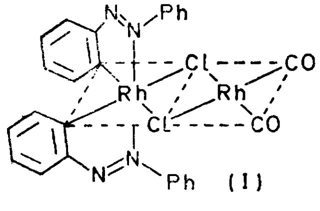
Carbon Compounds of the Transition Metals. Part XXVI.[1] Crystal and Molecular Structure of Di-μ-chloro-dicarbonylrhodium(I)bis(phenylazophenyl-2*C*,*N*′)rhodium(III)

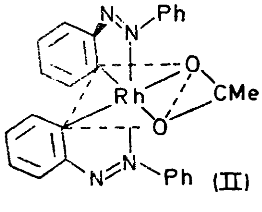
By **R. J. Hoare** and **O. S. Mills,*** Department of Chemistry, University of Manchester, Manchester M13 9PL

The crystal structure of the title compound (I) contains an octahedral bis(phenylazophenyl)rhodium moiety (with two five-membered Rh–C–C–N–N chelate rings) attached to a square planar dicarbonylrhodium group *via* two chlorine bridge atoms. The Rh · · · Rh distance is 3·551(2) Å and the molecule is folded about the chlorine bridge by 27°. The Rh–Cl distances *trans* to the Rh–C(CO) and Rh–C(Ph_2N_2) bonds respectively are 2·374(5) and 2·532(5) Å. The crystals are trigonal with *a* = 23·363(7) and *c* = 17·689(5) Å, space group $P\bar{3}c1$. The structure was solved from diffractometer data by Patterson and Fourier methods and refined by large-block-diagonal least-squares techniques to *R* 6·3% for 1797 unique reflections.

AMONGST recently reported[2] complexes of rhodium which contain azobenzene is di-μ-chloro-dicarbonylrhodium(I)bis(phenylazophenyl-2*C*,*N*′)rhodium(III) (I). We have subjected (I) to structure analysis to confirm the different environments of the rhodium atoms, for comparison of the bonded azobenzene ligands with those in acetatobis(phenylazophenyl-2*C*,*N*′),[1,2a] and to study the nature of the chlorine bridge which, in other rhodium complexes, has been shown to be capable of considerable variation.



(I)



(II)

EXPERIMENTAL

Crystal Data.—$C_{26}H_{18}Cl_2N_4O_2Rh_2$, $M = 695{\cdot}2$, Trigonal, $a = 23{\cdot}363(7)$, $c = 17{\cdot}689(5)$ Å, $U = 8361{\cdot}4$ Å^3, $D_m = 1{\cdot}68(2)$, $Z = 12$, $D_c = 1{\cdot}66$, $F(000) = 4080$. Space group $P\bar{3}c1$ (D^4_{3d}, No. 165). Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) = 13·8 cm^{-1}.

Fine yellow needles of (I) had hexagonal cross-section. Intensity data were collected on a Hilger and Watts

---

[1] Part XXV, R. J. Hoare and O. S. Mills, preceding paper.

[2] (*a*) A. R. M. Craik, G. R. Knox, P. L. Pauson, R. J. Hoare, and O. S. Mills, *Chem. Comm.*, 1971, 168; (*b*) M. I. Bruce, B. L. Goodall, M. Z. Iqbal, and F. G. A. Stone, *Chem. Comm.*, 1971, 661.

computer-controlled four-circle diffractometer[3] as far as $\theta = 25°$ with Mo-K_α radiation. 1797 unique reflexions with intensities $>3\sigma(F^2)$ were obtained in five shells which were scaled together by counting times. Corrections were applied for Lorentz and polarisation factors.

Solution and Refinement.—The diffraction symbol is $P\,.\,.\,c$ and the absence of a mirror plane perpendicular to the unique axis eliminated the hexagonal Laue groups $6/m$ and $6/mmm$ so that the only space groups to be considered were $P3c1$ and $P\bar{3}c1$ which contain 6 and 12 general positions respectively. As chemical evidence suggested that the molecule was at most a dimer of the unit [phenylazophenyl(chloro)carbonylrhodium], and the unit cell corresponded to 24 such units, the most likely situation involved one dimer per asymmetric unit of the space group $P\bar{3}c1$, although the other possibilities were not excluded. The foregoing was confirmed from a Patterson synthesis which contained a complete vector set for two rhodium atoms *ca.* 3·3 Å apart in accord with the symmetry of the space group $P\bar{3}c1$. In addition vectors attributable to the chlorine atoms were recognised so that with these four atoms, phases sufficiently accurate for the heavy-atom method to be effective were available and all 32 light atoms were obtained from two successive difference-Fourier syntheses after the heavy-atom positions had been corrected.

