

## The Crystal Structure of Di- $\mu$ -chloro-bis(triphenyl phosphite)-(cyclo-octa-1,5-diene)dirhodium(I)

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The crystal structure of di- $\mu$ -chloro-bis(triphenyl phosphite)(cyclo-octa-1,5-diene)dirhodium(I) has been determined by three-dimensional Patterson and Fourier techniques using automatic diffractometer data. The atomic parameters were refined by the least-squares method to a final  $R$  index of 0.066 for 2500 observed reflexions. The cell dimensions are  $a = 12.863 \pm 0.006$ ,  $b = 13.146 \pm 0.007$ ,  $c = 25.130 \pm 0.010$  Å,  $\beta = 99.98 \pm 0.01^\circ$  with the space group  $P2_1/c$  and 4 molecules per unit cell. The coordination of the Rh atoms is square planar, displaying a folded  $\text{RhCl}_2\text{Rh}$  bridge with an angle of  $122.6 \pm 0.2^\circ$  between the lines extending from the Rh atoms to the centre of the line joining the two Cl atoms.

### Introduction

The structure analysis of  $\text{Rh}_2[\text{P}(\text{OC}_6\text{H}_5)_3]_2(\text{C}_8\text{H}_{12})\text{Cl}_2$  (Haines, 1969) was undertaken at the request of Dr W. Robb and Mrs L. Haines of the National Chemical Research Laboratories as the structure of the  $\text{RhCl}_2\text{Rh}$  bridge is relevant to their kinetic studies of this and related compounds. Two structure analyses of compounds containing  $\text{RhCl}_2\text{Rh}$  bridges have hitherto been reported. Ibers & Snyder (1962) showed that the dimer of  $\text{RhCl}(\text{cyclo-octa-1,5-diene})$  is planar in that

the  $\text{RhCl}_2\text{Rh}$  bridge is planar and the centres of the C=C bonds (towards which the  $\sigma-\pi$  bonds between the rhodium atoms and the  $\text{C}_8\text{H}_{12}$  rings are directed) form square-planar arrays with the halves of the bridge. In contrast, Dahl, Martell & Wampler (1961) found a more complicated situation in  $\text{Rh}_2(\text{CO})\text{Cl}_2$ . Each rhodium atom is surrounded by two chlorine atoms and two carbonyl groups in a square-planar arrangement. The  $\text{RhCl}_2\text{Rh}$  bridge is severely bent with an angle of  $124^\circ$  between the two lines joining the rhodium atoms with the centre of the line between the

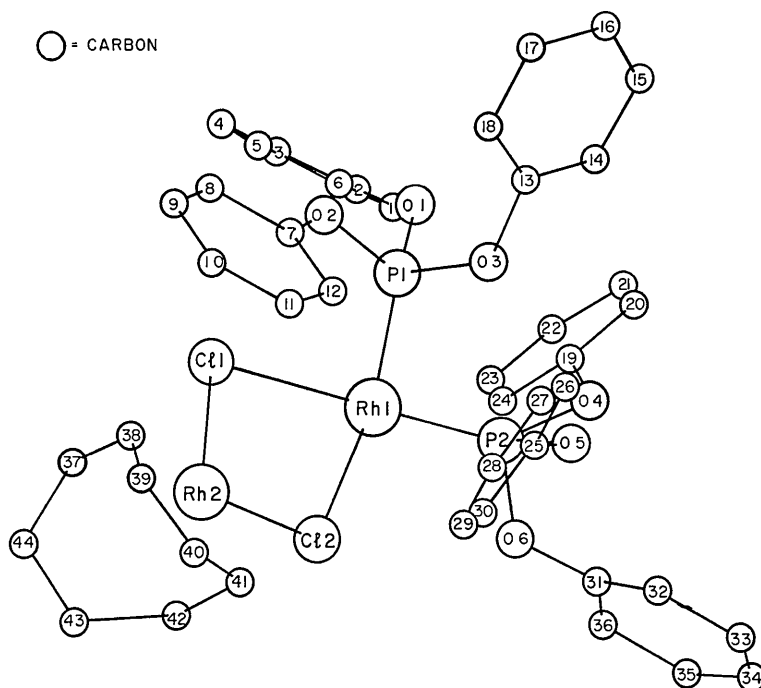


Fig. 1. A view of the molecule along the [221] axis showing the atomic numbering used.

chlorine atoms and they consider the rhodium atom to be six-coordinated. The increased coordination is caused by two rhodium atoms, *viz.* (a) one in an adjacent dimer at a distance of 3.31 Å which is in keeping with other metal-metal bonds as referenced by Dahl *et al.* (1961), and (b) the second rhodium atom of the bridge itself. Dahl *et al.* describe this atom as making a 'bent' bond with the central atom, and this is held responsible for the diamagnetism exhibited by the compound in the solid state.

