

LARSON, A. C. & CROMER, D. T. (1967). *Acta Cryst.* **22**, 793.  
 LEDSHAM, A. H. C. & STEEPLE, H. (1968a). *Acta Cryst.* **B24**, 320.  
 LEDSHAM, A. H. C. & STEEPLE, H. (1968b). *Acta Cryst.* **B24**, 1287.

LEDSHAM, A. H. C. & STEEPLE, H. (1969). *Acta Cryst.* **B25**, 398.  
 LIPSON, H. (1935). *Proc. Roy. Soc.* **A151**, 347.  
 LIPSON, H. & BEEVERS, C. A. (1935). *Proc. Roy. Soc.* **A148**, 664.  
 RAY, G. & RAY, S. (1965). *Z. Kristallogr.* **122**, 457.

*Acta Cryst.* (1970). **B26**, 1244

## The Crystal and Molecular Structure of Dichloro- $\pi$ -methylallyl-bis-(triphenylarsine)rhodium(III)

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A crystal structure analysis of dichloro- $\pi$ -methylallyl-bis(triphenylarsine)rhodium confirms that the two group V donor ligands are *trans* to the allyl ligand and reveals symmetrical rhodium-allyl bonding. The dihedral angle between the allyl plane and the As(1)-Rh-As(2) plane is  $126.6^\circ$  and the methyl group is displaced from the allyl plane  $0.2 \text{ \AA}$  towards the Rh<sup>III</sup> ion. The rhodium(III) ion is in only slightly distorted octahedral coordination and the rhodium-carbon distances show a lengthening due to the *trans* influence of the two arsine ligands.

### Introduction

Nuclear magnetic resonance, infrared and dipole moment studies of the series of compounds  $L_2\text{Rh}(\pi\text{-C}_3\text{H}_5\text{R})\text{Cl}_2$ , where  $L = \text{Ph}_3\text{As}$ ,  $\text{Ph}_3\text{Sb}$ ,  $\text{Ph}_3\text{P}$ ,  $[\text{p}-(\text{CH}_3)_2\text{NC}_6\text{H}_4]_3\text{As}$ ,  $[\text{p}-(\text{CH}_3)_2\text{NC}_6\text{H}_4]_3\text{Sb}$  and  $(\text{Ph}_2\text{CH}_3)\text{As}$  and  $\text{R} = \text{H}$ ,  $\text{CH}_3$ , have suggested that the group V donor ligands are *trans* to the allyl ligand (Volger & Vrieze, 1967). It has further been suggested that an increase in the total electron donor capacity decreases the activation energy in the intramolecular rearrangement of the allyl ligand and that this may therefore be a function of the '*trans* effect' of the group V ligand (Vrieze & Volger, 1967). The influence of *trans*-coordinated ligands has previously been invoked to explain the asymmetry of the bonding in such compounds as bis- $\pi$ -allylrhodium chloride and triphenylphosphinemethylallylpalladium chloride (Mason & Russel, 1966; Smith, 1968). The crystal structure analysis of one of the compounds in the above series,  $(\text{Ph}_3\text{As})_2\text{Cl}_2\text{Rh}(\pi\text{-C}_4\text{H}_7)$ , now confirms that the two arsine ligands are *trans* to the allyl group and revealed that the latter is symmetrically bonded. Furthermore the Rh-C and allyl C-C bond lengths indicate a considerable '*trans* effect' of the triphenylarsine group. Preliminary results of this analysis have been published previously (Hewitt & de Boer, 1968).

### Experimental

$(\text{Ph}_3\text{As})_2\text{Cl}_2\text{Rh}(\pi\text{-C}_4\text{H}_7)$  crystallizes from acetone in the form of red-brown rhombohedra. A suitable crystal of approximate dimensions,  $0.25 \times 0.15 \times 0.075 \text{ mm}$ , was selected and sealed in a  $0.2 \text{ mm}$  diameter glass capillary.

The estimated value of the linear absorption coefficient equals  $26.1 \text{ cm}^{-1}$ , which is sufficiently low for absorption corrections to be neglected. A preliminary study was carried out on the precession camera, which revealed that the complex crystallized in a triclinic space group and indicated that the crystal quality was good. The rough cell parameters obtained from the precession study were refined by least-squares calculations (Anzenhofer, de Boer & Hewitt, 1970) using values of  $\sin \theta$  and  $\sin(-\theta)$  measured on the diffractometer as observed data. The following refined cell parameters\* were obtained:

$$\begin{aligned} a &= 21.7816 \pm 5, & b &= 10.178 \pm 2, \\ c &= 10.233 \pm 3 \text{ \AA}, \\ \alpha &= 112.77 \pm 3, & \beta &= 111.48 \pm 3, \\ \gamma &= 102.60 \pm 5^\circ, \\ U &= 1707.0 \text{ \AA}^3, & D_x &= 1.592 \text{ g.cm}^{-3} \text{ for } Z=2, \\ M &= 847.4. \end{aligned}$$

No attempt was made to obtain a value for the measured density, the calculated value being of the order expected for this kind of compound.

The necessary arc orientation instructions for the Nonius three-circle automatic single-crystal diffractometer were calculated (Anzenhofer, de Boer & Hewitt, 1970) and complete three-dimensional data to  $\sin \theta = 0.42$  were collected using Zr-filtered Mo  $K\alpha$  radiation

\* The program refines six parameters,  $A, B, C, D, E, F$  where  $A = a^*2$ ,  $B = b^*2$ ,  $C = c^*2$ ,  $D = 2a^*b^* \cos \gamma^*$ ,  $E = 2b^*c^* \cos \alpha^*$ ,  $F = 2c^*a^* \cos \beta^*$ . Maximum and minimum values for the cell constants are calculated using standard deviations of the above parameters. The error estimates given above are five times this spread.

and the  $\theta$ - $2\theta$  scan method. The intensities of a number of reflexions were measured many times during the data collection in order to check any crystal decomposition. No such decomposition occurred and one crystal sufficed for the measurement of a total of 2694 independent reflexions. The intensities were corrected for Lorentz and polarization factors, but no absorption correction was applied. Structure amplitudes were obtained on a common arbitrary scale.