The structure was refined by the large-block-diagonal least-squares method in which the function minimised was $\Sigma w(F_o - k|F_c|)^2$. Scattering factors used[4,5] were corrected, where appropriate, for the real part of the anomalous dispersion effect.[6] Isotropic refinement converged after 6 cycles (the first with heavy-atom parameters only) at R 10·4%. For this, the 145 parameters which were refined were arranged in three matrices.

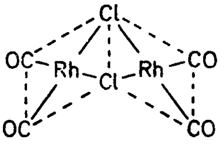
A difference-Fourier synthesis contained peaks which corresponded to the phenyl protons and indications of markedly anisotropic distribution about the heavy-atom positions. On this basis, supplemented by high B_{iso} values, anisotropic temperature factors were allowed for the rhodium and chlorine atoms and for the carbon and oxygen atoms in the two carbonyl groups in subsequent refinement. The eighteen phenyl protons were positioned geometrically assuming C–H 1·08 Å. The 186 parameters were grouped in six matrices for refinement. With weights given by $w^{-1} = 147 - 2{\cdot}38(F_o/k) + 0{\cdot}0132(F_o/k)^2$, refinement converged in four cycles in which seven weak reflexions with $F_o > 2{\cdot}5k\,.\,F_c$ were omitted. The final R was 6·3% and there were 9·6 observed data per parameter refined. A final difference-Fourier synthesis contained no difference density $>0{\cdot}6$ eÅ^{-3} in the body of the cell except close to the rhodium positions and to the three-fold axis, where values of *ca.* 1 eÅ^{-3} occurred.

RESULTS

Table 1 shows the atomic parameters after the final refinement, and Table 2 some results of molecular geometry calculations. A Table showing the agreement analyses and lists of observed and calculated structure factors are in Supplementary Publication No. SUP 20411 (13 pp., 1 microfiche).*

DISCUSSION

The structure of (I) can be considered as derived from those of (II) and $[Rh(CO)_2Cl]_2$ (III)[7] where the acetato-group in (II) has been replaced by a square planar $Rh(CO)_2Cl_2$ unit. On this basis one can assign formal oxidation states of +1 and +3 to atoms Rh(2) and Rh(1) respectively (Figure 1).



(III)

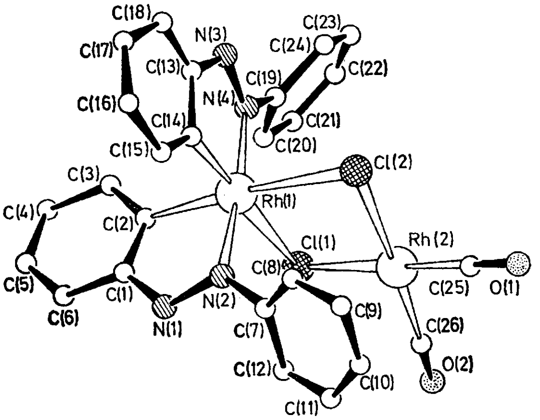


FIGURE 1 View of the molecule with atom numbering scheme

The rhodium atoms, 3·551(2) Å apart, are bridged by two chlorine atoms in a 'folded' configuration, like that in (III). The angle of fold, *i.e.* the dihedral angle

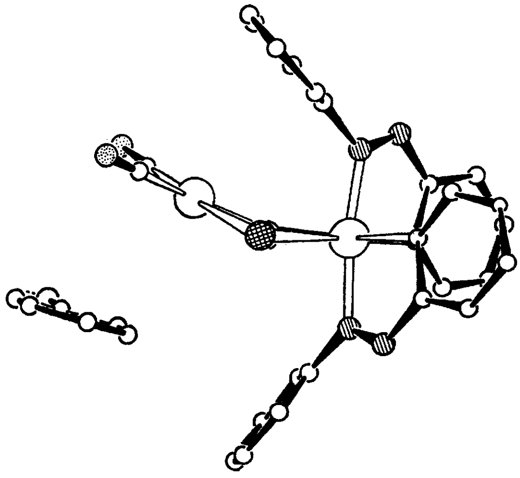
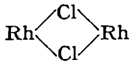


FIGURE 2 View of the molecule illustrating the folded  group and the packing of the square planar $Cl_2Rh(CO)_2$ group between two phenyl groups

---

* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

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

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

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

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

[7] L. F. Dahl, C. Martell, and D. L. Wampler, *J. Amer. Chem. Soc.*, 1961, **83**, 1761.

