preted as a dichloromethane molecule with a partial occupancy on two disordered sites.

We thank Dr P. Thomas for collecting the data. One of us (BM) thanks the Royal Society and the CNRS for support.

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Acta Cryst. (1979). B**35**, 174–177

Dimeric Chlorobis(triphenylphosphine)silver*

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(*Received* 21 *June* 1978; *accepted* 16 *October* 1978)

Abstract. $[Ag(C_{36}H_{30}P_2)Cl]_2$, triclinic, $P\bar{1}$, $a = 10{\cdot}308\,(5)$, $b = 12{\cdot}608\,(4)$, $c = 13{\cdot}893\,(6)$ Å, $\alpha = 113{\cdot}36\,(4)$, $\beta = 110{\cdot}29\,(3)$, $\gamma = 75{\cdot}02\,(3)°$, $V = 1539$ Å^3, $Z = 1$, $D_c = 1{\cdot}44$, $D_o = 1{\cdot}45$ Mg m^{-3}. Two Ag atoms are joined through a double Cl bridge. To each Ag are also coordinated two P atoms from two triphenylphosphine molecules. The coordination polyhedron around Ag is a distorted tetrahedron. The crystal structure is thus built up from discrete dimeric molecules.

Introduction. Prismatic crystals of the title compound were obtained on the slow cooling to room temperature of a warm CH_3CN solution of $AgNO_3$, $(C_2H_5)_4NCl$ and $P(C_6H_5)_3$; the molar ratio was 1:1:2. A single crystal defined by the six planes (001), (00$\bar{1}$), (10$\bar{1}$), ($\bar{1}$01), (110) and ($\bar{1}\bar{1}$0) was selected. The distances between parallel planes were 0·07, 0·08 and 0·08 mm.

The intensity measurements were carried out on a computer-controlled four-circle diffractometer (CAD-4) equipped with a graphite monochromator and using Cu $K\alpha$ radiation. The ω–2θ scan technique, with a scan interval of $\Delta\omega = (0{\cdot}60 + 0{\cdot}40\tan\theta)°$, was employed. The background was measured for one quarter of the scan time at each end of the peak-scan interval. 6181 reflections were recorded in the range $5° < \theta < 50°$, and 4821 with $I > 2\sigma(I)$ were used in the subsequent calculations. The standard deviation $\sigma(I)$ is based on counting statistics. The intensities of three standard reflections measured regularly were used to scale the intensities of the other reflections. The intensity decrease was linear with respect to exposure time and the total decrease was 17·6%. Corrections were made for Lorentz, polarization and absorption effects [μ(Cu $K\alpha$) = 7·32 mm^{-1}]. No corrections for anomalous dispersion or secondary extinction were made.

The positions of Ag, Cl, P and C were determined using the Patterson function, successive electron density syntheses and least-squares refinements. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Ag, Cl and P were refined anisotropically and C isotropically. The H atoms were not included. In the final difference synthesis no peaks larger than 1·8 e Å^{-3} were found. Two peaks of 1·8 and 1·6 e Å^{-3} are residuals from the electron density of silver. Apart from these no peaks larger than 1·1 e Å^{-3} were found. The quantity minimized was $\sum w_i(|F_o| - |F_c|)^2$ giving $R = \sum||F_o| -$

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* Structures of Complexes between Metal Halides and Phosphinothioethers or Related Ligands. VIII.

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$|F_c||/\sum|F_o| = 0{\cdot}065$ and $R_w = [\sum w_i(|F_o| - |F_c|)^2/\sum w_i|F_o|^2]^{1/2} = 0{\cdot}084$ in the final refinement. With $w_i^{-1} = \sigma^2(F_o) + 0{\cdot}020|F_o|^2$, $w_i(|F_o| - |F_c|)^2$ was nearly constant for different sin θ and $|F_o|$ intervals. The shifts in the positional parameters were less than 5% of the standard deviations. Final positional parameters are given in Table 1.* Selected and mean values of the interatomic distances and angles are given in Tables 2 and 3. All calculations were carried out on the Univac 1108 computer in Lund.

