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Key indicators

Single-crystal X-ray study
 $T = 100$ K
Mean $\sigma(C-C) = 0.004$ Å
 R factor = 0.032
 wR factor = 0.072
Data-to-parameter ratio = 20.2For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Tetrakis(triphenylarsine)silver(I) hexafluoro-
phosphate

The title compound, $[Ag(AsC_{18}H_{15})_4]PF_6$, crystallizes with the cation on a threefold rotation axis and the anions on positions with site symmetry $\bar{3}$. The Ag atom is surrounded by four arsine ligands forming a distorted tetrahedral configuration. The Ag–As distances are 2.6381 (6) and 2.6499 (9) Å, and the As–Ag–As angles are 108.91 (1) and 110.03 (1)°.

Received 6 September 2006

Accepted 7 September 2006

Comment

Complexes of silver(I) of the type $[AgXL_n]$ (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. The general method of preparation involves the reaction of appropriate amounts of the phosphine ligand with a silver(I) salt. Silver(I) salts of the classical non-coordinating anions (NO_3^- , ClO_4^- , BF_4^- , PF_6^-) are typically prepared by addition of the silver(I) salt to a hot solution of the phosphine in an alcohol (MeOH, EtOH). The desired complex then crystallizes from solution. These coordination complexes of silver(I) salts display a rich diversity of structural types. The interplay of parameters such as the geometrical flexibility of Ag^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.

Tetrakis(triarylphosphine) complexes have been isolated mainly with non-coordinating anions, *e.g.* $[Ag(PPh_3)_4]X$, where X is ClO_4^- , BrO_3^- and NO_3^- (Cotton & Goodgame, 1960). Crystallographic structural authentication has been undertaken for $[(PPh_3)_4Ag]X$ [$X = ClO_4^-$ (Engelhardt *et al.*, 1985) and NO_3^- (Barron *et al.*, 1986)]. Electron-rich ligands of the type $P(4-YC_6H_4)_3$, where Y is an electron donor, such as methyl or methoxy, most commonly form $[AgL_4][X]$ -type complexes where X is ClO_4^- or BF_4^- (Baiaida *et al.*, 1991). This was attributed to the large volume occupied by the $5sp^3$ orbitals of silver, enabling it to accommodate the lone pair from a fourth tertiary phosphine ligand. Attempts to isolate complexes with $[L]:[Ag] = 4:1$ stoichiometry with a halide have been problematic owing to their instabilities.

The structures of a relatively small number of tetrakis(triphenylarsine) complexes of silver(I), $[Ag(AsPh_3)_4]X$, have been reported [Cambridge Structural Database (CSD), Version 5.27, January 2006 update; Allen, 2002]. In the title complex, (I), the Ag atom is surrounded by four arsine ligands forming a distorted tetrahedral configuration. The Ag–As distances are 2.6381 (6) and 2.6499 (9) Å and the As–Ag–As angles 108.911 (10) and 110.026 (10)°. Two independent PF_6^- anions, each lying on a special position with site

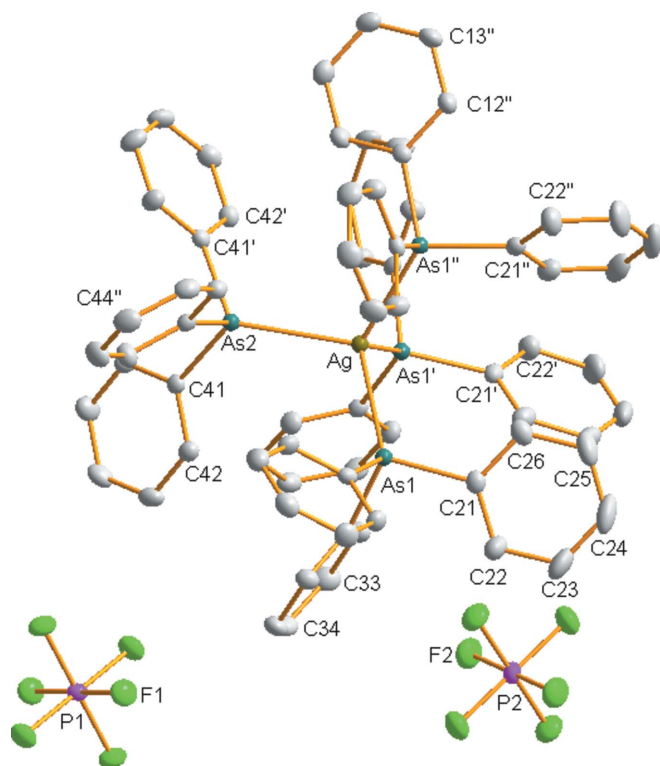
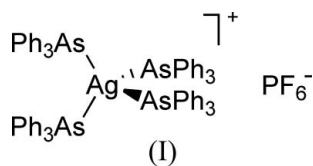


Figure 1
The structure of (I), showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity. For the C atoms, the first digit indicates ring number and the second digit indicates the position of the atom in the ring. Primed atoms were generated by three-fold rotation [symmetry codes: (i) $1 - y, x - y, z$; (ii) $1 - x + y, 1 - x, z$].

symmetry $\bar{3}$, are present in the current structure. Some weak interionic interactions are observed (Table 2). The current structure is compared with the previously reported structures in Table 3.



