

The X-ray Structure of  $\text{Rh}^{\text{I}}\text{Cl}(\text{C}_4\text{H}_6)_2$ 

BY A. IMMIRZI AND G. ALLEGRA

Istituto di Chimica Industriale del Politecnico and Centro Nazionale di Chimica delle Macromolecole,  
Sezione I, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

(Received 27 December 1967 and in revised form 26 February 1968)

$\text{RhCl}(\text{C}_4\text{H}_6)_2$  crystallizes in the tetragonal system, space group  $P4_21m$  ( $a=b=7.90\pm 0.03$ ;  $c=6.92\pm 0.02$  Å); two equivalent molecules, with crystallographic  $C_{2v}$  symmetry, are contained in the unit cell. The disagreement factor, calculated on 385 observed three-dimensional reflexions, is 0.062 after 4 cycles of least-squares refinement. Considering each butadiene group as a bidentate ligand, the metal coordination approximately corresponds to a square pyramid. The independent bond lengths and angles are (Å): Rh-Cl =  $2.44\pm 0.01$ ; Rh-C (external) =  $2.21\pm 0.01$ ; Rh-C (internal) =  $2.15\pm 0.01$ ; C-C (internal bond) =  $1.45\pm 0.02$ ; C-C (external bond) =  $1.38\pm 0.02$ ; C-C-C =  $117\pm 0.6^\circ$ .

## Introduction

In a previous short communication (Porri, Lionetti, Allegra & Immirzi, 1965), the chemical preparation

and the crystal structure of  $\text{Rh}^{\text{I}}\text{Cl}(\text{C}_4\text{H}_6)_2$  (I) were briefly described. Now we purpose to discuss in more detail the results of our X-ray investigation of (I) after the least-squares refinement.

Table 1. Fractional coordinates and thermal factors

	$x/a$	$y/b$	$z/c$	$B_{\text{iso}}$ (Å <sup>2</sup> )	$B_{11}=B_{22}$ (Å <sup>2</sup> )	$B_{33}$ (Å <sup>2</sup> )	$B_{12}$ (Å <sup>2</sup> )
Rh	0.5000	0.0000	0.2197	2.10	—	—	—
Cl	0.5000	0.0000	-0.1336	—	5.89	0.56	-1.54
C(1)	0.7077	-0.0779	0.4005	3.31	—	—	—
C(2)	0.7779	-0.0311	0.2250	2.98	—	—	—
Standard deviations							
	$\sigma(x)$ (Å)	$\sigma(y)$ (Å)	$\sigma(z)$ (Å)	$\sigma(B_{\text{iso}})$ (Å <sup>2</sup> )	$\sigma(B_{11})=$ $\sigma(B_{22})$ (Å <sup>2</sup> )	$\sigma(B_{33})$ (Å <sup>2</sup> )	$\sigma(B_{12})$ (Å <sup>2</sup> )
Rh	—	—	0.001	0.01	—	—	—
Cl	—	—	0.004	—	0.37	0.17	0.44
C(1)	0.011	0.011	0.015	0.19	—	—	—
C(2)	0.011	0.009	0.012	0.17	—	—	—

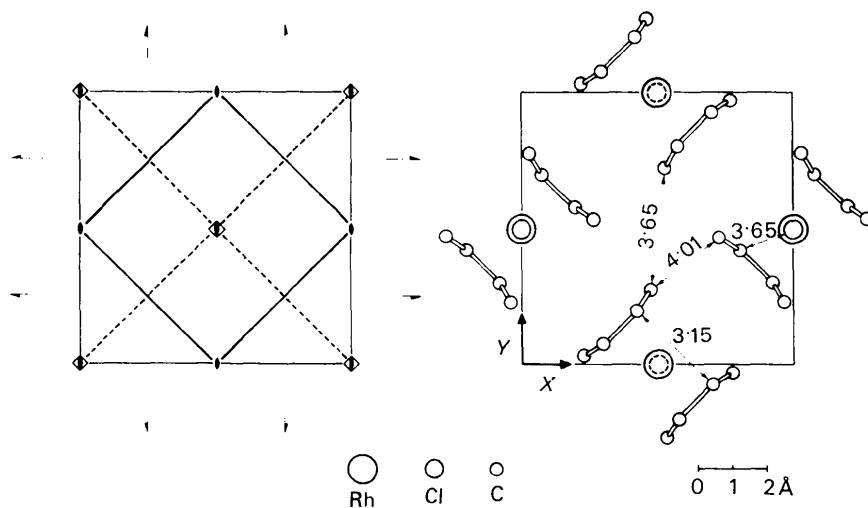


Fig. 1. Molecular packing of (I), in projection along the  $c$  axis. The shortest interatomic non-bonding distances are shown; only the 3.15 Å distance between C atoms is intramolecular.