### Structure determination and refinement

Examination of the plot of the three-dimensional Patterson synthesis (Anzenhofer *et al.*, 1970) revealed the positions of the rhodium, two arsenic and two chlorine atoms. Two cycles of full-matrix least-squares (Anzenhofer *et al.*, 1970) refinement in the space group  $P\bar{1}(C_1^1$ , No. 2) (*International Tables for X-ray Crystallography*, 1959) and with individual isotropic temperature fac-

Table 1. *Final weighting analysis\**

$F_{\text{obs}}$	$\sin \theta/\lambda$			Totals
	0-0-0.2	0.2-0.4	0.4-0.6	
0-3	1.063/(18)	1.359/(64)	2.152/(22)	1.476/(104)
3-7	1.119/(32)	0.958/(192)	1.034/(145)	1.002/(369)
7-10	1.973/(31)	0.612/(282)	0.659/(384)	0.698/(697)
10-13	0.926/(25)	0.414/(227)	0.556/(381)	0.520/(633)
13-16	1.871/(24)	0.435/(169)	0.577/(179)	0.596/(372)
16-20	1.524/(26)	0.587/(116)	0.624/(76)	0.712/(218)
20-23	0.941/(11)	0.618/(95)	0.562/(15)	0.640/(121)
23-26	1.681/(16)	0.677/(47)	0.678/(15)	0.883/(68)
26-30	2.022/(16)	0.869/(31)		1.262/(47)
30-33		1.035/(24)		2.330/(24)
33-36	6.853/(4)	1.375/(18)		2.323/(22)
36-40	3.554/(5)	1.277/(2)		2.903/(7)
40-43	0.805/(3)	2.135/(3)		1.470/(6)
43-46	7.816/(3)			2.605/(3)
46-49	8.961/(3)	8.397/(1)		11.76/(4)
Totals	1.798/(217)	0.660/(1271)	0.689/(1207)	

\* The numbers in brackets are the number of planes over which  $\sum wA^2$  is averaged.

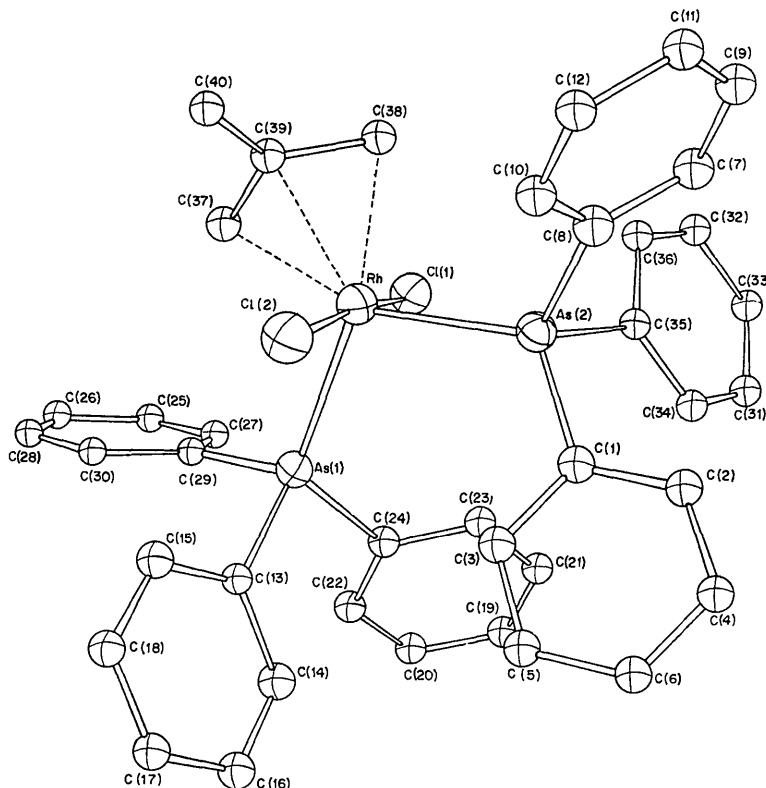


Fig. 1. The molecular structure of  $(\text{Ph}_3\text{As})_2\text{Cl}_2\text{Rh}(\pi\text{-C}_4\text{H}_7)$ ,

Table 2. Fractional atomic coordinates ( $\text{\AA}$ ) and mean-square amplitudes of vibration\* ( $\text{\AA}^2$ ) with their e.s.d.

