ELSEVIER

Journal of Organometallic Chemistry 486 (1995) 21–29

Journal of Organometallic Chemistry

Reactions of dicobalt octa(isocyanide) with 2-bromoacetophenone ☆

Yasuhiro Yamamoto *, Tomoaki Tanase, Kazuyoshi Sugano

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

Received 10 November 1993; in revised form 8 June 1994

Abstract

The reaction of $Co_2(XylNC)_8$ (Xyl = 2,6-$Me_2C_6H_3$) with 2-bromoacetophenone gave 2,3-bis(2,6-xylyl)imino-5-phenyl-2,3-dihydrofuran (**1a**) and the cobalta-azacyclopentane derivative $CoBr(PhCOCH)(XylNC)_6$ (**2a**). Structures of **1a** and **2a** were determined by X-ray analyses; **1a** is a furan derivative and **2a** has a distorted octahedral structure containing a five-membered metallacyclic moiety formed by an multiple insertion of isocyanide into a Co–C bond. Similar treatment at reflux in the presence of xylyl isocyanide gave two kinds of octahedral compounds, **3a** and **4a**, having similar formula composition $CoBr(PhCOCH)(XylNC)_5$; **3a** was found by X-ray analysis to have a cobaltacycle structure, containing a tridentate ligand consisting of sigma carbon, carbene and O-coordination sites, and **4a** was proposed to have a cobalta-azacyclobutane framework.

Keywords: Cobalt; Isocyanide; Insertion; Oxidative addition

1. Introduction

Metal carbonyls are well-known for a variety of metals. They are good catalyst precursors for several organic syntheses [1]. Dicobalt octacarbonyl has been used as a catalyst precursor in important reactions such as hydroformylation and carbonylation. Isocyanide, which is isoelectronic with carbon monoxide could form a wide range of zerovalent mono-, di-, and high nuclear complexes, e.g., Ni, Pd, Pt, Fe, Rh, Ru, Cr, Mo, W, etc. [2,3]. Although dicobalt octa(isocyanide) was prepared in 1984 by Stone's group and by us [4,5], there have been only a few investigations of its reactivity. Reactions of polyhalogen compounds with $Co_2(CO)_8$ gave trinuclear complexes such as $XCCo_3(CO)_9$ [6], whereas reactions with $Co_2(RNC)_8$ formed organic compounds such as indolenine or ketenimine derivatives [7,8]. We also reported briefly [7] that treatment of $Co_2(RNC)_8$ with benzyl bromide led to a multiple insertion of isocyanide into a cobalt–carbon bond to give 1,6-diphenyl-2,3,4,5-tetra(N-2,6-xylylimino)hexane. In an extensive investigation of reactions with halogen compounds we explored the reaction of $Co_2(XylNC)_8$ with 2-bromoacetophenone containing active methylene protons. Here we wish to describe formation of cobaltacyclic compounds through multiple insertion of isocyanide into a cobalt–carbon bond. A part of this reaction has been described in a preliminary report [9].

2. Experimental section

Dicobalt octa(2,6-xylyl isocyanide) [5] and xylyl isocyanide [10] were prepared according to literature methods. Hexane and benzene were purified by distillation over calcium hydride and THF was distilled over lithium aluminium hydride. Other reagents were of the best commercial grade and were used without further purification. Electronic and infrared spectra were recorded on U best-30 and Jasco A-100 spectrometers, respectively. Proton nmr spectra were recorded on JEOL G-400 and Hitachi CW-R1100 spectrometers; using TMS as an internal reference. GC mass spectra were measured by the Hitachi M-80. All experiments were carried out under nitrogen atmosphere.

2.1. Reaction of dicobalt octa(2,6-xylyl isocyanide) with 2-bromoacetophenone

(a) A mixture of $Co_2(XylNC)_8$ (0.102 g, 0.087 mmol) and 2-bromoacetophenone (0.516 g, 3.94 mmol) was

---

☆ Studies on Interaction of Transition-Metal Complexes with Isocyanides 40. For part 39, see K. Katsuki, M. Okamoto, Y. Ooyama and Y. Yamamoto, *Inorg. Chim. Acta, 217* (1994) 181.

* Corresponding author.

SSDI 0022-328X(94)05033-8

stirred in benzene (15 ml) at room temperature. After 3 h, the reaction mixture was chromatographed on alumina. Two bands were observed. The first eluting with benzene gave an orange solution. The solvent was removed to dryness in vacuo and the residue was crystallized from benzene/hexane to give orange crystals of **1a** (20 mg, 30%). Work-up of the second eluting with CH_2Cl_2 gave an orange solution, from which orange crystals of **2a** (22 mg, 11%) (containing 1/2-CH_2Cl_2) were obtained by crystallization from CH_2Cl_2/ether/hexane. **1a**: Mass spectrum: M^+, m/z 389; IR(nujol): 1705, 1596, 1581, and 1573 (C=N) cm^{-1}; electronic spectrum(AB)(hexane): λ 339 (log ϵ 4.2) and 256 nm; ^1H NMR($CDCl_3$): δ 2.13 (s, 6H, o-Me), 2.25 (s, 6H, o-Me) 5.93 (s, 1H, C=CH), and ca. 7.0 (c, aromatic proton(ap)). Found C, 82.09; H, 6.79; N, 7.24. Calcd. for $C_{26}H_{24}N_2O$: C, 82.20; H, 6.35; N, 7.36%. **2a** $1/2CH_2Cl_2$: IR(nujol): 2169, 2145sh, 2139(N≡C), 1651, 1626, 1590, 1580 (C=N and C=O) cm^{-1}. AB(benzene): λ 455sh (3.40) and 384sh(3.82) nm. ^1H NMR($CDCl_3$): δ 1.77(s, 3H, o-Me), 1.79(s, 3H, o-Me), 2.07(s, 6H, o-Me), 2.09(s, 3H, o-Me), 2.22(s, 6H, o-Me), 2.39(s, 3H, o-Me), 2.54(s, 6H, o-Me), 2.55(s, 3H, o-Me), 2.78(s, 3H, o-Me), 4.85(s, 1H, C=CH), 5.30(s, CH_2Cl_2), and ca. 7.0(c, ap). Found: C, 68.43; H, 5.74; N, 7.59. Calcd for $C_{62.5}H_{61}N_6BrClOCo$: C, 69.09; H, 5.66; N, 7.74%.

