Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Cd—N(1)	2·35 (5)	N(2)—C(2)	1·01 (7)
Cd—N(2)	2·38 (5)	N(3)—C(3)	1·36 (2)
Cd—N(3)	2·34 (2)	C(3)—C(4)	1·38 (3)
Cd—N(4)	2·27 (2)	C(4)—C(5)	1·39 (3)
Ni—C(1)	1·73 (5)	C(5)—Cl	1·76 (3)
Ni—C(2)	1·99 (4)	C(3)—H(C3)	1·09 (2)
N(1)—C(1)	1·32 (6)	C(4)—H(C4)	1·09 (2)
N(1)—Cd—N(1^{i})	92 (2)	C(1)—Ni—C(1^{i})	95 (3)
N(1)—Cd—N(2)	91 (2)	C(1)—Ni—C(2)	92 (2)
N(2)—Cd—N(2^{i})	85 (2)	C(2)—Ni—C(2^{i})	82 (3)
N(1)—Cd—N(4)	88 (1)	C(3)—N(3)—C(3^{i})	118 (2)
N(2)—Cd—N(4)	95 (1)	N(3)—C(3)—C(4)	122 (1)
N(1)—Cd—N(3)	92 (1)	C(3)—C(4)—C(5)	117 (2)
N(2)—Cd—N(3)	85 (1)	C(4)—C(5)—C(4^{i})	120 (4)

Symmetry code: (i) $\frac{1}{2} - x, y, z$.

octahedron. The 4-chloropyridine and the ammonia molecules bound to Cd in *trans* positions are located on both sides of the network. The ligands of one network fit into the spaces of the other, so that the layers are arranged as closely as possible. The plane of the four cyanide C atoms surrounding Ni at an average distance of 1·86 Å is tilted so that its normal makes an angle of 46° to the *a* axis. The bending in the networks occurs because of a departure of the Ni—C—N—Cd sequence of atoms from linearity at the C and N positions. Similar corrugated polymeric layers are also observed in some other related compounds (Rayner & Powell, 1952; Ülkü, 1975). This compound has a structure closely related to but distinct from that of the 'Hofmann pyridine complexes' with the general formula $M(C_5H_5N)_2Ni(CN)_4$ (Ülkü, 1975; Morehouse *et al.*, 1977) as far as the unit-cell symmetry is concerned. As can be seen from Table 2 the bond distances and angles which were calculated from the final coordinates using the *ORFFE*3 program (Busing, Martin & Levy, 1971) generally agree with those observed in related compounds. Because of some differences in the bond lengths and angles within the pyridine ring from their ideal values, the ligand appears slightly distorted.

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cis-Dicarbonylbis[(2-phenylazo)phenyl]ruthenium(II)

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Abstract. $[Ru(C_{12}H_9N_2)_2(CO)_2]$, $[\overline{\mathrm{Ru\{C_6H_4N{=}N}}\mathrm{C_6H_5\}_2(CO)_2}]$, $M_r = 519·5$, monoclinic, $P2_1/c$, $a = 9·987\ (1)$, $b = 13·891\ (1)$, $c = 17·242\ (3)$ Å, $\beta = 101·58\ (2)°$, $V = 2345\ (2)$ Å^3, $Z = 4$, $D_m = 1·49\ (1)$, $D_x = 1·472$ Mg m^{-3}, $\lambda(\mathrm{Mo}\ K\bar{\alpha}) = 0·7107$ Å, $\mu = 0·656$ mm^{-1}, $F(000) = 1048$, $T = 295\ (2)$ K, $R = 0·056$ for 3259 observed reflections. The distorted octahedral environment about the Ru atom consists of two cyclometallated azobenzene ligands and two mutually *cis* carbonyl ligands. The donor atoms are arranged such that the N atoms are respectively *trans* to a carbonyl ligand and an aryl C atom.

Introduction. The title compound, $C_{26}H_{18}N_4O_2Ru$, was isolated as a minor product from the reaction of $Ru_3(CO)_{12}$ and azobenzene in refluxing *n*-octane; the

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major product is the known cluster complex $\mathrm{Ru_3(\mu_3\text{-}NC_6H_5)_2(CO)_9}$ (Clegg, Sheldrick, Stalke, Bhaduri & Gopalkrishnan, 1984). Two strong ν(CO) absorptions (cyclohexane) at 2036 and 1986 $\mathrm{cm^{-1}}$ indicated the presence of two mutually *cis* carbonyl groups. The crystal structure was investigated to ascertain the relative disposition of the remaining C and N donor atoms of the two cyclometallated azobenzene ligands.

