

Tetrakis(tri-*p*-tolylphosphine- $\kappa P$ )silver(I)  
hexafluorophosphateGertruida J. S. Venter, Reinout  
Meijboom and Andreas Roodt\*Department of Chemistry, University of the Free  
State, PO Box 339, Bloemfontein 9300, South  
AfricaCorrespondence e-mail:  
roodta.sci@mail.uovs.ac.za

The title compound,  $[\text{Ag}(\text{P}(p\text{-tol})_3)_4]\text{PF}_6$  or  $[\text{Ag}(\text{C}_{21}\text{H}_{21}\text{P})_4]\text{PF}_6$ , crystallizes with parts of two independent formula units in the asymmetric unit. The Ag—P distances range between 2.5665 (13) and 2.6142 (7) Å, and the P—Ag—P angles between 109.310 (18) and 109.632 (18)°, indicating a distorted tetrahedral geometry. Both Ag atoms and both  $\text{PF}_6^-$  anions lie on threefold rotation axes.

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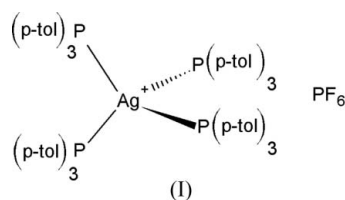
## Key indicators

Single-crystal X-ray study  
 $T = 295 \text{ K}$   
 Mean  $\sigma(\text{C}-\text{C}) = 0.007 \text{ \AA}$   
 $R$  factor = 0.038  
 $wR$  factor = 0.102  
 Data-to-parameter ratio = 21.3

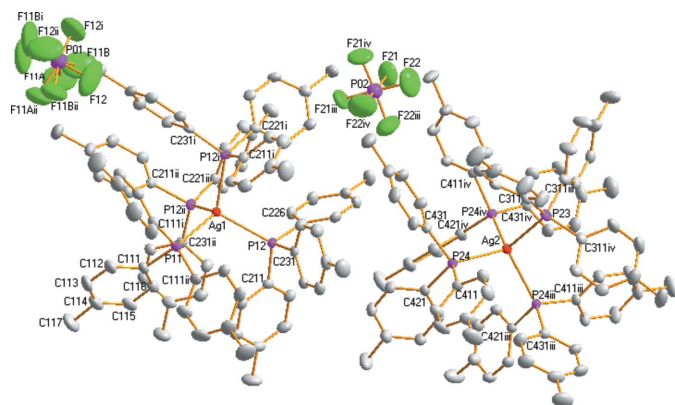
For details of how these key indicators were  
 automatically derived from the article, see  
<http://journals.iucr.org/e>.

## Comment

Tertiary phosphine complexes of  $\text{Ag}^{\text{I}}$  of the type  $[\text{Ag}XL_n]$  ( $L$  = tertiary phosphine;  $n = 1-4$ ;  $X$  = coordinating or non-coordinating anion) were first prepared by Mann *et al.* (1937) and are the first crystallographically characterized examples of metal phosphine complexes. Few structures, however, were reported in the form  $[\text{Ag}L_4]\text{PF}_6$  (Cotton & Luck, 1989; Bowmaker *et al.*, 1990). The general method of preparation involves the reaction of appropriate amounts of the phosphine ligand with an  $\text{Ag}^{\text{I}}$  salt.  $\text{Ag}^{\text{I}}$  complex salts of the classical weakly or non-coordinating anions ( $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ) are typically prepared by addition of the  $\text{Ag}^{\text{I}}$  salt to a hot solution of the phosphine in an alcohol (MeOH, EtOH). The desired complex then readily crystallizes from solution. The resulting coordination complexes of  $\text{Ag}^{\text{I}}$  salts display a rich diversity of structural types. The interplay of parameters such as the geometrical flexibility of  $\text{Ag}^{\text{I}}$ , bite angle, electronic properties of the phosphine and the coordination mode of the supporting ligands often renders predictions concerning the structural properties of silver-phosphine complexes, both in solution and in the solid state, difficult.



Efforts to study the solution behaviour of  $[\text{L}_n\text{AgX}]$  ( $n = 1-4$ ) complexes were initiated by Muetterties & Alegrianti (1972). A series of complexes with a wide range of counteranions was studied by NMR spectroscopy. The coordinating ligands were labile in all the complexes studied. Rapid ligand exchange reactions have additionally been reported for all NMR investigations of ionic monodentate phosphine complexes, thus making NMR spectroscopy of limited use for the characterization of these types of complexes.


**Figure 1**

The asymmetric unit of (I) (50% probability displacement ellipsoids) with H atoms omitted for clarity. The first digit of the P-atom labels indicates the Ag atom to which it is bonded, the second digit the number of the P atom. The first digit of the C-atom labels indicates the phosphine number, the second digit the ring number, the third digit the atom position in the ring. Atoms generated by symmetry are indicated by lower case roman numerical labels corresponding to the symmetry codes reported in Table 1. Some labels have been omitted for clarity, but all rings are numbered in the same consistent way.

The title compound, (I) (Fig. 1), is one of the first silver complexes in the literature with tri-*p*-tolylphosphine as ligand (Meijboom *et al.*, 2006; Meijboom, 2006). The Ag atom is in a formally four-coordinate environment, and adopts a distorted tetrahedral geometry, with parts of two independent formula units in the asymmetric unit, both Ag atoms and both PF<sub>6</sub><sup>−</sup> anions on threefold rotation axes.