Table 2 (cont.)

H	K	L	FO	FC	PH	H	K	L	FO	FC	PH	H	K	L	FO	FC	PH
6	6	5	24	23	9857	10	2	6	10	9	5131	2	1	7	4	5	2166
7	6	5	20	20	7801	11	2	6	17	16	7570	3	1	7	28	29	186
8	6	5	23	19	93	3	3	6	21	21	536	4	1	7	7	6	6970
9	6	5	13	17	7915	4	3	6	71	64	2304	5	1	7	20	21	294
10	6	5	13	12	9824	5	3	6	17	16	9960	6	1	7	6	2	6894
7	7	5	24	22	5000	6	3	6	41	43	2459	7	1	7	21	25	38
8	7	5	12	13	2452	7	3	6	16	15	32	8	1	7	7	4	6193
9	7	5	13	12	5024	8	3	6	29	29	2417	9	1	7	14	15	9874
8	8	5	13	15	327	9	3	6	10	8	144	10	1	7	7	5	7110
1	0	6	104	100	7500	10	3	6	19	18	2487	2	2	7	23	20	5215
2	0	6	18	17	5000	4	4	6	18	17	4800	3	2	7	5	4	5263
3	0	6	86	82	7500	5	4	6	43	43	7530	4	2	7	25	25	4891
4	0	6	22	23	5000	6	4	6	8	11	4514	5	2	7	5	6	3186
5	0	6	61	57	7500	7	4	6	34	33	7567	6	2	7	18	20	5073
6	0	6	16	11	5000	8	4	6	9	10	4397	7	2	7	6	6	3141
7	0	6	40	39	7500	9	4	6	20	19	7559	8	2	7	17	19	4808
8	0	6	9	8	5000	5	5	6	8	9	8801	9	2	7	7	4	2708
9	0	6	23	23	7500	6	5	6	31	30	2537	10	2	7	11	15	4913
10	0	6	10	9	5000	7	5	6	9	10	9599	3	3	7	29	10	9554
11	0	6	20	16	7500	8	5	6	22	23	2535	4	3	7	5	6	7729
1	1	6	23	22	9515	9	5	6	10	6	3681	5	3	7	20	22	9839
2	1	6	81	75	2660	6	6	6	9	9	5204	6	3	7	6	8	8876
3	1	6	18	17	9514	7	6	6	26	26	7344	7	3	7	18	22	9934
4	1	6	78	71	2612	8	6	6	10	8	4924	8	3	7	7	5	7970
5	1	6	17	17	9349	9	6	6	19	16	7277	9	3	7	12	14	9878
6	1	6	46	45	2661	7	7	6	15	11	9985	4	4	7	24	28	4745
7	1	6	14	12	9594	8	7	6	20	18	2535	5	4	7	6	2	1440
8	1	6	34	30	2479	1	0	7	*****	9	2500	6	4	7	19	21	5060
9	1	6	10	9	9874	2	0	7	28	27	5000	7	4	7	7	5	2890
10	1	6	22	21	2484	3	0	7	4	2	2500	8	4	7	15	17	5046
11	1	6	11	7	9780	4	0	7	30	32	5000	5	5	7	19	21	93
2	2	6	10	6	4762	5	0	7	5	3	2500	6	5	7	7	3	9635
3	2	6	75	68	7432	6	0	7	20	24	5000	7	5	7	16	19	9983
4	2	6	19	20	4919	7	0	7	6	1	2500	8	5	7	7	3	6783
5	2	6	57	52	7543	8	0	7	18	21	5000	6	6	7	16	17	4835
6	2	6	16	15	4868	9	0	7	7	3	2500	7	6	7	7	6	3398
7	2	6	42	39	7455	10	0	7	13	14	5000	8	6	7	12	14	4832
8	2	6	14	11	5070	1	1	7	26	24	368	7	7	7	16	14	9866
9	2	6	23	23	7328												

instead of 8 as in the remaining space groups. Each molecule must therefore contain only 2 crystallographically different carbon atoms, and the Rh and Cl atoms must lie on highly special sites. Condition (b) suggests that, in the structural projection along  $c$ , Rh and Cl of each molecule are superposed giving rise to a centered arrangement. The above conditions are fulfilled only by the space groups Nos. 90, 113 and 115. The first of these is readily discarded because the Rh-Cl axis would coincide with a fourfold symmetry axis; this is physically impossible unless an improbable statistical disorder is present; the last space group has been discarded on the basis of packing considerations, which will not be discussed further here.

