# Carbon Compounds of the Transition Metals. Part XXV.[1] Crystal and Molecular Structure of Acetatobis(phenylazophenyl-2C,N')rhodium(II)

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The crystal structure of the title compound (I) shows rhodium co-ordinated octahedrally by the acetate and two azobenzene ligands. This is the first direct confirmation that azobenzene chelates by means of σ-bonds at an ortho-carbon and the lone pair of the further nitrogen, forming a five-membered chelate ring. The crystals are monoclinic with space group Cc, and have $a = 8.847(4)$, $b = 16.760(8)$, $c = 15.710(8)$ Å, and $\beta = 96.14(3)°$. The structure was solved by Patterson and Fourier methods from diffractometer data, and refined by least-squares techniques to R 5.0% for 2318 unique reflections.

SINCE the preparation[2] of the azobenzene complex $(C_{12}H_9N_2)(C_5H_5)Ni$, complexes of many metals have been prepared in which azobenzene is thought to act as a bidentate ligand. A metal–carbon bond was shown[3] to be present in palladium and platinum complexes, and a five-membered chelate ring system was suggested, with the metal bonded to an ortho-carbon atom and the non-adjacent nitrogen atom. We have confirmed this mode of bonding in the crystal structures of two complexes: acetatobis(phenylazophenyl-2C,N')rhodium(III) (I),[4] and the related di-μ-chloro-dicarbonylrhodium(I)bis-(phenylazophenyl-2C,N')rhodium(I) (II),[5] in which acetate has been replaced by the group $Cl_2Rh(CO)_2$. We now report in full the X-ray crystal structure of (I).

(I)   (II)
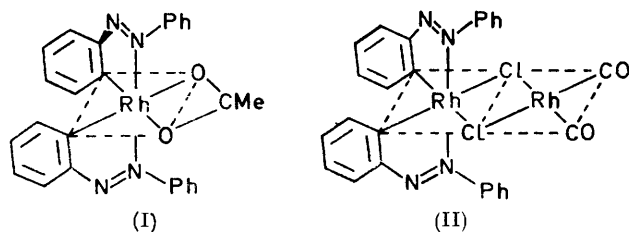
EXPERIMENTAL

Crystal Data.—$C_{26}H_{21}N_4O_2Rh$, $M = 524.4$, Monoclinic, $a = 8.847(4)$, $b = 16.760(8)$, $c = 15.710(8)$ Å, $\beta = 96.14(3)°$, $U = 2316.1$ Å^3, $D_m = 1.50(2)$, $Z = 4$, $D_c = 1.50$, $F(000) = 1064$. Space group $Cc(C_s^4$, No. 9) by systematic absences

and structure solution. Mo-K_α radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) = 7.5 cm^{-1}.

X-Ray intensity data from a deep purple crystal of (I) were collected on a Hilger and Watts computer-controlled four-circle diffractometer[6] as far as $\theta = 28°$ with Mo-K_α radiation. 2318 Unique reflections with intensities $> 3\sigma(F^2)$ were obtained in four shells which were scaled together by counting times. Corrections were applied for Lorentz and polarisation factors.

Solution and Refinement.—Systematic absences indicated space groups Cc or $C2/c$. Co-ordinates for a heavy atom in a general position in Cc, or on a two-fold axis in $C2/c$, were obtained from a Patterson synthesis. A Fourier synthesis was performed with symmetry $C2/c$ using phases calculated for a rhodium atom lying on a two-fold axis. The electron-density map showed an azobenzene ligand superposed on its two-fold rotation image, and the space group Cc was subsequently adopted. The rest of the structure was found in two successive difference-Fourier maps with phases from rhodium and (respectively) eight atoms of the azobenzene group, and all twelve carbon and nitrogen atoms of the same group. The second difference map still showed doubling of the light-atom peaks in pseudo two-fold symmetry because of the dominance of phases by the metal atom. However, the second azobenzene ligand and acetate group were readily located by taking the stronger of thirteen of the pairs of peaks, and the weaker of the remaining three. The structure was confirmed by a further difference-Fourier synthesis.

