

The X-ray Structure of Rh^ICl(C₄H₆)₂

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RhCl(C₄H₆)₂ crystallizes in the tetragonal system, space group $P\bar{4}1m$ ($a=b=7.90 \pm 0.03$; $c=6.92 \pm 0.02$ 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 ± 0.01 ; Rh–C (external) = 2.21 ± 0.01 ; Rh–C (internal) = 2.15 ± 0.01 ; C–C (internal bond) = 1.45 ± 0.02 ; C–C (external bond) = 1.38 ± 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 Rh^ICl(C₄H₆)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_{iso} (Å ²)	$B_{11}=B_{22}$ (Å ²)	B_{33} (Å ²)	B_{12} (Å ²)
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)	$\sigma(B_{iso})$ (Å ²)	$\sigma(B_{11}) = \sigma(B_{22})$ (Å ²)	$\sigma(B_{33})$ (Å ²)	$\sigma(B_{12})$ (Å ²)
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	—	—	—

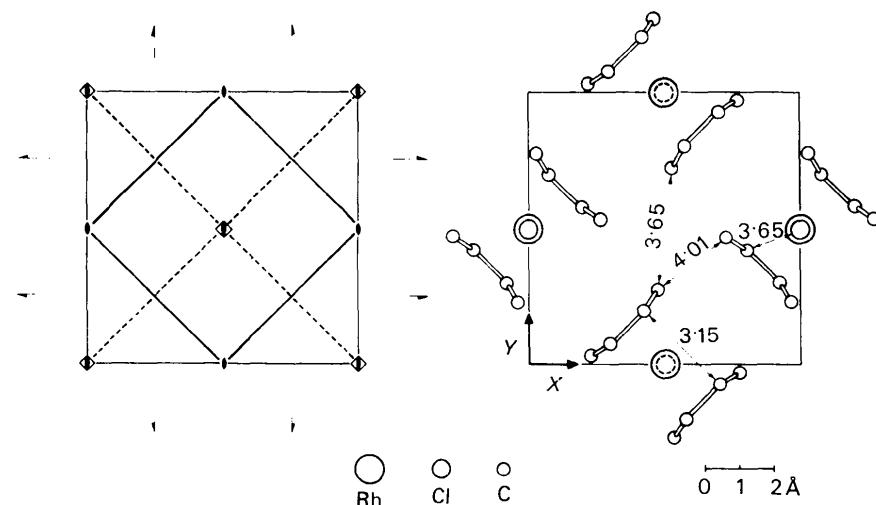


Fig. 1. Molecular packing of (I), in projection along the c axis. The shortest interatomic non-bonding distances are shown; only the 3.15 Å distance between C atoms is intramolecular.

Table 2. Observed and calculated structure factors

$2\pi \times PH/1000$ is the angle of phase of each reflexion; * means 'less than'. ***** means unobserved for geometrical reasons.

