Carbene Complexes. Part VI.[1] Complexes from Imidoyl Chloride and Rhodium(I) Precursors, and the Crystal and Molecular Structure of Carbonyltri-iodo-[α-(*N*-methyl-α-methyliminobenzylamino)benzylidene-*N*,*C*]rhodium, $I_3(OC)\overline{Rh–CPh(NMe)CPh:N}Me$

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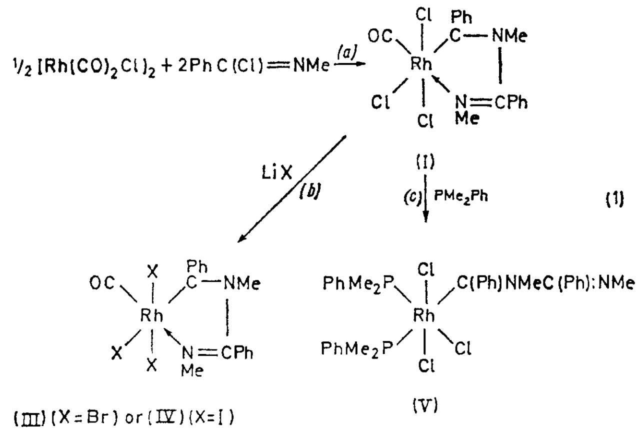
The reaction of an imidoyl chloride $R^1C(Cl):NR^2$ with the Rh^I complex $[Rh(CO)_2Cl]_2$ in the rigorous absence of hydrogen chloride affords the Rh^{III} carbene chelate $Cl_3(OC)\overline{Rh{\cdot}CR^1(NR^2)CR^1:N}R^2$. The chloride ligands are replaceable by Br^- or I^-, and the chelate bridge is cleaved by reaction with a tertiary phosphine. A single-crystal *X*-ray analysis of (IV) $I_3(OC)\overline{Rh{\cdot}CPh(NMe)CPh:N}Me$ by the heavy-atom method has been refined to *R* 0·047 for 2400 independent terms measured on a diffractometer: the complex has an approximately octahedral Rh environment, with Rh–C(carb) 1·968(13), C(carb)–N 1·328(16), Rh–N 2·047(9), Rh–I 2·662(4)—2·774(4), and Rh–C(O) 1·892(14) Å. Crystals are monoclinic, *a* = 10·83(1), *b* = 17·24(2), *c* = 11·52(1) Å, β = 97·3(2)°, *Z* = 4, space group $P2_1/n$.

It was previously shown that the reaction of a Rh^I complex, such as $(Ph_3P)_2(OC)RhCl$, with an imidoyl chloride, such as $PhC(Cl):NMe$, in the presence of hydrogen chloride yields a Rh^{III} carbene complex, such as $Cl_3(Ph_3P)(OC)Rh{\cdot}C(Ph)NHMe$.[1] The product may have been formed by the prior formation of either a salt, such as $[PhC(Cl)NHMe]^+Cl^-$ (see ref. 2), or an imidoyl–rhodium(III) complex, such as $Cl_2(Ph_3P)_2(OC)Rh{\cdot}C(Ph):NMe$. We now describe Rh^I/Rh^{III}–imidoyl chloride systems in which hydrogen chloride is rigorously excluded, and selected chemical and spectroscopic results on the products (see ref. 3, for preliminary data). Final confirmation of a metal carbene structure for such a product comes from a single-crystal *X*-ray analysis; an iodide was chosen only because of the superior quality of the crystals.

presumably CO, was observed [equation (1*a*)]. This reaction may obviously be regarded as similar to that shown in equation (2),[1] except that a second molecule of imidoyl chloride adds in place of hydrogen chloride. The stoicheiometry of both reactions is conveniently described by the term 'three-fragment oxidative addition.'[1-3] The product (I), of reaction (1*a*) is shown as a chelate on the basis of analogy with the crystal data on an analogue (*vide infra*), as is the stereochemistry, also of (III) and (IV).

The dichloromethane-free product (I) was only obtained by drying the crystalline solvated product (II) in a high vacuum for several days.

By reaction with lithium bromide or iodide, (I) readily undergoes exchange of all halide ligands to afford (III) or (IV), respectively [equation (1*b*)]. A more soluble monoreflux with excess of dimethylphenylphosphine in toluene [equation (1*c*)].



$$\tfrac{1}{2}[Rh(CO)_2Cl]_2 + PhC(Cl){:}NMe + HCl$$

$$\frac{1}{n}\,[Cl_3(OC)Rh{\cdot}C(Ph)NHMe]_n \qquad (2)$$

Although *X*-ray structural data show (IV) to be monomeric in the crystal, a molecular-weight determination in chloroform solution implies some association.