### Experimental

Crystals of suitable size and quality were prepared and provided by Mrs L. Haines. The crystals were amber coloured and had intricate faceting which resulted in many of them being nearly spherical. Preliminary oscillation, Weissenberg and precession photographs showed them to be monoclinic with space group  $P2_1/c$  ( $h0l$  absent for  $l$  odd,  $0k0$  absent for  $k$  odd). Spot positions were accurately measured with a Hilger &

Table 1. Final atomic parameters (fractional coordinates and isotropic temperature factors)

	Standard deviations are given in parentheses.			
	$x/a$	$y/b$	$z/c$	$B$
Rh(1)	0.7077 (1)	0.2180 (1)	0.6085 (1)	3.74 (3)
Rh(2)	0.7348 (1)	0.4218 (1)	0.5473 (1)	4.52 (4)
Cl(1)	0.5832 (3)	0.3503 (4)	0.5758 (1)	4.68 (10)
Cl(2)	0.7690 (4)	0.2495 (4)	0.5252 (2)	5.16 (11)
P(1)	0.6480 (4)	0.2054 (4)	0.6825 (2)	3.78 (10)
P(2)	0.8165 (3)	0.0954 (3)	0.6316 (2)	3.36 (9)
O(1)	0.5510 (8)	0.1317 (8)	0.6876 (4)	4.53 (24)
O(2)	0.6018 (9)	0.3070 (8)	0.7056 (4)	4.58 (25)
O(3)	0.7289 (8)	0.1610 (9)	0.7334 (4)	4.62 (26)
O(4)	0.7763 (8)	-0.0141 (8)	0.6475 (4)	4.24 (24)
O(5)	0.9048 (8)	0.1015 (8)	0.6857 (4)	4.08 (24)
O(6)	0.8827 (8)	0.0689 (8)	0.5857 (4)	4.36 (23)
C(1)	0.4543 (13)	0.1304 (13)	0.6510 (6)	4.6 (4)
C(2)	0.4322 (16)	0.0393 (16)	0.6255 (8)	6.4 (5)
C(3)	0.3239 (22)	0.0314 (22)	0.5921 (11)	10.2 (7)
C(4)	0.2622 (20)	0.1132 (21)	0.5901 (10)	8.8 (6)
C(5)	0.2857 (18)	0.2009 (18)	0.6177 (8)	7.4 (5)
C(6)	0.3907 (17)	0.2108 (18)	0.6488 (8)	6.9 (5)
C(7)	0.6567 (13)	0.3995 (13)	0.7159 (6)	4.0 (4)
C(8)	0.5928 (15)	0.4826 (15)	0.7203 (7)	5.4 (4)
C(9)	0.6442 (15)	0.5775 (15)	0.7331 (7)	5.9 (4)
C(10)	0.7518 (15)	0.5870 (15)	0.7417 (7)	5.4 (4)
C(11)	0.8120 (14)	0.5033 (15)	0.7361 (7)	4.9 (4)
C(12)	0.7674 (13)	0.4041 (13)	0.7238 (6)	4.6 (4)
C(13)	0.7036 (13)	0.1382 (14)	0.7842 (7)	4.1 (4)
C(14)	0.6971 (15)	0.0375 (16)	0.7975 (8)	6.3 (5)
C(15)	0.6770 (17)	0.0123 (17)	0.8503 (9)	7.1 (5)
C(16)	0.6618 (15)	0.0893 (17)	0.8850 (8)	6.2 (5)
C(17)	0.6670 (15)	0.1902 (16)	0.8720 (8)	6.0 (5)
C(18)	0.6881 (14)	0.2158 (15)	0.8193 (7)	4.9 (4)
C(19)	0.6954 (14)	-0.0720 (14)	0.6157 (7)	4.3 (4)
C(20)	0.6651 (15)	-0.1557 (15)	0.6426 (7)	5.4 (4)
C(21)	0.5856 (16)	-0.2184 (17)	0.6136 (8)	6.6 (5)
C(22)	0.5448 (15)	-0.1981 (16)	0.5602 (8)	5.7 (5)
C(23)	0.5760 (14)	-0.1128 (14)	0.5347 (7)	5.2 (4)
C(24)	0.6555 (14)	-0.0493 (14)	0.5616 (7)	4.7 (4)
C(25)	0.9632 (13)	0.1888 (13)	0.7022 (7)	4.0 (4)
C(26)	0.9787 (15)	0.2041 (16)	0.7579 (8)	5.5 (5)
C(27)	1.0418 (15)	0.2922 (16)	0.7765 (8)	6.3 (4)
C(28)	1.0791 (16)	0.3541 (16)	0.7420 (9)	6.7 (5)
C(29)	1.0616 (15)	0.3367 (16)	0.6864 (8)	6.6 (5)
C(30)	0.9994 (14)	0.2502 (14)	0.6656 (7)	5.0 (4)
C(31)	0.9482 (13)	-0.0153 (13)	0.5850 (7)	4.3 (4)
C(32)	1.0349 (18)	-0.0273 (18)	0.6215 (9)	7.5 (6)
C(33)	1.1014 (20)	-0.1159 (21)	0.6179 (11)	9.1 (7)
C(34)	1.0771 (17)	-0.1816 (16)	0.5761 (9)	7.2 (5)
C(35)	0.9945 (23)	-0.1639 (23)	0.5367 (11)	10.7 (8)
C(36)	0.9267 (20)	-0.0776 (21)	0.5408 (10)	9.6 (7)
C(37)	0.6645 (13)	0.5659 (14)	0.5358 (7)	4.7 (4)
C(38)	0.7254 (14)	0.5615 (14)	0.5888 (7)	6.1 (4)
C(39)	0.8292 (17)	0.6136 (16)	0.6047 (8)	6.9 (5)
C(40)	0.9236 (18)	0.5452 (18)	0.6014 (9)	6.9 (6)
C(41)	0.8943 (14)	0.4596 (14)	0.5566 (7)	6.0 (4)
C(42)	0.8448 (15)	0.4827 (14)	0.5029 (7)	5.3 (4)
C(43)	0.8153 (14)	0.5925 (15)	0.4824 (7)	5.9 (4)
C(44)	0.7027 (15)	0.6228 (15)	0.4895 (7)	5.5 (4)