H	K	L	FO	FC	PH	H	K	L	FO	FC	PH	H	K	L	FO	FC	PH			
0	0	0	*****	439	0	9	8	0	*	17	5	5000	7	7	1	*	13	5	3728	
2	0	0	174	196	0	10	8	0	*	18	16	0	8	7	1	*	31	28	2444	
4	0	0	166	173	0	9	9	0	*	18	18	5000	9	7	1	*	15	6	4617	
6	0	0	87	83	0	1	0	1	*****	176	7500	10	7	1	*	15	17	2452		
8	0	0	52	53	0	2	0	1	80	70	0	11	7	1	*	16	4	4776		
10	0	0	40	38	0	3	0	1	145	124	7500	8	8	1	*	15	7	1466		
12	0	0	*	17	18	0	4	0	1	43	42	0	9	8	1	*	23	19	7594	
1	1	0	*****	231	5000	5	0	1	81	78	7500	10	8	1	*	16	4	9962		
2	1	0	52	47	0	6	0	1	30	31	0	9	9	1	*	16	4	5276		
3	1	0	162	162	5000	7	0	1	64	58	7500	1	0	2	*****	24	2500			
4	1	0	21	25	0	8	0	1	19	19	0	2	0	2	133	131	5000			
5	1	0	113	111	5000	9	0	1	33	34	7500	1	0	2	*	35	10	7500		
6	1	0	12	15	0	10	0	1	*	11	5	0	4	0	2	*	117	121	5000	
7	1	0	73	73	5000	11	0	1	30	26	7500	5	0	2	*	8	12	7500		
8	1	0	*	11	2	0	12	0	1	*	15	4	0	6	0	2	74	72	5000	
9	1	0	38	43	5000	1	1	1	*****	62	5920	7	0	2	*	27	29	7500		
10	1	0	*	15	0	0	2	1	71	67	3079	8	0	2	*	52	50	5000		
11	1	0	36	30	5000	3	1	1	80	63	5417	9	0	2	*	11	8	7500		
12	1	0	*	17	1	0	4	1	1	113	103	2556	10	0	2	*	28	28	5000	
13	1	0	*	18	15	5000	5	1	1	25	27	6041	11	0	2	*	13	7	7500	
2	2	0	89	104	0	6	1	1	66	61	2584	12	0	2	*	14	16	5000		
3	2	0	15	10	0	7	1	1	27	26	5145	1	1	2	*****	124	291			
4	2	0	145	140	0	8	1	1	50	46	2282	2	1	2	*	12	13	2188		
5	2	0	11	8	5000	9	1	1	*	13	8	5204	3	1	2	*	131	121	139	
6	2	0	87	88	0	10	1	1	32	33	2389	4	1	2	*	15	15	3618		
7	2	0	*	12	1	0	11	1	1	*	15	6	5464	5	1	2	*	72	71	123
8	2	0	55	58	0	12	1	1	*	15	18	2438	6	1	2	*	16	16	2977	
9	2	0	*	14	5	0	2	2	81	65	107	7	1	2	*	70	66	9949		
10	2	0	42	37	0	3	2	1	90	82	7475	8	1	2	*	20	18	3238		
11	2	0	*	16	1	5000	4	2	1	33	28	9766	9	1	2	*	30	33	9732	
12	2	0	*	17	18	0	5	2	1	71	68	7581	10	1	2	*	12	8	3080	
3	3	0	145	149	5000	6	2	1	21	15	9719	11	1	2	*	27	25	9937		
4	3	0	25	21	5000	7	2	1	67	61	7500	12	1	2	*	14	7	2849		
5	3	0	97	101	5000	8	2	1	*	12	12	9500	2	2	2	*	99	90	5172	
6	3	0	*	11	1	5000	9	2	1	45	35	7328	1	2	2	*	19	20	6810	
7	3	0	72	75	5000	10	2	1	*	13	7	9370	4	2	2	*	93	90	4982	
8	3	0	*	13	2	5000	11	2	1	29	26	7536	5	2	2	*	8	2	4028	
9	3	0	38	38	5000	12	2	1	*	15	6	9972	6	2	2	*	60	58	5293	
10	3	0	*	16	0	5000	3	3	1	62	52	3956	7	2	2	*	15	14	7138	
11	3	0	33	25	5000	4	3	1	110	96	2206	8	2	2	*	46	45	4861		
12	3	0	*	17	0	0	5	3	1	20	20	4426	9	2	2	*	12	8	7520	
4	4	0	115	110	0	6	3	1	65	62	2644	10	2	2	*	27	29	5043		
5	4	0	15	9	5000	7	3	1	17	15	4291	11	2	2	*	19	10	7405		
6	4	0	66	68	0	8	3	1	49	44	2428	12	2	2	*	21	18	4991		
7	4	0	*	13	7	5000	9	3	1	*	13	9	4205	3	3	2	*	113	109	9827
8	4	0	48	47	0	10	3	1	29	28	2655	4	3	2	*	12	15	2815		
9	4	0	*	15	4	5000	11	3	1	*	15	6	5079	5	3	2	*	68	68	47
10	4	0	28	28	0	12	3	1	*	16	16	2520	6	3	2	*	14	14	1037	
11	4	0	*	17	5	5000	4	4	1	28	32	9879	7	3	2	*	56	55	190	
12	4	0	*	18	17	0	5	4	1	62	59	7343	8	3	2	*	11	10	2375	
5	5	0	61	57	5000	6	4	1	23	20	79	9	3	2	*	12	10	91		
6	5	0	*	13	6	0	7	4	1	58	51	7519	10	3	2	*	13	10	1748	
7	5	0	55	53	5000	8	4	1	*	12	12	5042	11	3	2	*	23	23	241	
8	5	0	*	14	5	0	9	4	1	28	28	7460	12	3	2	*	14	7	2428	
9	5	0	34	30	5000	10	4	1	*	14	7	219	4	4	2	*	86	88	4733	
10	5	0	*	16	0	0	11	4	1	28	27	7625	5	4	2	*	22	22	8189	
11	5	0	20	24	5000	12	4	1	*	16	3	1024	6	4	2	*	59	57	5205	
12	5	0	*	18	2	0	5	5	1	29	27	5423	7	4	2	*	17	16	7656	
6	6	0	51	51	0	6	5	1	45	42	2561	8	4	2	*	39	39	4967		
7	6	0	*	14	4	0	7	5	1	*	12	13	5042	9	4	2	*	12	10	7814
8	6	0	40	38	0	8	5	1	34	35	2317	10	4	2	*	25	24	5235		
9	6	0	*	16	4	0	9	5	1	*	14	9	5000	11	4	2	*	14	6	7673
10	6	0	19	22	0	10	5	1	27	24	2480	12	4	2	*	14	14			
11	6	0	*	18	1	0	11	5	1	*	15	4	5700	5	5	2	*	55	55	73
7	7	0	45	44	5000	8	6	1	18	15	4988	6	5	2	*	17	17	2338		
8	7	0	*	16	3	0	7	6	1	47	40	7648	7	5	2	*	42	43	74	
9	7	0	29	23	5000	8	6	1	*	13	7	9452	8	5	2	*	12	13	3315	
10	7	0	*	17	2	5000	9	6	1	28	24	7339	9	5	2	*	27	27	9829	
11	7	0	*	18	15	5000	10	6	1	*	15	8	8920	10	5	2	*	13	9	2410
8	8	0	31	27	0	11	6	1	*	16	18	7430	11	5	2	*	22	19	50	

