Dimeric Chloro-[1,5-bis(diphenylphosphine)pentane]silver*

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Abstract. $(AgClP_2C_{29}H_{30})_2$, monoclinic, $P2_1/n$, $a = 13\cdot428$ (1), $b = 33\cdot263$ (4), $c = 12\cdot414$ (1) Å, $\beta = 99\cdot30$ (1)°, $V = 5472$ Å^3, $Z = 4$, $D_c = 1\cdot43$, $D_o = 1\cdot45$ g cm^{-3}. Two Ag atoms are joined both by doubly bridging Cl atoms and by two molecules of 1,5-bis(diphenylphosphine)pentane. Each Ag is thus coordinated to two Cl and two P atoms, the latter belonging to different ligand molecules. The coordination round the Ag and P atoms is distorted tetrahedral.

Introduction. The preparation of 1,5-bis(diphenylphosphine)pentane was made by the route given by

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* Part VII in the series Structures of Complexes between Metal Halides and Phosphinothioethers or Related Ligands.

Degischer (1968) for bis(diphenylphosphinoethyl) sulphide. Single crystals of $(AgClP_2C_{29}H_{30})_2$ were obtained on slow evaporation at 50°C of a CH_3CN solution containing $AgNO_3$, $(C_2H_5)_4NCl$ and the above ligand in equimolar amounts. A single crystal, $0\cdot07 \times 0\cdot13 \times 0\cdot13$ mm, was selected for intensity measurements. A computer-controlled four-circle diffractometer (CAD-4) equipped with a graphite monochromator (Cu $K\alpha$ radiation) was used. The ω–2θ scan technique, with a scan interval of $(0\cdot70 + 0\cdot60 \tan \theta)°$, was employed. At each end of the interval the background was measured for one quarter of the scan time. In the range $5° < \theta < 60°$, 8764 reflexions were recorded. Of these, 4119 with $I > 2\sigma(I)$ were considered significantly above background and were used in the subsequent calculations. $\sigma(I)$ is the standard deviation based on

Table 1. *Fractional coordinates and isotropic thermal parameters of* $(AgClP_2C_{29}H_{30})_2$

The coordinates for silver are multiplied by 10^5, the others by 10^4. Estimated standard deviations are given in parentheses.