Discussion. The crystal structure is built up from dimeric molecules: $[Ag(C_{36}H_{30}P_2)Cl]_2$, '$AgClP_2$'. A stereoview of the molecule is shown in Fig. 1. When the H atoms in '$AgClP_2$' were geometrically located 1·00 Å from the corresponding C atoms, no H···H or Cl···H intermolecular distances shorter than 2·28 or 2·99 Å, respectively, were found. The van der Waals H···H and Cl···H distances are 2·4 and 3·0 Å (Pauling, 1960). Baur (1972) suggests 1·00 Å for the van der Waals radius of H. This indicates that there should be no intermolecular repulsive interactions. The Ag atom prefers a tetrahedral to a trigonal configuration. Using the bridging property of the Cl atom, Ag can maintain the tetrahedral configuration through a dimerization over a double Cl bridge. In '$AgClP_2$' Ag is coordinated to two Cl and two P atoms in the form of a distorted tetrahedron. The smallest and the largest angles and the distances in the coordination polyhedron are shown in Fig. 2 and Table 2. If steric hindrances are applied to the complex formation the dimerization can, however, be cancelled and three-coordinated Ag is formed (Barrow, Bürgi, Johnson & Venanzi, 1976).

The Ag—Cl distances [2·741 (2) and 2·596 (2) Å] in '$AgClP_2$' differ by almost 0·15 Å. The average value (2·669 Å) agrees well with Ag—Cl distances found in

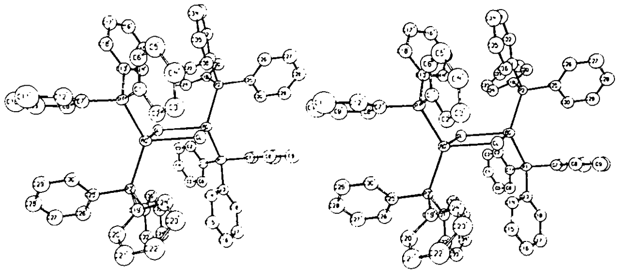

Fig. 1. A stereoview of the $[Ag(C_{36}H_{30}P_2)Cl]_2$ molecule showing the nonhydrogen atoms. The thermal ellipsoids are drawn to enclose 50% probability.

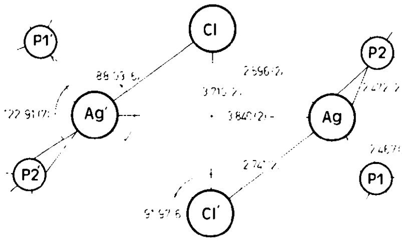

Fig. 2. Schematic drawing of the $P_2AgCl_2AgP_2$ fragment of $[Ag(C_{36}H_{30}P_2)Cl]_2$. Distances (Å) and selected angles (°) are given.

Table 1. *Fractional coordinates* (×10^4, *for* Ag ×10^5) *in* $[Ag(C_{36}H_{30}P_2)Cl]_2$

Standard deviations are given in parentheses.