Table 1

Final atomic parameters, with estimated standard deviations in parentheses (in the units of the last decimal place)

Atom	x/a	y/b	z/c	B/Å^2
Rh(1)	0·12650(7)	0·41065(7)	0·08827(8)	
Rh(2)	0·21425(8)	0·32338(8)	0·07372(10)	
Cl(1)	0·13375(25)	0·33034(24)	−0·00122(29)	
Cl(2)	0·23719(21)	0·42533(23)	0·12931(28)	
N(1)	0·0015(8)	0·3011(8)	0·1335(9)	6·29(36)
N(2)	0·0660(8)	0·3284(8)	0·1478(9)	6·06(35)
C(1)	−0·0125(9)	0·3387(9)	0·0844(10)	5·31(40)
C(2)	0·0385(8)	0·3933(8)	0·0527(9)	4·42(35)
C(3)	0·00260(10)	0·4287(10)	0·0017(11)	6·44(45)
C(4)	−0·0401(11)	0·4095(12)	−0·0183(12)	7·47(54)
C(5)	−0·0884(11)	0·3561(10)	0·0186(11)	6·61(47)
C(6)	−0·0779(10)	0·3193(10)	0·0674(11)	6·19(45)
C(7)	0·0833(10)	0·2908(10)	0·1937(11)	5·67(43)
C(8)	0·1257(11)	0·3199(11)	0·2520(12)	6·83(49)
C(9)	0·1474(12)	0·2882(12)	0·2981(13)	8·19(55)
C(10)	0·1277(12)	0·2255(13)	0·2852(13)	8·20(58)
C(11)	0·0852(13)	0·1933(13)	0·2245(14)	8·78(61)
C(12)	0·0619(11)	0·2248(12)	0·1778(13)	7·49(52)
N(3)	0·1960(8)	0·5523(8)	0·0673(9)	6·62(38)
N(4)	0·1827(8)	0·4976(7)	0·0322(9)	5·87(35)
C(13)	0·1607(9)	0·5407(10)	0·1333(11)	5·64(41)
C(14)	0·1221(9)	0·4738(9)	0·1594(10)	4·83(37)
C(15)	0·0888(10)	0·4594(10)	0·2279(11)	5·97(43)
C(16)	0·0897(12)	0·5122(12)	0·2693(12)	7·78(56)
C(17)	0·1231(12)	0·5751(12)	0·2406(13)	8·01(56)
C(18)	0·1629(12)	0·5918(12)	0·1773(13)	8·10(58)
C(19)	0·2145(9)	0·5071(9)	−0·0378(11)	5·29(40)
C(20)	0·1817(10)	0·4685(10)	−0·0970(12)	6·31(45)
C(21)	0·2133(11)	0·4791(11)	−0·1642(12)	6·88(49)
C(22)	0·2772(11)	0·5266(11)	−0·1724(11)	6·78(49)
C(23)	0·3115(11)	0·5640(11)	−0·1124(13)	7·35(52)
C(24)	0·2840(11)	0·5567(11)	−0·0422(11)	6·87(47)
C(25)	0·2790(11)	0·3197(11)	0·1281(12)	
C(26)	0·1922(11)	0·2438(12)	0·0335(14)	
O(1)	0·3191(10)	0·3181(10)	0·1613(11)	
O(2)	0·1734(10)	0·1928(9)	0·0079(14)	
H(3)	0·0660	0·4721	−0·0246	5
H(4)	−0·0515	0·4372	−0·0586	6
H(5)	−0·1386	0·3430	0·0063	6
H(6)	−0·1193	0·2758	0·0922	5
H(8)	0·1427	0·3718	0·2636	6
H(9)	0·1821	0·3156	0·3433	7
H(10)	0·0770	0·1868	0·2816	7
H(11)	0·0707	0·1421	0·2125	7
H(12)	0·0282	0·2005	0·1315	6
H(15)	0·0629	0·4092	0·2495	5
H(16)	0·0638	0·5020	0·3218	6
H(17)	0·1192	0·6132	0·2702	6
H(18)	0·1954	0·6433	0·1611	5
H(20)	0·1308	0·4295	−0·0912	6
H(21)	0·1865	0·4486	−0·2118	7
H(22)	0·3011	0·5357	−0·2275	7
H(23)	0·3628	0·6021	−0·1203	7
H(24)	0·3125	0·5871	0·0056	6