X-ray analysis of the single crystals. Determination of the space group

Transparent, yellow-orange, elongated single crystals of (I) form directly from the reaction described by Porri *et al.* (1965). In order to be able to record the X-ray spectra, the crystals, which rapidly decompose in air, were put in thin glass tubes, under an inert atmos-

sphere. hkl reflexions with l ranging from 0 to 7 were collected by the usual Weissenberg equi-inclination technique (Mo $K\alpha$ radiation); the c axis coincides with the axis of elongation of the crystals. The old data consisting of the (hkl) layers with $h+k=0$ and $h+k=1$ (Porri *et al.* 1965) were disregarded in the least-squares refinement, because of the less favourable crystal shape used.

Table 2 (cont.)

H	K	L	F0	Fc	Ph	H	K	L	F0	Fc	Ph	H	K	L	F0	Fc	Ph
6	6	2	45	41	5242	7	5	3	21	26	127	6	5	4	22	24	7166
7	6	2	• 12	9	6737	8	5	3	25	31	7290	7	5	4	22	23	4959
6	6	2	28	29	4940	9	5	3	14	17	386	8	5	4	20	20	7795
9	6	2	• 13	9	7296	10	5	3	23	21	7477	9	5	4	17	17	5019
10	6	2	24	21	9015	11	5	3	• 12	11	136	10	5	4	14	14	7371
11	6	2	• 14	6	7416	6	6	1	21	26	4595	6	6	4	18	21	247
7	7	2	32	30	91	7	6	3	25	30	2516	7	6	4	21	23	2212
8	7	2	• 11	6	2849	8	6	3	18	18	5281	8	6	4	13	16	138
9	7	2	27	20	70	9	6	3	20	22	2466	9	6	4	14	14	2406
10	7	2	• 14	8	2115	10	6	3	• 11	12	4854	10	6	4	13	14	293
11	7	2	• 14	14	9976	11	6	3	• 12	14	2466	7	7	4	17	15	5175
8	8	2	25	21	5128	7	7	3	18	17	9954	8	7	4	17	17	7500
9	8	2	• 16	7	7736	8	7	3	19	20	7372	9	7	4	17	13	5061
10	8	2	• 14	15	5107	9	7	3	15	12	0	8	8	4	• 10	12	9588
9	9	2	• 14	16	212	10	7	3	17	16	7530	9	8	4	• 10	11	2397
1	0	3	79	12	2500	8	6	3	13	12	5273	1	0	5	68	84	7900
2	0	3	95	94	5000	9	6	3	15	16	7430	2	0	5	49	47	0
1	0	3	131	135	2500	9	9	3	• 12	9	9769	1	0	5	65	73	7500
4	0	3	76	77	5000	1	0	4	81	82	2500	4	0	5	50	53	0
5	0	3	67	74	2500	2	0	4	44	42	0	5	0	5	63	46	7500
6	0	3	47	48	5000	3	0	4	47	61	2500	6	0	5	31	29	0
7	0	3	66	70	2500	4	0	4	50	48	0	7	0	5	30	35	7500
8	0	3	29	31	5000	5	0	4	41	45	2500	8	0	5	22	22	0
9	0	3	25	27	2500	6	0	4	32	35	0	9	0	5	21	17	7500
10	0	3	20	16	5000	7	0	4	28	30	2500	10	0	5	18	20	0
11	0	3	19	20	2500	8	0	4	27	29	0	11	0	5	15	12	7500
12	0	3	• 12	9	5000	9	0	4	21	20	2500	1	1	5	56	53	5113