(b) A mixture of xylyl isocyanide (0.053 g, 0.41 mmol), $Co_2(XylNC)_8$ (0.102 g, 0.087 mmol), and 2-bromoacetophenone (0.516 g, 3.94 mmol) was heated at reflux in benzene. After 3 h, the solvent was removed to dryness and the residue was chromatographed on alumina. Three bands (orange, red, and violet) were observed. Each was eluted with CH_2Cl_2, THF and MeOH. Eluting with CH_2Cl_2 gave an orange solution. The solvent was removed to dryness in vacuo, and the residue was recrystallized from benzene/hexane to give reddish orange crystals of **1a** (29 mg, 43%). The second eluting with THF gave orange red crystals of **3a** (58 mg, 10%). The last eluting with MeOH gave a violet solution, from which violet crystals of **4a** (containig $1/4CH_2Cl_2$) were obtained by crystallization from CH_2Cl_2/ ether/ hexane. **3a**: IR(nujol): 2136sh, 2106 (N≡C), 1633, 1589, 1522 (C=N) cm^{-1}; AB(benzene): λ 454sh (3.29) nm; ^1H NMR($CDCl_3$): δ 2.03(s, 3H, o-Me), 2.11(s, 3H, o-Me), 2.12(s, 3H, o-Me), 2.23(s, 3H, o-Me), 2.28(s, 6H, o-Me), 2.33(s, 6H, o-Me), 2.39(s, 3H, o-Me), 2.70(s, 3H, o-Me), 5.30 (s, CH_2Cl_2), 6.27(s, 1H, C=CH), and ca. 7 (c, ap). Found: C, 69.36; H, 5.47; 7.57. Calcd. for $C_{53}H_{51}N_5BrOCo$: C, 69.73; H, 5.63; N, 7.67%. **4a**'$1/4CH_2Cl_2$: IR(nujol): 2166, 2138 (N≡C), 1632, and 1591 (C=N, C=O, and C=C) cm^{-1}. AB(benzene): λ 904 (2.69), 581(4.11) and 410sh (3.82) nm. ^1H NMR($CDCl_3$): δ 1.87(s, 6H, o-Me), 2.20(s, 12H, o-Me), 2.31(s, 6H, o-Me), 2.43(s, 3H, o-Me), 5.3 s, CH_2Cl_2), 5.96 (s, 1H, C=CH), and ca. 7 (c, ap). Found: C, 68.35; H, 5.68; N, 7.43; Calcd for $C_{53.25}H_{51.5}N_5BrCl_{0.5}OCo$: C, 68.47; H, 5.56; N, 7.50%.

2.2. Structure determination

Compound **1a** was recrystallized from benzene/hexane, **2a** from benzene/ether, and **3a** from benzene /hexane. Cell constants were determined from 20 reflections on an Enraf-Nonius four-circle automated diffractometer (CAD4). The scan rates are 4° min^{-1}

Table 1
Crystallographic and Experimental Data for Compounds **1a**, **2a** and **3a**

compd.	**1a**	**2a**	**3a**C_6H_6
formula	$C_{26}H_{24}N_2O$	$C_{62}H_{60}N_6BrOCo$	$C_{59}H_{57}N_5BrOCo$
mol. wt.	389.5	1044.0	1147.2
crys. dimens.(mm)	0.30 × 0.30 × 0.25	0.2 × 0.2 × 0.38	0.30 × 0.54 × 0.18
cryst. syst.	monoclinic	monoclinic	monoclinic
space group	$C2/c$(No15)	$P2_1/n$ (No. 14)	$P2_1/n$(No. 14)
lattice parameters			
a(A)	28.479(5)	21.956(10)	21.214(7)
b(A)	9.648(1)	16.909(2)	22.232(11)
c(A)	19.274(7)	14.534(2)	13.181(3)
β(deg)	123.74(3)	98.85(2)	90.30(2)
V(A^3)	4404	5332	6217
Z	8	4	4
D_{calcd}(gcm^{-3})	1.148	1.301	1.226
scan method	$\omega(2\theta < 30°)$, $\omega - 2\theta$ $(30° < 2\theta < 52°)$	$\omega(2\theta < 30°)$, $\omega - 2\theta$ $(30° < 2\theta < 50°)$	$\omega(2\theta < 30°)$, $\omega - 2\theta$ $(30° < 2\theta < 50°)$
no. of data	2430	4050	4223
no. of obsd. data	1846 $(F_o > 5.0\sigma(F_o))$	2485 $(F_o > 5.0\sigma(F_o))$	2314 $(F_o > 5.0\sigma(F_o))$
R [a]	0.061	0.094	0.085
R_w [b]	0.051 ($w = 1$)	0.067 ($w = 1/\sigma^2(F_o)$)	0.077 ($w = 1/\sigma^2(F_o)$)

[a] $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$.
[b] $R_w = [\Sigma w(| F_o | - | F_c |)^2 / \Sigma w | F_o |^2]^{1/2}$.

for **1a**, **2a** and **3a**. The crystal parameters along with data collection are summarized in Table 1. Throughout the data collection the intensities of the three standard reflections were measured every 100 reflections as a check of the stability of the crystals and decay was not observed. Of totals of 2932 (for **1a**, $2\theta < 50°$), 4333 (for **2a**, $2\theta < 50°$), and 6677 (for **3a**, $2\theta < 45°$) independent intensities measured, 1571, 2149, and 2583 reflections ($F > 5\sigma(F_o)$) were used in the solutions and refinements of the structures. Intensities were corrected for Lorentz and polarization effects. The linear absorption coefficients for Mo Kα radiation were 0.07 (for **1a**), 0.31 (for **2a**), and 0.84 (for **3a**). The absorption correction of **3a** was made and those of the other compounds were not made. The structures were solved by direct methods (MULTAN78), by using the UNICS II program system [11]. Atomic scattering factors and anomalous dispersion effects were taken from the usual tabulations [12].

2.3. Structure of 1a

All nonhydrogen atoms were located in the initial E map and refined by the block-diagonal least-squares method. Hydrogen atoms were calculated at the ideal positions with the C–H distance of 0.95 Å, and were not refined. Final refinement with anisotropic thermal parameters for non-hydrogen atoms converged to $R = 0.061$ and $R_w = 0.051$, where $R = \| F_o | - | F_o \| / \Sigma | F_o |$ and $R_w = [\Sigma w(| F_o | - | F_c |)^2 / \Sigma w | F_o |^2)^{1/2}$ ($w = 1$). A final difference Fourier synthesis showed peaks at heights up to 0.18 eÅ^{-3}.