An *N*-ethyl derivative (VI), analogous to (I), was formed from PhC(Cl):NEt. Analytical and synthetic data for compounds (I)—(VI) are in Table 1 and spectroscopic results in Table 2. By use of the more hindered imidoyl chlorides, PhC(Cl):NR (R = Pr^i or *o*-$Me{\cdot}C_6H_4$), analogues of (I) were not formed and only very slow formation of $[Cl_3(OC)Rh{\cdot}C(Ph)NHR]_n$ was observed; this is clearly due to the slow hydrolytic production of hydrogen chloride.[1]

Compounds (I), (II), and (VI) show carbonyl stretching modes which are higher than those observed for $Cl_3(OC)Ph_3PRh{\cdot}C(Ph)NHMe$ and similar Rh^{III} carbene complexes.[1] As ν(CO) for Rh^{III} complexes is influenced primarily by the group *trans* to CO, we suggest that either the latter compounds have a different stereochemistry or possibly that the chelating carbene system [*e.g.*, in (I)] removes extra π-electron density from rhodium. Exchange of the chloride ligands of compound (I) for less-electronegative halides results in a lowering of ν(CO) in the bromide (III) and iodide (IV).

Within the C–N–C–N system, the imino N=C bond is expected to give rise to a single absorption band in the 1600—1700 cm^{-1} region, while another band in this region should result from the C(carb)$\overset{...}{-}$N bond;[1] this is consistent with the data of Table 2.

Structural information on compounds (I)—(V) is inferred not only by analogy with the crystal data, but also

TABLE 1

Analytical data, melting points, colours, and yields

	Compound	M.p./°C	Colour	Yield (%)	Found (%)			Required (%)		
					C	H	N	C	H	N
(I)	$Cl_3(OC)Rh{\cdot}C(Ph)N(Me)C(Ph)NMe$ [a]	>300	Yellow	73	43·1	3·40	5·95	43·1	3·41	5·92
(II)	$Cl_3(OC)Rh{\cdot}C(Ph)N(Me)C(Ph)NMe,CH_2Cl_2$ [b]	>300 [b]	Yellow	73	38·5	3·65	5·00	38·7	3·25	5·02
(III)	$Br_3(OC)Rh{\cdot}C(Ph)N(Me)C(Ph)NMe$	>300	Orange	82	33·9	2·85	4·50	33·6	2·66	4·62
(IV)	$I_3(OC)Rh{\cdot}C(Ph)N(Me)C(Ph)NMe$	240—242	Red	57	27·4	2·15	3·70	27·3	2·16	3·75
(V)	$Cl_3(Me_2PhP)_2Rh{\cdot}C(Ph)N(Me)C(Ph)NMe$	187—189	Yellow	34	52·8	5·50	3·90	53·2	5·31	3·88
(VI)	$Cl_3(OC)Rh{\cdot}C(Ph)N(Et)C(Ph)NEt$	>300	Yellow	69	45·2	4·35	5·60	45·5	4·02	5·58

[a] Found: *M*, 685. $C_{17}H_{16}Cl_3N_2ORh$ requires *M*, 474. [b] Compound loses CH_2Cl_2 at lower temperature.

TABLE 2

I.r.[a] and ^1H n.m.r.[b] data

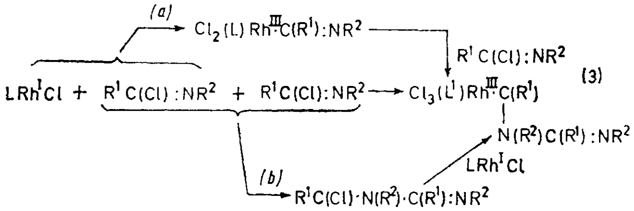
	Compound	ν(CO)	ν(CN)	ν(RhCl)	τ(Ph) [c]	τ(NCH)	τ(CMe)	τ(PMe)
(I)	$Cl_3(OC)Rh{\cdot}C(Ph)N(Me)C(Ph)NMe$	2120	1656, 1502	355vs, 332m, 315w	2·37	6·18s, 6·65s		
(II)	$Cl_3(OC)Rh{\cdot}C(Ph)N(Me)C(Ph)NMe{\cdot}CH_2Cl_2$ [d]	2120	1656, 1502	355vs, 332m, 315w	2·37	6·18s, 6·65s		
(III)	$Br_3(OC)Rh{\cdot}C(Ph)N(Me)C(Ph)NMe$	2115	1648, 1492		2·43	6·10s 6·70s		
(IV)	$I_3(OC)Rh{\cdot}C(Ph)N(Me)C(Ph)NMe$	2080	1638, 1470 [e]		2·53	5·92s, 6·72s		
(V)	$Cl_3(Me_2PhP)_2Rh{\cdot}C(Ph)N(Me)C(Ph)NMe$		1651, 1470 [e]	323w, 298m	2·55	6·58 7·25d [f]		8·00dd [g] 8·53dd [h]
(VI)	$Cl_3(OC)Rh{\cdot}C(Ph)N(Et)C(Ph)NEt$	2120	1648, 1497	349s, 316m	2·52	5·90q [i] 6·23q [i]	8·52t [i] 8·98t [i]	

[a] I.r. spectra ($\nu_{max.}$, cm^{-1}) obtained as Nujol mull. [b] ^1H N.m.r. spectra (τ and *J* Hz) in $CDCl_3$ with tetramethylsilane as internal standard. [c] Complex resonances: CH_2Cl_2. [d] Singlet at τ 4·7 due to CH_2Cl_2. [e] Band obscured by Nujol peak. [f] Separation is 1·4 Hz. [g] $J(P_1)$ 16·6, $J(P_2)$ 4·6. [h] $J(P_2)$ 11·6, $J(P_1)$ 4·2. [i] All coupling, 7·2 Hz.

from the ^1H n.m.r. characteristics due to the two *N*-methyl groups. The compounds have a single NMe resonance which changes little in chemical shift (τ 6·58—6·75) and another NMe resonance more structurally sensitive. Thus, the latter is assigned to the NMe directly attached to rhodium; this resonance undergoes a particularly large shift in compound (V), where in order to maintain a stable octahedral d^6 configuration the CNCN unit is considered to be unidentate.