Atom	x	y	z	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Rh	0.24455(6)	0.06158(13)	0.11432(13)	0.00188(3)	0.00937(15)	0.00906(16)	0.00162(6)	0.00201(6)	0.00498(13)
As(1)	0.16186(7)	0.08160(17)	-0.11439(16)	0.00147(4)	0.00896(21)	0.00801(22)	0.00158(8)	0.00166(8)	0.00472(18)
As(2)	0.33539(7)	-0.00819(16)	0.04334(18)	0.00170(4)	0.00869(21)	0.00854(23)	0.00182(8)	0.00174(8)	0.00475(19)
C1(1)	0.3111(2)	0.3316(4)	0.2859(4)	0.0022(1)	0.0179(5)	0.0115(6)	0.0014(2)	0.0021(2)	0.0045(5)
C1(2)	0.1717(2)	-0.2096(4)	-0.0233(5)	0.0022(1)	0.0093(6)	0.0135(7)	0.0008(2)	0.0017(2)	0.0063(5)
C(1)	0.3061(7)	0.8503(14)	0.8172(15)	0.0024(15)	0.0268(20)	0.0056(21)	0.0010(8)	0.0023(8)	0.0026(18)
C(2)	0.3533(8)	0.8076(19)	0.7719(17)	0.0022(5)	0.0175(30)	0.0078(24)	0.0036(10)	0.0019(9)	0.0022(22)
C(3)	0.2340(8)	0.7840(17)	0.6961(18)	0.0024(5)	0.0103(24)	0.0144(29)	0.0021(10)	0.0030(10)	0.0046(22)
C(4)	0.3316(9)	0.7089(21)	0.6104(20)	0.0037(7)	0.0212(34)	0.0175(34)	0.0059(13)	0.0047(13)	0.0093(29)
C(5)	0.2113(8)	0.6826(18)	0.5346(17)	0.0031(6)	0.0133(27)	0.0073(25)	0.0034(10)	0.0012(10)	0.0010(21)
C(6)	0.2594(9)	0.6427(20)	0.4901(19)	0.0031(6)	0.0213(32)	0.0139(30)	0.0060(12)	0.0037(11)	0.0096(26)
C(7)	0.4543(9)	0.9319(22)	0.2301(24)	0.0037(7)	0.0220(37)	0.0296(44)	0.0061(14)	0.0061(15)	0.0182(35)
C(8)	0.3811(8)	0.8870(18)	0.1476(16)	0.0029(5)	0.0178(28)	0.0090(24)	0.0046(10)	0.0032(10)	0.0093(23)
C(9)	0.4828(11)	0.8516(26)	0.2992(26)	0.0045(8)	0.0332(51)	0.0321(51)	0.0039(18)	0.0043(17)	0.0240(45)
C(10)	0.3376(9)	0.7560(21)	0.1365(26)	0.0024(6)	0.0167(33)	0.0392(51)	0.0022(12)	0.0022(14)	0.0209(36)
C(11)	0.4400(11)	0.7221(24)	0.2834(24)	0.0053(10)	0.0235(41)	0.0243(44)	0.0052(17)	0.0054(17)	0.0147(36)
C(12)	0.3654(12)	0.6735(25)	0.1963(32)	0.0058(10)	0.0243(44)	0.0478(68)	0.0062(18)	0.0069(22)	0.0272(49)
C(13)	0.0829(7)	0.8940(16)	0.6772(16)	0.0012(4)	0.0112(24)	0.0102(24)	0.0023(8)	0.0005(8)	0.0061(20)
C(14)	0.0758(8)	0.8696(18)	0.5260(18)	0.0032(6)	0.0147(28)	0.0105(26)	0.0030(11)	0.0027(10)	0.0051(23)
C(15)	0.0343(7)	0.7808(16)	0.6771(17)	0.0018(5)	0.0094(23)	0.0094(25)	0.0007(9)	0.0007(9)	0.0025(20)
C(16)	0.0210(9)	0.7392(19)	0.3813(17)	0.0034(6)	0.0153(29)	0.0077(25)	0.0028(11)	0.0016(10)	0.0028(23)
C(17)	0.0262(8)	0.3690(19)	0.6132(19)	0.0025(6)	0.0144(29)	0.0105(28)	0.0023(11)	-0.0002(10)	-0.0005(24)
C(18)	0.0213(8)	0.3498(19)	0.4689(21)	0.0025(6)	-0.0146(29)	0.0198(35)	0.0037(11)	0.0028(12)	0.0096(27)
C(19)	0.2728(19)	0.3759(21)	0.7079(23)	0.0042(7)	0.0227(36)	0.0292(44)	0.0050(14)	0.0076(16)	0.0208(36)
C(20)	0.2039(9)	0.3499(22)	0.6732(22)	0.0040(7)	0.0261(39)	0.0268(40)	0.0062(14)	0.0068(14)	0.0217(35)
C(21)	0.3098(9)	0.3171(23)	0.7930(24)	0.0029(6)	0.0277(41)	0.0330(46)	0.0043(13)	0.0077(15)	0.0231(39)
C(22)	0.1690(8)	0.2605(19)	0.7232(20)	0.0025(5)	0.0215(32)	0.0246(36)	0.0054(11)	0.0055(12)	0.0202(31)