Table 2
Positional Parameters of **1a** [a]

Atom	x	y	z	B_{eq} [b]
O	1104(2)	237(3)	6922(2)	4.4
N(1)	1285(2)	719(4)	5261(2)	3.9
N(2)	1202(2)	2385(4)	6551(3)	4.5
C(1)	1224(2)	202(4)	5820(3)	3.4
C(2)	1177(2)	1115(5)	6413(3)	3.8
C(3)	1185(2)	−1186(5)	6051(3)	3.7
C(4)	1122(2)	−1113(5)	6693(3)	3.5
C(11)	1340(2)	−230(5)	4737(3)	3.6
C(12)	1861(2)	−340(6)	5859(3)	4.9
C(13)	1913(3)	−1248(7)	4320(4)	6.4
C(14)	1457(3)	−1936(6)	3695(4)	6.2
C(15)	952(3)	−1784(6)	3580(3)	5.7
C(16)	871(2)	−921(5)	4095(3)	4.3
C(17)	290(3)	−731(7)	3905(4)	6.9
C(18)	2362(3)	474(9)	5529(4)	8.3
C(21)	1307(2)	3370(5)	6096(3)	3.6
C(22)	857(2)	3897(5)	5346(3)	4.1
C(23)	969(3)	4982(6)	4980(3)	5.3
C(24)	1498(3)	5499(6)	5332(4)	6.0
C(25)	1927(3)	4967(6)	6065(4)	6.3
C(26)	1845(2)	3876(6)	6477(3)	4.8
C(27)	2329(3)	3294(8)	7305(4)	8.2
C(28)	274(3)	3331(7)	4932(4)	6.7
C(41)	1078(2)	−2180(5)	7190(3)	3.7
C(42)	1097(2)	−3566(5)	7015(3)	4.6
C(43)	1044(3)	−4589(5)	7462(4)	5.9
C(44)	982(3)	−4231(6)	8103(4)	7.2
C(45)	973(3)	−2865(6)	8295(4)	7.5
C(46)	1013(3)	−1837(5)	7834(4)	5.9

[a] Values are multiplied by 10^4. Estimated standard deviations in parentheses.
[b] $B_{eq} = (8\pi^2/3)\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* a_i a_j$.

2.4. Structure of 2a and 3a

The cobalt and bromine atoms were solved by each initial E map of **2a** and **3a** and refined by the block-diagonal least-squares method. Subsequent Fourier maps gave the positions of the remaining non-hydrogen atoms. The hydrogen atoms were calculated in the ideal positions with a C–H distance of 0.95 Å, and were not refined. Non-hydrogen atoms were refined anisotropically. The final R and R_w values converged to 0.094 and 0.077 ($w = 1/\sigma^2(F_o)$) for **2a**, and 0.85 and 0.67 ($w = 1/\sigma^2(F_o)$) for **3a**, where $R = \Sigma \| F_o | - | F \| / \Sigma | F_o |$ and $R_w = [\Sigma w(| F_o | - | F_o |)^2 / \Sigma w | F_o |^2)^{1/2}$. Final difference Fourier synthesis showed peaks at heights up to 0.60 eÅ^{-3} (around Br atom) for **2a** and 0.58 eÅ^{-3} (around Br) for **3a**.

The positional parameters of **1a**, **2a** and **3a** are listed in Tables 2–4, and their selected bond angles and distances are in Tables 5–7.

3. Results and discussion

3.1. Reaction of dicobalt octa(2,6-xylyl isocyanide) with 2-bromoacetophenone

(a) Dicobalt octa(2,6-xylyl isocyanide), $Co_2(XylNC)_8$ (Xyl = $2,6\text{-}Me_2C_6H_3$) was treated with an excess amount of 2-bromoacetophenone in benzene at room temperature. After 3 h, two compounds **1a** (reddish orange) and **2a** (orange red) were isolated in 30% and 11% yields respectively, formulated as $(PhCOCH)(XylNC)_2$ and $CoBr(PhCOCH)(XylNC)_6$ from their elementary analyses and mass spectrum.

The infrared spectrum of **1a** showed the presence of C=N (or C=O) and C=C bonds at 1707, 1596, 1581, and 1573 cm^{-1}. The ^1H NMR spectrum showed three singlets at δ 2.13, 2.25, and 5.93; the two singlets at ca. δ 2.1 are assigned to *o*-methyl protons and the last one to an olefinic proton. The spectral data suggested that compound **1a** is 2,3-bis(2,6-xylyl)imino-5-(phenyl)-2.3-dihydrofuran, and its structure was finally confirmed by an X-ray analysis (Fig. 1).

The infrared spectrum of **2a** showed three characteristic bands at 2169, 2145sh, and 2139 cm^{-1} due to the terminal isocyanide groups and four bands at 1651, 1626, 1590, and 1580 cm^{-1}, assignable to the C=N and

Table 3
Positional parameters of **2a** [a]