* Anisotropic thermal parameters defined in the expression

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

Atom	10^5b_{11}	10^5b_{22}	10^5b_{33}	10^5b_{12}	10^5b_{31}	10^5b_{23}
Rh(1)	219(4)	213(4)	445(6)	94(3)	0(4)	−33(4)
Rh(2)	340(5)	303(5)	562(7)	184(4)	94(5)	56(5)
Cl(1)	372(16)	317(15)	550(21)	169(13)	−5(15)	−81(15)
Cl(2)	243(13)	309(14)	541(22)	114(11)	−8(14)	−36(15)

	10^4b_{11}	10^4b_{22}	10^4b_{33}	10^4b_{12}	10^4b_{31}	10^4b_{23}
C(25)	40(8)	54(9)	69(11)	27(7)	−6(7)	−4(8)
C(26)	48(9)	42(8)	87(13)	29(7)	9(8)	−4(8)
O(1)	68(8)	76(9)	107(11)	45(8)	−17(8)	10(8)
O(2)	75(9)	47(6)	140(13)	31(6)	8(9)	−19(8)

Table 2

Molecular geometry

(*a*) Bond distances (Å)

Rh(1)–Cl(1)	2·525(5)	Rh(1)–Cl(2)	2·539(5)
Rh(1)–N(2)	2·021(16)	Rh(1)–N(4)	2·042(15)
Rh(1)–C(2)	1·988(16)	Rh(1)–C(14)	1·980(17)
Rh(2)–Cl(1)	2·372(5)	Rh(2)–Cl(2)	2·377(5)
Rh(2)–C(25)	1·830(23)	Rh(2)–C(26)	1·809(23)
N(1)–C(1)	1·383(22)	N(3)–C(13)	1·376(22)
N(1)–N(2)	1·335(22)	N(3)–N(4)	1·311(22)
N(2)–C(7)	1·396(22)	N(4)–C(19)	1·403(21)
C(1)–C(6)	1·393(25)	C(13)–C(18)	1·405(27)
C(1)–C(2)	1·358(22)	C(13)–C(14)	1·435(24)
C(2)–C(3)	1·351(24)	C(14)–C(15)	1·388(23)
C(3)–C(4)	1·419(27)	C(15)–C(16)	1·425(27)
C(4)–C(5)	1·358(28)	C(16)–C(17)	1·373(29)
C(5)–C(6)	1·326(25)	C(17)–C(18)	1·382(28)
C(7)–C(12)	1·392(27)	C(19)–C(24)	1·452(26)
C(7)–C(8)	1·356(25)	C(19)–C(20)	1·344(24)
C(8)–C(9)	1·358(28)	C(20)–C(21)	1·354(25)
C(9)–C(10)	1·317(30)	C(21)–C(22)	1·351(26)
C(10)–C(11)	1·400(29)	C(22)–C(23)	1·353(26)
C(11)–C(12)	1·384(30)	C(23)–C(24)	1·369(26)
C(25)–O(1)	1·123(23)	C(26)–O(2)	1·138(24)
Rh(1)–Rh(2)	3·551(2)	Cl(1)–Cl(2)	3·276(7)

(*b*) Bond Angles (°)