Efforts to study the solution behaviour of $[L_nAgX]$ complexes were initiated by Muetterties & Alegranti (1972). A series of complexes with a wide range of counter-anions 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 Ag^I monodentate phosphine complexes, thus making NMR spectroscopy of limited use for this type of complex.

Experimental

A solution of triphenylarsine (126 mg, 0.41 mmol) in warm ethanol (3.0 ml) was added to a solution of $AgPF_6$ (26.0 mg, 0.10 mmol) in

warm ethanol (2.0 ml). Colourless crystals of the title compound were obtained in quantitative yield on cooling and standing of the solution.

Crystal data

$[Ag(C_{18}H_{15}As)_4]PF_6$
 $M_r = 1477.72$
 Trigonal, $R\bar{3}$
 $a = 14.276 (5) \text{ \AA}$
 $c = 51.421 (5) \text{ \AA}$
 $V = 9076 (5) \text{ \AA}^3$
 $Z = 6$

$D_x = 1.622 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 2.59 \text{ mm}^{-1}$
 $T = 100 (2) \text{ K}$
 Cuboid, colourless
 $0.43 \times 0.32 \times 0.22 \text{ mm}$

Data collection

Bruker X8 APEX-II diffractometer
 ω and φ scans
 Absorption correction: multi-scan (SADABS; Bruker, 2004)
 $T_{min} = 0.379, T_{max} = 0.565$

12694 measured reflections
 4969 independent reflections
 4358 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.021$
 $\theta_{max} = 28.3^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.072$
 $S = 1.05$
 4969 reflections
 246 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0232P)^2 + 59.264P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.002$
 $\Delta\rho_{max} = 2.53 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -1.9 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters ($\text{\AA}, ^\circ$).

P1–F1	1.6018 (16)	As1–C21	1.937 (2)
P2–F2	1.5995 (17)	As1–C31	1.946 (3)
Ag–As2	2.6381 (6)	As1–C11	1.947 (3)
Ag–As1	2.6499 (9)	As2–C41	1.941 (3)
As2–Ag–As1 ⁱ	108.911 (10)	As1 ⁱⁱ –Ag–As1	110.026 (10)
As2–Ag–As1 ⁱⁱ	108.911 (10)	C21–As1–C31	103.03 (11)
As1 ⁱ –Ag–As1 ⁱⁱ	110.026 (10)	C21–As1–C11	101.42 (10)
As2–Ag–As1	108.911 (10)	C31–As1–C11	100.55 (11)
As1 ⁱ –Ag–As1	110.026 (10)		

Symmetry codes: (i) $-y + 1, x - y, z$; (ii) $-x + y + 1, -x + 1, z$.

Table 2

Hydrogen-bond geometry ($\text{\AA}, ^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C13–H13 \cdots F2 ⁱⁱⁱ	0.95	2.55	3.373 (3)	145

Symmetry code: (iii) $-y + 1, x - y + 1, z$.

Table 3

Comparative geometrical parameters for selected $[Ag(AsPh_3)_4]X$ complexes..

X	Ag–As (\AA)	Ag–As (\AA)	Ag–As (\AA)	Ag–As (\AA)	Notes
NO_3	2.650	2.649	–	–	(i)
ClO_4	2.680	2.652	–	–	(i)
PF_6	2.6381 (6)	2.6499 (9)	–	–	TW
BF_4	2.6451 (10)	2.6578 (5)	–	–	(ii)
BrO_3	2.655 (1)	2.637 (1)	2.659 (1)	2.644 (1)	(iii)

Notes: TW is this work; (i) Bowmaker *et al.* (1997), extracted from CSD; (ii) Tripathi *et al.* (1997); (iii) Cingolani *et al.* (2003).

H atoms were placed in geometrically idealized positions (C–H = 0.95 Å) and constrained to ride on their parent atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The deepest residual electron-density hole is located 0.41 Å from atom As2 and the highest peak is 0.01 Å from the Ag atom.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINTE-Plus* (Bruker, 2004); data reduction: *SAINTE-Plus* and *XPREP* (Bruker 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *SHELXL97*.

Financial assistance from the South African National Research Foundation, THRIP, the Research Fund of the University of the Free State and SASOL is gratefully acknowledged. The authors are grateful to Professor A. Roodt (University of the Free State) for the freedom to pursue their own research within his group. Part of this material is based on work supported by the South African National Research Foundation (SA NRF, GUN 2038915). Opinions, findings, conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the NRF.

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