Watts four-circle diffractometer and all the cell constants were determined from these by means of least-squares methods to give:

$$\begin{aligned} a &= 12.863 \pm 0.006 \text{ \AA} \\ b &= 13.146 \pm 0.007 \\ c &= 25.130 \pm 0.010 \\ \beta &= 99.98 \pm 0.01^\circ. \end{aligned}$$

The density measured by flotation was  $1.59 \text{ g.cm}^{-3}$  indicating four formula units of mass 1005.5 in the unit cell which gave a calculated density of  $1.60 \text{ g.cm}^{-3}$ .

A crystal of spherical shape with a diameter of 0.2 mm was selected for the intensity measurements. The intensities of 2500 independent reflexions with  $\theta \leq 20^\circ$  were measured. Mo  $K\alpha$  (Zr,  $\beta$ -filtered) radiation was used in conjunction with the  $\omega$ -scan technique. The intense 102 reflexion was used as a reference standard and remeasured after each set of 5 reflexions. Maximum variation over the 14 days taken to collect the intensities was  $\pm 2\%$ . Background corrections were made from slow scans of intensity against  $\theta$  parallel to central lattice rows but sufficiently far from them in  $\omega$  to ensure that the tails of the diffraction peaks were not intersected. The usual  $L_p$  corrections were made and absorption corrections were obviated by the low value of  $\mu R \approx 0.10$ .

### Structure refinement

The trial structure which followed from three-dimensional Patterson and Fourier syntheses was refined to  $R=0.066$ ,  $[R=(\sum(|F_o|-|F_c|)/\sum|F_o|)]$ , by using a full-matrix least-squares program which minimizes the function  $\sum w(|F_o|-|kF_c|)^2$  (Busing, Martin & Levy, 1962) with individual isotropic thermal parameters for all the atoms. The form factors used were those of Hanson, Herman, Lea & Skillman (1964) after minimal adjustment for anomalous dispersion according to *International Tables for X-ray Crystallography* (1962).

All measurable intensities were included in the refinement with equal weight and those of magnitude less than three times the background count (the unobserved

Table 2. Bond distances ( $\text{\AA}$ )

Standard deviations in parentheses.			
Rh(1)-Cl(1)	2.410 (5)	C(11)-C(12)	1.43 (2)
Rh(1)-Cl(2)	2.398 (5)	C(12)-C(7)	1.40 (2)
Rh(1)-P(1)	2.138 (5)		
Rh(1)-P(2)	2.146 (5)	C(13)-C(14)	1.37 (2)
Rh(2)-Cl(1)	2.383 (5)	C(14)-C(15)	1.43 (3)
Rh(2)-Cl(2)	2.391 (5)	C(15)-C(16)	1.37 (3)
		C(16)-C(17)	1.37 (3)
Rh(2)-C(37)	2.10 (2)	C(17)-C(18)	1.43 (2)
Rh(2)-C(38)	2.12 (2)	C(18)-C(13)	1.39 (2)
Rh(2)-C(41)	2.08 (2)		
Rh(2)-C(42)	2.10 (2)	C(19)-C(20)	1.38 (2)
		C(20)-C(21)	1.41 (2)
Rh(2)···Rh(1)*	3.138 (2)	C(21)-C(22)	1.38 (2)
Cl(1)···Cl(2)*	3.185 (7)	C(22)-C(23)	1.38 (2)
		C(23)-C(24)	1.40 (2)
P(1)-O(1)	1.61 (1)	C(24)-C(19)	1.40 (2)
P(1)-O(2)	1.59 (1)		
P(1)-O(3)	1.61 (1)	C(25)-C(26)	1.39 (2)
P(2)-O(4)	1.60 (1)	C(26)-C(27)	1.44 (3)
P(2)-O(5)	1.60 (1)	C(27)-C(28)	1.35 (3)
P(2)-O(6)	1.61 (1)	C(28)-C(29)	1.39 (3)
		C(29)-C(30)	1.43 (2)
O(1)-C(1)	1.41 (2)	C(30)-C(25)	1.37 (2)
O(2)-C(7)	1.41 (2)		
O(3)-C(13)	1.40 (2)	C(31)-C(32)	1.33 (4)
O(4)-C(19)	1.42 (2)	C(32)-C(33)	1.45 (3)
O(5)-C(25)	1.41 (2)	C(33)-C(34)	1.35 (3)
O(6)-C(31)	1.39 (2)	C(34)-C(35)	1.34 (3)
		C(35)-C(36)	1.44 (3)
C(1)-C(2)	1.37 (3)	C(36)-C(31)	1.37 (3)
C(2)-C(3)	1.48 (4)		
C(3)-C(4)	1.34 (3)	C(37)-C(38)	1.42 (2)
C(4)-C(5)	1.35 (3)	C(38)-C(39)	1.49 (3)
C(5)-C(6)	1.44 (3)	C(39)-C(40)	1.52 (3)
C(6)-C(1)	1.34 (3)	C(40)-C(41)	1.59 (3)
		C(41)-C(42)	1.42 (2)
C(7)-C(8)	1.38 (2)	C(42)-C(43)	1.56 (3)
C(8)-C(9)	1.42 (2)	C(43)-C(44)	1.54 (3)
C(9)-C(10)	1.37 (2)	C(44)-C(37)	1.53 (2)
C(10)-C(11)	1.37 (2)	Mean aromatic	
		C=C	1.39 (3)