Therefore, the resulting space group is  $P\bar{4}_2m$  (No. 113); the molecule is placed on two crystallographic mirror planes, intersecting at right angles. The Rh-Cl axis coincides with the intersection line, which is also a twofold axis in the structure (Fig. 1); the (rigorous) molecular symmetry is therefore represented by the  $C_{2v}$  group. The butadiene group must assume a *cis* conformation, because the two halves of each group must be mirror images.

#### Structural resolution and refinement

The Rh and Cl  $z$  coordinates were first derived from a two-dimensional Patterson synthesis on the (110) projection; then location of all non-hydrogen atoms was

completed by the usual Fourier methods on the same projection.

From the data previously collected (Porri *et al.* 1965), consisting of the ( $hkl$ ) layers with  $h+k=0$  and  $h=k=1$ , a fairly well resolved image of the molecular electron density has been obtained with the use of the modulated Fourier synthesis method (Buerger, 1960). The electron density about the Rh atom position showed an essentially spherical symmetry ( $\partial^2\rho/\partial z^2 \approx$

$$\partial^2\rho/\partial \left( \begin{matrix} x+y \\ 12 \end{matrix} \right)^2 = 26 \text{ e.}\text{\AA}^{-2}), \text{ while only about the Cl}$$

atom the contours were markedly ellipsoidal

$$(\partial^2\rho/\partial z^2 = 11; \partial^2\rho/\partial \left( \begin{matrix} x+y \\ 12 \end{matrix} \right)^2 = 5.5 \text{ e.}\text{\AA}^{-2}). \text{ The final Weis-$$

senberg equi-inclination data were collected by turning the crystal about the  $c$  axis, and we decided to refine the 8 layer scale factors independently; under these conditions, as it has been stressed by Lingafelter & Donohue (1966), the anisotropic refinement of the Rh atom would have been incorrect, because of its large average contribution to the reflexions. For the above reasons we decided to apply anisotropic thermal factors to the Cl atom only.

The full-matrix least-squares refinement was carried out with the aid of a general program prepared by one of us (Immirzi, 1967). The atomic scattering factors were calculated according to Vand, Eiland & Pepinsky

(1957), using the values suggested by Moore (1963) for the constants  $A_i$ ,  $B_i$ ,  $C_i$ ,  $a_i$ ,  $b_i$ . After four cycles during which  $\sum_w [|F_{\text{obs}}(hkl)| - |F_{\text{calc}}(hkl)|]^2$  was minimized, the final shifts were less than 10% of the corresponding standard deviations for the atomic coordinates and less than 50% for the thermal factors. The weighting scheme suggested by Cruickshank (1965) was used, yielding a final disagreement factor  $R=0.062$  for 385 independent observed reflexions out of 535 reciprocal lattice points with  $d > 0.60 \text{ \AA}$ , giving a ratio of 17.5 observed reflexions per parameter. Giving the non-observed reflexions an arbitrary structure factor equal to one half of the observable limit, increases the total disagreement factor to 0.093. Table 1 reports the resulting fractional coordinates and thermal factors together with their standard deviations.

The full list of observed and calculated structure factors is reported in Table 2.

#### Considerations on the crystal packing and on the molecular structure

By assuming each butadiene group as a bidentate ligand, linked to the metal through its outer C-C bonds, the fivefold coordination around the Rh atom approximately corresponds to a square pyramid (Fig. 2). As has been observed for other organometallic complexes (Mills & Robinson, 1963; Allegra, Logiudice, Natta, Giannini, Fagherazzi & Pino, 1967), the distances from the metal atom to the atoms of the ligands are significantly shorter than to the outer atoms. This seems to be in qualitative agreement with the observation that the central (C-C) bond of each ligand is almost significantly longer than the adjacent bonds: the  $\pi$  electron contribution of the central bond to the coordination with the metal seems larger than that of the other (C-C) bonds. According to Churchill & Mason (1967), in the case of the M-butadiene coordination, the electron back-donation to the conjugated ligands should be very small since it should involve the  $b_2(2)$  ligand combination, which tends to increase the double bond character of the inner bond.