Atom	*x*	*y*	*z*	B_{eq}^{b}
Co	7081(1)	2363(1)	9526(2)	3.3
Br	6993(1)	3720(1)	8982(1)	4.4
O	9347(6)	3161(8)	8209(10)	6.4
N(1)	7442(6)	2861(8)	11520(9)	3.7
N(2)	8213(6)	2863(7)	10616(10)	3.3
N(3)	8029(6)	2209(7)	8276(9)	3.0
N(4)	6304(6)	1802(9)	7691(11)	4.7
N(5)	5741(6)	2558(9)	9946(10)	4.5
N(6)	7351(7)	718(8)	10201(10)	4.7
C(1)	7577(7)	2717(9)	10729(11)	2.8
C(2)	8373(8)	2690(10)	9756(11)	3.8
C(3)	7874(8)	2375(10)	9059(11)	3.6
C(4)	6616(8)	2009(10)	8367(13)	4.3
C(5)	6246(7)	2488(11)	9896(11)	3.6
C(6)	7228(8)	1385(10)	9941(12)	3.9
C(7)	8947(7)	2822(11)	9581(12)	3.9
C(8)	9192(7)	2618(11)	8699(12)	3.7
C(11)	6871(8)	2727(11)	11859(11)	4.0
C(12)	6804(8)	2012(12)	12338(13)	4.9
C(13)	6227(9)	1958(13)	12669(13)	6.0
C(14)	5823(10)	2576(15)	12612(14)	7.9
C(15)	5943(10)	3273(14)	12209(14)	7.4
C(16)	6502(9)	3400(12)	11822(13)	5.8
C(17)	6631(10)	4193(12)	11466(14)	6.6
C(18)	7265(10)	1403(12)	12474(13)	6.1
C(21)	8668(8)	3160(12)	11380(13)	4.7
C(22)	9031(9)	2637(14)	11933(12)	6.1
C(23)	9486(9)	2963(13)	12616(13)	6.3
C(24)	9551(10)	3758(15)	12648(14)	7.9
C(25)	9205(10)	4259(13)	12067(13)	6.7
C(26)	8723(9)	4012(12)	11410(13)	5.3
C(27)	8351(11)	4552(12)	10785(15)	6.9
C(28)	8929(10)	1770(13)	11810(14)	7.0
C(31)	7748(7)	1921(10)	7399(11)	2.5
C(32)	7671(8)	1099(10)	7244(12)	4.5
C(33)	7466 ())	866(11)	6374(12)	4.8
C(34)	7301(8)	1366(12)	5641(12)	5.4
C(35)	7400(8)	2173(12)	5809(13)	5.0
C(36)	7628(7)	2483(11)	6682(11)	3.8
C(37)	7769(9)	3341(10)	6834(12)	4.5
C(38)	7862(9)	522(11)	8022(13)	4.9
C(41)	6000(7)	1578(11)	6768(12)	4.1
C(42)	5922(9)	758(12)	6668(15)	6.4
C(43)	5644(10)	575(13)	5747(15)	7.3
C(44)	5523(9)	1156(16)	5081(14)	8.4
C(45)	5609(8)	1939(15)	5288(14)	6.9
C(46)	5860(8)	2217(13)	6158(12)	5.6
C(47)	5932(10)	3045(12)	6387(15)	6.6
C(48)	6089(10)	157(12)	7368(17)	7.9
C(51)	5108(8)	2802(10)	9980(12)	3.7
C(52)	4745(8)	2227(12)	10307(13)	5.5
C(53)	5127(9)	2474(13)	10324(13)	6.4
C(54)	3929(9)	3182(14)	9971(16)	7.5
C(55)	4304(9)	4718(15)	9628(14)	7.4
C(56)	4922(10)	3531(12)	9625(13)	6.1
C(57)	5333(11)	4059(13)	9242(15)	7.7
C(58)	4873(10)	1461(13)	10725(15)	7.6
C(61)	7325(9)	−81(11)	10541(12)	4.7
C(62)	7885(9)	−488(10)	10674(12)	4.9
C(63)	7818(9)	−1254(12)	11017(13)	5.7
C(64)	7277(10)	−1526(12)	11193(13)	6.4
C(65)	6758(9)	−1082(12)	11072(13)	5.5
C(66)	6749(10)	−313(11)	10712(12)	5.5
C(67)	6191(10)	173(13)	10545(15)	7.1
C(68)	8486(10)	−167(14)	10481(15)	7.4
C(71)	9311(8)	1757(10)	8465(13)	4.2
C(72)	9284(9)	1561(13)	7543(12)	5.7
C(73)	9378(11)	788(14)	7297(16)	8.5
C(74)	9551(11)	248(13)	7979(15)	7.9
C(75)	9565(11)	429(13)	8875(15)	7.2
C(76)	9456(9)	1190(13)	9158(13)	6.1

[a] Values are multiplied by 10^4. Estimated standard deviations in parentheses.
[b] $B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i a_j$.

C=O groups. The ^{1}H NMR spectrum showed nine singlets at δ 1.77, 1.79, 2.07, 2.09, 2.22, 2.39, 2.54, 2.55, and 2.78, consisting of a 3 : 3 : 6 : 3 : 6 : 3 : 6 : 3 : 3 intensity ratio and one singlet at δ 4.85 due to an olefinic proton. Three singlets having a 6 intensity ratio were assigned to the terminal isocyanide groups, and the six signals having a 3 intensity ratio, to three kinds of the inserted isocyanide groups, in which three inserted isocyanides would have a steric rotation-barrier based on the presence of six kinds of signals. The structure was confirmed by an X-ray analysis. As expected, the molecule is a six-coordinated cobaltacycle compound containing the bidentate ligand, produced by the multiple insertion of three isocyanide molecules (Fig. 2).

(b) After the similar reaction was carried out in the presence of 2,6-xylyl isocyanide (XylNC) in benzene at reflux, three compounds **1a** (reddish orange), **3a** (red), and **4a** (violet) were obtained, which were separated by the column chromatography on alumina. Compounds **3a** and **4a** had similar composition, formulated as CoBr(PhCOCH)(XylNC)$_5$.

It was determined by an X-ray analysis that the structure of **3a** is a six-coordinated cobaltacycle compound containing a tridentate ligand, which was produced by a multiple insertion of isocyanide (Fig. 3).

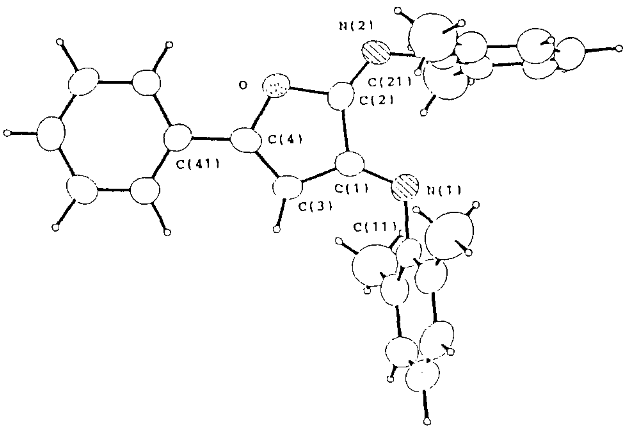


Fig. 1. Structure of **1a**.

Table 4
Positional parameters of **3a** C_6H_6 [a]