The Ag–P bond length for this tri-*p*-tolylphosphine-containing silver compound is shorter than in related compounds (Table 3) with Ag–P ranging between 2.5665 (13) Å and 2.6142 (7) Å. The P–Ag–P angles of the title compound vary between 109.310 (18)° and 109.632 (18)°.

## Experimental

The title compound was synthesized by heating four equivalents of P(*p*-tol)<sub>3</sub> (0.4178 g, 1.373 mmol) with AgPF<sub>6</sub> (0.0861 g, 0.3405 mmol) in acetonitrile under reflux. Recrystallization from acetone produced white crystals suitable for X-ray diffraction in quantitative yield (0.4873 g). M.p. 362–364 K.

### Crystal data

[Ag(C<sub>21</sub>H<sub>21</sub>P)<sub>4</sub>]PF<sub>6</sub>  
*M<sub>r</sub>* = 1470.23  
 Cubic, *P*2<sub>1</sub>3  
*a* = 24.6842 (4) Å  
*V* = 15040.3 (4) Å<sup>3</sup>  
*Z* = 8

*D<sub>x</sub>* = 1.299 Mg m<sup>−3</sup>  
 Mo *K*α radiation  
 $\mu$  = 0.43 mm<sup>−1</sup>  
*T* = 101 (2) K  
 Cuboid, white  
 0.40 × 0.37 × 0.36 mm

### Data collection

Bruker X8 APEX2 diffractometer  
 $\omega$  and  $\varphi$  scans  
 Absorption correction: multi-scan  
 (SADABS; Bruker, 2004)  
*T<sub>min</sub>* = 0.846, *T<sub>max</sub>* = 0.860

122435 measured reflections  
 12538 independent reflections  
 10906 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.064  
 $\theta_{\text{max}}$  = 28.4°

### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.038  
*wR*(*F*<sup>2</sup>) = 0.102  
*S* = 1.09  
 12538 reflections  
 588 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0501P)^2 + 9.1168P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 ( $\Delta/\sigma$ )<sub>max</sub> = 0.003  
 $\Delta\rho_{\text{max}} = 1.58 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.55 \text{ e } \text{Å}^{-3}$   
 Absolute structure: Flack (1983),  
 5852 Friedel pairs  
 Flack parameter: −0.024 (17)

**Table 1**

Selected geometric parameters (Å, °).

P11–Ag1	2.5695 (13)	P23–Ag2	2.5665 (13)
P12–Ag1	2.5737 (7)	P24–Ag2	2.6142 (7)
P11–Ag1–P12	109.310 (18)	P23–Ag2–P24	109.502 (18)
P12 <sup>i</sup> –Ag1–P12	109.631 (18)	P24 <sup>iii</sup> –Ag2–P24	109.441 (18)
P12 <sup>i</sup> –Ag1–P12 <sup>ii</sup>	109.631 (18)	P24 <sup>iii</sup> –Ag2–P24 <sup>iv</sup>	109.441 (18)

Symmetry codes: (i) *z, x, y*; (ii) *y, z, x*; (iii)  $-z + 1, x + \frac{1}{2}, -y + \frac{3}{2}$ ; (iv)  $y - \frac{1}{2}, -z + \frac{3}{2}, -x + 1$ .

**Table 2**

Hydrogen-bond geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
C213–H213···F21 <sup>v</sup>	0.95	2.54	3.439 (4)	159

Symmetry code: (v)  $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$ .

**Table 3**

Comparative geometrical parameters for similar [Ag(PR<sub>3</sub>)<sub>4</sub>]X structures (*R* = *p*-tol, Ph; *X* = PF<sub>6</sub><sup>−</sup>, NO<sub>3</sub><sup>−</sup>, ClO<sub>4</sub><sup>−</sup>), indicated as *X, R* in column headings..

Parameters	PF <sub>6</sub> , <i>p</i> -tol <sup>i</sup>	PF <sub>6</sub> , Ph <sup>ii</sup>	NO <sub>3</sub> , Ph <sup>iii</sup>	ClO <sub>4</sub> , Ph <sup>iv</sup>
Ag1–P11	2.570 (1)	2.639 (2)	2.642 (3)	2.651 (3)
Ag1–P12	2.5737 (7)	2.674 (1)	2.671 (4)	2.668 (6)
Ag2–P21	2.567 (1)	–	–	–
Ag2–P22	2.6142 (7)	–	–	–
P11–Ag1–P12	109.31 (2)	109.31 (3)	109.52 (9)	109.3 (2)
P12–Ag1–P12 <sup>i</sup>	109.63 (2)	109.73 (3)	109.42 (7)	109.6 (2)
P23–Ag2–P24	109.50 (2)	–	–	–
P24–Ag2–P24 <sup>i</sup>	109.44 (2)	–	–	–

(i) This work. (ii) Bowmaker *et al.* (1990). (iii) Barron *et al.* (1986). (iv) Engelhardt *et al.* (1985).

H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C–H = 0.95–0.98 Å and *U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(C) and 1.2*U*<sub>eq</sub>(C) for methyl and aromatic H atoms, respectively. The methyl H atoms were positioned to fit the difference electron density and the groups were then refined as rigid rotors. The highest residual electron-density peak is 1.68 Å from F12.

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT-Plus (Bruker, 2004); data reduction: SAINT-Plus and XPREP (Bruker, 2004); program(s) used to solve structure: SIR97 (Altomare *et al.*, 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: DIAMOND (Brandenburg & Putz, 2005); software used to prepare material for publication: WinGX (Farrugia, 1999).

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