Refinement of the structure was carried out by the block-diagonal least-squares method, in which the function minimised was $\Sigma w(F_o - |F_c|)^2$. Scattering factors[7,8] were

[1] Part XXIV, R. J. Hoare and O. S. Mills, *J.C.S. Dalton*, 1972, 653.

[2] J. P. Kleiman and M. Dubeck, *J. Amer. Chem. Soc.*, 1963, 85, 1544.

[3] A. C. Cope and R. W. Siekman, *J. Amer. Chem. Soc.*, 1965, 87, 3272.

[4] A. R. M. Craik, G. R. Knox, P. L. Pauson, R. J. Hoare, and O. S. Mills, *Chem. Comm.*, 1971, 168.

[5] R. J. Hoare and O. S. Mills, following paper.

[6] D. B. G. Edwards, K. Bowden, J. Standeven, and O. S. Mills, *Computer Bulletin*, 1966, 10, 54.

[7] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, 42, 3175.

[8] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, 18, 104.

corrected. where appropriate, for the real part of the anomalous dispersion.[9] The imaginary part was ignored in the structure-factor calculation.
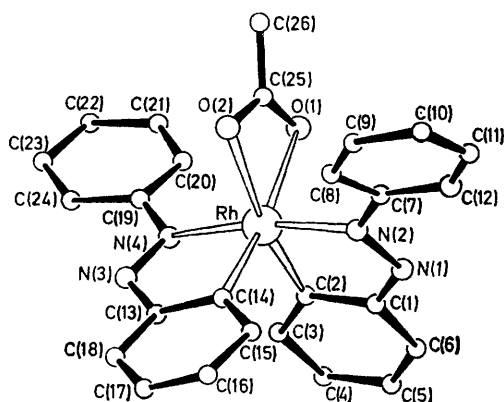

FIGURE 1 A view of the molecule showing the approximate molecular two-fold symmetry

For isotropic refinement of the structure, the 132 refined parameters were grouped in four matrices. Refinement converged (all parameter shifts $<1\sigma$) at R 9·6%, with a weighting scheme $w^{-1} = 12\cdot32 + 0\cdot1691\ F_0$. A difference-Fourier map showed peaks for phenyl protons, some electron density near the acetate methyl carbon, and evidence of anisotropic motion around rhodium.
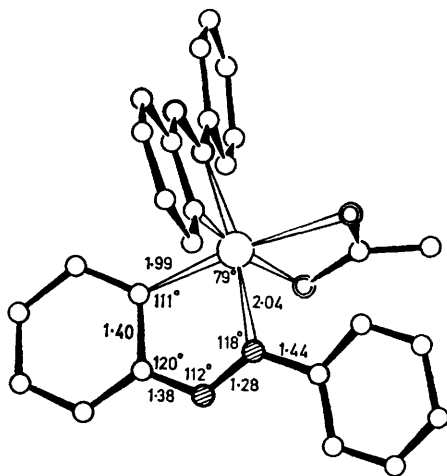

FIGURE 2 A view of the molecule showing mean bonding parameters for the chelate rings

Refinement was continued allowing anisotropic temperature factors to rhodium and the two carbon atoms of the acetate group, the latter having high isotropic temperature factors. The eighteen phenyl hydrogens were placed geometrically, and included in the structure-factor calculation. Refinement converged after four cycles at R 4·99%. In the final refinements, the six largest structure factors were omitted on the grounds of likely extinction, and two weak reflections with $F_0 > 2\cdot5\ kF_c$ were also omitted. The 147 parameters were arranged in four matrices and the weighting function used was $w^{-1} = 5\cdot6 - 0\cdot18\ F_0 + 0\cdot00436\ F_0{}^2$. A final difference-Fourier synthesis revealed no peaks $>0\cdot5$ eÅ^{-3}, except for density of 0·6 eÅ^{-3} which could be attributed to the hydrogen atoms of the methyl group.

[9] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

RESULTS

Table 1 contains the final atomic parameters, and the atom numbering scheme is shown in Figure 1. Molecular geometry calculations are shown in Table 2. There were no intermolecular contacts $<3\cdot5$ Å (ignoring hydrogen atoms).