Cl(1)–Rh(1)–Cl(2)	80·6(2)	N(2)–Rh(1)–N(4)	174·6(6)
N(2)–Rh(1)–C(2)	79·1(7)	N(4)–Rh(1)–C(14)	79·3(7)
Cl(1)–Rh(1)–C(14)	179·1(5)	Cl(2)–Rh(1)–C(2)	176·0(5)
C(25)–Rh(2)–C(26)	88·7(10)	Cl(1)–Rh(2)–Cl(2)	87·2(2)
C(25)–Rh(2)–Cl(1)	177·5(7)	C(26)–Rh(2)–Cl(2)	176·8(7)
Rh(1)–Cl(1)–Rh(2)	92·9(2)	Rh(1)–Cl(2)–Rh(2)	92·4(2)
C(1)–N(1)–N(2)	112·6(15)	C(13)–N(3)–N(4)	112·6(16)
N(1)–N(2)–Rh(1)	116·2(12)	N(3)–N(4)–Rh(1)	117·4(12)
N(1)–N(2)–C(7)	115·0(16)	N(3)–N(4)–C(19)	114·6(15)
N(1)–C(1)–C(2)	118·8(17)	N(3)–C(13)–C(14)	118·4(17)
C(1)–C(2)–Rh(1)	113·1(13)	C(13)–C(14)–Rh(1)	111·6(13)
C(1)–C(2)–C(3)	119·7(17)	C(13)–C(14)–C(15)	121·0(17)
C(2)–C(3)–C(4)	120·4(19)	C(14)–C(15)–C(16)	118·4(18)
C(3)–C(4)–C(5)	116·4(20)	C(15)–C(16)–C(17)	119·4(20)
C(4)–C(5)–C(6)	124·7(22)	C(16)–C(17)–C(18)	123·0(23)
C(5)–C(6)–C(1)	117·3(19)	C(17)–C(18)–C(13)	118·4(22)
N(2)–C(7)–C(8)	119·8(19)	N(4)–C(19)–C(20)	120·2(18)
N(2)–C(7)–C(12)	121·6(19)	N(4)–C(19)–C(24)	117·7(17)
C(7)–C(8)–C(9)	124·2(21)	C(19)–C(20)–C(21)	119·0(20)
C(8)–C(9)–C(10)	119·0(23)	C(20)–C(21)–C(22)	121·5(21)
C(9)–C(10)–C(11)	119·3(24)	C(21)–C(22)–C(23)	120·0(21)
C(10)–C(11)–C(12)	122·3(24)	C(22)–C(23)–C(24)	122·8(21)
C(11)–C(12)–C(7)	116·7(21)	C(23)–C(24)–C(19)	114·6(19)
Rh(2)–C(25)–O(1)	179·3(22)	Rh(2)–C(26)–O(2)	174·8(22)

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

Plane (i):

Rh(1), Cl(1), Cl(2) $-0{\cdot}1122X - 0{\cdot}7316Y + 0{\cdot}6725Z = -4{\cdot}8219$

Plane (ii):

Rh(2), Cl(1), Cl(2) $-0{\cdot}5101X - 0{\cdot}4967Y + 0{\cdot}7022Z = -2{\cdot}9606$

Plane (iii):

Rh(2), Cl(1), Cl(2), C(25) C(26), O(1), O(2) $-0{\cdot}4919X - 0{\cdot}4608Y + 0{\cdot}7387Z = -2{\cdot}6491$

[Rh(2) −0·007, Cl(1) −0·086, Cl(2) 0·091, C(25) −0·026, C(26) 0·006, O(1) −0·049, O(2) 0·070, Rh(1) 0·880]

TABLE 2 (*Continued*)

Plane (iv):
N(1), N(2), C(1)–C(2) $-0.3794X + 0.5392Y + 0.7519Z = 6.4053$
[N(1) −0·023, N(2) 0·012, C(1) 0·023, C(2) −0·013, Rh(1) −0·053]

Plane (v):
N(3), N(4), C(13), C(14) $0.8810X + 0.0440Y + 0.4710Z = -0.6311$
[N(3) 0·034, N(4) −0·018, C(13) −0·033, C(14) 0·017, Rh(1) 0·110]

Plane (vi):
C(1)—(6) $-0.3503X + 0.5736Y + 0.7404Z = 6.5364$
[C(1) −0·012, C(2) 0·012, C(3) 0·003, C(4) −0·020, C(5) 0·021, C(6) −0·005, Rh(1) 0·031, N(1) −0·073, N(2) 0·013]

Plane (vii):
C(7)—(12) $-0.7471X - 0.2717Y + 0.6066Z = 1.5537$
[C(7) 0·010, C(8) −0·011, C(9) 0·002, C(10) 0·007, C(11) −0·007, C(12) −0·001, N(2) −0·060]

Plane (viii):
C(13)—(18) $0.8537X + 0.1182Y + 0.5071Z = 0.3064$
[C(13) −0·003, C(14) −0·033, C(15) 0·028, C(16) 0·016, C(17) −0·053, C(18) 0·046, Rh(1) −0·104, N(3) 0·020, N(4) −0·145]