\* Interatomic distance across  $\text{RhCl}_2\text{Rh}$  bridge.

Table 3. Bond angles ( $^\circ$ )

Standard deviations in parentheses.

Rh(1)-Cl(1)-Rh(2)	81.8 (2)		
Rh(1)-Cl(2)-Rh(2)	81.9 (2)		
Cl(1)-Rh(1)-Cl(2)	82.9 (2)	P(2)-O(4)-C(19)	125.4 (1.0)
Cl(1)-Rh(1)-P(1)	91.9 (2)	P(2)-O(5)-C(25)	123.7 (1.0)
Cl(2)-Rh(1)-P(2)	94.0 (2)	P(2)-O(6)-C(31)	125.8 (9)
Cl(1)-Rh(2)-Cl(2)	83.7 (2)		
P(1)-Rh(1)-P(2)	91.3 (2)	C(37)-C(38)-C(39)	123.6 (1.6)
		C(38)-C(39)-C(40)	113.5 (1.8)
Rh(1)-P(1)-O(1)	121.1 (5)	C(39)-C(40)-C(41)	113.2 (1.7)
Rh(1)-P(1)-O(2)	117.4 (5)	C(40)-C(41)-C(42)	122.3 (1.7)
Rh(1)-P(1)-O(3)	116.0 (5)	C(41)-C(42)-C(43)	123.7 (1.6)
Rh(1)-P(2)-O(4)	121.2 (5)	C(42)-C(43)-C(44)	112.4 (1.5)
Rh(1)-P(2)-O(5)	121.4 (5)	C(43)-C(44)-C(37)	113.1 (1.5)
Rh(1)-P(2)-O(6)	112.1 (5)	C(44)-C(37)-C(38)	122.2 (1.6)
P(1)-O(1)-C(1)	124.4 (1.0)	Mean O-P-O	99.5 (6)
P(1)-O(2)-C(7)	125.2 (1.0)	Mean O-C-C	117.4 (1.6)
P(1)-O(3)-C(13)	125.4 (1.0)	Mean C-C-C (benzene)	119.5 (2.0)
Rh(1)Cl(1)Cl(2)/Rh(2)Cl(1)Cl(2) interplanar angle			122.6 (2)

reflexions) were excluded according to the suggestion of Dunning & Vand (1969). The final positional and thermal parameters are listed in Table 1.

Interatomic distances and bond angles were calculated (Fig. 1) with the aid of the crystallographic program ORFFE of Busing, Martin & Levy (1964). These values are summarized in Tables 2 and 3. Observed and calculated structure factors are listed in Table 4.

The atomic numbering and the molecular geometry are illustrated in Figs. 1 and 2. Fig. 1 shows a view of the molecule perpendicular to the (221) crystal plane, while the molecular geometry can be seen from the stereoscopic diagram in Fig. 2. The principal bonding parameters of the structure are given in Fig. 3.

Table 4. Observed and calculated structure factors

The columns are  $\sqrt{I_0}/|F_{obs}|$  and  $10F_{calc}$ .

Table with multiple columns of numerical data representing observed and calculated structure factors. The table is organized into several vertical sections, each starting with a header like 'O, 0, L' or 'O, 0, L' followed by a list of values. The data is presented in a grid-like format with varying column widths.

Table 4 (cont.)