The stereochemistry of (V) is revealed by its PMe resonances, which appear as a pair of double doublets. Thus the dimethylphenylphosphine ligands are mutually *cis* and to maintain a magnetic non-equivalence between these phosphorus ligands, one such ligand is *cis* and the other *trans* to the carbene moiety. The difference in stereochemistry between (V) and (I), (II), or (VI) is further confirmed by a significant change in position and intensity of the Rh–Cl stretching modes.

As regards the mechanism of formation of the metal carbene complexes such as (I) or (VI) from appropriate imidoyl chlorides, it is likely to be as shown in equation (3*a*); the alternative, (3*b*), is much less plausible than for the comparable reaction [1] of the free imidoyl chloride with hydrogen chloride. The coupling of two imidoyl fragments within the co-ordination sphere of a transition metal might have synthetic use if it were possible to make the reaction catalytic, and alternative reagents, such as a carboxylic acid chloride, might serve in place of the second molecule of imidoyl chloride.



(3)

DISCUSSION

Crystal and molecular structure of $I_3(OC)$-$\overline{\mathrm{Rh{-}CPh(NMe)C(Ph){:}N}}$Me. As with other carbene complexes studied,[4] the bonding environment of the ' carbene carbon,' C(carb), is essentially trigonal, being planar to within 0·012 Å of its substituents [Table 3, plane (a)] and subtending angles of 115(1), 120(1), and 125(1)° with them. The Rh–C(2) distance [1·968(13) Å] is similar to that found for Rh^{III}–C(carb) [1·961(11) Å] in $Cl_3(Et_3P)_2$-Rh–CHNMe [5] and is significantly longer than the Rh–C(O) distance [1·892(14) Å], but also signifiantly shorter than the Rh^{III}–C(alkyl) single-bond distances (2·05—2·08 Å),[6-8] even allowing for a decrease of 0·04 Å in covalent radii for the change C(sp^3) to C(sp^2). [The Rh–C(O) distance may be compared with the 1·97(3) Å reported for (π-C_5H_5)(C_2F_5)IRhCO.][9] As with carbene complexes of other metals, these features are attributed to a small degree of metal–C(carb) d_π–p_π bonding, and competing p_π–p_π N–C(carb) bonding. This is borne out by the C(carb)–N(1) distance [1·328(16) Å] which is comparable with the corresponding distance in organic amides, *e.g.*, 1·35 Å in acetanilide, and C(carb)–N bond lengths of 1·31—1·36 Å found in other monocarbene complexes, but much shorter than the N–C single-bond distance of 1·47(2) Å in, *e.g.*, diethylamine.[4] It is also not significantly different from the C(3)–N(2) value of 1·305(17) Å, indicating that these two chelate bonds have a similar amount of double-bond character. The N(1)–C(3) length [1·432(15) Å] is, however, significantly longer and close to the normal single-bond value. The C(carb)–C(6) bond distance [1·457(17) Å] is consistent with a single bond between two trigonal carbons and is virtually the same as the C(3)–C(12) length [1·464(17) Å]. A comparison of the Rh–N(2) distance of 2·047(9) with Rh^{III}–N(sp^2) distances of 2·09—2·12 Å in pyridine complexes [6-8, 10] indicates some shortening from the single-bond value, the sum of the covalent radii being 2·08 Å.

The five-membered Rh^{III}–carbene chelate ring is essentially planar, the maximum deviation from the plane being 0·003 Å [Table 5, plane (*b*)], and shows similar geometry to five-membered carbene chelate ring complexes of Pd [11] and Mo.[12] The angle subtended at Rh is 79·3(5)°, *cf.* 87° for the Pd complex and 71—73° for the Mo complexes. The remaining internal angles range from 114(1) to 117(1)°, *cf.* 108—124° in the Pd and Mo complexes. The similarity of the present ring to the five-membered Rh^{III}–chelate rings in acetobis(phenylazophenyl-2*C*,*N*')rhodium(III) [13] and di-μ-chloro-dicarbonylrhodium(I)-bis(phenylazophenyl-2*C*,*N*')rhodium(III),[14] where the angles subtended at Rh vary from 79·1 to 79·7° and other internal angles range from 111 to 120°, is even more striking, especially since the mean Rh–N and Rh–C distances of 2·04(1) and 1·99(1) Å, are virtually the same as in the present compound. Their shortness is attributed in part to d_π–p_π interaction between filled metal orbitals and the π-bonding system of the chelate ring, and also to a chelate effect.