Atom	x	y	z	B_{eq} [b]
Co	2090(2)	2912(2)	6293(3)	3.2
Br	2563(1)	2530(2)	4791(2)	5.1
O	1638(7)	3576(7)	5439(11)	3.9
N(1)	2794(9)	1987(8)	7492(14)	4.6
N(2)	1893(10)	1085(8)	6842(15)	4.8
N(3)	1318(8)	1898(8)	6239(13)	3.9
N(4)	1384(8)	3458(8)	8006(13)	3.4
N(5)	3269(9)	3699(8)	6622(15)	4.5
C(1)	2344(10)	2154(10)	6950(17)	3.8
C(2)	1855(11)	1659(10)	6704(17)	3.8
C(3)	1344(10)	2491(12)	5933(15)	3.7
C(4)	1700(11)	3207(10)	7347(16)	3.2
C(5)	2843(10)	3382(11)	6527(18)	3.8
C(6)	903(11)	2790(10)	5347(18)	4.5
C(7)	1114(11)	3383(11)	5115(17)	4.0
C(11)	3331(11)	2337(10)	7878(18)	4.1
C(12)	3179(11)	2586(11)	8836(18)	4.9
C(13)	3727(15)	2926(12)	9268(22)	8.2
C(14)	4251(14)	2942(13)	8673(21)	7.3
C(15)	4388(13)	2676(12)	7774(23)	7.7
C(16)	3893(11)	2323(11)	7310(19)	5.1
C(17)	3965(13)	1999(14)	6330(21)	8.1
C(18)	2611(12)	2514(14)	9447(16)	5.8
C(21)	2421(11)	769(10)	7230(9)	4.2
C(22)	2347(10)	619(10)	8281(18)	3.5
C(23)	2798(12)	212(12)	8664(21)	6.1
C(24)	3293(13)	11(12)	8093(23)	7.2
C(25)	3339(12)	193(10)	7066(20)	4.9
C(26)	2889(12)	579(10)	6594(21)	4.8
C(27)	2899(12)	734(12)	5493(18)	5.4
C(28)	1834(13)	832(12)	8951(20)	6.3
C(31)	745(12)	1519(11)	6012(18)	4.5
C(32)	779(12)	1227(10)	5029(9)	4.8
C(33)	195(13)	862(12)	4886(21)	6.1
C(34)	−253(12)	837(11)	5624(19)	5.4
C(35)	−260(13)	1142(12)	6531(22)	6.4
C(36)	306(12)	1522(11)	6789(20)	5.3
C(37)	344(13)	1829(13)	7755(20)	7.1
C(38)	1268(13)	1272(13)	4271(20)	6.8
C(41)	949(10)	3753(10)	8656(16)	3.1
C(42)	307(13)	3825(12)	8359(22)	6.7
C(43)	−101(15)	4083(14)	9068(25)	9.0
C(44)	114(16)	4247(14)	10005(23)	8.7
C(45)	744(14)	4212(12)	10285(20)	6.8
C(46)	1209(14)	3960(12)	9614(19)	6.9
C(47)	1880(16)	3926(14)	9925(23)	9.1
C(48)	158(14)	3660(13)	7264(23)	8.1
C(51)	3793(11)	4063(11)	6679(20)	4.8
C(52)	3777(12)	4464(11)	7551(19)	5.0
C(53)	4312(12)	4855(11)	7599(20)	5.1
C(54)	4784(13)	4828(14)	6903(20)	7.2
C(55)	4787(14)	4465(14)	6089(23)	8.2
C(56)	4278(12)	4019(12)	5934(20)	5.7
C(57)	4233(14)	3591(14)	5061(20)	8.1
C(58)	3311(13)	4475(12)	8341(20)	5.6
C(71)	715(12)	3775(12)	4443(18)	5.2
C(72)	91(13)	3628(12)	4144(22)	7.0
C(73)	−227(12)	4035(13)	3545(21)	6.8
C(74)	15(14)	4546(13)	3236(24)	8.3
C(75)	626(15)	4719(14)	3520(27)	10.6
C(76)	973(14)	4322(13)	4149(24)	8.5
C(11′)	797(14)	2588(17)	10861(23)	10.1
C(12′)	1390(14)	2711(14)	12356(23)	8.8
C(13′)	927(16)	2912(15)	11717(24)	10.0
C(14′)	1731(14)	2212(14)	12118(20)	8.2
C(15′)	1088(17)	2019(17)	10667(24)	11.3
C(16′)	1587(16)	1840(16)	11316(25)	10.8

[a] Values are multiplied by 10^4. Estimated standard deviations in parentheses.

[b] $B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i a_j$.

The spectroscopic data were in agreement with the structure in the solid state. The infrared spectrum showed two N≡C bands at 2136sh and 2106 cm^{-1}, suggesting the presence of two terminal isocyanide ligands. The ^{1}H NMR spectrum showed eight singlets due to *o*-methyl protons at δ 2.03, 2.11, 2.12, 2.23, 2.28, 2.33, 2.39 and 2.70, consisting of a 3:3:3:3:6:6:3:3 intensity ratio, in addition to a singlet at δ 6.27 due to an olefinic proton. The singlets at δ 2.28 and 2.33 consisting of a 6 intensity ratio are assigned to two terminal isocyanides and other singlets, to three 2,6-xylylimino and -amino groups; each group of the latter is suggested to be in a different environment by means of steric hindrance of the rotation of the aryl groups.

Compound **4a** showed the characteristic bands of the terminal isocyanide groups at 2166 and 2138 cm^{-1}, and the bands due to the double bonds (C=N, C=O, and C=C), at 1632 and 1591 cm^{-1}. The ^{1}H NMR spectrum showed six singlets at δ 1.87, 2.20, 2.31, 2.36, 2.43 and 5.96, consisting of a 6:12:3:6:3:1 intensity ratio. The last signal was assigned to an olefinic proton and other signals, to *o*-methyl groups. From an intensity ratio of the *o*-methyl protons, the presence of four kinds of isocyanide ligands was inferred. Among five isocyanide ligands, two isocyanides are in a similar environment and one is in the rotational barrier. Based

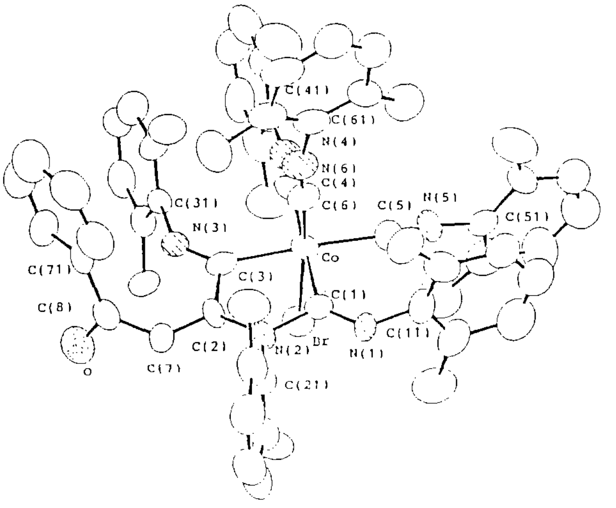


Fig. 2. Structure of **2a**.