	x	y	z		x	y	z
Ag	41837 (5)	16099 (5)	3204 (4)	C(17)	2500 (8)	1340 (7)	−4383 (6)
Cl	6496 (2)	440 (2)	−134 (1)	C(18)	2152 (7)	1894 (7)	−3391 (6)
P(1)	2443 (2)	2120 (2)	−1228 (1)	C(19)	3068 (7)	3110 (6)	2790 (5)
P(2)	4503 (2)	2930 (1)	2233 (1)	C(20)	2625 (8)	4179 (7)	3526 (6)
C(1)	769 (7)	1679 (6)	−1487 (5)	C(21)	1500 (9)	4233 (8)	3900 (7)
C(2)	495 (8)	1507 (7)	−653 (6)	C(22)	801 (9)	3307 (8)	3550 (7)
C(3)	−744 (9)	1175 (8)	−786 (7)	C(23)	1224 (9)	2247 (8)	2828 (7)
C(4)	−1745 (9)	986 (8)	−1770 (7)	C(24)	2369 (8)	2144 (7)	2429 (6)
C(5)	−1476 (9)	1138 (8)	−2618 (7)	C(25)	4623 (7)	4432 (6)	2472 (5)
C(6)	−241 (8)	1475 (7)	−2487 (6)	C(26)	5683 (8)	5044 (7)	3324 (6)
C(7)	2041 (7)	3663 (6)	−1117 (6)	C(27)	5706 (9)	6209 (8)	3478 (7)
C(8)	3173 (8)	4175 (8)	−985 (7)	C(28)	4696 (9)	6757 (8)	2816 (7)
C(9)	2950 (10)	5320 (9)	−972 (8)	C(29)	3642 (9)	6160 (8)	1980 (7)
C(10)	1668 (11)	5964 (9)	−1016 (8)	C(30)	3615 (8)	4990 (7)	1800 (6)
C(11)	522 (12)	5469 (11)	−1128 (9)	C(31)	6054 (7)	2525 (6)	3229 (5)
C(12)	728 (9)	4299 (8)	−1162 (7)	C(32)	6120 (7)	2871 (7)	4313 (6)
C(13)	2864 (7)	1467 (6)	−2528 (5)	C(33)	7341 (8)	2541 (7)	5038 (6)
C(14)	3941 (7)	533 (6)	−2655 (6)	C(34)	8478 (9)	1872 (8)	4652 (7)
C(15)	4285 (8)	1 (7)	−3656 (6)	C(35)	8409 (9)	1536 (8)	3562 (7)
C(16)	3545 (8)	412 (7)	−4495 (6)	C(36)	7192 (7)	1857 (7)	2841 (6)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33955 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic distances* (Å) *and angles* (°) *in* $[Ag(C_{36}H_{30}P_2)Cl]_2$

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

Ag—Ag'	3·840 (2)	Cl—Cl'	3·710 (2)
Silver coordination			
Ag—P(1)	2·467 (2)	Ag—Cl	2·596 (2)
—P(2)	2·472 (2)	—Cl'	2·741 (2)
Phosphorus coordination			
P(1)—Ag	2·467 (2)	P(2)—Ag	2·472 (2)
—C(1)	1·823 (7)	—C(19)	1·822 (7)
—C(7)	1·835 (8)	—C(25)	1·818 (7)
—C(13)	1·818 (7)	—C(31)	1·826 (7)

Mean C—C distances in the phenyl rings*

1·384 (4)	1·391 (9)	1·392 (7)	1·401 (8)
1·395 (7)	1·388 (4)		

Mean C—C—C angles in the phenyl rings*

119·9 (7)	120·0 (3)	120·0 (4)	119·9 (6)
120·0 (1)	120·0 (3)		

Angle in the double bridge

Ag—Cl—Ag' 91·97

Angles in the distorted tetrahedra around the Ag and P atoms

P(1)—Ag—P(2)	122·91 (7)	P(2)—Ag—Cl	113·92 (7)
P(1)—Ag—Cl'	103·59 (7)	P(2)—Ag—Cl'	108·70 (7)
P(1)—Ag—Cl	112·97 (7)	Cl—Ag—Cl'	88·03 (6)
Ag—P(1)—C(1)	110·7 (2)	Ag—P(2)—C(19)	114·3 (2)
Ag—P(1)—C(7)	117·6 (2)	Ag—P(2)—C(25)	115·3 (2)
Ag—P(1)—C(13)	116·3 (2)	Ag—P(2)—C(31)	116·2 (2)
C(1)—P(1)—C(7)	105·2 (3)	C(19)—P(2)—C(25)	102·0 (3)
C(1)—P(1)—C(13)	105·4 (3)	C(19)—P(2)—C(31)	104·1 (3)
C(7)—P(1)—C(13)	100·2 (3)	C(25)—P(2)—C(31)	103·2 (3)

