.424(1)	−0.1291(5)	0.7025(6)	6.1(4)

$$^a B_{eq} = (8\pi^2/3)[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos \gamma + 2U_{13}aa^*cc^* \cos \beta + 2U_{23}bb^*cc^* \cos \alpha].$$

$\text{cm}^{-1}$ ) as well as the C=N and C=O bonds in the range 1648–1579  $\text{cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum showed five resonances for the methyl groups at  $\delta$  1.74, 2.06, 2.11, 2.17 and 2.32 ppm in a 6:6:3:6:6 intensity ratio, assigned to four isocyanides and an acetyl group. Olefinic and two N–H protons also appeared at  $\delta$  5.19, 4.31 and 9.87 respectively. Finally it was determined by X-ray analysis that the molecule consists of a heterocyclic ring, 1-(N-2',6'-xylyl)-2-(2',6'-xylylimino)-3,4-di-(2',6'-xylylamino)-5-exo(acetylmethylene)-1-azacyclopent-3-ene, derived from the successive insertion of isocyanide molecules (Fig. 1).

Table 3  
Positional parameters for 5-C<sub>6</sub>H<sub>6</sub>

Atom	x	y	z	B <sub>eq</sub> <sup>a</sup>
O(1)	0.3863(4)	-0.1081(5)	0.0924(3)	6.8(5)
O(2)	0.4779(4)	-0.1790(6)	0.0918(4)	8.1(6)
N(1)	0.5804(4)	-0.0788(6)	0.1153(3)	4.9(5)
N(2)	0.5958(3)	0.1589(6)	0.1202(3)	3.4(4)
N(3)	0.4448(4)	0.0718(6)	0.1073(3)	3.9(5)
N(4)	0.4674(4)	0.3150(6)	0.1259(2)	3.2(4)
N(5)	0.6043(3)	0.3233(6)	0.1109(3)	3.3(4)
C(1)	0.4747(5)	-0.0160(7)	0.1060(4)	4.4(6)
C(2)	0.4469(6)	-0.108(1)	0.0963(4)	5.7(8)
C(3)	0.3612(7)	-0.204(1)	0.0831(6)	10(1)
C(4)	0.5385(5)	-0.0042(7)	0.1134(4)	4.1(6)
C(5)	0.5461(4)	0.0944(7)	0.1167(3)	3.2(5)
C(6)	0.4906(6)	0.1388(7)	0.1143(3)	3.3(5)
C(7)	0.4996(4)	0.2406(6)	0.1180(3)	3.1(5)
C(8)	0.5709(4)	0.2511(7)	0.1159(3)	3.0(5)
C(11)	0.6311(5)	-0.0764(7)	0.1467(4)	4.3(3)
C(12)	0.6237(6)	-0.0527(8)	0.1912(4)	4.5(6)
C(13)	0.6753(7)	-0.0540(8)	0.2183(4)	5.4(7)
C(14)	0.7327(6)	-0.0803(9)	0.2024(4)	5.3(7)
C(15)	0.7383(5)	-0.1083(8)	0.1593(4)	4.(7)
C(16)	0.6886(6)	-0.1080(8)	0.1311(4)	4.4(6)
C(17)	0.6962(6)	-0.142(1)	0.083(8)	6.6(8)
C(18)	0.5615(6)	-0.029(1)	0.2104(4)	7.1(8)
C(21)	0.6606(4)	0.1387(7)	0.1090(4)	4.0(6)
C(22)	0.7034(5)	0.1517(7)	0.1425(4)	4.0(6)
C(23)	0.7646(5)	0.1316(9)	0.1316(5)	5.8(7)
C(24)	0.7800(6)	0.103(1)	0.0901(5)	6.6(8)
C(25)	0.7364(7)	0.092(1)	0.0577(4)	6.7(8)
C(26)	0.6737(5)	0.1130(8)	0.0664(4)	5.0(7)
C(27)	0.6272(6)	0.100(1)	0.0309(4)	6.0(7)
C(28)	0.6857(5)	0.1838(8)	0.1875(4)	5.1(7)
C(31)	0.3843(5)	0.0952(7)	0.0907(4)	3.8(6)
C(32)	0.3329(5)	0.0817(7)	0.1181(4)	4.6(6)
C(33)	0.2750(5)	0.104(1)	0.0995(5)	6.0(8)
C(34)	0.2687(6)	0.138(1)	0.0584(5)	6.8(9)
C(35)	0.3193(7)	0.153(1)	0.0329(4)	6.7(8)
C(36)	0.3785(5)	0.1299(8)	0.0489(4)	4.7(7)
C(37)	0.4335(6)	0.142(1)	0.0190(4)	6.5(7)
C(38)	0.3386(5)	0.0406(9)	0.1634(4)	6.2(7)
C(41)	0.4041(4)	0.3104(7)	0.1378(4)	3.3(5)
C(42)	0.3867(5)	0.2770(7)	0.1791(4)	4.0(6)
C(43)	0.3247(6)	0.2850(9)	0.1909(4)	5.4(7)
C(44)	0.2825(5)	0.3230(8)	0.1625(5)	5.5(7)
C(45)	0.3001(5)	0.3598(8)	0.1223(5)	5.0(7)
C(46)	0.3616(5)	0.3554(7)	0.1087(4)	4.3(6)
C(47)	0.3833(6)	0.398(1)	0.0666(4)	6.5(8)
C(48)	0.4333(6)	0.240(1)	0.2108(4)	6.3(7)
C(51)	0.5817(4)	0.4158(7)	0.1034(4)	3.7(6)
C(52)	0.5735(5)	0.4799(8)	0.1361(4)	4.6(6)
C(53)	0.5557(5)	0.574(1)	0.1257(6)	6.2(8)
C(54)	0.5469(6)	0.601(1)	0.836(7)	8(1)
C(55)	0.5557(6)	0.536(1)	0.0507(5)	5.8(8)
C(56)	0.5741(5)	0.4438(8)	0.0591(5)	4.7(7)
C(57)	0.5845(6)	0.376(1)	0.0222(4)	7.0(8)
C(58)	0.5815(6)	0.450(1)	0.1837(5)	6.8(8)
C(111)	0.3287(7)	0.383(1)	0.7307(6)	9(1)
C(112)	0.3590(8)	0.438(1)	0.7016(6)	8(1)
C(113)	0.409(1)	0.411(2)	0.6844(7)	14(2)
C(114)	0.435(1)	0.328(2)	0.699(1)	29(3)
C(115)	0.401(1)	0.269(1)	0.725(1)	17(2)
C(116)	0.3514(8)	0.298(1)	0.7424(6)	8(1)