C(23)	0.2782(8)	0.2311(18)	0.8451(18)	0.0024(5)	0.0182(29)	0.0158(30)	0.0036(10)	0.0036(10)	0.0132(26)
C(24)	0.2063(7)	0.2000(15)	0.8080(16)	0.0025(5)	0.0084(21)	0.0088(23)	0.0020(9)	0.0027(9)	0.0057(19)
C(25)	0.1048(9)	0.4542(19)	0.0839(19)	0.0044(7)	0.0141(29)	0.0118(29)	0.0042(12)	0.0023(12)	0.0049(24)
C(26)	0.0287(9)	0.3770(19)	0.0667(19)	0.0032(6)	0.0168(31)	0.0136(29)	0.0041(12)	0.0031(11)	0.0074(26)
C(27)	0.1410(8)	0.3658(17)	0.0284(19)	0.0029(6)	0.0112(25)	0.0166(31)	0.0040(10)	0.0034(11)	0.0060(24)
C(28)	0.0087(9)	0.2189(20)	-0.0067(20)	0.0031(6)	0.0218(34)	0.0189(34)	0.0049(12)	0.0057(12)	0.0134(30)
C(29)	0.1097(7)	0.2023(17)	0.9547(17)	0.0017(5)	0.0144(26)	0.0134(27)	0.0028(9)	0.0028(9)	0.0083(23)
C(30)	0.0420(8)	0.1256(18)	0.9334(19)	0.0023(6)	0.0175(29)	0.0197(32)	0.0043(11)	0.0042(11)	0.0116(27)
C(31)	0.4975(9)	0.3395(22)	0.0704(22)	0.0026(6)	0.0263(39)	0.0244(40)	0.0034(13)	0.0049(13)	0.0196(35)
C(32)	0.4777(8)	0.5842(20)	0.6985(21)	0.0024(6)	0.0178(32)	0.0206(36)	0.0038(11)	0.0037(12)	0.0087(29)
C(33)	0.4620(8)	0.5608(19)	0.7653(22)	0.0018(5)	0.0155(30)	0.0245(40)	0.0018(10)	0.0029(12)	0.0104(30)
C(34)	0.4384(7)	0.1989(17)	0.0681(18)	0.0021(5)	0.0127(26)	0.0154(30)	0.0022(9)	0.0030(10)	0.0077(24)
C(35)	0.4210(7)	0.1701(16)	0.1156(16)	0.0016(4)	0.0110(23)	0.0118(25)	0.0022(8)	0.0026(9)	0.0063(21)
C(36)	0.4635(7)	0.2841(17)	0.0018(5)	0.0018(5)	0.0105(24)	0.0132(28)	0.0015(9)	0.0022(10)	0.0027(22)
C(37)	0.1955(9)	0.1484(19)	0.2704(18)	0.0035(6)	0.0206(32)	0.0123(29)	0.0048(12)	0.0053(12)	0.0097(26)
C(38)	0.3116(7)	0.1148(18)	0.3682(16)	0.0018(5)	0.0189(29)	0.0072(23)	0.0032(10)	0.0018(9)	0.0082(22)
C(39)	0.2358(9)	0.0703(20)	0.3313(17)	0.0043(7)	0.0195(33)	0.0061(24)	0.0033(12)	0.0033(11)	0.0044(24)
C(40)	0.1994(10)	0.9273(21)	0.3343(21)	0.0048(8)	0.0237(36)	0.0200(36)	0.0031(14)	0.0057(14)	0.0200(32)
H(2)	0.4099	0.8978	0.8670	3.4					
H(3)	0.1950	0.8145	0.7304	3.2					
H(4)	0.3708	0.6766	0.5758	4.5					
H(5)	0.1548	0.6266	0.4398	3.5					
H(6)	0.2408	0.5597	0.3601	3.9					
H(7)	0.4904	0.0359	0.2440	5.2					
H(9)	0.5412	0.8906	0.3666	6.9					
H(10)	0.2794	0.7177	0.0661	5.5					
H(11)	0.4635	0.6574	0.3388	6.3					
H(12)	0.3294	0.5700	0.1833	7.9					
H(14)	0.1150	0.9580	0.5244	4.0					
H(15)	0.0394	0.7974	0.7942	3.0					
H(16)	0.0156	0.0722	0.2656	3.9					
H(17)	-0.0693	0.5249	0.2696	4.4					
H(18)	-0.0603	0.5624	0.5331	4.2					
H(19)	0.2991	0.4453	0.6684	4.8					
H(20)	0.1782	0.3974	0.6089	4.7					
H(21)	0.3657	0.3390	0.8205	4.9					
H(22)	0.1131	0.2379	0.6953	3.6					
H(23)	0.3077	0.1832	0.9115	3.3					
H(25)	0.1293	0.5816	-0.2444	4.5					
H(26)	0.0111	0.4440	-0.2768	4.0					
H(27)	0.1940	0.4246	0.0423	3.6					
H(28)	-0.0442	0.1601	-0.0209	4.1					
H(30)	0.0171	-0.0030	0.2604	3.5					
H(31)	0.4889	0.6400	0.0145	4.8					
H(32)	0.4438	0.4966	0.5237	4.3					
H(33)	0.4158	0.4543	0.7184	4.6					
H(34)	0.5994	0.8881	0.1257	3.3					
H(36)	0.5500	0.7376	0.6296	3.3					