The two mutually *trans*-Rh–I distances of 2·662(4) and 2·680(4) Å compare with the values of 2·653(18) Å in (π-C_5H_5)(C_2F_5)IRhCO [9] and 2·643(3) in $[I_2(Me)(Ph_3P)_2Rh]$-C_6H_6.[8] The Rh^{III}–I(3) bond length of 2·774(4) *trans* to C(carb) demonstrates the magnitude of the *trans*-influence of this carbene ligand. The Rh octahedron is

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slightly distorted, the principal axes deviating from linearity as follows: I(1)–Rh–I(2) 171·5(1), I(3)–Rh–C(2) 176·3(4), and N(2)–Rh–C(1) 176·5(5)°. The planes of the phenyl groups [Table 5, planes (*c*) and (*d*)] make angles of 65 and 84° with the plane of the chelate ring; there is therefore no overlap with the aromatic π system.

EXPERIMENTAL

Preparation of starting materials and general techniques were described in Part V.[1]

Preparation of $Cl_3(OC)Rh{\cdot}C(Ph)N(Me)C(Ph){:}NMe$, (I), *and an Analogue*, (VI).—*N*-Methylbenzimidoyl chloride (0·784 g, 5·19 mmol) in dichloromethane (5 ml) was added to a dichloromethane solution (15 ml) of $[Rh(CO)_2Cl]_2$ (0·447 g, 1·15 mmol). After 16 h, diethyl ether (50 ml) was added and, upon cooling to 0°, pale yellow crystals separated out. These were washed with diethyl ether (10 ml) and dried under nitrogen. Thus the solvated *complex* $[Cl_3(OC)Rh{-}C(Ph)N(Me)C(Ph){:}NMe]_2,2CH_2Cl_2$, (II) (0·939 g, 73%) was obtained. By crushing these crystals and placing them in a high vacuum for 3 days, solvent was removed to give (I) quantitatively.

The closely analogous *compound* $Cl_3(OC)Rh{\cdot}C(Ph)N(Et)C(Ph){:}NEt$, (VI), was prepared by this method from *N*-ethylbenzimidoyl chloride.

Preparation of $I_3(OC)Rh{\cdot}C(Ph)N(Me)C(Ph){:}NMe$, (IV), *and the Bromo-analogue*, (III).—Powdered anhydrous lithium iodide (7·0 g, 52·3 mmol) was placed in a solution of compound (I) (0·166 g, 0·175 mmol) in dichloromethane (15 ml).

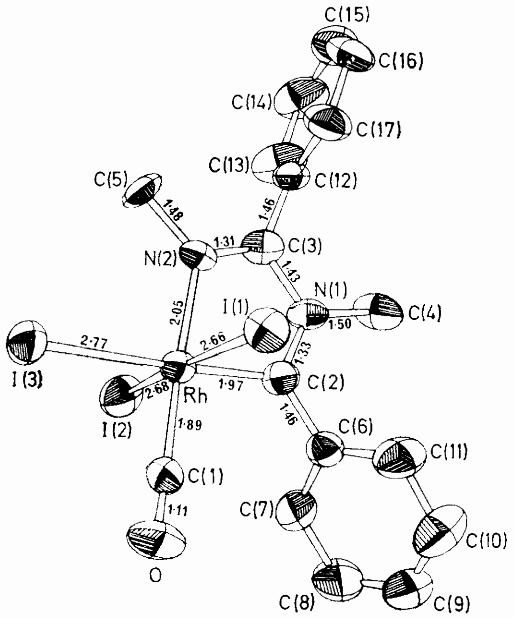

FIGURE 1 View of the molecule (IV) approximately down *c** axis, showing numbering system used and thermal motion. Ellipsoids are scaled to enclose 50% probability