* The mean values of the distances and angles in the phenyl rings ($\bar{b}$) and corresponding mean values of the standard deviations $\sigma(\bar{b})$ are calculated according to the formulae:

$$\bar{b}=\sum_{i=1}^{6}\frac{b_i}{\sigma_i^2}\bigg/\sum_{i=1}^{6}\frac{1}{\sigma_i^2},$$

$$\sigma(\bar{b})=\left\{\frac{1}{5}\left[\sum_{i=1}^{6}(b_i-\bar{b})^2\frac{1}{\sigma_i^2}\bigg/\sum_{i=1}^{6}\frac{1}{\sigma_i^2}\right]\right\}^{1/2}.$$

Table 3. *Selected intramolecular distances* (Å) *in* $[Ag(C_{36}H_{30}P_2)Cl]_2$

H···H distances <3·00 Å			
H(C2)···H(C24)	2·56	H(C26)···H(C32)	2·88
H(C6)···H(C18)	2·36	H(C32)···H(C20)	2·79
H···C distances <3·00 Å			
H(C2)···C(24)	2·93	H(C26)···C(31)	2·56
H(C6)···C(13)	2·83	H(C26)···C(32)	2·71
H(C6)···C(18)	2·60	H(C30)···C(7)	2·83
H(C12)···C(1)	2·67	H(C30)···C(8)	2·98
H(C12)···C(6)	2·92	H(C32)···C(19)	2·72
H(C18)···C(7)	2·70	H(C32)···C(20)	2·79
H(C20)···C(25)	2·60	H(C35)···C(6)'	2·97
C···C distances <3·50 Å			
C(15)'···C(32)	3·47 (1)	C(14)'···C(36)	3·39 (1)
Cl···H distances <3·50 Å			
Cl···H(C2)'	3·04	Cl···H(C24)'	2·83
Cl···H(C14)	2·71	Cl···H(C36)	2·72

similar dimeric molecules (Aurivillius, Cassel & Fälth, 1974; Cassel, 1976).

The Ag—P distances [2·467 (2) and 2·472 (2) Å] are also in good agreement with values found in similar compounds containing two P atoms (Aurivillius, Cassel & Fälth, 1974; Cassel, 1975, 1976; Teo & Calabrese, 1976). In the latter, $[AgBr(C_{36}H_{30}P_2)]_2.CHCl_3$, '$AgBrP_2$', one Ag—P distance is somewhat elongated [2·513 (7) Å] compared with those in '$AgClP_2$'. The Ag—P—C angles in '$AgClP_2$' are all smaller and the C—P—C angles are all greater than 109·5° as a consequence of repulsive interactions between the phenyl rings. The P—C and C—C distances have normal values, as have the C—C—C angles (see Table 2).

Both the Cl···Cl and the Br···Br distances in '$AgClP_2$' and '$AgBrP_2$', respectively, are approximately 0·1 Å longer than the corresponding van der Waals values (Pauling, 1960). This means that the halogen···halogen repulsive interactions in the two compounds are similar and weak.

In both structures there are intramolecular non-bonding repulsions; however, for '$AgBrP_2$' no details of these are reported. In '$AgClP_2$' the intramolecular H···H, H···C, C···C and Cl···H distances were calculated and selected values are given in Table 3. On comparing these with the van der Waals distances reported in the literature (Pauling, 1960; Gieren & Dederer, 1977), it is found that several H···H, C···H and Cl···H distances have low values. The Cl atom which is the closest bonded to Ag is in close contact with H(C14), H(C24)' and H(C36). Close H···H and H···C contacts are H(C6)—H(C18), H(C6)—C(18), H(C12)—C(1), H(C20)—C(25) and H(C26)—C(31). With a radius of 1·00 Å for H there are still close contacts between Cl and H(C14), H(C24)' and H(C36).

There are noticeable differences between '$AgClP_2$' and '$AgBrP_2$'. In the former the Ag—Ag distance [3·840 (2) Å] is longer than that in the latter [3·720 (4) Å]. In '$AgClP_2$', as mentioned above, the Ag—Cl distances differ by 0·15 Å, whereas in '$AgBrP_2$' the Ag—Br distances are equal.