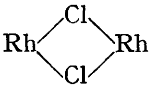
Plane (ix):
C(19)—(24) $0.7019X - 0.6676Y + 0.2484Z = -8.9412$
[C(19) −0·025, C(20) 0·014, C(21) 0·006, C(22) −0·013, C(23) 0·001, C(24) 0·017, N(4) −0·034]

(*d*) Dihedral angles between planes (°)

(i)—(ii)	26·77	(i)—(iii)	27·24
(iv)—(vi)	2·67	(v)—(viii)	4·98
(iv)—(vii)	53·63	(v)—(ix)	45·09

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

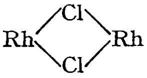
$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} a & b\cos\gamma & 0 \\ 0 & b\sin\gamma & 0 \\ 0 & 0 & c \end{bmatrix} \begin{bmatrix} x/a \\ y/b \\ z/c \end{bmatrix}$$

between the normals to the planes defined by Rh(1), Cl(1), Cl(2) and Rh(2), Cl(1), Cl(2), is 26·8°. Table **3** lists the angles of fold found for other compounds which contain the  bridging arrangement. It is clear that considerable flexibility is possible and that this is not simply related to the formal oxidation state of the metal. It seems that the arrangement adopted reflects steric or crystal-packing factors rather than metal–metal bonding as suggested for the case of (III).

Within the square-co-ordinate $[Rh(CO)_2Cl_2]$ group of (I), mean bond lengths of 1·82(2) and 2·374(5) Å for Rh–C and Rh–Cl respectively agree well with values of 1·81 and 2·355 Å reported for (III).[7] The group is not strictly planar (Figure 2), with a maximum atomic deviation of 0·09 Å from the least-squares plane (iii), Table 2(*c*).

The two azobenzene groups co-ordinate Rh(1) in a way similar to that reported for (II). Each azobenzene ligand forms a five-membered chelate ring with Rh, σ-bonding through an *ortho*-carbon and the lone pair of the nitrogen atom. The two Rh–C bonds are *cis* and the two Rh–N bonds *trans* to one another. Each free phenyl group is twisted out of the plane of the rest of the azobenzene ligand by rotation about the C–N bond. The dihedral angles between the phenyl groups and the chelate rings to which they are attached are 53·6 and 45·1° for the two ligands [Table 2(*c*), planes (iv), (v), (vii), (ix)].

TABLE 3

Compounds with the  group

	Angle of fold/deg.
(cyclo-octa-1,5-diene)$Rh^{I}Cl_2Rh^{I}$(cyclo-octa-1,5-diene)	*ca.* 0 [a]
(cyclo-octa-1,5-diene)$Rh^{I}Cl_2Rh^{I}[(PhO)_3P]_2$	57·4 [b]
$(CO)_2Rh^{I}Cl_2Rh^{I}(CO)_2$	56 [c]
$(C_8H_{15}O_2)$(4-picoline)$_2$$ClRh^{III}Cl_2Rh^{III}Cl$(4-picoline)$_2$-$(C_8H_{15}O_2)$	0 [d]
$(C_6H_{11}O)ClRh^{III}Cl_2Rh^{III}Cl(C_6H_{11}O)$,MeOH	18·2 [e]
(azobenzene)$_2$$Rh^{III}Cl_2Rh^{I}(CO)_2$	26·8 [f]

[a] J. A. Ibers and R. G. Snyder, *Acta Cryst.*, 1962, **15**, 923. [b] J. Coetzer and G. Gafner, *Acta Cryst.* 1970, **B26**, 985. [c] Ref. 7. [d] J. A. Evans, D. R. Russell, A. Bright, and B. L. Shaw, *Chem. Comm.*, 1971, 841. [e] A. Bright, J. F. Malone, J. K. Nicholson, J. Powell, and B. L. Shaw, *Chem. Comm.*, 1971, 712. [f] This work.