1 1304 1866	-8 329 -355	3 196 127	9 887 -894	1 333 524	6 274 178	5 332 131	11 363 357	-1 622 -041	10 791 701	-3 717 817
6 736 418	-9 366 -376	4 915 -388	13 495 426	5 401 -446	7 522 519	6 515 387	-1 604 -659	-1 851 -457	11 111 112	-5 592 678
7 3 311 -840	-10 282 301	5 122 -237	13 371 -817	6 133 -256	8 450 -814	7 632 431	-1 237 -303	-1 118 115	-1 323 122	-5 381 371
8 394 607	-11 355 368	6 1647 -1626	15 789 732	7 295 133	9 551 -937	8 509 519	-1 047 -512	-1 114 115	-1 323 122	-5 381 371
9 227 -216	-13 376 399	9 340 -183	-7 573 487	9 822 -837	10 367 -474	10 348 -351	-5 241 -311	-7 645 -118	-2 611 -274	-6 761 828
10 682 391	-14 667 -657	10 185 969	-5 914 969	11 107 -582	11 590 -522	11 576 -570	-6 605 602	-7 645 -118	-1 314 -124	-13 481 -416
15 571 579	-16 319 -257	12 861 834	-7 472 468	11 440 -937	11 590 -482	11 590 -482	-6 605 602	-1 314 -124	-1 314 -124	-15 314 -124
16 073 -632	-1 101 1	16 430 -446	-9 834 -917	12 331 267	-5 888 984	16 403 384	-17 283 304	-10 267 -560	-7 565 574	-17 382 -392
22 476 -184	-2 264 -328	17 283 -293	-11 274 269	14 413 404	-8 232 -193	17 283 267	-7 486 1	-11 673 690	-10 277 267	10% -3, 1
24 360 -328	3 731 -090	-2 980 1070	5 -8, 1	15 603 571	-9 884 -931	-2 763 798	3 358 379	-13 267 325	-13 267 325	
-57 330 260	-4 414 -1	-4 785 -272	10 521 569	16 307 -395	-10 704 390	-10 704 390	3 358 379	-13 267 325	-16 279 268	
-7 338 163	-1 864 848	-5 937 611	1 255 323	-1 878 958	-12 501 -528	-11 311 -278	-9 926 901	-1 439 -497	-15 618 593	5 578 -539
-10 500 -522	-6 704 -878	-6 1735 167	4 462 399	-11 274 663	-11 274 663	-11 274 663	-9 926 901	-2 338 -179	-19 573 -112	6 312 308
-8 320 387	-1 864 848	-5 937 611	1 255 323	-1 878 958	-12 501 -528	-11 311 -278	-9 926 901	-1 439 -497	-19 573 -112	-1 255 304
-11 392 619	-2 262 328	-7 474 857	5 643 667	-5 1031 1099	-18 262 541	-18 262 541	-7 208 939	-3 357 -419	0 420 -413	-1 508 519
-13 519 526	-9 484 478	-8 2545 2534	2091 -261	-6 1206 1309	-6 1206 1309	-6 1206 1309	-9 741 -578	-5 290 313	2 484 -282	-4 631 696
-14 535 526	-4 -11, 1	-11 573 -527	10 268 -347	-8 1484 1542	6 -7, 1	6 -7, 1	-11 418 -635	-7 315 167	3 450 -620	-5 455 -446
-15 301 -385	-11 573 -527	-11 648 -648	10 268 -347	-8 1484 1542	6 -7, 1	6 -7, 1	-11 418 -635	-7 315 167	3 450 -620	-5 455 -446
-17 371 -339	0 571 -507	-13 320 317	12 323 215	-9 777 -539	6 659 732	6 659 732	-15 172 341	-14 292 273	5 795 -726	-7 276 771
-19 521 -197	1 716 -609	-14 427 634	13 740 -609	-13 758 -754	6 331 331	6 331 331	-16 290 -235	6 444 -523	6 794 536	-9 277 302
-20 425 -137	4 122 378	-18 064 -608	-11 576 -623	-20 204 319	-19 320 -334	-19 320 -334	-16 842 -899	4 608 -626	16 291 198	-2 360 -412
0 201 -208	-2 602 -598	-19 265 -313	-2 303 385	-20 715 -823	-20 715 -823	-20 715 -823	-21 474 422	5 604 673	-2 461 -218	-10 320 -733
0 1005 -1059	-4 414 -1	-20 804 -720	-7 698 -703	-22 731 -709	-12 435 330	-12 435 330	-21 474 422	5 604 673	-2 461 -218	-10 320 -733
1 720 685	-4 652 200	-22 700 -567	-9 647 -688	-22 731 -709	-12 435 330	-12 435 330	-21 474 422	5 604 673	-2 461 -218	-10 320 -733
2 1609 -1613	-6 151 651	5 254 346	-12 400 -410	-2 447 -352	-11 303 363	-11 303 363	-2 426 446	-4 443 499	-8 504 -475	7 361 359
3 701 -828	-8 376 389	3 143 1507	-16 337 381	1 871 -841	4 795 810	4 795 810	-3 634 713	4 301 370	-16 496 514	8 463 447
4 811 -789	5 0, 1	4 209 955	-14 489 -456	4 795 810	6 328 -394	6 328 -394	-7 995 -1075	6 747 776	7 -10, 1	-12 388 391
5 399 -606	-6 1557 -1547	7 496 554	-5 -4, 1	7 523 544	8 1305 -1265	8 1305 -1265	-9 312 300	1 417 -487	-11 276 313	4 332 352
6 731 721	4 2454 2523	10 256 211	2 532 554	8 1305 -1265	10 347 -269	10 347 -269	-10 312 300	1 417 -487	-11 276 313	4 332 352
8 628 618	8 284 345	11 262 239	3 498 623	14 345 218	14 345 218	14 345 218	-12 519 -509	3 702 -671	-11 553 -670	-2 281 -287
9 784 957	8 284 345	11 262 239	3 498 623	14 345 218	14 345 218	14 345 218	-12 519 -509	3 702 -671	-11 553 -670	-2 281 -287
11 279 191	10 404 -326	14 544 527	5 579 -554	15 310 278	1 440 416	1 440 416	-13 278 -266	-8 207 556	-17 514 -273	6 259 278