As shown in Fig. 1 the most characteristic feature of the molecular packing consists of the fourfold arrangement of *up* and *down* molecules around each  $\bar{4}$  axis. No  $\text{C} \cdots \text{C}$  intermolecular distance is shorter than  $3.65 \text{ \AA}$ ; the shortest  $\text{Cl} \cdots \text{C}$  contact distance between molecules superposed along *c* is also  $3.65 \text{ \AA}$ . As for the intramolecular non-bonding distances, it seems worth mentioning that, as a result of the coordination to the metal, one  $\text{C} \cdots \text{C}$  contact between different butadiene ligands is shorter ( $3.15 \text{ \AA}$ ) than that found in graphite ( $3.40 \text{ \AA}$ ) (Wyckoff, 1963).

The authors acknowledge the helpful assistance of Dr Porri and Dr Lionetti, who supplied as with the samples.

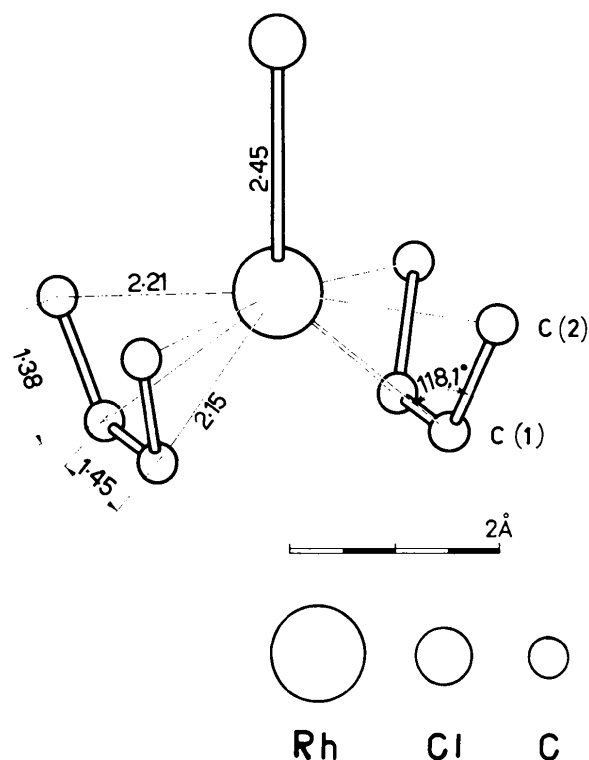


Fig. 2. Resulting molecular structure of (I). Average estimated standard deviations are:

Rh-Cl	0.005 Å
Rh-C	0.012
C-C	0.019
C-C-C	0.6°

#### References

- ALLEGRA, G., LOGIUDICE, F., NATTA, G., GIANNINI, U., FAGHERAZZI, G. & PINO, P. (1967). *Chem. Comm.* 1263.  
 BUERGER, M. J. (1960). *Crystal Structure Analysis*, chapter 14. New York: John Wiley.  
 CHURCHILL, N. R. & MASON, R. (1967). *Advanc. Organometallic Chem.* **5**, 93.  
 CRUICKSHANK, D. W. J. (1965). *Computing Methods in Crystallography*, Chap. 14. Editor, J. S. ROLLETT. London: Pergamon.  
 IMMIRZI, A. (1967). *Ric. Sci.* **37**, 743.  
*International Tables for X-Ray Crystallography*, (1965). Vol. III. Birmingham: Kynoch Press.  
 LINGAFELTER, G. C. & DONOHUE, J. (1966). *Acta Cryst.* **20**, 321.  
 MILLS, O. S. & ROBINSON, G. (1963). *Acta Cryst.* **16**, 758.  
 MOORE, F. H. (1963). *Acta Cryst.* **16**, 1169.  
 PORRI, L., LIONETTI, A., ALLEGRA, G. & IMMIRZI, A. (1965). *Chem. Comm.* 336.  
 VAND, V., EILAND, P. E. & PEPINSKY, R. (1957). *Acta Cryst.* **10**, 303.  
 WYCKOFF, R. W. G. (1963). *Crystal Structures*, Vol. I p. 11. New York: Interscience.