TABLE 1

Atomic parameters

Atom	x/a	y/b	z/c	$B/\text{Å}^2$
Rh	0·0000	0·06283(3)	0·2500	*
N(1)	0·0389(10)	−0·1031(5)	0·2916(6)	4·65(15)
N(2)	0·1094(9)	−0·0358(5)	0·2982(6)	3·97(13)
C(1)	−0·1070(11)	−0·0948(6)	0·2521(6)	4·09(15)
C(2)	−0·1624(10)	−0·0187(5)	0·2308(6)	3·79(15)
C(3)	−0·3132(13)	−0·0106(7)	0·1952(7)	4·96(19)
C(4)	−0·4033(14)	−0·0790(7)	0·1816(8)	5·67(23)
C(5)	−0·3454(19)	−0·1532(7)	0·2056(8)	5·39(21)
C(6)	−0·1997(13)	−0·1620(7)	0·2403(7)	5·02(19)
C(7)	0·2627(11)	−0·0298(6)	0·3427(6)	4·11(16)
C(8)	0·3211(14)	0·0283(8)	0·3804(8)	5·55(22)
C(9)	0·4629(17)	0·0252(9)	0·4275(10)	6·94(28)
C(10)	0·5444(17)	−0·0448(9)	0·4311(10)	6·71(28)
C(11)	0·4819(16)	−0·1128(9)	0·3923(9)	6·65(27)
C(12)	0·3399(13)	−0·1115(7)	0·3473(7)	5·11(20)
N(3)	−0·2110(10)	0·1912(6)	0·2662(6)	5·00(16)
N(4)	−0·1389(8)	0·1571(4)	0·2104(5)	3·58(12)
C(13)	−0·1843(12)	0·1571(6)	0·3464(7)	4·81(18)
C(14)	−0·0847(11)	0·0912(6)	0·3591(6)	3·95(15)
C(15)	−0·0583(13)	0·0570(7)	0·4388(7)	5·03(19)
C(16)	−0·1225(16)	0·0946(8)	0·5063(9)	6·05(25)
C(17)	−0·2146(16)	0·1577(9)	0·4935(9)	6·83(29)
C(18)	−0·2489(15)	0·1900(9)	0·4144(9)	6·46(25)
C(19)	−0·1633(10)	0·1914(6)	0·1275(6)	3·93(15)
C(20)	−0·1145(12)	0·1516(7)	0·0598(7)	4·97(20)
C(21)	−0·1299(14)	0·1842(8)	−0·0233(8)	5·92(23)
C(22)	−0·1955(15)	0·2570(8)	−0·0373(8)	6·08(24)
C(23)	−0·2473(16)	0·3001(9)	0·0321(9)	6·74(27)
C(24)	−0·2313(14)	0·2654(7)	0·1149(8)	5·64(22)
O(1)	0·1388(9)	0·0483(5)	0·1398(5)	5·28(14)
O(2)	0·1991(9)	0·1410(5)	0·2382(5)	5·08(13)
C(25)	0·2250(12)	0·1066(6)	0·1697(7)	*
C(26)	0·3567(20)	0·1361(9)	0·1249(13)	*
H(3)	−0·360	0·048	0·179	6
H(4)	−0·519	−0·074	0·152	7
H(5)	−0·419	−0·205	0·196	7
H(6)	−0·156	−0·221	0·258	6
H(8)	0·258	0·083	0·374	7
H(9)	0·510	0·078	0·460	8
H(10)	0·543	−0·104	0·457	8
H(11)	0·546	−0·168	0·397	8
H(12)	0·291	−0·165	0·317	7
H(15)	0·010	0·004	0·449	6
H(16)	−0·098	0·071	0·570	7
H(17)	−0·262	0·184	0·548	7
H(18)	−0·328	0·240	0·406	6
H(20)	−0·063	0·094	0·070	7
H(21)	−0·089	0·152	−0·076	8
H(22)	−0·208	0·282	−0·100	8
H(23)	−0·298	0·358	0·002	8
H(24)	−0·271	0·297	0·168	7

* Anisotropic thermal parameters ($\times 10^4$)

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Rh †	1459(7)	226(1)	302(2)	−71(7)	86(3)	−17(4)
C(25)	167(15)	38(4)	65(5)	14(6)	26(7)	17(4)
C(26)	275(29)	64(7)	145(14)	17(11)	132(17)	23(8)

These are defined in the expression

$$\exp-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{23}kl + 2b_{31}lh + 2b_{12}hk)$$

† Rh parameters $\times 10^5$.