\* Expression for anisotropic temperature factor is  $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ .

tors resulted in an  $R$  index of 0.215 ( $R' = 0.291$ ), where

$$R = \frac{\sum |F_o - F_c|}{\sum F_o}, \quad R' = \sqrt{\frac{\sum w(F_o - F_c)^2}{\sum wF_o^2}}$$

Table 3. *Molecular dimensions and e.s.d.'s*

<b>Rhodium octahedron</b>	
Rh - C(1) = 2.261 (4) Å	C(1) - Rh - C(2) = 174.03 (14)°
Rh - As(2) = 2.492 (2) Å	As(2) - Rh - As(1) = 106.25 (6)°
Rh - C(39) = 2.267 (14) Å	C(1) - Rh - As(1) = 83.26 (10)°
Rh - C(12) = 2.258 (4) Å	C(1) - Rh - As(2) = 92.24 (10)°
Rh - C(37) = 2.246 (16) Å	C(2) - Rh - As(1) = 91.02 (11)°
Rh - As(1) = 2.494 (2) Å	As(2) - Rh - C(2) = 87.84 (11)°
Rh - C(38) = 2.226 (13) Å	As(1) - Rh - C(37) = 94.4 (4)°
	C(1) - Rh - C(37) = 83.8 (4)°
	C(2) - Rh - C(37) = 98.3 (4)°
	As(2) - Rh - C(38) = 90.2 (4)°
	C(1) - Rh - C(38) = 84.3 (4)°
	C(2) - Rh - C(38) = 101.7 (4)°
	C(37) - Rh - C(38) = 68.3 (6)°
<b>Arsenic tetrahedra</b>	
As(1) - C(29) = 1.958 (15) Å	As(2) - C(1) = 1.941 (13) Å
As(2) - C(8) = 1.958 (16) Å	As(1) - C(13) = 1.967 (14) Å
As(1) - C(24) = 1.950 (13) Å	As(2) - C(35) = 1.948 (14) Å
Rh - As(1) - C(29) = 110.6 (4)°	C(29) - As(1) - C(24) = 100.2 (6)°
C(24) - As(1) - C(13) = 101.6 (6)°	Rh - As(1) - C(24) = 117.6 (4)°
Rh - As(1) - C(13) = 121.7 (4)°	C(29) - As(1) - C(13) = 102.2 (6)°
Rh - As(2) - C(35) = 114.9 (4)°	Rh - As(2) - C(1) = 120.2 (4)°
Rh - As(2) - C(8) = 114.8 (4)°	C(35) - As(2) - C(1) = 103.5 (6)°
C(1) - As(2) - C(8) = 100.2 (6)°	C(8) - As(2) - C(35) = 100.5 (6)°
<b>Phenyl groups</b>	
<b>Group I</b>	
C(1) - C(2) = 1.36 (2) Å	C(3) - C(1) - C(2) = 117.6 (1.3)°
C(1) - C(3) = 1.39 (2) Å	C(2) - C(4) - C(6) = 119.8 (1.6)°
C(2) - C(4) = 1.38 (2) Å	C(6) - C(5) - C(3) = 120.6 (1.4)°
C(3) - C(5) = 1.38 (2) Å	C(1) - C(2) - C(4) = 121.9 (1.4)°
C(4) - C(6) = 1.38 (2) Å	C(4) - C(6) - C(5) = 118.8 (1.5)°
C(5) - C(6) = 1.36 (2) Å	C(5) - C(3) - C(1) = 121.2 (1.4)°
Avg. C-C = 1.38 Å	Avg. C-C-C = 120.0°
<b>Group II</b>	
C(8) - C(7) = 1.36 (2) Å	C(10) - C(8) - C(7) = 116.9 (1.6)°
C(8) - C(10) = 1.372 Å	C(7) - C(9) - C(11) = 122.0 (1.9)°
C(7) - C(9) = 1.38 (3) Å	C(11) - C(12) - C(10) = 120.7 (2.1)°
C(10) - C(12) = 1.36 (3) Å	C(8) - C(7) - C(9) = 121.1 (1.8)°
C(9) - C(11) = 1.35 (3) Å	C(9) - C(11) - C(12) = 117.2 (2.0)°
C(12) - C(11) = 1.39 (3) Å	C(12) - C(10) - C(8) = 122.1 (1.7)°
Avg. C-C = 1.37 Å	Avg. C-C-C = 120.0°
<b>Group III</b>	
C(13) - C(15) = 1.38 (2) Å	C(14) - C(13) - C(15) = 118.7 (1.3)°
C(13) - C(14) = 1.41 (2) Å	C(18) - C(17) - C(16) = 122.5 (1.5)°
C(15) - C(18) = 1.36 (2) Å	C(16) - C(14) - C(13) = 121.1 (1.4)°
C(14) - C(16) = 1.37 (2) Å	C(13) - C(15) - C(18) = 120.1 (1.3)°
C(18) - C(17) = 1.37 (2) Å	C(17) - C(16) - C(14) = 118.2 (1.4)°
C(16) - C(17) = 1.37 (2) Å	C(15) - C(18) - C(17) = 119.3 (1.5)°
Avg. C-C = 1.38 Å	Avg. C-C-C = 120.0°
<b>Group IV</b>	
C(24) - C(23) = 1.40 (2) Å	C(22) - C(24) - C(23) = 119.0 (1.3)°
C(24) - C(22) = 1.38 (2) Å	C(23) - C(21) - C(19) = 121.4 (1.9)°
C(23) - C(21) = 1.37 (2) Å	C(19) - C(20) - C(22) = 121.7 (1.7)°
C(22) - C(20) = 1.39 (2) Å	C(24) - C(23) - C(21) = 119.7 (1.5)°
C(21) - C(19) = 1.37 (3) Å	C(21) - C(19) - C(20) = 118.9 (2.0)°
C(20) - C(19) = 1.35 (4) Å	C(20) - C(22) - C(24) = 119.2 (1.40)°
Avg. C-C = 1.38 Å	Avg. C-C-C = 120.0°
<b>Group V</b>	
C(29) - C(27) = 1.40 (2) Å	C(30) - C(29) - C(27) = 120.3 (1.4)°
C(29) - C(30) = 1.40 (2) Å	C(25) - C(26) - C(28) = 120.0 (1.6)°
C(27) - C(25) = 1.41 (2) Å	C(26) - C(28) - C(30) = 120.7 (1.6)°
C(30) - C(28) = 1.41 (2) Å	C(29) - C(27) - C(25) = 119.9 (1.4)°
C(25) - C(26) = 1.39 (2) Å	C(29) - C(30) - C(28) = 117.7 (1.5)°
C(28) - C(26) = 1.35 (3) Å	C(26) - C(25) - C(27) = 119.3 (1.6)°
Avg. C-C = 1.39 Å	Avg. C-C-C = 119.7°
<b>Group VI</b>	
C(35) - C(34) = 1.39 (2) Å	C(36) - C(35) - C(34) = 118.3 (2.0)°
C(35) - C(36) = 1.41 (2) Å	C(34) - C(31) - C(33) = 119.0 (1.6)°
C(34) - C(31) = 1.41 (2) Å	C(36) - C(32) - C(33) = 119.4 (1.5)°
C(36) - C(32) = 1.37 (2) Å	C(35) - C(34) - C(31) = 119.5 (1.4)°
C(31) - C(33) = 1.36 (2) Å	C(35) - C(36) - C(32) = 120.7 (1.4)°
C(32) - C(33) = 1.34 (2) Å	C(32) - C(33) - C(31) = 123.0 (1.6)°
Avg. C-C = 1.38 Å	Avg. C-C-C = 120.0°
<b>Methyllyl ligand</b>	
C(39) - C(37) = 1.44 (2) Å	C(37) - C(39) - C(38) = 119.2 (1.4)°
C(39) - C(38) = 1.47 (2) Å	C(37) - C(39) - C(40) = 121.8 (1.5)°
C(39) - C(40) = 1.52 (2) Å	C(38) - C(39) - C(40) = 118.3 (1.5)°

The corresponding unweighted difference Fourier synthesis revealed the positions of the 40 expected carbon atoms, *i.e.* one methylallyl group and six phenyl groups. Block-diagonal least-squares refinement with individual isotropic temperature factors gave an  $R$  index of 0.073 ( $R' = 0.109$ ). This reduced to 0.062 ( $R' = 0.071$ ) upon anisotropic approximation for the temperature factors of the five heavy atoms and further to 0.057 ( $R' = 0.065$ ) with anisotropic temperature factors for the carbon atoms.

Up to this stage only unit weights had been used and a weighting analysis indicated that this was satisfactory. A difference Fourier synthesis showed distinct areas of electron density corresponding to hydrogen atom positions around the phenyl rings. Peak positions were not, however, sufficiently distinct to allow the hydrogen atom coordinates to be obtained from the Fourier synthesis. The phenyl hydrogen atoms were therefore included in calculated positions in the refinement and given the temperature factor (isotropic) of the carbon atom to which they were attached. The C-H distance was assumed to be 1.08 Å and the scattering factors for hydrogen, carbon, chlorine, arsenic and rhodium were taken from *International Tables for X-ray Crystallography* (1962). Neither positional nor thermal parameters of the hydrogen atoms were refined. The final value of the  $R$  index was 0.056 ( $R' = 0.063$ ), unit weights still being satisfactory (Table 1). The final difference Fourier synthesis did not reveal the positions of the remaining hydrogen atoms unambiguously, although there were areas of positive electron density in the positions where the hydrogen atoms were expected. The remainder of the difference Fourier synthesis consisted of random fluctuations of electron density.

The final atomic coordinates, thermal parameters and corresponding estimated standard deviations are given in Table 2. These coordinates determine the structural parameters given in Table 3. The coordinate standard deviations were taken directly from the inverse of the  $10 \times 10$  atom matrix in the block-diagonal least-squares program. A list of structure factors may be obtained upon request.