$$^a B_{eq} = (8\pi^2/3)[U_{11}(aa')^2 + U_{22}(bb')^2 + U_{33}(cc')^2 + 2U_{12}aa'bb' \cos \gamma + 2U_{13}aa'cc' \cos \beta + 2U_{23}bb'cc' \cos \alpha].$$

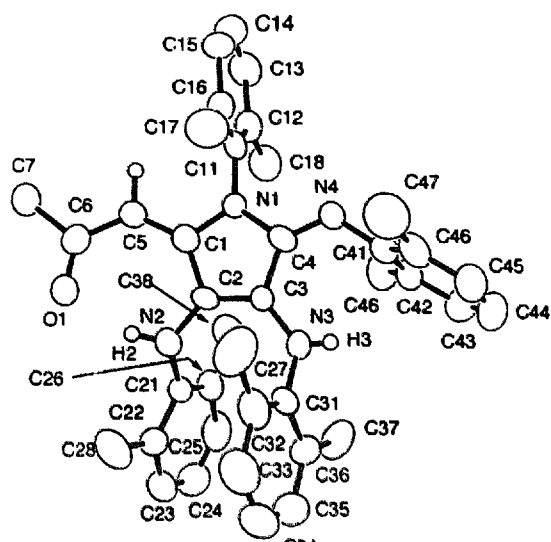


Fig. 1. Molecular structure of 1.