1	1	3	95	93	9818	10	0	4	18	15	0	2	1	5	59	63	2200
2	1	3	118	110	7530	11	0	4	17	15	2500	3	1	5	46	44	5131
3	1	3	87	84	9939	12	0	4	• 10	10	0	4	1	5	53	59	2298
4	1	3	95	94	7434	1	1	4	36	31	4400	5	1	5	40	40	5226
5	1	3	49	51	82	2	1	4	46	47	7218	6	1	5	36	36	2246
6	1	3	57	61	7468	3	1	4	48	47	4766	7	1	5	28	29	5196
7	1	3	40	41	251	4	1	4	54	56	7560	8	1	5	22	25	2551
8	1	3	41	45	7340	5	1	4	25	25	4502	9	1	5	25	21	5168
9	1	3	19	21	562	6	1	4	31	35	7495	10	1	5	18	15	2941
10	1	3	19	24	7387	7	1	4	35	36	4902	11	1	5	15	16	5122
11	1	3	18	14	286	8	1	4	22	26	7928	2	2	5	33	28	9983
12	1	3	• 12	16	7419	9	1	4	15	17	5048	3	2	5	54	58	7479
2	2	3	77	77	4660	10	1	4	18	19	7715	4	2	5	47	46	55
3	2	3	99	100	2521	11	1	4	17	16	4929	5	2	5	36	39	7422
4	2	3	61	62	5108	12	1	4	• 10	10	7700	6	2	5	34	35	9959
5	2	3	47	52	2497	2	2	4	41	30	9779	7	2	5	31	32	7485
6	2	3	39	40	4606	3	2	4	48	48	2102	8	2	5	26	26	49
7	2	3	48	51	2509	4	2	4	29	32	91	9	2	5	• 12	17	7843
8	2	3	25	28	5299	5	2	4	39	43	2305	10	2	5	23	19	9940
9	2	3	21	27	2435	6	2	4	22	22	9949	11	2	5	• 13	13	7462
10	2	3	17	17	6847	7	2	4	30	34	2376	3	3	5	49	46	4869
11	2	3	19	21	2507	8	2	4	21	23	181	4	3	5	49	54	2863
12	2	3	• 12	10	5061	9	2	4	19	21	2569	5	3	5	37	38	5021
3	3	3	67	71	152	10	2	4	17	17	111	6	3	5	30	33	2577
4	3	3	77	84	7398	11	2	4	14	15	2379	2	3	5	31	32	4975
5	3	3	41	46	14	3	3	4	41	46	5493	8	3	5	23	22	2671
6	3	3	66	50	7617	4	3	4	51	52	7666	9	3	5	22	19	4931
7	3	3	30	34	9694	5	3	4	21	26	5171	10	3	5	• 12	13	2524
8	3	3	32	36	7660	6	3	4	31	38	6977	11	3	5	• 13	13	4976
9	3	3	19	18	9835	7	3	4	26	27	5113	4	4	5	41	39	244
10	3	3	21	23	7623	8	3	4	23	25	7412	5	4	5	35	35	7473
11	3	3	16	13	9607	9	3	4	14	16	5179	6	4	5	28	27	123
12	3	3	• 12	14	7500	10	3	4	15	17	7015	7	4	5	24	27	7593
4	4	3	54	60	5606	11	3	4	16	14	4910	8	4	5	25	22	298
5	4	3	58	64	2343	4	4	4	39	41	140	9	4	5	21	16	7411
6	4	3	33	36	4881	5	4	4	30	33	2688	10	4	5	• 13	15	54
7	4	3	41	45	2437	6	4	4	28	28	9899	11	4	5	• 13	10	7125
8	4	3	20	26	5412	7	4	4	27	28	2376	5	5	5	22	22	5426
9	4	3	22	26	2400	8	4	4	22	21	9843	6	5	5	23	25	2448
10	4	3	• 11	14	4733	9	4	4	18	16	2510	7	5	5	26	23	5163
11	4	3	11	17	2471	10	4	4	15	15	9870	8	5	5	22	18	2473
5	5	3	35	37	261	11	4	4	14	13	2374	9	5	5	• 12	15	5184
6	5	3	47	46	7476	5	5	4	29	30	4795	10	5	5	• 13	12	2568