### Molecular structure

The molecular structure of  $(\text{Ph}_3\text{As})_2\text{Cl}_2\text{Rh}(\pi\text{-C}_4\text{H}_7)$  is shown in Fig. 1 and bond lengths and angles in Table 3. The rhodium(III) ion is in slightly distorted octahedral coordination (Fig. 2) the methylallyl anion (with four  $\pi$ -electrons available for bonding) occupying two coordination sites. The two group V ligands are *trans* to the methylallyl ligand, which is symmetrically  $\pi$ -bonded. The increase in the As(2)-Rh-As(1) angle compared with the octahedral angle is due presumably to crowding of the phenyl groups. Similarly the small C(37)-Rh-C(38) angle reflects the requirements of the allyl ligand. The angles Cl(2)-Rh-C(37) and Cl(2)-Rh-C(38) are both greater than the corresponding Cl(1) angles, which is probably due to the presence

of the methyl group on the allyl group. The two Rh–Cl bond lengths are not significantly different and compare well with other values found for Rh–Cl, for instance 2.386 (3) in RhCl(CS) (PPh<sub>3</sub>)<sub>2</sub> (De Boer, Rogers, Skapski & Troughton, 1967) and 2.38 (1) in [Rh(C<sub>8</sub>H<sub>12</sub>)Cl]<sub>2</sub> (Ibers & Snyder, 1962). The Rh–As bonds are not significantly different in length either and agree well with the value expected from a simple covalent radii sum (Pauling, 1960). The Rh–C bond lengths will be discussed later (see *Discussion*).

The stereochemistry around each arsenic atom reflects in general the requirements of minimum inter- and intramolecular contact – it is shown in detail in Fig. 3. The C–As–C angles are slightly larger than in As(CH<sub>3</sub>)<sub>3</sub>, for example, but show no significant deviations from the mean value, 101.3°, thus maintaining

the trigonal symmetry of the As–C group. The trigonal

axis does not, however, coincide with the direction of the Rh–As bond (Table 5), nor is there equal rotation of the phenyl groups about their respective C–As bonds (dihedral angles, I–II=90.6, II–VI=114.8, I–VI=112.4, III–IV=113.6, IV–V=57.2, III–V=65.9°). The phenyl groups themselves are planar (Table 4) but for

groups V and VI the arsenic atom does not lie in the plane of the benzene ring (Table 5).

The As–C and C–C bonds are all normal in length.

### Molecular packing

The molecular packing on the (001) and (010) planes is shown in Figs. 4 and 5 respectively. It is immediately evident that the unit cell is evenly packed. The only strict crystallographic symmetry present is that of a centre of symmetry, although it can be seen that the molecule does possess an approximate twofold rotation axis perpendicular to the (001) plane if the allyl ligand is not included. The non-bonded intra- and intermolecular contacts less than 4 Å are also shown in Figs. 4 and 5. As far as intramolecular contacts are concerned, the shortest distances are found between carbon atoms of the phenyl groups bonded to the same arsenic atom: these are all about 3 Å. The shortest intermolecular contact is that between two symmetry related phenyl groups (III and III'). The two groups are nearly parallel and the distance between them, 3.28 Å, is close to the 'thickness' of benzene. In terms of van der Waals forces a phenyl group can be given an effective thickness of about 3.4 Å (Pauling, 1960). The shortest C–C contact with 'side on' approach of the phenyl groups is 4.0 Å, assuming a van der Waals

Table 4. Mean-plane deviations (Å) for phenyl groups

Group I		Group II		Group III	
C(1)	0.0115	C(7)	−0.0143	C(13)	0.0089
C(2)	−0.0106	C(8)	0.0057	C(14)	−0.0045
C(3)	−0.0064	C(9)	0.0103	C(15)	−0.0113
C(4)	0.0044	C(10)	0.0070	C(16)	0.0024
C(5)	0.0004	C(11)	0.0024	C(17)	−0.0046
C(6)	0.0008	C(12)	−0.0111	C(18)	0.0091
Group IV		Group V		Group VI	
C(19)	−0.0092	C(25)	−0.0110	C(31)	−0.0200
C(20)	0.0125	C(26)	0.0099	C(32)	0.0066
C(21)	−0.0030	C(27)	0.0007	C(33)	0.0138
C(22)	−0.0036	C(28)	0.0014	C(34)	0.0068
C(23)	0.0115	C(29)	0.0105	C(35)	0.0126
C(24)	−0.0081	C(30)	−0.0116	C(36)	−0.0197

Table 5. Structure details of arsine stereochemistry

Deviation of As from phenyl plane (Å)	Distance from As to nearest C neighbours (Å)		Deviation of As from phenyl plane (Å)	Distance from As to nearest C neighbours (Å)	
	I	II		IV	V
−0.007*	As(2)–C(2)	2.909	0.046	As(1)–C(23)	2.909
	As(2)–C(3)	2.892		As(1)–C(22)	2.914
−0.046	As(2)–C(7)	2.949	0.090	As(1)–C(27)	2.915
	As(2)–C(10)	2.884		As(1)–C(30)	2.924
−0.003	As(1)–C(15)	2.920	−0.123	As(2)–C(36)	2.892
	As(1)–C(14)	2.952		As(2)–C(34)	2.954

\* These numbers correspond with those in Table 4.

radius of 1.2 Å for hydrogen and a C–H bond length of 1.08 Å. Since there are no other short intermolecular contacts it can be concluded that intermolecular contacts are not important in determining the molecular geometry.

### Discussion

The methylallyl group is clearly symmetrically bonded to the rhodium(III) ion, the difference between the Rh–C(37) and the Rh–C(38) bond distances not being significant. There is in fact no significant deviation from the mean of all three Rh–C distances. In most cases the left–right asymmetry observed in metal–allyl bonding may be explained in terms of the so-called ‘*trans* influence’ of other ligands bonded to the transition metal ion. Thus in triphenylphosphinemethylallylpalladium(II) chloride (Mason & Russel, 1966; Smith, 1968) and bis- $\pi$ -allylrhodium chloride (McPartlin & Mason, 1967) the shortest metal–carbon bonds are *trans* to the chlorine ion. In  $\pi$ -2-methylallyl and

$\pi$ -1,1,3,3-tetramethylallylpalladium(II) chloride dimers (Mason & Wheeler, 1968), however, the allyl ligands are symmetrically bonded. The one exception is  $\pi$ -1,3-dimethylallylpalladium(II) chloride dimer (Davies, Mais, O’Brien & Owston, 1967). This compound has a non-planar Pd–Cl bridging system and the asymmetrically bonded allyl ligands are *syn* (Kilbourn, Mais & Owston, 1967) with respect to the chlorine bridge. It is suggested that crystal packing forces may be responsible for the asymmetry in bonding. Whatever the explanation may be, it seems unlikely that this compound is representative in terms of metal–allyl bonding. The symmetry of the  $(\text{Ph}_3\text{As})_2\text{Cl}_2\text{Rh}(\pi\text{-C}_4\text{H}_7)$  molecule [mirror plane through Rh, Cl(1), Cl(2), C(39) and C(40)] means that any *trans* influence should be evident in the rhodium–carbon and allyl carbon–carbon bond lengths.