Table 1. *Fractional atomic coordinates and* B_{eq} ($\mathrm{Å^2}$) *values*

$$B_{\rm eq} = 8\pi^2(U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	$B_{\rm eq}$
Ru	0·29559 (5)	0·18787 (4)	0·22738 (3)	4·01
C(1)	0·4640 (9)	0·1653 (6)	0·2961 (5)	5·43
O(1)	0·5670 (6)	0·1438 (5)	0·3347 (3)	6·72
C(2)	0·1934 (11)	0·1721 (5)	0·3104 (5)	5·80
O(2)	0·1333 (10)	0·1609 (6)	0·3591 (5)	9·89
N(1)	0·1233 (6)	0·1852 (3)	0·1344 (3)	4·18
N(2)	0·0959 (5)	0·1057 (4)	0·0960 (3)	4·38
N(3)	0·3136 (6)	0·3420 (5)	0·2192 (3)	4·89
N(4)	0·3570 (6)	0·3792 (5)	0·1637 (3)	5·32
C(3)	0·0399 (6)	0·2647 (4)	0·1029 (4)	4·24
C(4)	−0·0118 (8)	0·3219 (5)	0·1543 (5)	5·56
C(5)	−0·0964 (8)	0·3991 (6)	0·1233 (7)	7·00
C(6)	−0·1224 (9)	0·4170 (7)	0·0420 (7)	6·75
C(7)	−0·0686 (9)	0·3616 (6)	−0·0069 (6)	6·40
C(8)	0·0155 (9)	0·2837 (6)	0·0214 (5)	5·64
C(9)	0·1740 (6)	0·0301 (5)	0·1301 (4)	4·52
C(10)	0·1478 (7)	−0·0615 (6)	0·0965 (5)	5·57
C(11)	0·2180 (10)	−0·1388 (6)	0·1328 (6)	7·16
C(12)	0·3230 (9)	−0·1265 (7)	0·1998 (7)	6·87
C(13)	0·3431 (9)	−0·0372 (6)	0·2338 (5)	5·58
C(14)	0·2746 (8)	0·0447 (5)	0·1984 (4)	4·97
C(15)	0·2662 (7)	0·4153 (5)	0·2712 (5)	4·70
C(16)	0·2219 (9)	0·5043 (7)	0·2392 (6)	6·56
C(17)	0·1886 (10)	0·5745 (7)	0·2890 (9)	8·24
C(18)	0·1988 (9)	0·5518 (7)	0·3688 (8)	7·64
C(19)	0·2440 (10)	0·4648 (7)	0·3989 (6)	7·36
C(20)	0·2790 (7)	0·3941 (6)	0·3493 (5)	5·25
C(21)	0·4109 (9)	0·3068 (7)	0·1179 (5)	6·24
C(22)	0·4041 (8)	0·2101 (7)	0·1362 (4)	5·27
C(23)	0·4638 (8)	0·1452 (9)	0·0909 (5)	6·45
C(24)	0·5218 (10)	0·1778 (11)	0·0301 (6)	8·52
C(25)	0·5323 (11)	0·2761 (14)	0·0133 (6)	9·27
C(26)	0·4727 (10)	0·3414 (9)	0·0572 (6)	7·60

Table 2. *Interatomic distances* (Å) *and angles* (°)