The tetragonal unit cell of (I) has the following parameters: $a=b=7.90 \pm 0.03 \text{ \AA}$; $c=6.92 \pm 0.02 \text{ \AA}$; $Z=2$; $V=432 \pm 4 \text{ \AA}^3$. The calculated density ($D_{\text{calc}}=1.67 \text{ g.cm}^{-3}$) agrees with the experimental value, measured by floating crystal techniques, to within a few per cent. Systematic relationships among the X-ray intensities are:

- (a) $|F(hkl)| = |F(khl)|$;
- (b) $|F(hk0)|$ with $h+k=2n+1$ are very weak;
- (c) $|F(h00)| \neq 0$ only if $h=2n$.

Because of (b), relationship (c) has not been assumed as generally valid. Since no systematic absences are observed on the $00l$ reflexions, possible space groups are those corresponding to the numbers (*International Tables for X-ray Crystallography*, 1952): 89 (*P422*), 90 (*P4212*); 99 (*P4mm*), 111 (*P42m*), 113 (*P421m*), 115 (*P4m2*) and 123 (*P4/mmm*). Since only two molecules are present per unit cell, and all the carbon atoms cannot be placed on an element of crystallographic symmetry, the last group must be discarded; in fact, it contains too many general positions, 16,

Table 2 (cont.)