TABLE 3

Final fraction co-ordinates (× 10^4) and thermal parameters (Å^2 × 10^3) *

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	1182(1)	2380(1)	3001(1)	52(1)	53(1)	50(1)	−2(1)	13(1)	−4(1)
I(2)	−230(1)	1736(1)	−1493(1)	72(1)	61(1)	54(1)	9(1)	−7(1)	−3(1)
I(3)	−2150(1)	2265(1)	1176(1)	43(1)	54(1)	79(1)	3(1)	12(1)	14(1)
Rh	305(1)	2045(1)	796(1)	38(1)	32(1)	50(1)	−1(1)	8(1)	3(1)
O	−173(10)	408(6)	1493(10)	95(8)	47(6)	96(8)	−16(6)	19(6)	21(6)
N(1)	2627(10)	2588(5)	316(8)	56(6)	32(6)	36(5)	1(5)	14(5)	−5(4)
N(2)	719(9)	3161(5)	374(9)	46(6)	28(6)	62(7)	−9(5)	7(5)	−1(5)
C(1)	26(12)	1000(8)	1188(13)	41(7)	44(8)	74(10)	−6(6)	−4(7)	15(7)
C(2)	2078(12)	1940(7)	606(11)	51(7)	36(7)	51(8)	2(6)	−4(6)	0(6)
C(3)	1871(12)	3271(7)	190(9)	60(8)	38(7)	30(6)	−3(6)	16(6)	7(5)
C(4)	3961(13)	2628(8)	103(15)	51(8)	46(8)	117(13)	−11(7)	58(8)	−12(8)
C(5)	−203(11)	3795(7)	285(13)	44(8)	33(8)	92(11)	20(6)	12(7)	17(7)
C(6)	2796(11)	1226(7)	797(11)	42(7)	40(8)	54(8)	−2(6)	12(6)	3(6)
C(7)	2494(13)	578(9)	139(15)	57(9)	53(9)	97(12)	10(8)	−1(8)	−12(8)
C(8)	3162(17)	−124(9)	383(18)	86(12)	46(10)	138(17)	7(9)	3(12)	−38(10)
C(9)	4081(16)	−157(9)	1274(17)	78(12)	50(10)	99(13)	12(8)	9(10)	6(9)
C(10)	4364(16)	460(10)	1990(15)	91(12)	80(12)	76(12)	36(10)	6(9)	2(9)
C(11)	3760(15)	1169(8)	1731(13)	90(11)	51(9)	67(10)	13(8)	9(8)	−13(7)
C(12)	2430(11)	4024(6)	−18(12)	44(7)	27(6)	67(9)	−1(6)	12(6)	−3(6)
C(13)	2534(15)	4252(8)	−1156(13)	103(12)	55(9)	58(9)	8(9)	42(8)	20(7)
C(14)	2995(17)	4990(10)	−1335(18)	98(14)	57(11)	107(15)	4(10)	47(11)	30(10)
C(15)	3343(16)	5464(9)	−436(23)	72(12)	43(10)	148(19)	−13(9)	11(12)	18(12)
C(16)	3252(17)	5235(9)	678(19)	100(14)	39(10)	120(16)	−16(9)	−31(12)	−16(10)
C(17)	2797(15)	4504(8)	889(13)	90(12)	45(9)	69(9)	−8(8)	−14(8)	−15(7)
H(7) †	1721	596	−532						
H(8)	2949	−633	−126						
H(9)	4578	−690	1452						
H(10)	5070	420	2753						
H(11)	4036	1681	2215						
H(13)	2236	3858	−1873						
H(14)	3086	5206	−2203						
H(15)	3743	6011	−552						
H(16)	3479	5632	1388						
H(17)	2761	4306	1764						

* In the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. † The positional parameters for these hydrogens were calculated and isotropic temperature factors of $U = 0{\cdot}076$ were assigned. These were not refined.

After 4 days in the dark at 20°, the solid was filtered off and the volume of filtrate reduced by evaporation to *ca.* 5 ml. Addition of diethyl ether (10 ml) and cooling to 0° afforded deep red cubes of the *iodo-complex*, (IV) (0·149 g, 57%).

This procedure was repeated, with lithium bromide in place of the iodide and a reaction time of 1 week, to afford the *bromo-complex*, (III).

Preparation of $Cl_3(Me_2PhP)_2Rh{\cdot}C(Ph)N(Me)C(Ph){:}NMe$, (V).—Dimethylphenylphosphine (0·253 g, 1·83 mmol) was added to compound (I) (0·274 g, 0·240 mmol) in toluene (25 ml). This mixture was heated under reflux for 2 h and, after cooling, the resulting solid was recrystallised (CH_2Cl_2/Et_2O) to yield the lemon-yellow *compound*, (V) (0·143 g, 0·198 mmol).

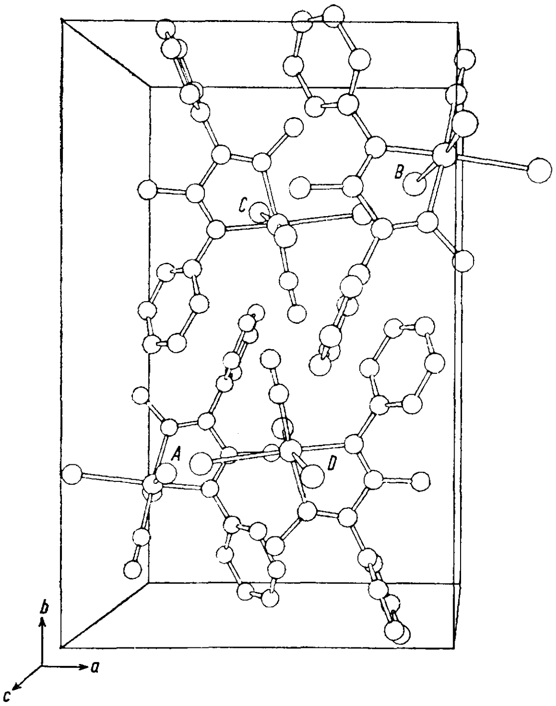

FIGURE 2 Unit-cell contents, viewed down mean *c** axis. Molecule A has approximately the same orientation as in Figure 1 and the atomic co-ordinates listed in Table 3. Molecule B is related to A by a centre of symmetry at the centre of the cell. Molecule C is related to A by a 2_1 screw along *b*, and molecule D is related to C again by a centre of symmetry at the centre of the cell.