	x	y	z	B (Å^2)		x	y	z	B (Å^2)
Ag(1)	29204 (7)	17360 (3)	8542 (7)	[5·2]	C(26)	2117 (11)	2711 (5)	5147 (12)	7·0 (3)
Ag(2)	19433 (8)	8582 (3)	23598 (8)	[6·0]	C(27)	2150 (11)	3112 (5)	4775 (13)	7·6 (4)
Cl(1)	1609 (2)	1140 (1)	313 (2)	[6·0]	C(28)	1222 (10)	3345 (4)	4584 (11)	6·5 (3)
Cl(2)	3206 (2)	1466 (1)	2948 (2)	[5·6]	C(29)	3631 (8)	1613 (3)	8168 (9)	4·5 (3)
P(1)	2453 (2)	2433 (1)	1246 (2)	[4·2]	C(30)	2609 (10)	1516 (4)	7840 (11)	6·2 (3)
P(2)	4130 (3)	1552 (1)	9610 (3)	[4·8]	C(31)	2169 (11)	1534 (4)	6707 (12)	7·4 (4)
P(3)	3191 (3)	332 (1)	3101 (3)	[6·2]	C(32)	2763 (10)	1660 (4)	5955 (11)	6·6 (3)
P(4)	141 (3)	926 (1)	2609 (3)	[6·0]	C(33)	3786 (10)	1761 (4)	6266 (11)	6·4 (3)
C(1)	1502 (8)	2449 (4)	2179 (9)	5·1 (3)	C(34)	4217 (9)	1745 (4)	7388 (11)	5·9 (3)
C(2)	460 (10)	2266 (4)	1616 (11)	6·6 (3)	C(35)	1921 (11)	4790 (4)	2246 (12)	7·2 (3)
C(3)	4798 (10)	2832 (4)	7490 (12)	7·2 (3)	C(36)	2735 (13)	4694 (5)	3017 (14)	9·0 (4)
C(4)	66 (11)	1760 (5)	2960 (12)	7·6 (4)	C(37)	2841 (14)	4238 (6)	3278 (16)	10·5 (5)
C(5)	4565 (10)	3596 (4)	7141 (12)	7·1 (3)	C(38)	2160 (15)	4004 (6)	2691 (16)	10·1 (5)
C(6)	4427 (11)	1011 (4)	9595 (12)	7·4 (4)	C(39)	1384 (17)	4092 (7)	1971 (19)	12·1 (6)
C(7)	4933 (15)	882 (7)	850 (18)	12·3 (6)	C(40)	1182 (13)	4527 (6)	1677 (14)	9·6 (5)
C(8)	4547 (23)	426 (11)	1066 (27)	18·3 (10)	C(41)	3209 (9)	332 (4)	4568 (11)	6·0 (3)
C(9)	4990 (23)	337 (9)	1996 (29)	18·5 (10)	C(42)	2748 (10)	20 (5)	5075 (12)	7·0 (3)
C(10)	4553 (12)	449 (5)	3028 (14)	8·8 (4)	C(43)	2721 (11)	49 (5)	6210 (13)	7·9 (4)
C(11)	1988 (9)	2775 (4)	121 (10)	5·0 (3)	C(44)	3131 (12)	377 (6)	6808 (14)	8·8 (4)
C(12)	2306 (10)	2686 (4)	9139 (11)	6·6 (3)	C(45)	3615 (12)	675 (5)	6306 (14)	8·9 (4)
C(13)	1962 (12)	2941 (5)	8202 (14)	8·7 (4)	C(46)	3640 (11)	671 (5)	5176 (12)	7·3 (4)
C(14)	1324 (12)	3261 (5)	8348 (14)	9·1 (4)	C(47)	4344 (11)	4451 (5)	6834 (11)	6·6 (3)
C(15)	965 (12)	3345 (5)	9339 (14)	8·9 (4)	C(48)	4740 (16)	4807 (7)	6785 (18)	12·1 (6)
C(16)	1342 (10)	3087 (4)	259 (11)	6·1 (3)	C(49)	850 (17)	158 (7)	8850 (19)	13·1 (6)
C(17)	3478 (8)	2716 (4)	2048 (9)	4·2 (2)	C(50)	1820 (13)	85 (6)	9220 (13)	8·8 (4)
C(18)	3709 (11)	3104 (5)	1820 (12)	7·5 (4)	C(51)	2790 (15)	4729 (7)	5859 (17)	11·5 (6)
C(19)	4515 (12)	3306 (5)	2536 (13)	8·2 (4)	C(52)	3383 (14)	4377 (6)	6404 (15)	10·2 (5)
C(20)	12 (11)	1891 (5)	8443 (13)	7·7 (4)	C(53)	4827 (10)	4150 (4)	8977 (11)	6·2 (3)
C(21)	4811 (11)	2719 (5)	3628 (12)	7·6 (4)	C(54)	520 (12)	688 (5)	4735 (13)	8·1 (4)
C(22)	4005 (9)	2517 (4)	2940 (11)	5·7 (3)	C(55)	280 (14)	609 (6)	5845 (16)	10·3 (5)
C(23)	343 (9)	3177 (4)	4817 (10)	5·1 (3)	C(56)	4340 (14)	4270 (5)	1074 (15)	9·6 (5)
C(24)	340 (10)	2796 (4)	5239 (11)	6·4 (3)	C(57)	3638 (12)	4095 (5)	313 (14)	8·4 (4)
C(25)	1245 (11)	2563 (4)	5408 (12)	7·4 (4)	C(58)	3859 (11)	4018 (5)	9235 (13)	7·6 (4)

Table 2. *Vibrational parameters for the silver, chlorine and phosphorus atoms of* $(AgClP_2C_{29}H_{30})_2$

The expression for the anisotropic thermal parameters is of the form $\exp\left[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})\right]$.
The β_{ij} values are multiplied by 10^5. Estimated standard deviations are given in parentheses. R_i denotes the r.m.s. components.