Table 5
Selected Bond Distances and Angles of **1a**

Bond Distances (Å)					
O–C(2)	1.396(8)	O–C(4)	1.386(6)	N(1)–C(1)	1.284(8)
N(1)–C(11)	1.435(8)	N(2)–C(2)	1.247(6)	N(2)–C(21)	1.433(8)
C(1)–C(2)	1.506(9)	C(1)–C(3)	1.435(7)	C(3)–C(4)	1.347(9)
C(4)–C(41)	1.459(8)				
Bond Angles (deg.)					
C(2)–O–C(4)	107.4(5)	C(1)–N(1)–C(11)	117.5(4)		
C(2)–N(2)–C(21)	120.8(6)	N(1)–C(1)–C(2)	121.3(4)		
N(1)–C(1)–C(3)	133.9(5)	C(2)–C(1)–C(3)	104.8(5)		
O–C(2)–N(2)	117.3(6)	O–C(2)–C(1)	106.8(4)		
N(2)–C(2)–C(1)	135.9(6)	C(1)–C(3)–C(4)	108.0(5)		
O–C(4)–C(3)	113.0(5)	O–C(4)–C(41)	115.0(5)		
C(3)–C(4)–C(41)	132.1(5)				

on the spectroscopic data and the structure of **3a**, the three possible structures with a four-membered cobalta-azacyclobutane core were considered for compound **4a** (Fig. 4). Structures **4a-A** and **4a-B** are due to difference of the position of a Br atom in the equatorial plane. The structure **4a-C** is based on the structures of **2a** and **3a** in which a halogen atom has been occupied in the *trans*-position to the terminal isocyanide. Since three isocyanide ligands are nonequivalent in the structure **4a-C**, the chemical shift of *o*-methyl protons for the two isocyanide ligands is due to an accidental degeneracy. For the structures **4a-A** and **4a-B**, the ^{1}H NMR spectrum is in agreement with the proposed structure. For the time being we assume that the structure of **4a** is **A** or **B**. Thus, the singlet at δ 2.20 having a 12 intensity ratio was due to the axial terminal isocyanide ligands, and the band at δ 2.36 to an equatorial terminal one. The amino-N-2,6-xylyl group appeared at δ 1.87. The imino-N-2,6-xylyl group accepted a steric hindrance similar to those of **2a** and **3a**. The electronic spectrum showed a characteristic band at 904 nm, reminiscent of violet colour. When complex **2a** was refluxed in benzene, the loss of isocyanide from **2a** occurred and the furan derivative **1a** was obtained in a low yield, suggesting that **2a** is one of the precursors of the furan derivative. The loss of the inserted isocyanide has been observed in some reactions of the imino-complexes [2,13]. The thermal decompositions of **3a** or **4a**

Table 6
Selected Bond Distances and Angles of **2a**

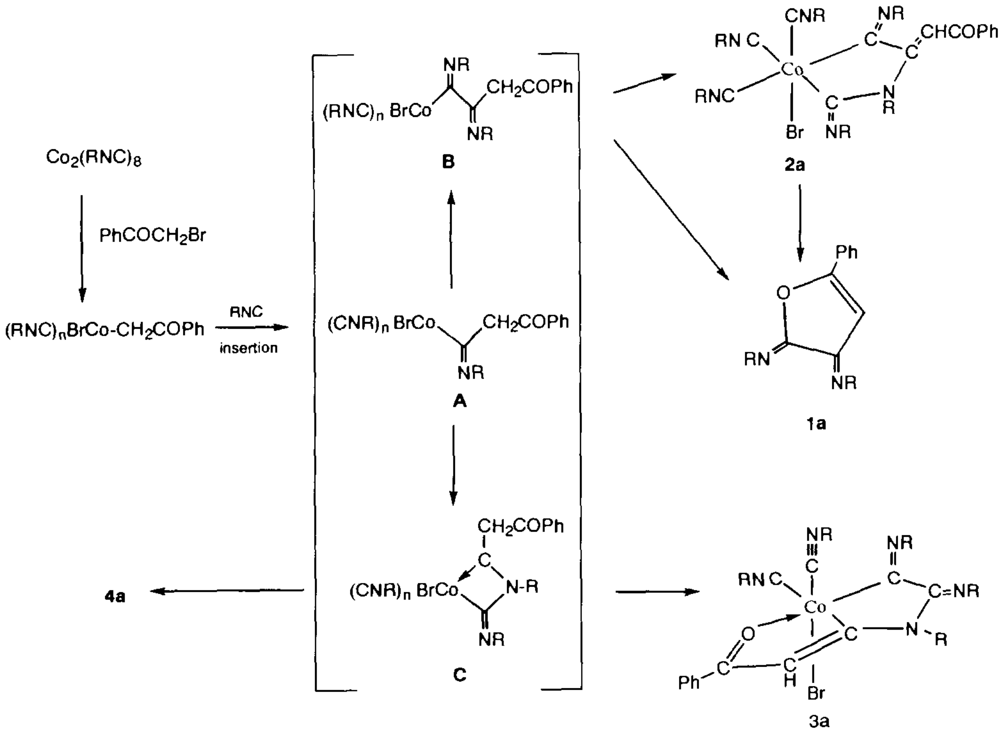
Bond distances (Å)					
Co–Br	2.426(3)	Co–C(1)	2.004(15)	Co–C(3)	1.964(18)
Co–C(4)	1.927(18)	Co–C(5)	1.999(17)	Co–C(6)	1.772(18)
O–C(8)	1.24(2)	N(1)–C(1)	1.25(2)	N(1)–C(11)	1.43(2)
N(2)–C(1)	1.45(2)	N(2)–C(2)	1.38(2)	N(3)–C(3)	1.27(2)
N(4)–C(4)	1.16(2)	N(5)–C(5)	1.13(2)	N(6)–C(6)	1.21(2)
C(2)–C(3)	1.47(2)	C(2)–C(8)	1.49(2)		
Bond angles (deg.)					
Br–Co–C(1)	90.4(5)	Br–Co–C(3)	84.7(5)		
Br–Co–C(4)	90.2(5)	Br–Co–C(5)	87.6(5)		
Br–Co–C(6)	174.1(6)	C(1)–Co–C(3)	84.7(7)		
C(1)–Co–C(4)	179.0)7)	C(1)–Co–C(5)	97.6(7)		
C(1)–Co–C(6)	86.4(7)	C(3)–Co–C(4)	94.5(7)		
C(3)–Co–C(5)	172.0(7)	C(3)–Co–C(6)	90.1(8)		
C(4)–Co–C(5)	83.3(7)	C(4)–Co–C(6)	97.7(8)		
C(1)–N(1)–C(11)	128.6(14)	C(1)–N(2)–C(2)	116.7(13)		
C(1)–N(2)–C(21)	121.9(14)	C(2)–N(2)–C(21)	121.4(14)		
C(3)–N(3)–C(31)	138.1(14)	C(4)–N(4)–C(41)	170.5(18)		
C(5)–N(5)–C(51)	169.4(18)	C(6)–N(6)–C(61)	164.6(18)		
Co–C(1)–N(1)	133.2(12)	Co–C(1)–N(2)	110.8(11)		
N(1)–C(1)–N(2)	115.9(13)	N(2)–C(2)–C(7)	120.8(14)		
C(3)–C(2)–C(7)	123.5(16)	Co–C(3)–N(3)	133.1(12)		
Co–C(3)–C(2)	111.1(2)	N(3)–C(3)–C(2)	115.1(15)		
Co–C(4)–N(4)	175.9(17)	Co–C(5)–N(5)	168.3(14)		
Co–C(6)–N(6)	177.1(17)	C(2)–C(7)–C(8)	125.5(14)		
O–C(8)–C(7)	118.8(16)	O–C(8)–C(71)	120.4(16)		