TABLE 4

Molecular geometry

(*a*) Bond lengths (Å)

Rh–I(1)	2·662(4)	C(3)–C(12)	1·464(17)
Rh–I(2)	2·680(4)	C(6)–C(7)	1·366(20)
Rh–I(3)	2·774(4)	C(6)–C(11)	1·405(19)
Rh–N(2)	2·047(9)	C(7)–C(8)	1·421(22)
Rh–C(1)	1·892(14)	C(8)–C(9)	1·337(25)
Rh–C(2)	1·968(13)	C(9)–C(10)	1·357(23)
O–C(1)	1·108(18)	C(10)–C(11)	1·401(22)
N(1)–C(2)	1·328(16)	C(12)–C(13)	1·386(20)
N(1)–C(3)	1·432(15)	C(12)–C(17)	1·353(19)
N(1)–C(4)	1·497(18)	C(13)–C(14)	1·393(23)
N(2)–C(3)	1·305(17)	C(14)–C(15)	1·336(29)
N(2)–C(5)	1·476(16)	C(15)–C(16)	1·358(33)
C(2)–C(6)	1·457(17)	C(16)–C(17)	1·385(22)

TABLE 4 (*Continued*)

(*b*) Bond angles (°)

I(1)–Rh–I(2)	171·5(1)	Rh–C(2)–N(1)	115·1(9)
I(1)–Rh–I(3)	93·1(1)	Rh–C(2)–C(6)	124·8(9)
I(1)–Rh–N(2)	87·7(3)	N(1)–C(2)–C(6)	120·1(12)
I(1)–Rh–C(1)	91·6(4)	N(1)–C(3)–N(2)	114·2(10)
I(1)–Rh–C(2)	83·7(4)	N(1)–C(3)–C(12)	120·2(11)
I(2)–Rh–I(3)	95·2(1)	N(2)–C(3)–C(12)	125·4(11)
I(2)–Rh–N(2)	88·9(3)	C(2)–C(6)–C(7)	121·4(11)
I(2)–Rh–C(1)	91·4(4)	C(2)–C(6)–C(11)	120·4(12)
I(2)–Rh–C(2)	88·0(4)	C(7)–C(6)–C(11)	118·0(12)
I(3)–Rh–N(2)	98·8(3)	C(6)–C(7)–C(8)	120·5(14)
I(3)–Rh–C(1)	84·7(4)	C(7)–C(8)–C(9)	119·9(16)
I(3)–Rh–C(2)	176·3(4)	C(8)–C(9)–C(10)	121·6(15)
N(2)–Rh–C(1)	176·5(5)	C(9)–C(10)–C(11)	119·4(15)
N(2)–Rh–C(2)	79·3(5)	C(6)–C(11)–C(10)	120·4(13)
C(1)–Rh–C(2)	97·3(5)	C(3)–C(12)–C(13)	119·4(11)
C(2)–N(1)–C(3)	116·7(11)	C(3)–C(12)–C(17)	120·2(12)
C(2)–N(1)–C(4)	123·5(10)	C(13)–C(12)–C(17)	120·4(12)
C(3)–N(1)–C(4)	119·8(10)	C(12)–C(13)–C(14)	118·2(14)
Rh–N(2)–C(3)	114·7(8)	C(13)–C(14)–C(15)	121·0(19)
Rh–N(2)–C(5)	123·1(8)	C(14)–C(15)–C(16)	120·5(17)
C(3)–N(2)–C(5)	122·2(10)	C(15)–C(16)–C(17)	120·0(17)
Rh–C(1)–O	174·6(13)	C(12)–C(17)–C(16)	119·8(15)

(*c*) Intermolecular contacts (Å) within the limits of the contact radii: Rh, I, 2·2 Å; O, N, C, 1·9 Å

C(9) ··· C(8^{I})	3·772(28)	C(16) ··· O($^{\mathrm{IV}}$	3·651(23)
C(15) ··· C(5^{II})	3·657(22)	I(1) ··· I(2^{V})	4·146(4)
C(16) ··· C(5^{II})	3·742(22)	C(4) ··· I(2^{V})	4·061(17)
O ··· I(2^{III})	3·722(10)	C(17) ··· I(2^{V})	4·076(15)
O ··· $\mathrm{O}^{\mathrm{III}}$	3·779(16)	I(1) ··· I(3^{V})	3·918(4)
C(7) ··· $\mathrm{O}^{\mathrm{III}}$	3·399(18)	C(4) ··· I(1^{VI})	3·622(17)
C(8) ··· $\mathrm{O}^{\mathrm{III}}$	3·691(21)	C(13) ··· I(3^{VI})	4·082(15)
C(16) ··· I(1^{IV})	4·017(17)	C(14) ··· O^{VI}	3·452(24)

Roman numeral superscripts refer to the following co-ordinate transformations:

I $1 - x, -y, -z$
II $-x, 1 - y, -z$
III $-x, -y, -z$
IV $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$
V $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$
VI $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$