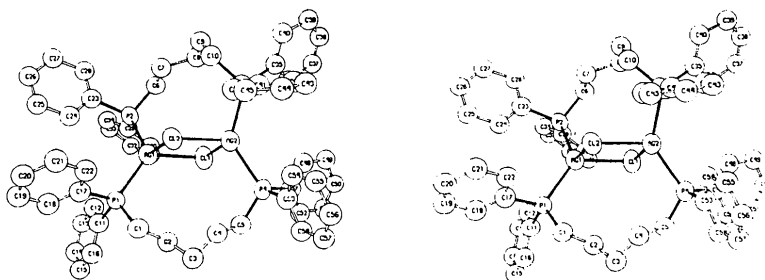|	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1 (Å)	R_2 (Å)	R_3 (Å)
Ag(1)	937 (8)	115 (1)	802 (8)	−15 (3)	277 (6)	−40 (3)	0·295	0·225	0·256
Ag(2)	936 (8)	137 (1)	975 (9)	−21 (3)	171 (7)	64 (3)	0·300	0·245	0·286
Cl(1)	1059 (28)	146 (5)	794 (26)	−87 (9)	10 (21)	54 (9)	0·339	0·235	0·260
Cl(2)	997 (26)	120 (4)	785 (26)	−36 (8)	−2 (21)	22 (8)	0·311	0·237	0·253
P(1)	663 (22)	98 (4)	629 (24)	−4 (8)	82 (18)	−22 (8)	0·242	0·213	0·239
P(2)	917 (27)	103 (4)	721 (26)	−13 (9)	288 (21)	−25 (9)	0·291	0·214	0·241
P(3)	1252 (34)	114 (5)	961 (32)	27 (10)	196 (27)	53 (10)	0·333	0·237	0·281
P(4)	904 (28)	128 (5)	1106 (33)	−49 (10)	317 (25)	−3 (11)	0·308	0·243	0·276

Fig. 1. A stereo view of $(AgClP_2C_{29}H_{30})_2$ showing the non-hydrogen atoms. The thermal ellipsoids are drawn to enclose 50% probability.

counting statistics. Corrections were made for the decay of the intensities by means of three standard reflexions, and for Lorentz, polarization and absorption effects $[\mu(Cu\ K\alpha)=82\cdot1\ cm^{-1}]$.

The structure was solved from the Patterson function and successive electron density syntheses. The Ag, Cl and P atoms were refined anisotropically and the C atoms isotropically by least squares. H atoms were excluded. Scattering factors for the neutral atoms were taken from Hanson, Herman, Lea & Skillman (1964). The refinement reduced $R=\sum||F_o|-|F_c||/\sum|F_o|$ to 0·071 and $R_w=[\sum w_i(|F_o|-|F_c|)^2/\sum w_i|F_o|^2]^{1/2}$ to 0·086. An anomalous dispersion correction (*International Tables for X-ray Crystallography*, 1974) for Ag, Cl and P did not affect R and R_w. The quantity minimized was $\sum w_i(|F_o|-|F_c|)^2$, with $w_i^{-1}=\sigma^2(F_o)+a|F_o|^2$. With $a=0\cdot001$, the average values of $w_i(|F_o|-|F_c|)^2$ were nearly constant in different $|F_o|$ and $\sin\theta$ intervals. There were no peaks larger than $1\cdot3\ e\ \text{Å}^{-3}$ in the final difference map. Final positional and thermal parameters are presented in Tables 1 and 2* and interatomic distances and angles in Table 3. For all

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31730 (17 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

calculations the Univac 1108 computer in Lund was used.