TABLE 2

Molecular geometry

(a) Intramolecular distances (Å)

Rh–N(2)	2·022(8)	Rh–N(4)	2·057(9)
Rh–C(2)	1·982(9)	Rh–C(4)	2·000(9)
Rh–O(1)	2·241(8)	Rh–O(2)	2·220(8)
C(1)–C(2)	1·39(1)	C(13)–C(14)	1·41(1)
C(2)–C(3)	1·40(1)	C(14)–C(15)	1·37(1)
C(3)–C(4)	1·40(2)	C(15)–C(16)	1·40(2)
C(4)–C(5)	1·38(2)	C(16)–C(17)	1·34(2)
C(5)–C(6)	1·35(2)	C(17)–C(18)	1·36(2)
C(1)–C(6)	1·40(1)	C(13)–C(18)	1·38(2)
C(1)–N(1)	1·38(1)	C(13)–N(3)	1·38(1)
N(1)–N(2)	1·29(1)	N(3)–N(4)	1·27(1)
N(2)–C(7)	1·46(1)	N(4)–C(19)	1·42(1)
C(7)–C(12)	1·38(1)	C(19)–C(24)	1·38(2)
C(7)–C(8)	1·36(2)	C(19)–C(20)	1·36(1)
C(8)–C(9)	1·39(2)	C(20)–C(21)	1·41(2)
C(9)–C(10)	1·37(2)	C(21)–C(22)	1·36(2)
C(10)–C(11)	1·38(2)	C(22)–C(23)	1·42(2)
C(11)–C(12)	1·37(2)	C(23)–C(24)	1·42(2)
C(25)–O(1)	1·30(1)	C(25)–O(2)	1·26(1)
C(25)–C(26)	1·51(2)		

(b) Intramolecular angles (°)

N(2)–Rh–C(2)	78·7(3)	N(4)–Rh–C(14)	79·1(3)
O(1)–Rh–O(2)	59·6(3)	N(2)–Rh–N(4)	171·2(3)
O(1)–Rh–C(2)	104·8(3)	O(2)–Rh–C(14)	107·8(3)
Rh–C(2)–C(1)	111·3(6)	Rh–C(14)–C(13)	110·5(7)
C(2)–C(1)–N(1)	119·3(8)	C(14)–C(13)–N(3)	119·7(9)
C(1)–N(1)–N(2)	111·7(8)	C(13)–N(3)–N(4)	113·1(9)
N(1)–N(2)–Rh	118·5(6)	N(3)–N(4)–Rh	117·6(6)
C(1)–C(2)–C(3)	118·8(9)	C(13)–C(14)–C(15)	119·8(9)
C(2)–C(3)–C(4)	119·0(10)	C(14)–C(15)–C(16)	117·3(10)
C(3)–C(4)–C(5)	120·5(11)	C(15)–C(16)–C(17)	122·1(13)
C(4)–C(5)–C(6)	121·2(11)	C(16)–C(17)–C(18)	121·7(14)
C(5)–C(6)–C(1)	119·1(10)	C(17)–C(18)–C(13)	118·5(13)
C(6)–C(1)–C(2)	121·4(9)	C(18)–C(13)–C(14)	120·5(10)
C(6)–C(1)–N(1)	119·2(9)	C(18)–C(13)–N(3)	119·8(10)
N(1)–N(2)–C(7)	114·6(8)	N(3)–N(4)–C(19)	114·3(8)
N(2)–C(7)–C(3)	117·4(9)	N(4)–C(19)–C(20)	119·2(9)
C(7)–C(8)–C(9)	118·7(12)	C(19)–C(20)–C(21)	121·7(11)
C(8)–C(9)–C(10)	119·6(14)	C(20)–C(21)–C(22)	119·7(12)
C(9)–C(10)–C(11)	120·2(14)	C(21)–C(22)–C(23)	119·9(13)
C(10)–C(11)–C(12)	120·9(13)	C(22)–C(23)–C(24)	119·1(13)
C(11)–C(12)–C(7)	117·5(11)	C(23)–C(24)–C(19)	119·9(11)
C(12)–C(7)–C(8)	122·9(10)	C(24)–C(19)–C(20)	119·7(9)
Rh–O(1)–C(25)	89·3(6)	Rh–O(2)–C(25)	91·1(7)
O(1)–C(25)–C(26)	122·2(12)	O(2)–C(25)–C(26)	117·9(12)
O(1)–C(25)–O(2)	119·9(9)		