TABLE 5

Least-squares planes expressed in the form $Px + Qy + Rz = S$, with displacements (Å) of atoms from these planes. σ is the standard deviation of the atoms (those defining the plane) from the plane

(*a*) Displacements

Plane (*a*): C(2), Rh, C(6), N(1)

C(2) −0·012, Rh 0·003, C(6) 0·004, N(1) 0·004, I(3) 0·181, O 0·043, N(2) 0·047, C(1) −0·026, C(3) 0·042, C(4) −0·036, C(5) 0·082, C(9) 0·138, C(12) 0·190, C(15) 0·433

Plane (*b*): Rh, C(2), N(1), C(3), N(2)

Rh −0·001, C(2) 0·003, N(1) −0·003, C(3) 0·001, N(2) 0, I(3) 0·149, O 0·101, C(1) 0·010, C(4) −0·033, C(5) 0·002, C(6) 0·054, C(9) 0·254, C(12) −0·033, C(15) 0·316

Plane (*c*): C(6)—(11)

C(6) −0·006, C(7) 0·071, C(8) −0·002, C(9) −0·002, C(10) 0·031, C(11) −0·017, C(2) 0·089

Plane (*d*): C(12)—(17)

C(12) −0·008, C(13) 0·005, C(14) −0·001, C(15) −0·002, C(16) 0, C(17) 0·005

(*b*) Equations

	P	*Q*	*R*	*S*	σ
(*a*)	1·313	4·000	10·853	1·178	0·008
(*b*)	1·400	3·607	10·899	1·648	0·002
(*c*)	−8·119	−4·683	7·986	−2·201	0·020
(*d*)	10·011	−6·451	−0·494	−0·155	0·005

(*c*) Angles (°) between the planes

(*b*)–(*a*)	1·4	(*c*)–(*a*)	64·6	(*c*)–(*b*)	64·5
(*d*)–(*a*)	84·4	(*d*)–(*b*)	83·5	(*d*)–(*c*)	56·9

Crystal Structure Analysis of (IV), $\mathrm{I_3(OC)Rh{-}CPh(NMe)C(Ph){:}NMe}$.

Data are in Tables 3—6 and Figures 1 and 2

Crystal Data.—$C_{17}H_{16}I_3N_2ORh$, $M = 747{\cdot}95$, Monoclinic, $a = 10{\cdot}83(1)$, $b = 17{\cdot}24(2)$, $c = 11{\cdot}52(1)$ Å, $\beta = 97{\cdot}3(2)°$ (standard deviations from the spread of measurements), $U = 2133{\cdot}7$ Å^3, $D_m > 2{\cdot}2$, $Z = 4$, $D_c = 2{\cdot}33$, g cm^{-3} $F(000) = 1376$. Space group $P2_1/n$ (a non-standard form of $P2_1/c$, No. 14) [15] (C_{2h}^5) from systematic absences: $h0l$ for $h + l = 2n + 1$, and $0k0$ for $k = 2n + 1$. Mo-K_α radiation (silicon crystal monochromator), $\lambda = 0{\cdot}71069$ Å, μ(Mo-K_α) = 51·72 cm^{-1}. Lattice parameters derived from precession photographs.

TABLE 6

Torsion angles (°). The angle A–B–C–D is defined as positive if, when viewed along the B–C bond, Atom A must be rotated clockwise to eclipse atom D

C(1)–Rh–N(2)–C(3)	6·5(10)
C(1)–Rh–N(2)–C(5)	−173·4(11)
C(2)–Rh–N(2)–C(3)	0·1(9)
C(2)–Rh–N(2)–C(5)	−179·8(11)
N(2)–Rh–C(1)–O	120·4(13)
C(2)–Rh–C(1)–O	126·7(14)
N(2)–Rh–C(2)–N(1)	−0·3(9)
N(2)–Rh–C(2)–C(6)	177·5(12)
C(1)–Rh)C(2)–N(1)	−179·9(10)
C(1)–Rh–C(2)–C(6)	−2·0(12)
C(3)–N(1)–C(2)–Rh	0·5(14)
C(3)–N(1)–C(2)–C(6)	−177·5(11)
C(4)–N(1)–C(2)–Rh	−178·5(9)
C(4)–N(1)–C(2)–C(6)	3·4(18)
C(2)–N(1)–C(3)–N(2)	−0·4(16)
C(2)–N(1)–C(3)–C(12)	174·1(11)
C(4)–N(1)–C(3)–N(2)	178·6(11)
C(4)–N(1)–C(3)–C(12)	−6·7(17)
Rh–N(2)–C(3)–N(1)	0·1(13)
Rh–N(2)–C(3)–C(12)	−174·1(10)
C(5)–N(2)–C(3)–N(1)	−179·9(11)
C(5)–N(2)–C(3)–C(12)	5·8(19)
Rh–C(2)–C(6)–C(7)	62·0(17)
Rh(1)–C(2)–C(6)–C(11)	−112·8(13)
N(1)–C(2)–C(6)–C(7)	−120·1(15)
N(1)–C(2)–C(6)–C(11)	65·0(17)
N(1)–C(3)–C(12)–C(13)	87·6(15)
N(1)–C(3)–C(12)–C(17)	−94·9(15)
N(2)–C(3)–C(12)–C(13)	−98·4(16)
N(2)–C(3)–C(12)–C(17)	79·0(17)
C(2)–C(6)–C(7)–C(8)	−176·4(14)
C(11)–C(6)–C(7)–C(8)	−1·4(22)
C(2)–C(6)–C(11)–C(10)	173·3(14)
C(7)–C(6)–C(11)–C(10)	−1·7(21)
C(6)–C(7)–C(8)–C(9)	1·0(25)
C(7)–C(8)–C(9)–C(10)	2·7(27)
C(8)–C(9)–C(10)–C(11)	−5·9(26)
C(9)–C(10)–C(11)–C(6)	5·3(24)
C(3)–C(12)–C(13)–C(14)	175·9(14)
C(17)–C(12)–C(13)–C(14)	−1·5(22)
C(3)–C(12)–C(17)–C(16)	−175·9(14)
C(13)–C(12)–C(17)–C(16)	1·5(22)
C(12)–C(13)–C(14)–C(15)	0·8(26)
C(13)–C(14)–C(15)–C(16)	−0·1(29)
C(14)–C(15)–C(16)–C(17)	0·1(29)
C(15)–C(16)–C(17)–C(12)	−0·8(26)