12 381 399	14 926 902	15 741 759	10 473 413	16 020 807	4 509 519	4 509 519	-15 267 -208	0 673 376	8 451 376	-13 491 -520
13 825 -848	16 471 -848	-1 248 -200	-1 396 422	-2 975 1044	-3 001 -486	-3 001 -486	-1 278 -193	2 134 114	0 485 -468	-3 554 588
14 353 362	20 558 -574	-2 807 -790	-1 396 422	-2 975 1044	-3 001 -486	-3 001 -486	-1 278 -193	2 134 114	0 485 -468	-3 554 588
15 365 353	20 558 -574	-2 807 -790	-1 396 422	-2 975 1044	-3 001 -486	-3 001 -486	-1 278 -193	2 134 114	0 485 -468	-3 554 588
17 206 338	-2 162 -1617	-5 245 196	-6 468 -455	-8 125 1938	11 501 441	11 501 441	-2 201 -304	8 1233 -1248	2 497 497	-2 333 333
-1 553 545	-4 539 -450	-4 1207 1254	-19 370 431	-5 365 324	-6 102 326	-6 102 326	-6 1452 -1371	-2 500 -519	4 616 -309	-11 311 362
-3 879 700	-6 287 -247	-5 245 196	-12 321 -320	-7 247 -257	-6 422 -499	-6 422 -499	-6 1452 -1371	-2 500 -519	4 616 -309	-11 311 362
-5 628 674	-8 134 -1445	-7 339 -380	-13 570 -380	-11 611 -1282	-9 299 -249	-9 299 -249	-6 1452 -1371	-2 500 -519	4 616 -309	-11 311 362
-6 624 639	-10 134 -1445	-7 339 -380	-13 570 -380	-11 611 -1282	-9 299 -249	-9 299 -249	-6 1452 -1371	-2 500 -519	4 616 -309	-11 311 362
-8 451 400	-12 439 472	-9 456 571	-5 -10, 1	-10 1342 -1429	-8 285 334	-8 285 334	-11 444 -418	-18 523 491	-1 212 206	9 -5, 1
-9 765 852	-14 459 886	-10 981 -1009	-1 917 863	-11 566 461	-10 134 336	-10 134 336	-11 444 -418	-18 523 491	-1 212 206	9 -5, 1
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-12 534 476	-20 558 -574	-12 320 318	-2 320 318	-5 334 509	-19 429 402	-19 429 402	-13 305 -337	0 644 888	-3 276 -878	2 549 545
-13 553 -636	-22 641 -636	-13 320 318	-2 320 318	-5 334 509	-19 429 402	-19 429 402	-13 305 -337	0 644 888	-3 276 -878	2 549 545
-15 371 -375	-24 724 -375	-14 320 318	-3 320 318	-6 334 509	-20 429 402	-20 429 402	-13 305 -337	0 644 888	-3 276 -878	2 549 545
-16 390 -321	-26 807 -321	-15 320 318	-4 320 318	-7 334 509	-21 429 402	-21 429 402	-13 305 -337	0 644 888	-3 276 -878	2 549 545
-18 396 -425	-28 890 -425	-16 320 318	-5 320 318	-8 334 509	-22 429 402	-22 429 402	-13 305 -337	0 644 888	-3 276 -878	2 549 545
-19 537 498	-30 973 -498	-17 320 318	-6 320 318	-9 334 509	-23 429 402	-23 429 402	-13 305 -337	0 644 888	-3 276 -878	2 549 545
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-34 427 498	-41 388 -498	-22 320 318	-11 320 318	-14 334 509	-28 429 402	-28 429 402	-13 305 -337	0 644 888	-3 276 -878	2 549 545
-37 611 498	-43 471 -498	-23 320 318	-12 320 318	-15 334 509	-29 429 402	-29 429 402	-13 305 -337	0 644 888	-3 276 -878	2 549 545
-40 795 498	-45 554 -498	-24 320 318	-13 320 318	-16 334 509	-30 429 402	-30 429 402	-13 305 -337	0 644 888	-3 276 -878	2 549 545
-43 979 498	-47 637 -498	-25 320 318	-14 320 318	-17 334 509	-31 429 402	-31 429 402	-13 305 -337	0 644 888	-3 276 -878	2 549 545
-47 163 498	-49 720 -498	-26 320 318	-15 320 318	-18 334 509	-32 429 402	-32 429 402	-13 305 -337	0 644 888	-3 276 -878	2 549 545
-50 347 498	-51 803 -498	-27 320 318	-16 320 318	-19 334 509	-33 429 402	-33 429 402	-13 305 -337	0 644 888	-3 276 -878	2 549 545
-53 531 498	-53 886 -498	-28 320 318	-17 320 318	-20 334 509	-34 429 402	-34 429 402	-13 305 -337	0 644 888	-3 276 -878	2 549 545
-56 715 498	-55 969 -498	-29 320 318	-18 320 318	-21 334 509	-35 429 402	-35 429 402	-13 305 -337	0 644 888	-3 276 -878	2 549 545
-59 899 498	-58 052 -498	-30 320 318	-19 320 318	-22 334 509	-36 429 402	-36 429 402	-13 305 -337	0 644 888	-3 276 -878	2 549 545
-63 083 498	-60 135 -498	-31 320 318	-20 320 318	-23 334 509	-37 429 402	-37 429 402	-13 305 -337	0 644 888	-3 276 -878	2 549 545
-66 267 498	-62 218 -498	-32 320 318	-21 320 318	-24 334 509	-38 429 402	-38 429 402	-13 305 -337	0 644 888	-3 276 -878	2 549 545
-69 451 498	-64 301 -498	-33 320 318	-22 320 318	-25 334 509	-39 429 402	-39 429 402	-13 305 -337	0 644 888	-3 276 -878	2 549 545
-72 635 498	-66 384 -498	-34 320 318	-23 320 318	-26 334 509	-40 429 402	-40 429 402	-13 305 -337	0 644 888	-3 276 -878	2 549 545
-75 819 498	-68 467 -498	-35 320 318	-24 320 318	-27 334 509	-41 429 402	-41 429 402	-13 305 -337	0 644 888	-3 276 -878	2