(c) Least-squares planes defined by atomic positions,* with distances (Å) of relevant atoms from the planes given in square brackets

Plane (i):

N(1), N(2), C(1), C(2) $-0.4108X + 0.1132Y + 0.9047Z$
$= 9.9646$

[Rh -0.140, N(1) 0.020, N(2) -0.011, C(1) -0.020, C(2) 0.011]

Plane (ii):

N(3), N(4), C(13), C(14) $0.7503X + 0.6226Y + 0.2222Z$
$= 1.1822$

[Rh 0.026, N(3) 0.001, N(4) 0.000, C(13) -0.001, C(14) 0.000]

Plane (iii):

C(1)—(6) $-0.3895X + 0.1120Y + 0.9142Z$
$= 3.9666$

[C(1) -0.012, C(2) 0.005, C(3) 0.008, C(4) -0.013, C(5) 0.007, C(6) 0.006, Rh -0.115, N(1) 0.061, N(2) 0.042]

TABLE 2 (Continued)

Plane (iv):

C(7)—(12) $-0.5037X - 0.2386Y + 0.8303Z$
$= 3.7229$

[C(7) 0.000, C(8) -0.012, C(9) 0.019, C(10) -0.013, C(11) 0.001, C(12) 0.006, N(2) 0.052]

Plane (v):

C(13)—(18) $-0.7738X - 0.6085Y - 0.1758Z$
$= -0.8452$

[C(13) 0.004, C(14) -0.024, C(15) 0.029, C(16) -0.013, C(17) -0.007, C(18) 0.012, Rh -0.157, N(3) -0.045, N(4) -0.110]

Plane (vi):

C(19)—(24) $-0.8817X - 0.4340Y - 0.1853Z$
$= -0.2946$

[C(19) -0.004, C(20) 0.000, C(21) 0.001, C(22) 0.001, C(23) -0.005, C(24) 0.006, N(4) -0.062]

Plane (vii):

O(1), O(2), C(25), C(26) $0.5514X - 0.6491Y + 0.5241Z$
$= 1.1674$

[O(1) -0.001, O(2) -0.001, C(25) 0.003, C(26) -0.001, Rh -0.036]

* In the following equations, X, Y, Z refer to orthogonal co-ordinates obtained by the transformation

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} a & 0 & c\cos\beta \\ 0 & b & 0 \\ 0 & 0 & c\sin\beta \end{bmatrix} \begin{bmatrix} x/a \\ y/b \\ z/c \end{bmatrix}$$

The agreement analysis at the final cycle of refinement and the list of observed and calculated structure factors are published in Supplementary Publication No. SUP 20410 (23 pp., 1 microfiche).†

DISCUSSION

The rhodium atom is surrounded by two azobenzene molecules and an acetate ion, all of which act as bidentate ligands. Each azobenzene σ-bonds to rhodium through an *ortho*-carbon atom and the lone pair of the further nitrogen, forming a five-membered chelate ring. [This ring skeleton is similar to that found in the diazo-ester adduct $(\pi\text{-}C_5H_5)(CO)_2MoN(H)NC(CO_2Et)COH$.[10]] The acetate group lies on an idealised molecular two-fold axis, and completes a distorted octahedral co-ordination about the metal. The two Rh–N bonds are *trans*, and the two Rh–C bonds *cis* to one another. The bond distances and angles of the two azobenzene ligands related by the molecular symmetry do not differ significantly, and some mean values are shown in Figure 2.