The N(2)–C(2) and N(3)–C(3) bond distances (1.377(7) and 1.380(7) Å) are longer than the N(4)–C(4) one (1.276(6) Å). The C(2)–C(3) bond length (1.356(7) Å) in the ring is shorter by 0.11 Å than the other C(1)–C(2) and C(3)–C(4) bond lengths. These results suggest that the double bonds are located at the N(4)–C(4) and C(2)–C(3) positions. The angles C(2)–N(2)–C(21) and C(3)–N(3)–C(31) (126.2(5) and 126.4(5)°) are larger than C(4)–N(4)–C(41) (121.9(5)°). Since two hydrogen atoms, H(2) and H(3), located by the difference Fourier syntheses are connected with each N(2) and N(3) atom respectively, two amino groups exist in the N(2) and N(3) positions. The C(1)–C(5) bond length of 1.364(8) Å is similar to that of the C(2)–C(3) bond, and is assigned as a double bond. Dihedral angles between the heterocyclic ring and each xylyl group are in the range 68–83°, minimizing the steric repulsive-interaction among the aromatic rings. The O(1)···H(2) hydrogen bonding was supported by the facts that six atoms O(1)C(6)C(5)C(1)C(2)N(2) are located in the same plane (torsion angles O(1)C(6)C(5)C(1) and N(2)C(2)C(1)C(5) 0 and 7° respectively) and that the O(1)···H(2) bond length is 1.85(8) Å.

Compound 2 showed the presence of terminal isocyanides (2138 and 2108 cm<sup>-1</sup>) and C=N and C=O double bonds (1629 and 1598 cm<sup>-1</sup>). The electronic spectrum showed three peaks at 868, 551 and 370(sh) nm, and is comparable with that of CoBr(PhCOCH)(Xyl)NC, 3 [8], suggesting the structure to have a cobaltazaacyclobutane ring similar to that of 3 (Fig. 2). The <sup>1</sup>H NMR spectrum was in good agreement with the proposed structure and showed five singlets at δ 1.74, 1.79, 1.93, 2.22, and 2.26 ppm in a 12:6:3:6:6 intensity ratio and a singlet due to an olefinic proton at δ 5.14 ppm (1H). The signal at δ 1.74 ppm is assigned

Table 4  
Selected bond lengths and angles for **1**

<i>Bond lengths (Å)</i>			
O(1)–C(6)	1.232(6)	N(1)–C(1)	1.389(6)
N(1)–C(4)	1.389(7)	N(1)–C(11)	1.437(7)
N(2)–C(2)	1.377(7)	N(2)–C(21)	1.403(7)
N(3)–C(3)	1.380(7)	N(3)–C(31)	1.407(7)
N(4)–C(4)	1.276(6)	N(4)–C(41)	1.426(7)
C(1)–C(2)	1.471(7)	C(1)–C(5)	1.364(8)
C(3)–C(4)	1.474(7)	C(5)–C(6)	1.449(8)
C(6)–C(7)	1.512(9)	N(2)–H(2)	0.88(7)
N(3)–H(3)	0.74(5)	C(5)–H(51)	1.04(6)
<i>Intramolecular length (Å)</i>			
O(1)⋯H(2)	1.85(8)		
<i>Bond angles (°)</i>			
C(1)–N(1)–C(4)	110.9(4)	C(1)–N(1)–C(11)	124.9(4)
C(4)–N(1)–C(11)	124.0(4)	C(2)–N(2)–C(21)	126.2(5)
C(3)–N(3)–C(31)	126.4(5)	C(4)–N(4)–C(41)	121.9(5)
N(1)–C(1)–C(2)	106.0(5)	N(1)–C(1)–C(5)	121.0(5)
C(2)–C(1)–C(5)	133.0(5)	N(2)–C(2)–C(1)	121.3(5)
N(2)–C(2)–C(3)	130.5(5)	C(1)–C(2)–C(3)	108.2(5)
N(3)–C(3)–C(2)	129.1(5)	N(3)–C(3)–C(4)	122.3(5)
C(2)–C(3)–C(4)	108.5(5)	N(1)–C(4)–N(4)	120.9(5)
N(1)–C(4)–C(3)	105.8(5)	N(4)–C(4)–C(3)	133.3(6)
C(1)–C(5)–C(6)	129.5(6)	O(1)–C(6)–C(5)	126.2(5)
C(5)–C(6)–C(7)	116.3(6)	C(2)–N(2)–H(2)	113(5)
C(21)–N(2)–H(2)	118(5)	C(3)–N(3)–H(3)	122(4)
C(31)–N(3)–H(3)	110(4)	C(1)–C(5)–H(51)	111(3)
C(6)–C(5)–H(51)	118(3)		