Discussion. A stereo view of $(AgClP_2C_{29}H_{30})_2$ is given in Fig. 1. As in $(AgXP_2SC_{28}H_{28})_2$, $X=Cl$ and I (Aurivillius, Cassel & Fälth, 1974; Cassel, 1975), the present
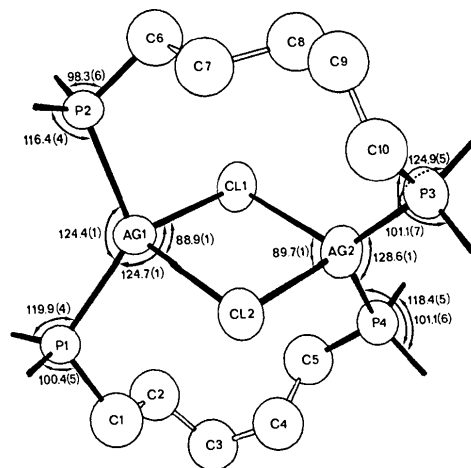

Fig. 2. Schematic drawing of $(AgClP_2C_{29}H_{30})_2$ showing the non-hydrogen atoms except the phenyl carbon atoms. The smallest and largest angles of the distorted tetrahedra around Ag(1), Ag(2), P(1), P(2), P(3) and P(4) are given.

Table 3. *Interatomic distances* (Å) *and angles* (°)
in $(AgClP_2C_{29}H_{30})_2$

Standard deviations are given in parentheses.
For notation, see Fig. 1.

Ag(1)–Ag(2)	3·812 (1)	Cl(1)–Cl(2)	3·769 (4)

Silver coordination

Ag(1)–P(1)	2·472 (3)	Ag(2)–P(3)	2·493 (4)
–P(2)	2·492 (3)	–P(4)	2·499 (4)
–Cl(1)	2·664 (4)	–Cl(1)	2·678 (3)
–Cl(2)	2·718 (3)	–Cl(2)	2·663 (3)

Phosphorus coordination

P(1)—Ag(1)	2·472 (3)	P(2)—Ag(1)	2·492 (3)
–C(1)	1·858 (12)	–C(6)	1·842 (15)
–C(11)	1·830 (13)	–C(23)	1·843 (12)
–C(17)	1·824 (11)	–C(29)	1·819 (11)
P(3)—Ag(2)	2·493 (4)	P(4)—Ag(2)	2·499 (4)
–C(10)	1·887 (16)	–C(5)	1·823 (15)
–C(35)	1·855 (15)	–C(47)	1·819 (15)
–C(41)	1·818 (14)	–C(53)	1·832 (14)

Carbon–carbon distances outside the phenyl rings

C(1)—C(2)	1·58 (2)	C(6)—C(7)	1·65 (3)
C(2)—C(3)	1·54 (2)	C(7)—C(8)	1·64 (4)
C(3)—C(4)	1·51 (2)	C(8)—C(9)	1·25 (5)
C(4)—C(5)	1·63 (2)	C(9)—C(10)	1·54 (4)

Mean carbon–carbon distances of the phenyl rings

1·411 (11), 1·394 (15), 1·399 (15), 1·411 (6), 1·412 (40),
1·408 (7), 1·381 (43), 1·410 (26)

Angles in the double bridge

Ag(1)–Cl(1)–Ag(2)	91·1 (1)	Ag(1)–Cl(2)–Ag(2)	90·2 (1)

Angles in the distorted tetrahedra around the silver and the
phosphorus atoms

P(1)—Ag(1)–P(2)	124·4 (1)	P(3)—Ag(2)–P(4)	128·6 (1)
P(1)—Ag(1)–Cl(1)	124·7 (1)	P(3)—Ag(2)–Cl(1)	126·6 (1)
P(1)—Ag(1)–Cl(2)	97·1 (1)	P(3)—Ag(2)–Cl(2)	94·1 (1)
P(2)—Ag(1)–Cl(1)	97·6 (1)	P(4)—Ag(2)–Cl(1)	94·0 (1)
P(2)—Ag(1)–Cl(2)	120·4 (1)	P(4)—Ag(2)–Cl(2)	119·0 (1)
Cl(1)–Ag(1)–Cl(2)	88·9 (1)	Cl(1)–Ag(2)–Cl(2)	89·7 (1)
Ag(1)–P(1)—C(1)	111·8 (4)	Ag(1)–P(2)—C(6)	114·2 (5)
Ag(1)–P(1)—C(11)	119·9 (4)	Ag(1)–P(2)—C(23)	116·4 (4)
Ag(1)–P(1)—C(17)	113·5 (4)	Ag(1)–P(2)—C(29)	114·2 (4)
C(1)—P(1)—C(11)	105·9 (5)	C(6)—P(2)—C(23)	106·9 (6)
C(1)—P(1)—C(17)	100·4 (5)	C(6)—P(2)—C(29)	98·3 (6)
C(11)–P(1)—C(17)	103·3 (5)	C(23)–P(2)—C(29)	105·0 (5)
Ag(2)–P(3)—C(10)	115·9 (5)	Ag(2)–P(4)—C(5)	114·1 (5)
Ag(2)–P(3)—C(35)	124·9 (5)	Ag(2)–P(4)—C(47)	111·8 (5)
Ag(2)–P(3)—C(41)	105·6 (5)	Ag(2)–P(4)—C(53)	118·4 (5)
C(10)–P(3)—C(35)	103·4 (7)	C(5)—P(4)—C(47)	104·5 (7)
C(10)–P(3)—C(41)	101·1 (7)	C(5)—P(4)—C(53)	105·4 (6)
C(35)–P(3)—C(41)	102·7 (7)	C(47)–P(4)—C(53)	101·1 (6)