TABLE 4

Some rhodium–chlorine distances with various *trans*-ligands

trans-Ligand	*d*(Rh–Cl)/Å	Rh oxidn. state	Cl type
CO	2·374(5) [a,b]	I	br
σ-Ph	2·532(5) [a,b]	III	br
ROH	2·301(6) [a,c]	III	term
Cl	2·32(1) [a,d]	III	term
R_3N	2·33(1) [d]	III	term
pyridine	2·339(4) [e]	III	term
Cl	2·340(7) [a,f]	III	term
Cl	2·34(1) [a,g]	III	term
Cl	2·347(6) [h]	III	term
Cl	2·365(6) [h]	III	br
Cl	2·360(4) [a,i]	III	term
π-olefin	2·386(4) [a,c]	III	br
R_3As	2·39(1) [g]	III	term
σ-alkyl	2·531(4) [e]	III	term
σ-alkyl	2·616(4) [a,c]	III	br
σ-alkyl	2·632(6) [h]	III	br
CO	2·355 [a,j]	I	br
π-olefin	2·38 [k,l]	I	br
π-olefin	2·387(5) [a,m]	I	br
$(PhO)_3P$	2·404(5) [a,m]	I	br

[a] Mean of two. [b] Compound (I), this work. [c] $[(C_6H_{11}O)Cl_2Rh^{III}]_2$,MeOH; Table 3, ref. *e*. [d] $(o\text{-}Me_2N\cdot C_6H_4\cdot AsMe_2)Cl_3Rh^{III}$; G. Bombieri, R. Graziani, C. Panattoni, and L. Volponi, *Chem. Comm.*, 1967, 977. [e] $[o\text{-}CH_2\cdot C_6H_4\cdot P(p\text{-}MeC_6H_4)_2](py)_2Cl_2Rh^{III}$; R. Mason and A. D. C. Towl, *J. Chem. Soc.* (*A*), 1970, 1601. [f] [*trans*-$(py)_4Cl_2Rh^{III}][H(NO_3)_2]$; G. C. Dobinson, R. Mason, and D. R. Russell, *Chem. Comm.*, 1967, 62. [g] $(o\text{-}MeO\cdot C_6H_4\cdot AsMe_2)ClRh^{III}$; G. Bombieri, R. Graziani, C. Panattoni, and L. Volponi, *Chem. Comm.*, 1967, 1284. [h] $[(C_8H_{15}O)$(4-picoline)$_2Cl_2Rh^{III}]_2$; Table 3, ref. *d*. [i] π-$[CH_2C(Me)CH_2](Ph_3As)_2Cl_2Rh^{III}$; T. G. Hewitt, J. J. de Boer, and K. Anzenhofer, *Acta Cryst.* 1970, **B26**, 1244. [j] $[Rh^{I}(CO)_2Cl]_2$; ref. 7. [k] Mean of four. [l] [(cyclo-octa-1,5-diene)$Rh^{I}Cl]_2$; Table 3, ref. *a*. [m] (cyclo-octa-1,5-diene)Rh^{I}-bis(μ-Cl)-$[(PhO)_3P]_2Rh^{I}$; Table 3, ref. *b*.

The two chlorine atoms complete an octahedral coordination of Rh(1). As in (II), this part of the molecule has an idealised C_{2v} symmetry. However, the dihedral angles in (I) are much larger than the corresponding ones (21·4 and 13·4°) in (II) and this reflects the greater bulk of the bridging chloro-group relative to the oxygen atoms of the acetato-group.

The chelating groups are planar [planes (iv) and (v), Table 2(*c*)] but Rh(1) lies slightly out of both planes. The bond distances and bond angles agree very well with those found in (II) and a detailed comparison and discussion is given elsewhere.[1] There we conclude that the mean distances for Rh–C 1·984(6) and Rh–N 2·031(16) Å are both 0·05 Å less than is found for similar single bonds which suggests some degree of metal–ligand multiple bonding in (I). The bond lengths between light atoms are also consistent with some redistribution of the π-electron density around the chelate rings.

The Rh–Cl distances in (I) emphasise the large variations that occur with different *trans*-ligands. Table 4 compares Rh–Cl distances for a number of compounds with a variety of *trans*-ligands, oxidation states, and chlorine types. It will be seen that the results from (I) agree with those from similar compounds and that for Rh^{III} compounds the ligands can be arranged according to their *trans*-bond lengthening effect in the series: ROH $\sim$ amines $\sim$ chlorine $<$ π-olefin $\sim$ arsine $\ll$ σ-alkyl.

We thank Professor P. L. Pauson, who supplied us with a sample of the crystals, and for additional information before publication, the N.A.T.O. and the S.R.C. for awards towards this work, and Drs. L. I. Hodgson and F. S. Stephens who have contributed to the computer programmes used.

[2/334 *Received*, 14*th February*, 1972]