Table 5  
Selected bond lengths and angles for **5** · C<sub>6</sub>H<sub>6</sub>

<i>Bond lengths (Å)</i>			
O(1)–C(2)	1.32(1)	O(1)–C(3)	1.48(1)
O(2)–C(2)	1.21(1)	N(1)–C(4)	1.39(1)
N(1)–C(11)	1.46(1)	N(2)–C(5)	1.41(1)
N(2)–C(8)	1.41(1)	N(2)–C(21)	1.47(1)
N(3)–C(1)	1.39(1)	N(3)–C(6)	1.38(1)
N(3)–C(31)	1.44(1)	N(4)–C(7)	1.28(1)
N(4)–C(41)	1.42(1)	N(5)–C(8)	1.25(1)
N(5)–C(51)	1.40(1)	C(1)–C(2)	1.45(1)
C(1)–C(4)	1.41(1)	C(4)–C(5)	1.40(1)
C(5)–C(6)	1.36(1)	C(6)–C(7)	1.45(1)
C(7)–C(8)	1.55(1)		
<i>Bond angles (°)</i>			
C(1)–O(1)–C(3)	113(1)	C(4)–N(1)–C(11)	120.2(9)
C(5)–N(2)–C(8)	106.9(7)	C(5)–N(2)–C(21)	125.8(8)
C(8)–N(3)–C(21)	121.3(8)	C(1)–N(3)–C(6)	105.8(8)
C(1)–N(3)–C(31)	127.9(9)	C(6)–N(3)–C(31)	123.4(8)
C(7)–N(4)–C(41)	122.6(9)	C(8)–N(5)–C(51)	124.4(8)
N(3)–C(1)–C(2)	127(1)	N(3)–C(1)–C(4)	110.3(9)
C(2)–C(1)–C(4)	123(1)	O(1)–C(2)–O(2)	123(1)
O(1)–C(2)–C(1)	116(1)	O(2)–C(2)–C(1)	122(1)
N(1)–C(4)–C(1)	124(1)	N(1)–C(4)–C(5)	132(1)
C(1)–C(4)–C(5)	104.2(9)	N(2)–C(5)–C(4)	137.1(9)
N(3)–C(6)–C(5)	109.4(8)	N(3)–C(6)–C(7)	141.3(9)
C(5)–C(6)–C(7)	109.3(8)	N(4)–C(7)–C(6)	138(1)
N(4)–C(7)–C(8)	118.2(9)	C(6)–C(7)–C(8)	103.0(8)
N(2)–C(8)–N(5)	122.3(9)	N(2)–C(8)–C(7)	106.8(8)
N(5)–C(8)–C(7)	130.9(9)		



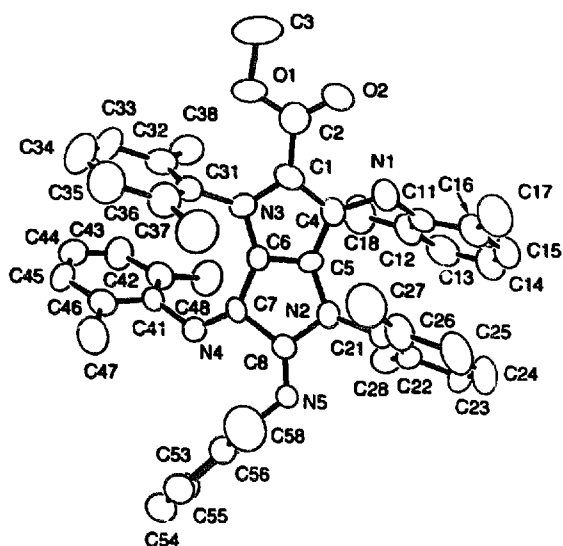


Fig. 3. Molecular structure of  $5 \cdot C_6H_6$ .