H	K	L	F0	FC	PH	H	K	L	F0	FC	PH	H	K	L	F0	FC	PH
6	6	5	24	23	9852	10	2	6	+ 10	9	5131	2	1	7	+ 4	5	2166
7	6	5	20	20	7801	11	2	6	+ 17	16	7520	3	1	7	+ 28	29	186
8	6	5	73	19	93	3	3	6	+ 21	21	536	4	1	7	+ 7	6	6470
9	6	5	+ 13	12	7915	4	3	6	+ 71	64	2304	5	1	7	+ 20	71	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	11	2452	7	3	6	+ 16	15	32	8	1	7	+ 7	4	4193
9	7	5	+ 13	12	5026	8	3	6	+ 29	29	2417	9	1	7	+ 14	15	9874
8	8	5	+ 13	15	327	9	1	6	+ 10	8	146	10	1	7	+ 7	5	7110
1	0	6	104	100	7500	10	1	6	+ 19	18	2482	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	5071
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	1	7	+ 29	10	5554
11	0	6	20	16	7500	8	5	6	+ 22	23	2535	4	1	7	+ 5	6	7779
1	1	6	23	22	9515	9	5	6	+ 10	6	9881	5	1	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	1	7	+ 12	14	9878
6	1	6	46	45	2641	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	2679	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	2684	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	4262	5	0	7	+ 5	3	2500	6	5	7	+ 7	3	9435
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	1	6783
5	2	6	57	52	7563	8	0	7	+ 18	21	5000	6	6	7	+ 16	17	6815
6	2	6	16	15	4888	9	0	7	+ 7	3	2500	7	6	7	+ 7	6	3398
7	2	6	42	39	7455	10	0	7	+ 14	14	5000	8	6	7	+ 12	14	4812
8	2	6	14	11	5070	1	1	7	+ 26	24	388	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 $P\bar{4}2_1m$ (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 ($\partial^2\varrho/\partial z^2 \approx \partial^2\varrho/\partial (x+y)^2 = 26 \text{ e.}\AA^{-2}$), while only about the Cl atom the contours were markedly ellipsoidal ($\partial^2\varrho/\partial z^2 = 11; \partial^2\varrho/\partial (x+y)^2 = 5.5 \text{ e.}\AA^{-2}$). The final Weissenberg 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, Loguidice, 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 π 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 C-C intermolecular distance is shorter than 3.65 Å; the shortest Cl-C contact distance between molecules superposed along c is also 3.65 Å. As for the intramolecular non-bonding distances, it seems worth mentioning that, as a result of the coordination to the metal, one C-C contact between different butadiene ligands is shorter (3.15 Å) than that found in graphite (3.40 Å) (Wyckoff, 1963).

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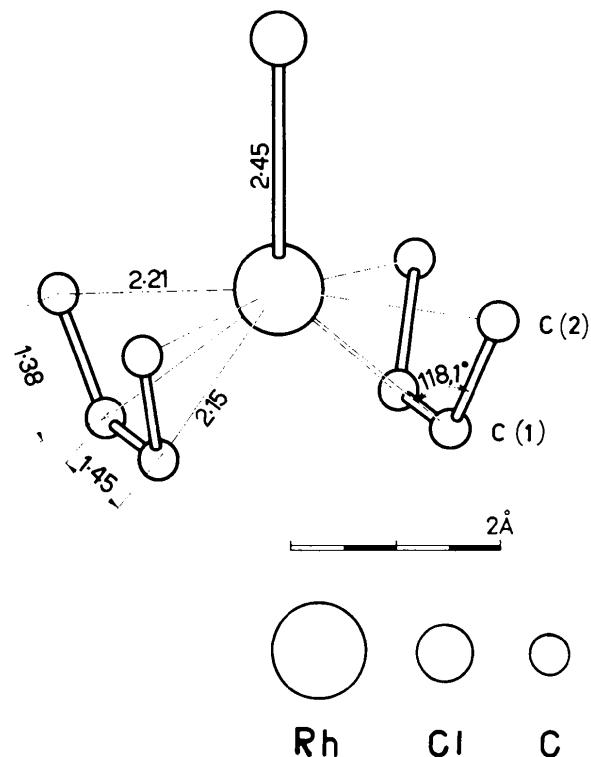


Fig. 2. Resulting molecular structure of (I). Average estimated standard deviations are:

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

References

- ALLEGRA, G., LOGUIDICE, 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.