Table 7
Selected Bond Distances and Angles of **3a**$_4$

Bond distances (Å)					
Co–Br	2.386(5)	Co–O	2.090(15)	Co–C(1)	1.965(23)
Co–C(3)	1.897(26)	Co–C(4)	1.743(23)	Co–C(5)	1.932(24)
O–C(7)	1.26(3)	N(1)–C(1)	1.25(3)	N(2)–C(2)	1.29(3)
N(3)–C(2)	1.40(3)	N(3)–C(3)	1.38(3)	N(4)–C(4)	1.23(3)
N(5)–C(5)	1.15(3)	C(1)–C(2)	1.55(3)	C(3)–C(6)	1.38(3)
C(6)–C(7)	1.43(3)				
Bond angles (deg.)					
Br–Co–O	89.6(4)	Br–Co–C(1)	86.8(7)		
Br–Co–C(3)	88.1(8)	Br–Co–C(4)	176.0(8)		
Br–Co–C(5)	88.3(7)	O–Co–C(1)	165.1(8)		
O–Co–C(3)	80.4(9)	O–Co–C(4)	86.9(9)		
O–Co–C(5)	94.5(8)	C(1)–Co–C(3)	85.1(10)		
C(1)–Co–C(4)	96.1(10)	C(1)–Co–C(5)	99.8(10)		
C(3)–Co–C(4)	89.4(11)	C(3)–Co–C(5)	173.8(11)		
C(4)–Co–C(5)	93.9(11)	Co–O–C(7)	110.1(14)		
C(1)–N(1)–C(11)	129.1(20)	C(2)–N(2)–C(21)	126.1(21)		
C(2)–N(3)–C(3)	117.2(20)	C(2)–N(3)–C(31)	122.0(19)		
C(4)–N(4)–C(41)	171.6(21)	C(5)–N(5)–C(51)	176.3(24)		
Co–C(1)–N(1)	135.6(18)	Co–C(1)–C(2)	109.7(15)		
N(1)–C(1)–C(2)	114.7(20)	N(2)–C(2)–N(3)	119.2(21)		
N(3)–C(2)–C(1)	111.4(19)	Co–C(3)–N(3)	115.7(18)		
Co–C(3)–C(6)	117.7(19)	N(3)–C(3)–C(6)	126.5(23)		
Co–C(4)–N(4)	172.2(20)	Co–C(5)–N(5)	174.6(22)		
O–C(7)–C(6)	121.2(21)	O–C(7)–C(71)	119.7(21)		
C(6)–C(7)–C(71)	119.1(21)				

did not give the furan derivative and the mutual interconversion between **3a** and **4a** did not occur either.

Based on these results, the overall reaction is assumed to proceed as depicted in Scheme 1. An initial oxidative addition of $PhCOCH_2Br$ to $Co_2(RNC)_8$ was followed by an insertion of isocyanide to give an intermediate **A**. After a double insertion of isocyanide, complex **2a** was formed by a nucleophilic attack of a



Scheme 1.

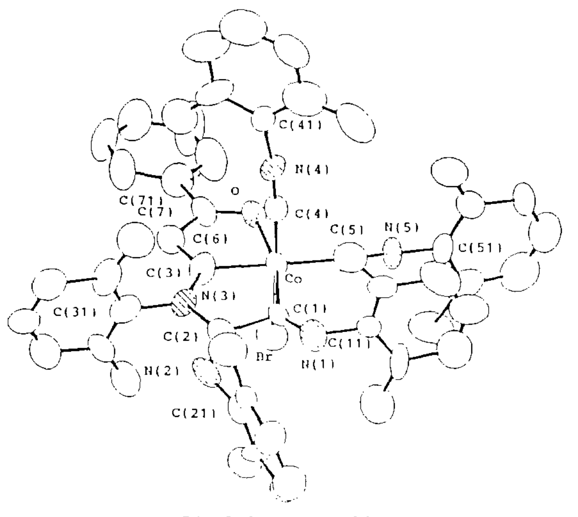


Fig. 3. Structure of **3a**.

β-imino-nitrogen onto a coordinated isocyanide and compound **1a** was formed by an attack of the carbonyl oxygen to the metal atom to give the metallacycle compound and by the reductive elimination of the furan derivative.

The second route from the species **A** is a nucleophilic attack of an imino nitrogen onto the coordinated isocyanide before a double insertion proceeds, producing a carbene species **C** and finally the species **C** was oxidized to give the metallacyclic compound **4a**. Since conversion of **4a** to **3a** was not observed, an insertion of isocyanide into a cobalt–carbon bond of the C species occurred independently to form a five-membered carbene species, and finally **3a** was obtained by the coordination of the carbonyl moiety and an oxidation of the cobalt(II) species, to Co^{III}. In these reactions the oxidation of Co^{II} to Co^{III} species was observed, probably occurring through radical processes. The detailed mechanism remains unknown.

3.2. Structure description. Structure of 1a

Two N-xylyl groups have a *syn*-configuration. The C-phenyl ring is coplanar to the five-membered C(1)C(2)C(3)C(4)O ring, whereas the N-phenyl rings are nearly perpendicular. Average C=N bond length of 1.266(8) Å and average C–N–C bond angle of 119.2(5)° are not significantly different from the respective expected values. No unusual bond lengths or angles were observed.

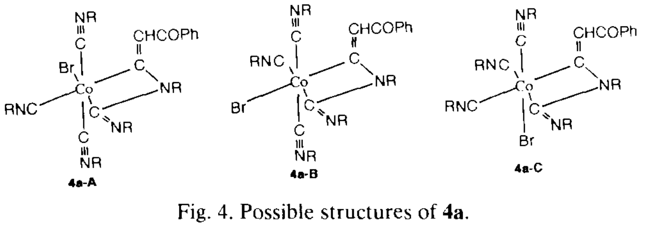


Fig. 4. Possible structures of **4a**.