double bond and the latter in the range of a C–N single bond. The C(5)–C(6) bond length is shorter at 1.36(1) Å than the single C(7)–C(8) bond length (1.55(1) Å) and is in agreement with the C–C double bond. Other C(1)–C(4), C(4)–C(5) and C(6)–C(7) bond lengths are in the range 1.41 to 1.45 Å, shorter than the C(7)–C(8) bond length. From the demands of the electronic structure, the C(1)–C(4) bond is assumed to be a double bond. The infrared spectrum showed a band at 3346  $cm^{-1}$  due to the N–H stretching frequency. The  $^1H$  NMR spectrum showed six singlets in the methyl region at  $\delta$  1.62, 1.89, 2.01, 2.05, 2.24 and 3.44 ppm; the last one is assigned to the OMe protons. The singlet due to the NH group appeared at  $\delta$  7.36 ppm.

A variety of possible routes is considered with regard to the aforementioned reactions. On the basis of compounds obtained, a possible path is depicted in Scheme 1. An oxidative addition of a chloro-compound to  $Co_2(XylNC)_8$  initially occurred, followed by successive insertion of five or four isocyanide molecules to give a six-membered intermediate (A or B) with N-coordination. The five-membered ring intermediate C was formed by isomerization of keto–enol type and nucleophilic attack of the coordinated nitrogen atom to the  $\alpha$ -imino carbon. Finally complex 1 or 4 was generated by addition of hydrogen. In contrast, the intermediate species D was formed by a nucleophilic attack to a  $\gamma$ -imino nitrogen via imino–enamine isomerization [14,15]. Then, the reaction led to the formation of 5 through the transfer and elimination of hydrogen.

The carbene intermediate was formed via nucleophilic attack of the  $\alpha$ -imino nitrogen on the coordinated isocyanide, followed by elimination of hydrogen to give the four-membered metallacycle 2.

Reactions of dicobalt octaisocyanide with alkyl (con-

taining carbonyl or ester group) halides were mainly classified into three categories: (1) in the reaction with benzyl bromide, the coupling reaction of bisimino alkyl groups occurred after the double insertion of isocyanides [4]; (2) in the reaction with 2-bromoacetophenone, a nucleophilic attack of the  $\beta$ -imino nitrogen to a coordinated isocyanide carbon occurred to give cobaltacycles [8]; and (3) as shown in the present reactions, N-coordinated chelating intermediates were formed by the normal multiple-insertion, and heterocyclic compounds were isolated through nucleophilic attack of the coordinated nitrogen to the  $sp^2$  carbon atom ( $\alpha$ -carbon atom) of inserted isocyanides.

The electron withdrawing ability of the functional groups decreases in the order  $CH_2COPh > CH_2COCH_3 > CH_2COOCH_3 > CH_2Ph$ . Complexes containing the carbonyl or alkoxy carbonyl group appear to contribute more to the stability of the polyimino groups than those containing the benzyl group. This stability results in the coordination of the imino nitrogen to the cobalt atom [16], probably suggesting the contribution of a back-bonding interaction from the metal to the C=N double bond. A trend was observed of the substrate with high electron withdrawing group favoring category (2), the substrate with low electron withdrawing group leading to cleavage of a cobalt–carbon bond before occurrence of the cyclization reaction (category (1)), and the medium substrate preferring the category (3). The different reactivities may be related to the delicate electronic effect, but the details remain unknown.

A listing of additional bond distances, bond angles, thermal parameters, and tables of observed and calculated structure factors is available from the authors.

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