A detailed examination of the interatomic parameters shows two points of interest. Firstly, the  $\text{RhCl}_2\text{Rh}$ -bridge atoms are not coplanar. Table 5 shows a comparison of the bonding parameters associated with the folded  $\text{RhCl}_2\text{Rh}$  bridge in the two species  $\text{Rh}_2(\text{CO})_4\text{Cl}_2$  and  $\text{Rh}_2[\text{P}(\text{OC}_6\text{H}_5)_3]_2(\text{C}_8\text{H}_{12})\text{Cl}_2$ . The intersecting angles of the two planes defined by the atoms  $\text{Rh}(1)\text{Cl}(1)\text{Cl}(2)$  and  $\text{Rh}(2)\text{Cl}(1)\text{Cl}(2)$  are almost equal in both molecules. This agreement between the interatomic distances and bond angles listed in Table 5 leads to the conclusion that the bridge geometry is essentially identical in the two molecules.

Secondly, whereas Dahl *et al.* observed an intermolecular Rh–Rh distance of 3.31 Å for  $\text{Rh}_2(\text{CO})_4\text{Cl}_2$  which led to their postulation of octahedral hybridization for the metal atoms, the closest approach of two Rh atoms in neighbouring molecules of the species  $\text{Rh}_2[\text{P}(\text{OC}_6\text{H}_5)_3]_2(\text{C}_8\text{H}_{12})\text{Cl}_2$  is found to be 6.4 Å. This result precludes the necessity of an intermolecular metal–metal bond in inducing the folded conformation.

The equation of the best plane through  $\text{Rh}(2)$  and its four ligands, *viz.* Cl(1), Cl(2), P(1) and P(2), is

$$0.5940X + 0.6717Y + 0.4427Z - 12.4198 = 0^*$$

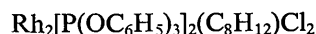
If it is assumed that the bonding of the metal to the cyclo-octadiene ring is directed towards the centre of the double bond, the best plane through  $\text{Rh}(1)$  and its 4 ligands, *viz.* Cl(1), Cl(2), the centre of  $\text{C}(37)=\text{C}(38)$  and the centre of  $\text{C}(41)=\text{C}(42)$ , is given by the equation

$$0.3281X - 0.1221Y + 0.9367Z - 14.3432 = 0.$$

The perpendicular distances from the atoms or ligands defined above to the corresponding planes are given in Table 6. In both cases the 5 sets of positional coordinates deviate from the respective planes by less

\*  $X$ ,  $Y$  and  $Z$  are the orthogonalized coordinates parallel to  $a$ ,  $b$  and  $c^*$ .

than 0.1 Å. It thus appears that the arrangement of the ligands around the two Rh atoms of



must be seen as square planar coordination.

Table 6. *Perpendicular distances ( $\sigma$ ) between the atoms or groups involved in the square-planar arrangement around the two Rh atoms and the best plane through each set of atoms*

	$\sigma$		$\sigma$
Rh(1)	0.002 Å	Rh(2)	-0.014 Å
Cl(1)	-0.054	Cl(1)	0.080
Cl(2)	0.052	Cl(2)	-0.075
P(1)	0.055	Centre of C(37)C(38)	-0.084
P(2)	-0.055	Centre of C(41)C(42)	0.093

The unusually long C=C bond distance of 1.42 Å in the cyclo-octadiene ring is a direct result of the  $\sigma-\pi$  bonding with the Rh atom (Ibers & Snyder, 1962). The mean Rh–P and O–P bond lengths of 2.142 (La Placa & Ibers, 1965) and 1.605 Å (Davies & Stanley, 1962) show consistency with literature values. The three phenyl rings on each of the two phosphite groups are arranged in a propeller-like manner (Fig. 2) with a mean aromatic C=C bond length of  $1.39 \pm 0.03$  Å. The shortest intermolecular contact distance (3.56 Å) occurs between the carbon atoms C(16) and C(42), the parent molecules of which are related by a glide plane. The closest approach of two rhodium atoms (6.4 Å) is observed between  $\text{Rh}(2)$  atoms in neighbouring molecules related by a centre of symmetry.