Ru—C(1)	1·879 (9)	Ru—C(2)	1·930 (8)
Ru—N(1)	2·103 (6)	Ru—N(3)	2·155 (7)
Ru—C(14)	2·052 (7)	Ru—C(22)	2·103 (8)
C(1)—O(1)	1·15 (1)	C(2)—O(2)	1·14 (1)
N(1)—C(3)	1·424 (8)	N(3)—C(15)	1·50 (1)
N(1)—N(2)	1·289 (7)	N(3)—N(4)	1·240 (8)
N(2)—C(9)	1·368 (8)	N(4)—C(21)	1·45 (1)
C(9)—C(14)	1·40 (1)	C(21)—C(22)	1·39 (1)
C(1)—Ru—C(2)	93·0 (4)	C(1)—Ru—N(1)	165·8 (3)
C(1)—Ru—N(3)	97·5 (3)	C(1)—Ru—C(14)	91·5 (3)
C(1)—Ru—C(22)	88·0 (3)	C(2)—Ru—N(1)	95·2 (3)
C(2)—Ru—N(3)	103·0 (3)	C(2)—Ru—C(14)	91·6 (3)
C(2)—Ru—C(22)	177·9 (3)	N(1)—Ru—N(3)	91·9 (2)
N(1)—Ru—C(14)	76·7 (3)	N(1)—Ru—C(22)	84·2 (3)
N(3)—Ru—C(14)	162·4 (3)	N(3)—Ru—C(22)	75·1 (3)
C(14)—Ru—C(22)	90·2 (3)		
Ru—C(1)—O(1)	173·9 (7)	Ru—C(2)—O(2)	178·6 (7)
Ru—N(1)—N(2)	117·6 (4)	Ru—N(3)—N(4)	120·8 (6)
Ru—N(1)—C(3)	127·1 (4)	Ru—N(3)—C(15)	126·6 (5)
C(3)—N(1)—N(2)	114·9 (5)	C(15)—N(3)—N(4)	112·4 (7)
N(1)—N(2)—C(9)	113·2 (5)	N(3)—N(4)—C(21)	110·9 (7)
N(2)—C(9)—C(14)	120·1 (6)	N(4)—C(21)—C(22)	120·6 (7)
N(2)—C(9)—C(10)	118·5 (6)	N(4)—C(21)—C(26)	115·8 (9)

Experimental. An orange crystal 0·28 × 0·60 × 0·98 mm grown from *n*-hexane, m.p. 423 K (dec.). Density measured in aqueous $\mathrm{ZnBr_2}$ solution. Enraf–Nonius CAD-4*F* diffractometer controlled by PDP8/A computer, graphite-monochromated Mo $K\bar{\alpha}$ radiation, ω:2θ scan technique. Cell parameters obtained by least-squares procedure on 25 reflections, $15 \leq \theta \leq 23°$. Total of 7335 reflections measured in range $1 \leq \theta \leq 25°$; $-11 \leq h \leq 11, -16 \leq k \leq 1, -20 \leq l \leq 8$. No significant changes in the net intensities of three standard reflections ($6\bar{5}\bar{1}$, $6\bar{1}\bar{2}$, $6\bar{2}\bar{4}$) monitored every 3600 s X-ray exposure time. Max. and min. transmission factors for analytical absorption correction 0·8504 and 0·6013 (Sheldrick, 1976). 3712 unique reflections ($R_{\rm int} = 0{\cdot}160$); 3259 satisfied $I \geq 2{\cdot}5\sigma(I)$. Structure solved from the Patterson synthesis and full-matrix least-squares refinement based on F (Sheldrick, 1976). Anisotropic thermal parameters for non-H atoms; H atoms located from difference map but positions not refined. Final refinement on 298 parameters: $R = 0{\cdot}056$, $wR = 0{\cdot}065$, $S = 0{\cdot}89$ for $w = [\sigma^2(F) + 0{\cdot}017|F|^2]^{-1}$, $(\Delta/\sigma)_{\max} \leq 0{\cdot}001$, $\Delta\rho_{\max} = 0{\cdot}70$, $\Delta\rho_{\min} = -0{\cdot}96$ e $\mathrm{Å^{-3}}$; no extinction correction. Scattering factors for H, C, N, O given in *SHELX76* (Sheldrick, 1976) and those for neutral Ru corrected for f' and f'' (Hamilton & Ibers, 1974). University of Adelaide's VAX11/780 VMS4·3 computer system with *SHELX76* (Sheldrick, 1976). Crystallographic results* are summarized in Tables 1 and 2 and Fig. 1.

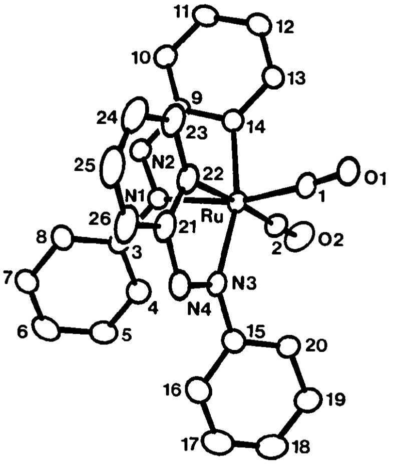

Fig. 1. *ORTEP* drawing (Johnson, 1971) showing the numbering scheme used for $\mathrm{Ru\{C_6H_4N{=}NC_6H_5\}_2(CO)_2}$. Atoms not otherwise indicated are C atoms.

