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Bis(trimethylphosphine)silver(I) hexafluorophosphate

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In the title two-coordinate silver compound, $[Ag(C_3H_9P)_2]PF_6$, the cation has crystallographically imposed mirror symmetry, and approximates very closely to $\overline{3}m$ (D_{3d}) symmetry with fully staggered methyl groups in the solid state. The Ag atom has a nearly linear coordination geometry, with a P—Ag—P angle of 178.70 (4)°. The Ag—P bond lengths are 2.3746 (12) and 2.3783 (12) Å, which are significantly longer than the Au—P bond length of 2.304 (1) Å in the analogous two-coordinate gold cation. The lack of intramolecular steric effects within the present cations containing trimethylphosphine (cone angle 118°), compared with those in known cations containing trimesitylphosphine (cone angle 212°), provides a better comparison of *M*—P distances and thus more conclusive evidence that Au really is smaller than Ag.

Comment

The concept of the 'lanthanide contraction' is commonly invoked to explain some observed radius discontinuities within the periodic table (Pyykko, 1988). The phenomenon called the 'relativistic contraction' (Schwerdtfeger *et al.*, 1990), which is predictable by theoretical calculations involving relativistic and correlational effects, is usually thought to be the specific cause of a third-row element having an expected radius that is similar to, if not less than, that of a second-row element. Experimental proof of this phenomenon has not been forthcoming, because a comparison of metal-to-ligand bond lengths is invalidated by changes in coordination number, geometry or crystal lattice in an apparently analogous set of second- and third-row complexes. Recently (Bayler *et al.*, 1996), an attempt was made to answer the question by making a direct comparison of analogous Ag and Au complexes. It was concluded from the crystal structure analyses of bis(trimesitylphosphine)silver(I) and bis(trimesitylphosphine)gold(I) tetrafluoroborate, that the Au^I atomic radius is almost 0.1 Å smaller than that of Ag^I. Although acknowledging that the Ag/Au—PR_3 distances were larger in these complexes than in other phosphine complexes with smaller *R* substituents, it was considered that the two trimesitylphosphine ligands were 'in a strain-free staggered conformation with deviations in their geometrical parameters within the limits of experimental error', and thus that the comparison was valid.

Our previous structural analysis of the two-coordinate bis(trimesitylphosphine)silver(I) cation (Alyea *et al.*, 1982) indicated, however, that significant intramolecular crowding occurs due to methyl–methyl interactions. The conformation adopted by the phosphine moieties in the molecule deviates from a fully staggered $C_3P—Ag—PC_3$ atom system by an average of 17°. Application of our 'ligand profile' concept (Ferguson *et al.*, 1998) also showed that repulsion led to displacement of the P atoms and *o*-methyl groups relative to the aromatic ring plane, as well as other angle bending. Similarly, our X-ray structural analysis of chloro(trimesitylphosphine)gold(I) (Alyea *et al.*, 1993) clearly showed that significant attractive interaction occurs between the Au atom and the immediately adjacent mesityl methyl groups. Hence, any comparison of Ag/Au—P bond distances within *M*($Pmes_3$) ($Pmes_3$ is trimesitylphosphine) moieties is flawed by the presence of steric interactions. Our recent comparison of the Ag/Au—P bond distances within the chloro[tris(2,4,6-trimethoxyphenyl)phosphine]silver(I) and chloro[tris(2,4,6-trimethoxyphenyl)phosphine]gold(I) complexes was still inadequate, due to the presence of weak *M*···O interactions (Alyea *et al.*, 2000). The present work compares the title complex, (I), with an analogous two-coordinate Au complex also involving the small phosphine ligand trimethylphosphine (cone angle 118°), for which no steric hindrance is expected.

$$[Me_3P \text{ —— } Ag \text{ —— } PMe_3]^+ \quad \cdot PF_6^-$$

(I)

The crystal structure of (I) contains discrete well resolved cations and anions located on independent mirror planes, with the PF_6^- anion disordered (Fig. 1). While the cation in (I) has crystallographically imposed mirror symmetry, it approximates very closely to $\overline{3}m$ (D_{3d}) symmetry with fully staggered methyl groups (Fig. 1). Examination of the structure with *PLATON* (Spek, 2002) showed that there were no solvent-accessible voids in the crystal lattice.