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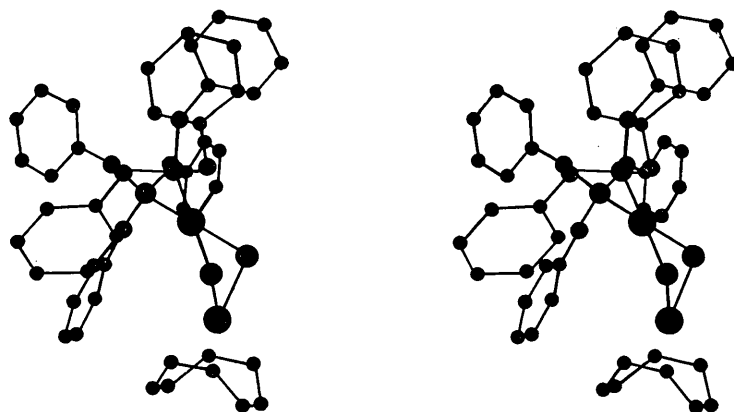


Fig. 2. Stereoscopic pair showing the molecular geometry of  $\text{Rh}_2[\text{P}(\text{OC}_6\text{H}_5)_3]_2(\text{C}_8\text{H}_{12})\text{Cl}_2$ .

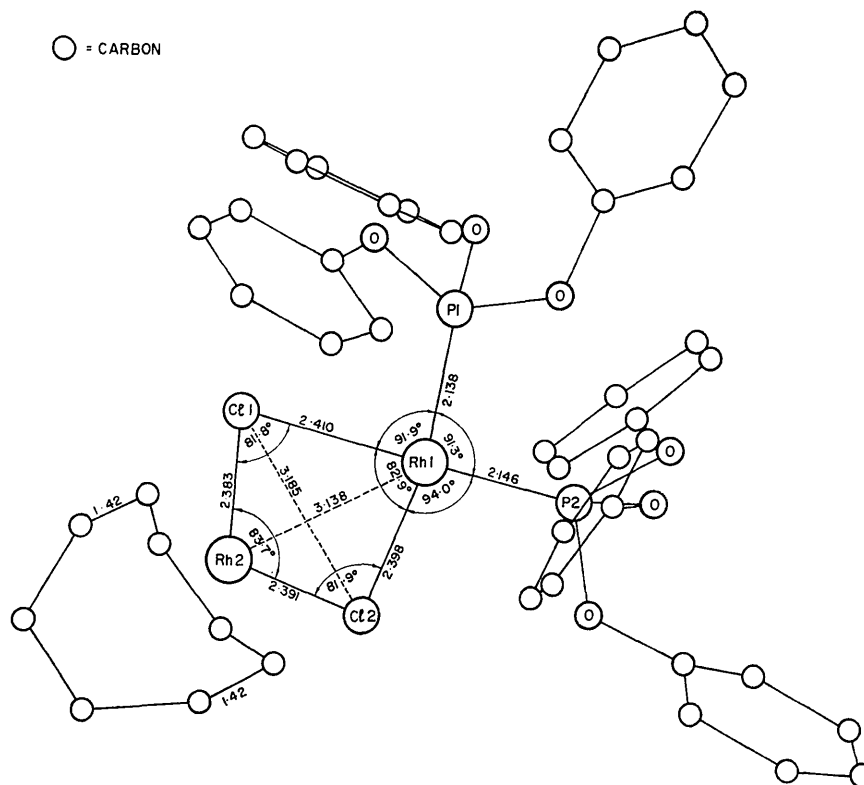


Fig. 3. The principal bond lengths and bond angles.

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## The Crystal and Molecular Structure of Coriose

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The crystal structure of coriose,  $C_7H_{14}O_7$ , a natural 3-heptulose, has been determined by the use of a symbolic addition procedure. The space group is  $P2_1$  with two molecules in the unit cell of dimensions  $a = 11.33$ ,  $b = 7.460$ ,  $c = 5.205$  Å and  $\beta = 90.75^\circ$ . The molecule is found in a novel  $\alpha$ -furanose form with three *cis* hydroxyl groups. Owing to the twist of the five-membered ring, similar to that in adenosine monophosphate, three groups attached to the ring are quasi-equatorial and the other two are quasi-axial.

### Introduction

Coriose,  $C_7H_{14}O_7$ , is a naturally occurring heptulose, extracted from *Coriaria japonica* A. Gray. The crystal

of coriose is obtained solvent-free either from aqueous ethanol, methanol or water. The same crystal (m.p. =  $169$ – $171^\circ$ ) is obtained also by evaporation of an aqueous solution to dryness at higher temperature, or by