Angles in the ligand chains

P(1)–C(1)–C(2)	111 (1)	P(2)–C(6)—C(7)	108 (1)
C(1)–C(2)–C(3)	110 (1)	C(6)–C(7)—C(8)	108 (2)
C(2)–C(3)–C(4)	110 (1)	C(7)–C(8)—C(9)	105 (3)
C(3)–C(4)–C(5)	111 (1)	C(8)–C(9)—C(10)	122 (3)
C(4)–C(5)–P(4)	109 (1)	C(9)–C(10)–P(3)	120 (2)

structure consists of dimeric molecules. The nearly
square plane formed by Ag(1), Ag(2), Cl(1) and Cl(2)
(Fig. 2) is almost equal to the plane in
$(AgClP_2SC_{28}H_{28})_2$. The deviations from a least-squares
plane are +0·011, +0·012, −0·011 and −0·011 Å for
the four atoms respectively. The smallest and largest
angles in the distorted tetrahedra around Ag(1), Ag(2),
P(1), P(2), P(3) and P(4) are shown in Fig. 2. These
values deviate considerably from 109·5°. It is noticeable
that all Ag–P–C angles in the present and the above-
mentioned structures, with one exception, are greater
than 109·5° while all C–P–C angles are smaller.
The steric hindrance when two P atoms, each bonded
to two phenyl rings, enter the coordination sphere of
Ag might cause the increase in the Ag–P–C angles. In the
Ag tetrahedra the angles P(1)–Ag(1)–P(2) and P(3)–
Ag(2)–P(4) are 124·4 (1) and 128·6 (1)°, respectively,
much larger than the corresponding 117·7 (1)° found in
$(AgClP_2SC_{28}H_{28})_2$. One explanation for these deviations
is that the strain in 1,5-bis(diphenylphosphine)pentane
is larger than in bis(diphenylphosphinoethyl) sulphide.
The latter is more movable around the S atom than the
former around a CH_2 group.

In the ligand chain from P(2) to P(3) the positions of
C(8) and C(9) could not be accurately determined
(Table 1). The possibility of disorder for the C atoms
due to different conformations of the chain must be
considered. However, it was not possible from the
difference maps to deduce alternative conformations.
In the other ligand chain, from P(1) to P(4), distances
and angles are in accordance with expected values.
Apart from the above-mentioned inaccuracy con-
cerning two C atoms, all interatomic distances between
bonded atoms in $(AgClP_2C_{29}H_{30})_2$ and
$(AgClP_2SC_{28}H_{28})_2$ are in good agreement.

References

Aurivillius, K., Cassel, A. & Fälth, L. (1974). *Chem. Script.* 5, 9–12.
Cassel, A. (1975). *Acta Cryst.* B31, 1194–1196.
Degischer, G. (1968). Diss. 4163, E.T.H., Zürich, Switzer-land.
Hanson, H. P., Herman, F., Lea, J. D. & Skillman, S. (1964). *Acta Cryst.* 17, 1040–1044.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.