If one assumes the same covalent radius for Pd<sup>II</sup> as for Rh<sup>III</sup>, then comparison of the Rh–C and C–C distances of dichloro- $\pi$ -methylallyl-bis(triphenylarsine)-

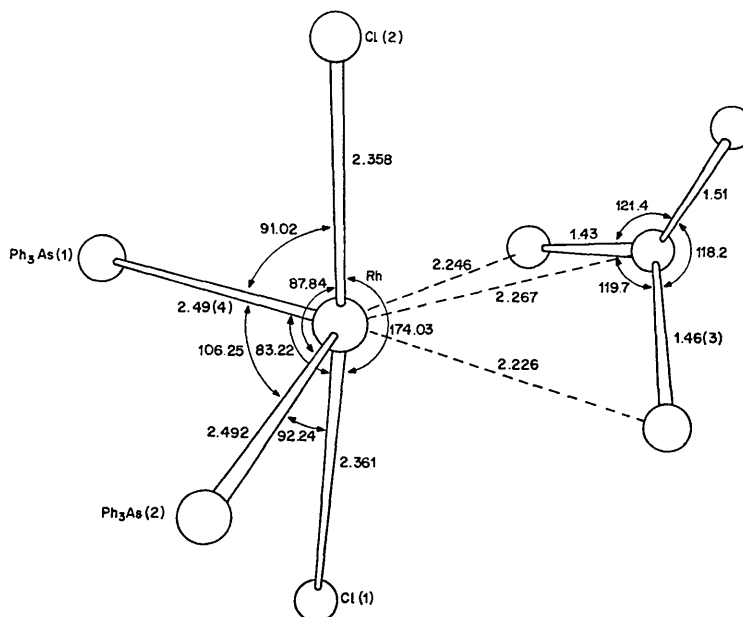


Fig. 2. Molecular geometry about the rhodium(III) ion.

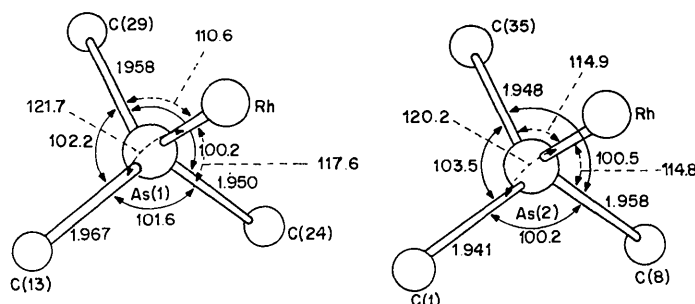


Fig. 3. Stereochemistry around the arsenic atoms.

rhodium with the Pd-C and C-C distances of triphenylphosphinemethylallylpalladium(II) chloride and the  $\pi$ -allyl palladium(II) chloride dimer indicates a reasonably large *trans* influence of the arsine ligands, *i.e.* triphenylphosphinemethylallylpalladium(II) chloride

Pd-C (*trans* to Ph<sub>3</sub>P)=2.28 (Mason & Russel, 1966)  
(2.20) (Smith, 1968)

C-C=1.40 (1.28)

Pd-C (*trans* to Cl) =2.14 (2.12) C-C=1.47 (1.50)  
and  $\pi$ -allylpalladium(II) chloride (Smith, 1965)

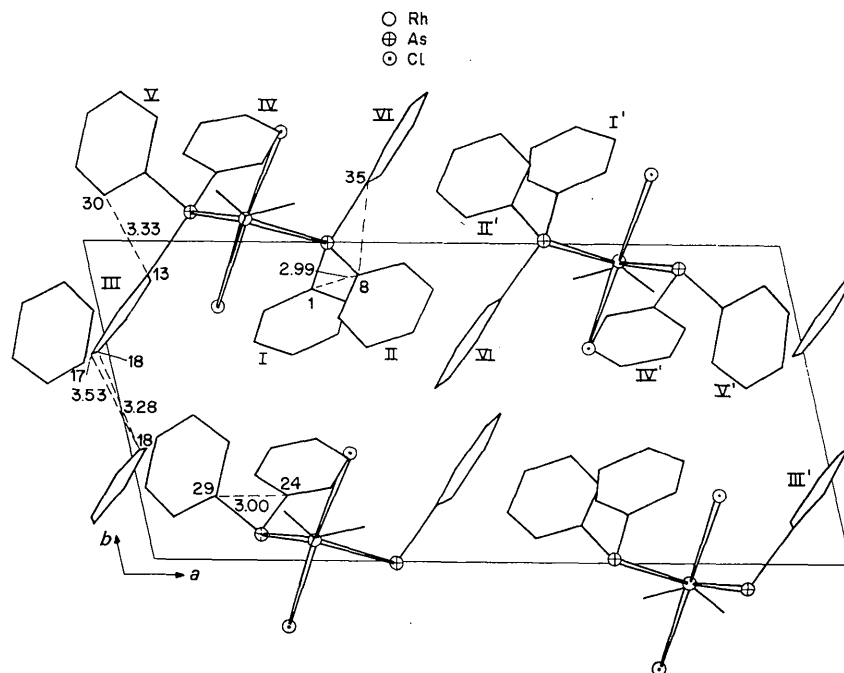


Fig. 4. The (001) plane of  $(\text{Ph}_3\text{As})_2\text{Cl}_2\text{Rh}(\pi\text{-C}_4\text{H}_7)$ .