As the Cl atom in '$AgClP_2$' is in close contact with three H atoms the replacement of the Cl atom by a Br should change these interactions. It is possible that the differences between '$AgClP_2$' and '$AgBrP_2$' could be explained from a more detailed study of the effect of this replacement on both inter- and intramolecular non-bonding repulsions.

The author thanks Dr Karin Aurivillius for valuable help. This investigation is part of a research project financially supported by the Swedish Natural Science Research Council.

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Acta Cryst. (1979). B**35**, 177–178

Tris(1-phenyl-3,5-dimethylpyrazole)silver(I) Nitrate

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(*Received* 25 *July* 1978; *accepted* 12 *September* 1978)

Abstract. $[Ag(C_{11}H_{12}N_2)_3]NO_3$, $C_{33}H_{36}AgN_7O_3$, trigonal, $R3$, hexagonal axis: $a = 15{\cdot}30\,(2)$, $c = 11{\cdot}87\,(1)$ Å, $\gamma = 120{\cdot}0\,(2)^\circ$, $V = 2406$ Å^3, $Z = 3$, $D_m = 1{\cdot}40$ (flotation), $D_x = 1{\cdot}42$ Mg m^{-3}. The final R was 0·047. The coordination around the Ag^+ corresponds to a trigonal bipyramid with the three N atoms of the ligands in the equatorial plane and NO_3^- groups at the apices.

Introduction. The crystals were prepared by Dr M. Molina and co-workers (Institute of Chemistry of Araraquara, UNESP). They are white and opaque, with prismatic habit. Chemical analysis showed a composition ratio of 1:3 between Ag^+ and the ligands (Molina, Angst, Garcia & Melios, 1972). The structure determination was undertaken in order to study the coordination around Ag^+ and the interaction between Ag^+ and NO_3^-. Cell dimensions were determined by a least-squares fit to settings for 25 reflexions ($\pm hkl$) on a CAD-4 automatic diffractometer. Intensity measurements were carried out up to 30° in θ, with graphite-monochromated Mo $K\alpha$ radiation and a crystal in the form of an elongated block 0·5 × 0·3 × 0·8 mm. Lorentz and polarization corrections were applied but no absorption correction [μ(Mo $K\alpha$) = 0·66 mm^{-1}] was made. 909 unique reflections were collected and after application of the acceptance criterion $F^2 \geq 2\sigma(F^2)$, 898 reflexions were retained for use in the structure analysis.*

The structure was solved by application of direct methods, using the program *MULTAN* (Germain, Main & Woolfson, 1971) and difference Fourier calculations. It was refined by a full-matrix least-squares method by minimization of $\sum w(k|F_o| - |F_c|)^2$ until all the atomic parameter shifts were smaller than a standard deviation. The final unweighted R factor omitting unobserved reflections is 0·047 and including them is 0·049. Anisotropic temperature factors were assigned to all non-hydrogen atoms. Complex neutral-atom scattering factors were employed (*International Tables for X-ray Crystallography*, 1974). Final positional parameters are shown in Table 1.

Discussion. The Ag^+ and the N of the nitrate group lie on the threefold axis.

Table 1. *Fractional atomic coordinates* (×10^4) *with their e.s.d.'s*

	x	y	z
Ag(1)	0	0	0
O(1)	10 (10)	741 (9)	5500 (10)
N(3)	0	0	4906 (62)
N(1)	2281 (3)	1833 (3)	427 (4)
N(2)	1689 (3)	924 (3)	−77 (4)
C(3)	2310 (4)	766 (4)	−731 (5)
C(4)	3301 (4)	1567 (4)	−608 (5)
C(5)	3263 (4)	2233 (4)	128 (5)
C(6)	1839 (4)	2205 (4)	1205 (5)
C(7)	1313 (5)	1628 (6)	2114 (7)
C(8)	858 (6)	1983 (8)	2860 (7)
C(9)	943 (6)	2922 (8)	2664 (9)
C(10)	1480 (7)	3488 (7)	1786 (12)
C(11)	1936 (6)	3151 (5)	1042 (8)
C(12)	1922 (6)	−159 (6)	−1448 (7)
C(13)	4083 (5)	3203 (5)	598 (8)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33897 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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