The four phenyl rings and the acetate group are planar [planes (iii)—(vii), Table 2], and have normal bond parameters (mean phenyl C–C 1·38 Å, range 1·34—1·42 Å). The free phenyl group of each azobenzene ligand is twisted away from the acetate group by rotation about the C–N bond, with torsion angles +22° [N(1)–N(2)–C(7)–C(12)] and +14° [N(3)–N(4)–C(19)–C(24)]. The chelate skeletons are planar [planes (i) and (ii), Table 2], but the rhodium atoms lie significantly out of those planes (by 0·140 and 0·026 Å respectively).

10 J. R. Knox and C. K. Prout, *Acta Cryst.*, 1969, **B25**, 1952.

Table 3 shows in detail the bond distances and angles of the four chelate rings occurring in (I) and (II). The last column shows the mean value for each parameter,

TABLE 3

Bonding parameters of chelate rings in (I) and (II)

(a) Distances (Å)

	(I)		(II)		
Rh–C	1·982(9)	2·000(9)	1·988(16)	1·980(17)	1·989
Rh–N	2·022(8)	2·057(9)	2·021(16)	2·042(15)	2·036
N–N	1·287(12)	1·274(11)	1·335(22)	1·311(23)	1·289
N–C	1·377(13)	1·381(14)	1·383(22)	1·376(22)	1·379
C–C	1·395(13)	1·415(14)	1·358(22)	1·435(24)	1·401
C–N (exocyclic)	1·460(12)	1·419(11)	1·396(22)	1·403(21)	1·429

(b) Angles (°)

	(I)		(II)		
C–Rh–N	79·7(3)	79·1(3)	79·1(7)	79·3(7)	79·4
Rh–N–N	118·5(6)	117·6(6)	116·2(12)	117·4(12)	117·8
N–N–C	111·7(8)	113·1(9)	112·6(15)	112·6(16)	112·4
N–C–C	119·3(8)	119·7(9)	118·8(17)	118·4(17)	119·3
C–C–Rh	111·3(6)	110·5(7)	113·1(13)	111·6(13)	111·2
N–C–N (exocyclic)	114·6(8)	114·3(8)	115·0(16)	114·6(15)	114·5

weighted according to their standard deviations (mean = $\Sigma p_i/\sigma_i^2/\Sigma 1/\sigma_i^2$). No parameter differs by $>2·5\sigma$ from the mean. Since the ring geometries agree thus satisfactorily, the mean values of the parameters only will be discussed.

[11] R. Mason and A. D. C. Towl, *J. Chem. Soc. (A)*, 1970, 1601.
[12] G. C. Dobinson, R. Mason, and D. R. Russell, *Chem. Comm.*, 1967, 62.

Both the Rh–N and Rh–C bond distances (Table 3) are shorter than Rh[III] co-ordination distances in comparable structures. The mean Rh–N distance of 2·036 Å may be compared with Rh[III]–N(sp^2) distances in pyridine (py) complexes: 2·112(14) and 2·123(13) in (py)$_2$-(CH$_2$·C$_6$H$_4$·PPh$_2$)Cl$_2$Rh; [11] 2·09(2) (mean) in [(py)$_4$Cl$_2$Rh]-[H(NO$_3$)$_2$],[12] and 2·09(2) Å (mean) in [(4-picoline)$_2$Cl$_2$-(C$_8$H$_{15}$O$_2$)Rh]$_2$.[13] The mean Rh–C distance of 1·989 Å is shorter than values of 2·07—2·08 Å found for five neutral Rh[III] complexes,[14] or 2·048(16) Å in [Rh(NH$_3$)$_5$-Et]Br$_2$,[15] even allowing for a decrease of 0·04 Å in covalent radius from C(sp^3) to C(sp^2). This shortening of the Rh–C and Rh–N bonds in both (I) and (II) can be interpreted in terms a d_π–p_π bonding interaction between filled metal orbitals and the π-bonding system of the chelate skeleton, or as a chelate effect.

[13] J. A. Evans, D. R. Russell, A. Bright, and B. L. Shaw, *Chem. Comm.*, 1971, 841.
[14] Ref. 11 and references therein.
[15] A. C. Skapski and P. G. H. Troughton, *Chem. Comm.*, 1969, 666.