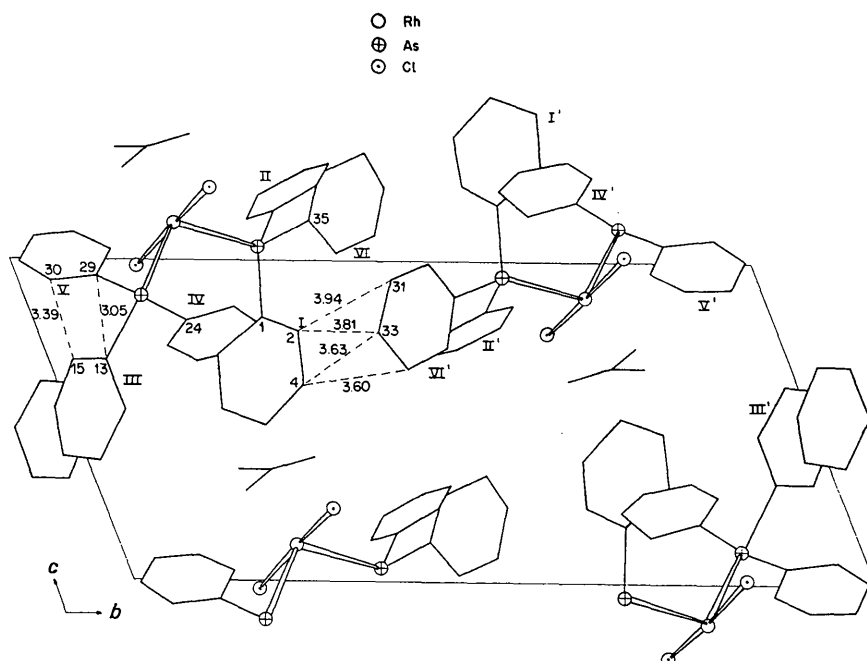


Fig. 5. The (010) plane of  $(\text{Ph}_3\text{As})_2\text{Cl}_2\text{Rh}(\pi\text{-C}_4\text{H}_7)$ .

Pd-C (*trans* to Cl) = 2.12      C-C = 1.36  
 Pd-C (*trans* to Cl) = 2.12      C-C = 1.40.

Although the lengthening of the C-C bonds is hardly significant ( $\Delta/\sigma = 3.8$ ) such lengthening is consistent with a 'trans influence' of the arsine ligands.

The dihedral angle between the plane of the allyl ligand and the As(1)-Rh-As(2) plane is 126.6°, in good agreement with the angle of 125° predicted on the basis of a trigonal model (Vrieze, McLean, Cossee & Hilbers, 1966). The methyl group is displaced from the allyl plane 0.2 Å towards the Rh<sup>III</sup> ion. Such distortions, which are common to methylallyl compounds (Churchill & Mason, 1967) were originally thought to be a consequence of asymmetric metal-allyl bonding (Canadine, 1967). This explanation, considered unlikely by us, is now seen to be incorrect.

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#### References

- ANZENHOFER, K., BOER, J. J. DE & HEWITT, T. G. (1970). Internal report.
- BOER, J. L. DE, ROGERS, D., SKAPSKI, A. C. & TROUGHTON, P. G. H. (1967). *Chem. Comm.* 756.
- CANADINE, R. M. (1967). Presented at *Allyl and Olefin Complexes of Metals*, Chemical Society Symposium, Sheffield, April 1967.
- CHURCHILL, M. R. & MASON, R. (1967). *Advanc. Organometal. Chem.* **5**, 95.
- DAVIES, G. R., MAIS, R. H. B., O'BRIEN, S. & OWSTON, P. G. (1967). *Chem. Comm.* p. 1151.
- HEWITT, T. G. & BOER, J. J. DE (1968). *Chem. Comm.* p. 1413.
- IBERS, J. A. & SNYDER, R. G. (1962). *Acta Cryst.* **15**, 708.
- International Tables for X-ray Crystallography* (1959). Vol. I. Birmingham: Kynoch Press.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- KILBOURN, B. T., MAIS, R. H. B. & OWSTON, P. G. (1967). *Chem. Comm.* p. 16.
- MCPARTLIN, M. & MASON, R. (1967). *Chem. Comm.* p. 16.
- MASON, R. & RUSSELL, D. R. (1966). *Chem. Comm.* p. 26.
- MASON, R. & WHEELER, A. G. (1968). *Nature, Lond.* **217**, 1253.
- PAULING, L. (1960). *The Nature of the Chemical Bond*. Ithica: Cornell Univ. Press.
- SMITH, A. E. (1965). *Acta Cryst.* **18**, 331.
- SMITH, A. E. (1968). Private communication.
- VOLGER, H. C. & VRIEZE, K. (1967). *J. Organometal. Chem.* **9**, 527.
- VRIEZE, K., MACLEAN, C., COSSEE, P. & HILBERS, C. W. (1966). *Rec. Trav. chim. Pays-Bas*, **85**, 1077.
- VRIEZE, K. & VOLGER, H. C. (1967). *J. Organometal. Chem.* **9**, 537.

*Acta Cryst.* (1970). B**26**, 1251

## Crystal Chemistry of the Ionic Thiourea Complexes

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Thiourea forms a series of stoichiometric complexes with the salts of alkali metals and related cations. For monovalent cations to which the discussion is restricted a cation: thiourea ratio of 1:4 is favoured and eightfold coordination occurs invariably. The cations occur in linear stacks at characteristic separations and each cation is surrounded by eight sulphur atoms at the corners of a cubically distorted antiprism. The thiourea molecules lie at right angles to the axis through the cationic chains which represent the spines of coordination columns with -NH<sub>2</sub> groups at the surface. These columns pack together in such a way as to create channels of appropriate dimensions for the associated anions to fit snugly into them. The complexes are stabilized by attractions between free ions and dipoles and the limited number of structure types corresponding to the nature of the anions all have very similar Madelung constants. The influence on the structures of factors such as ionic size and shape and hydrogen bonding is examined critically.

### Introduction

The series of thiourea complexes of ionic salts of monovalent cations is characterized by a small number of related structure types. The complexes usually crystallize in the form of delicate needles elongated along an axis (for convenience always called *c*) measuring about 8.2 Å. In structures containing heavy cations, oscillation X-ray photographs taken about this axis always show odd layer lines of relatively low intensity.

This suggests that the cations occur in linear stacks parallel to [001] and with a pitch of approximately *c*/2. It is thus not surprising to find that complexes with a common cation have virtually identical *c* axes, irrespective of the space group. On the other hand, complexes with a common anion usually have a common space group.

In (001) projection, the crystallographic unit cells are always simply related to a tetragonal cell of edge approximately 10 Å. This means that the chains of