3.3. Structure of 2a

The molecule has a distorted octahedral structure. One isocyanide and one bromine atom are occupied in an axial position. An equatorial position was occupied with two terminal isocyanide molecules and bidentate ligand formed by a multiple insertion of isocyanide, in which the molecule has a cobalta-azacyclopentane framework. The angles of the C(1)–Co–C(3) and C(4)–Co–C(5) bonds are 84.7(7)° and 83.3°, being narrower than the ideal angle. The C(3)–Co–C(14) and C(1)–Co–C(5) bond angles are 94.5° and 97.6° respectively, compensating the narrow angles. The C(1)–Co–C(4) angle is nearly linear, but the C(3)–Co–C(5) angle is 172°, bending to the less steric bromine side to minimize the steric repulsive interaction with the axial isocyanide as shown in the angles of the C(3)–Co–Br (84.7°) and C(5)–Co–Br (87.6°). The four phenyl rings of the bidentate ligand are nearly perpendicular to the equatorial plane CoC(1)C(2)C(3)N(2), also minimizing steric repulsion among the phenyl rings. The Co–C(6) bond length (1.772(18) Å) in the axial position is shorter than the average distance (1.963(18) Å) of those in the equatorial position. This result is traced back to the C(6)–N(6) bond being longer by ca. 0.06 Å in comparison with the C(4)–N(4) and C(5)–N(5) ones. These phenomena are responsible for less *trans*-influence being exerted by the bromine atom than the sp^3 carbon. The C=N double bond distances are not significantly different from those of the platina-azabutane derivative [11]. The Co–C–N and C–N–C bond angles fall in the usual range found in various isocyanide complexes.

3.4. Structure of 3a

The molecule has a distorted octahedral structure as well as **2a**. Of the six coordinated sites, three sites in an equatorial position are occupied by the tridentate ligand which was formed by a triple insertion of isocyanide molecules into a metal-acetophenone residue and another site is occupied by the terminal isocyanide. Axial positions are occupied by the isocyanide molecule and bromine atom. The tridentate ligand consists of two five-membered rings containing the cobalt atom, in which the two rings are nearly planar, and the N-aromatic rings lie perpendicularly to the ring planes. The two bite angles of the cobalt atom are 80.4(9)° and 85.1(10)° and two other angles have an angle greater than ca. 95°. The Co–C(3) bond length is 1.897(26) Å, shorter than the Co–C(1) single bond distance of 1.965(23) Å. The C(3)–C(6) and C(3)–N(3) bond lengths are 1.38 Å, slightly shorter than the C–C and C–N single bond lengths. Further the C(6)–C(7) bond length is longer than that of the usual double bond. These results suggest that the Co–C bond has carbene-like behaviour. The C(7)–O bond length is 1.26 Å, within the usual C=O double bond range, showing the coordination of the oxygen atom to the cobalt metal. The coordination mode of tridentate ligand may be depicted as Fig. 4. The Co–C(4) and Co–C(5) bond distances are 1.743(23) and 1.932(24) Å, respectively, also showing that the *trans*-influence of the carbene ligand is greater than that of the bromine ligand.

4. Supplementary material available

Listings of anisotropic thermal parameters, atomic parameters of hydrogen atoms and bond distances and angles, and a tables of structure factor amplitudes are available from the authors.

References

[1] For example, J. Falbe, *Carbon Monoxide in Organic Synthesis*, Springer, West Berlin, 1970.

[2] a) Y. Yamamoto, *Coord. Chem. Rev.*, *32* (1980) 193; b) E. Singleton and H.E. Oosthuizen, *Adv. Organomet. Chem.*, *22* (1983) 209

[3] a) M.G. Thomas, W.R. Pretzer, B.E. Beier, F.J. Hirsekorn and E.L. Muetterties, *J. Am. Chem. Soc.*, *99* (1977) 743; b) E.O. Fischer and H. Werner, *Chem. Ber.*, *95* (1962) 703; c) S. Otsuka, A. Nakamura and Y. Tatsuno, *J. Am. Chem. Soc.*, *91* (1969) 6994; c) M. Green, J.A.K. Howard, M. Murray, J.L. Spencer and F.G.A. Stone, *J. Chem. Soc., Dalton Trans.*, (1977) 1509; d) Y. Yamamoto, K. Aoki and H. Yamazaki, *Chem. Lett.*, (1979) 391; Y. Yamamoto, K. Aoki and H. Yamazaki, *Organometallics*, *2* (1983) 1377; e) Y. Yamamoto, H. Yamazaki and T. Sakurai, *J. Am. Chem. Soc.*, *104* (1982) 2329; f) J.-M. Bassett, D.E. Berry, G.K. Barker, M. Green, J.A. Howard and F.G.A. Stone, *J. Chem. Soc., Dalton Trans.*, (1979) 1003; g) Y. Yamamoto and H. Yamazaki, *Bull. Chem. Soc. Jpn.*, *57* (1984) 297; h) D.D. Klendworth, W.W. Welters III and R.A. Walton, *J. Organomet. Chem.*, *213* (1981) C13; i) Y. Yamamoto and H. Yamazaki, *J. Organomet. Chem.*, *282* (1985) 191.

[4] G.K. Barker, A.M.R. Galas, M. Green, J.A.K. Howard, F.G.A. Stone, T.W. Turney, A.J. Welch and P. Woodward, *J. Chem. Soc., Chem. Commun.*, (1977) 256.

[5] Y. Yamamoto and H. Yamazaki, *J. Organomet. Chem.*, *137* (1977) C31; Y. Yamamoto and H. Yamazaki, *Inorg. Chem.*, *17* (1978) 3111.

[6] R.D.W. Kemmitt and D.R. Russell, *Comprehensive Organometallic Chemistry*, Pergamon Oxford Vol. 5, 1982 p. 162.

[7] Y. Yamamoto and H. Yamazaki, *Organometallics*, *7* (1988) 2411.

[8] Y. Yamamoto and H. Yamazaki, *Bull. Chem. Soc. Jpn.*, *42* (1969) 2077.

[9] K. Sugano, T. Tanase, K. Kobayashi and Y. Yamamoto, *Chem. Lett.*, (1991) 921.

[10] H.M. Walborsky and G.E. Niznik, *J. Org. Chem.*, *37* (1972) 187.

[11] T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Hokoku*, *55* (1979) 69.

[12] D.T. Cramer and J.T. Waber, *International Tables for X-Ray Crystallography, Vol. 4*, Kynoch, Birmingham, 1974.

[13] Y. Yamamoto and H. Yamazaki, *Coord. Chem. Revs.*, *8* (1972) 225.