Crystals were well-formed, deep-red, diamond-shaped plates. The morphology of the data crystal was defined by all members of the {010} and {101} forms, distances between parallel faces being 0·0096 × 0·0276 × 0·0296 cm. Integrated intensities were measured on a PAILRED diffractometer. The crystal was oriented so that its c axis coincided with the instrumental ω axis; the layers $hk0$—14 were surveyed by the stationary-counter–moving-crystal method. Intensities of reflections with $2\theta \leqslant 60°$ were measured, the ω scan through the reflections varying from 1·6° on the zero layer to 3·4° on layer 14, at a scan velocity of 1° min^{-1}. Background was measured at both extremities of each scan for 40 s.

Reflections whose independent background intensities differed by $>3\sigma$ or which had $I/\sigma(I) < 3{\cdot}0$ were discarded. The remaining 2429 independent intensities were corrected for Lorentz and polarisation effects and, at a later stage, for absorption. Transmission factors for F_o, calculated by Alcock's [16] version of the analytical method of De Meulenaer and Tompa,[17] varied from 0·567 to 0·784.

The overlap of Harker and non-Harker peaks on the Harker section of the Patterson synthesis prevented the direct determination of co-ordinates for the heavy atoms. However, a set of prominent peaks around the origin yielded the overall geometry and orientation of a planar RhI_3 unit having two *trans*-iodine atoms. The position of this strongly scattering portion of the molecule in the unit cell (its orientation being defined from the Patterson synthesis) was determined by the minimum residual method [18] based on 100 reflections with $\sin\theta/\lambda \leqslant 0{\cdot}2$ and interval translations of 0·25 Å. The minimum value of R was 0·39 [the procedure was initially carried out using a translational increment of 0·5 Å; this gave a different, but higher (0·47) residual, see ref. 19].

A structure-factor calculation over all data based on positions derived from the minimum residual treatment gave R 0·51 which was reduced to R 0·21 after 3 cycles of positional and isotropic thermal parameter least-squares refinement. As expected, there were comparatively large shifts in positional parameters during the first 2 cycles. The positions of the remaining non-hydrogen atoms were obtained from the resulting difference-Fourier synthesis.

The structure was refined using the least-squares programme CRYLSQ [20] in the full-matrix mode minimising the function $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F)$. Atomic scattering factors were taken from ref. 21 except those for hydrogen, which were from ref. 22. The effects of anomalous dispersion from the rhodium and iodine atoms were included in the calculations by using values of $\Delta f'$ and $\Delta f''$ from ref. 23.

Refinement of positional and isotropic thermal parameters of all non-hydrogen atoms gave R 0·109, and the weighted value R' 0·127 [$R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$]. Allowance was then made for the anisotropic thermal vibration of the rhodium and iodine atoms which decreased R to 0·060 and R' to 0·069 upon further refinement. At this point data

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were corrected for absorption as described previously, refinement based on the corrected data reduced R to 0·052 and R' to 0·061. Phenyl group hydrogens were then included in the structure-factor calculations, but their parameters, deduced from the known stereochemistry of the benzene ring, were not refined. This caused a decrease in R' of 0·001. Finally, all non-hydrogen atoms were refined anisotropically, terminating at R 0·047 and R' 0·055. During the final cycle of refinement there were no parameter shifts $>0{\cdot}4\sigma$. The adequacy of the weighting scheme was confirmed by an analysis of the variation of the mean $w\Delta^2$ with $|F_o|$ and $\sin\theta/\lambda$. The function values in the final difference synthesis were in the range $-0{\cdot}8$ to 0·9e. All peaks of magnitude $>\pm0{\cdot}6$e were associated with the rhodium and iodine atoms.

Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20786 (3 pp., 1 microfiche).*

We thank S.R.C. for the award of a fellowship to A. J. O. and for other support.

[3/593 *Received, 21st March,* **1973**]

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