In the cation, the Ag—P distances (Table 1) have a mean value of 2.376 (2) Å. For comparison, Ag—P distances of 2.461 (6) Å (Alyea *et al.*, 1982) and 2.4409 (9) Å (Bayler *et al.*, 1996) have been reported for the bis(trimesitylphosphine)silver(I) cation. The Ag—P bond distance based on the sum of tetrahedral covalent radii is calculated as 2.44 Å (Pauling, 1960) or 2.64 Å (Cambridge Structural Database, Release of April 2002; Allen & Kennard, 1993), so that a shorter distance might be anticipated for a two-coordinate complex.

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Although several complexes of the type $[L_2\mathrm{Ag}]Y$ are primarily two-coordinate with other bulky phosphine ligands L, weak coordination of the anion Y occurs in the solid state. A search of the April 2002 release of the Cambridge Structural Database (CSD; Allen & Kennard, 1993) for structures containing the P_2Ag fragment showed no instances, other than the $(mes_3P)_2Ag$ cation, wherein the P—Ag—P bond angle was larger than 170°. The Ag—P distances in the authentically two-coordinate complexes chloro[tris(2,4,6-trimethoxyphenyl)phosphine]silver(I) and bromo[tris(2,4,6-trimethoxyphenyl)phosphine]silver(I) are 2.379 (1) and 2.374 (2) Å, respectively (Baker *et al.*, 1992).

In polymeric $[Ag_4Cl_4(PMe_3)_3]$ (Bowmaker *et al.*, 1999), the Ag—P distance is 2.362 (4) Å, though the coordination is not strictly two-coordinate. Likewise, for analogous gold complexes of the type $[L_2\mathrm{Au}]Y$, the only truly two-coordinate example found without significant anion interactions was $[(Me_3P)_2Au]Cl$ (Angermaier *et al.*, 1994), with Au—P 2.2304 (1) Å and P—Au—P 175.4 (1)°; the Au···Cl distance of 3.167 (1) Å indicated a weak 'ion-pair contact' interaction.

A 'ligand profile' of the Me_3P group in the present silver complex clearly indicates that steric hindrance does not affect the Ag—P bond distance. The mean cone angle is calculated to be 115°, compared with the 'CPK model cone angle' of 118° (Tolman, 1977). For comparison, the cone angles were calculated for the Ag—PMe_3 moiety in some other known complexes of Ag with trimethylphosphine. In the polymeric complexes $[Ag_4Cl_4(PMe_3)_3]$ (Bowmaker *et al.*, 1999) and $[Ag(PR_3)_2]_2[Ni(mnt)_2]$ (mnt is maleonitriledithiolate; Youm *et al.*, 2000), similar cone angles of 116 and 115°, respectively, reflect the absence of steric congestion. The cone angle in polymeric $[Me_3PAgCCSiMe_3]$, which has adjacent phosphine ligands [P—Ag—P 113.33 (9)°; Brasse *et al.*, 1996], is 111°.

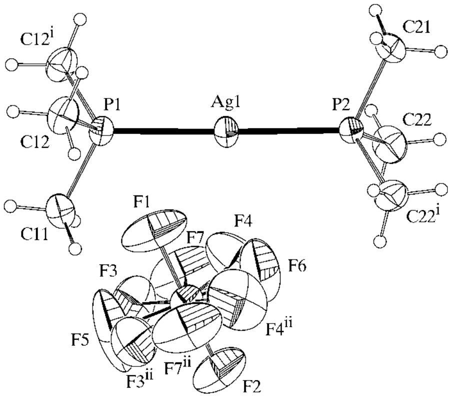

Figure 1
A view of complex (I) with the atom-numbering scheme; the central P atom of the anion (P3) is not labelled. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii [symmetry codes: (i) $x, \frac{3}{2} - y, z$; (ii) $x, \frac{1}{2} - y, z$].

Since no intramolecular interactions exist between the methyl substituents in either of the current $[(Me_3P)_2Ag]^+$ or $[(Me_3P)_2Au]^+$ cations, a valid comparison of M—P distances is possible, allowing the conclusion that Au really is smaller than Ag.