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* Lists of anisotropic thermal parameters, H-atom parameters, all interatomic parameters, mean-plane data, and a full listing of the structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43407 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The structure analysis confirms the stoichiometry of the title compound and the presence of two cyclometallated azobenzene ligands. The crystal structure consists of discrete molecular units; the closest intermolecular contact of 2·21 Å is between O(1) and H(25′) where H(25′) is related by the symmetry operation $x, \frac{1}{2}-y, \frac{1}{2}+z$.

The coordination geometry about the Ru atom is defined by the two pairs of C and N donor atoms from the cyclometallated azobenzene ligands and two mutually *cis* carbonyl groups. N(1) is *trans* to the carbonyl CO(1) and N(3) is *trans* to the metallated C atom, C(14), so that the overall geometry of the complex is similar to that reported for the analogous Os compound (Dawoodi, Mays & Raithby, 1981). The five-membered Ru—C—C—N—N rings are essentially planar; the dihedral angle between the planes is *ca* 109°. The greatest deviations from ideal octahedral geometry about the Ru atom arise as a result of the restricted bite distance of the cyclometallated ligands [N(1)···C(14) 2·58 and N(3)···C(22) 2·60 Å, N(1)—Ru—C(14) 76·7 (3) and N(3)—Ru—C(22) 75·1 (3)°].

The Ru—N(3) [2·155 (7) Å] and Ru—C(22) [2·103 (8) Å] bonds *trans* to CO are longer than those *trans* to N or C(aryl) [Ru—N(1) 2·103 (6), Ru—C(14) 2·052 (7) Å] as expected from the greater *trans* effect of the CO ligands. Similarly, the Ru—CO(2) [1·930 (8) Å] bond is longer than Ru—CO(1) [1·879 (9) Å] as a result of the greater *trans* effect of C(aryl) *vs* N.

For complexes of this type, *i.e.* with *cis* monodentate ligands and two cyclometallated groups, three different arrangements of the cyclometallated donor atoms are possible. The title compound, and the Os analogue, adopt a conformation similar to that found for $\overline{\mathrm{Ru}\{(\mathrm{C_6H_4O})\mathrm{P}}(\mathrm{OC_6H_5})_2\}_2(L)_2$ with $L = \mathrm{P(OC_6H_5)_3}$ (Garbauskas, Kasper & Lewis, 1984) and $L = \mathrm{CO}$ (Bruce, Snow & Tiekink, 1986). An alternative conformation, with the N atoms *trans* and the metallated C atoms *cis* to each other, has been reported for $\overline{\mathrm{Rh}\{\mathrm{C_6H_4N{=}N}}\mathrm{C_6H_5}\}_2(\mathrm{O_2CCH_3})$ (Craik, Knox, Pauson, Hoare & Mills, 1971). The third possible isomer has been found in $\mathrm{Ru(CO)_2(bq)_2}$ (bq = benzo[*h*]quinolin-10-yl), in which both of the N atoms are *trans* to carbonyl groups (Patrick, White, Bruce, Beatson, Black, Deacon & Thomas, 1983).

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Structures of Five *N,N′*-Bis[(dialkoxyphosphinoyl)methyl]-1,4-benzenediamines

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Abstract. *N,N′*-Bis[(diethoxyphosphinoyl)methyl]-1,4-benzenediamine, $\mathrm{C_{16}H_{30}N_2O_6P_2}$ (I), $M_r = 408{\cdot}4$, triclinic, $P\bar{1}$, $a = 5{\cdot}654$ (1), $b = 8{\cdot}732$ (1), $c = 11{\cdot}092$ (1) Å, $\alpha = 75{\cdot}95$ (1), $\beta = 86{\cdot}89$ (1), $\gamma = 84{\cdot}11$ (1)°, $V = 528{\cdot}2$ (4) Å^3, $Z = 1$, $D_x = 1{\cdot}28$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}24$ mm^{-1},

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