The P—C bond lengths and Ag—P—C and P—C—P angles (Table 1) are comparable with those reported for other trimethylphosphine complexes of Ag. Comparison with the angles in the analogous Au complex is not possible due to the reported disorder of the phosphine ligands.

The shortest Ag···F inter-ion distance of 3.392 (7) Å (Ag1···F7) is not compatible with any significant covalent bonding.

Experimental

Compound (I) was prepared by combining silver hexafluorophosphate with two equivalents of trimethylphosphine in dichloromethane at ambient temperature under an N_2 atmosphere. The colourless crystals obtained were kept in the dark under N_2 to avoid possible decomposition. The ^{31}P NMR solution spectrum in CH_2Cl_2/$CDCl_3$ (1:1) at a lowered temperature showed a peak at −34.07 p.p.m., attributable to the coordinated Me_3P, and at −143.28 p.p.m., due to the PF_6^- anion. A superposition of two doublets, due to coupling of the P nucleus with the two magnetic isotopes of Ag, occurs for the cation signal; $^1J(^{107}Ag–^{31}P) = 516$ Hz and $^1J(^{109}Ag–^{31}P) = 592$ Hz. For comparison, the $^1J(^{107}Ag–^{31}P)$ coupling constants for complexes $[L_n\mathrm{Ag}]Y$ of Ag^I with triphenylphosphine are 755 (n = 1), 507 (n = 2), 319 (n = 3) and 224 (n = 4) Hz (Alyea *et al.*, 1987). Hence, two-coordination is maintained in solution.

Crystal data

$[Ag(C_3H_9P)_2]PF_6$
$M_r = 404.98$
Orthorhombic, *Pnma*
$a = 11.7912\ (12)$ Å
$b = 8.4725\ (7)$ Å
$c = 14.768\ (4)$ Å
$V = 1475.3\ (4)$ Å^3
$Z = 4$
$D_x = 1.823$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10.0–18.9°$
$\mu = 1.73$ mm^{-1}
$T = 293\ (2)$ K
Block, colourless
0.55 × 0.31 × 0.25 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical *via* six ψ scans at 4° steps (North *et al.*, 1968)
$T_{\min} = 0.536$, $T_{\max} = 0.648$
1795 measured reflections
1795 independent reflections

1387 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 27.4°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 19$
3 standard reflections
frequency: 120 min
intensity variation: ±1.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.095$
$S = 1.09$
1795 reflections
108 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0567P)^2 + 0.3935P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.58$ e Å^{-3}
$\Delta\rho_{\min} = -0.62$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0107 (9)

Compound (I) crystallized in the orthorhombic system, with space group *Pnma* or $Pn2_1a$ being sugested by the systematic absences. *Pnma* was chosen and confirmed by the successful solution and refinement. The cation lies on a mirror plane, with atoms C11, P1, Ag1, P2 and C21 on the mirror. The PF_6^- anion also lies on a mirror plane and is disordered; atoms P3, F1, F2, F5 and F6 lie on the mirror

Table 1
Selected geometric parameters (Å, °).

Ag1—P1	2.3746 (12)	P1—C12	1.806 (4)
Ag1—P2	2.3784 (12)	P2—C22	1.806 (4)
P1—C11	1.799 (5)	P2—C21	1.819 (4)
P1—Ag1—P2	178.70 (4)	C22—P2—C21	103.94 (17)
C11—P1—C12	103.63 (17)	C22—P2—Ag1	114.00 (15)
C11—P1—Ag1	114.91 (18)	C21—P2—Ag1	114.84 (18)
C12—P1—Ag1	114.61 (13)		

plane. In the final refinement cycles, *DFIX* restraints (*SHELXL*97; Sheldrick, 1997) were employed to ensure octahedral geometry at P3. The P—F bond length was refined as a free variable [final value 1.53 (1) Å]. H atoms were treated as riding atoms (C—H = 0.96 Å).

Data collection: *CAD*-4-*PC Software* (Enraf–Nonius, 1992); cell refinement: *SET*4 and *CELDIM* in *CAD*-4-*PC Software*; data reduction: *DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989); program(s) used to solve structure: *NRCVAX*96 *via* the Patterson heavy-atom method; program(s) used to refine structure: *NRCVAX*96 and *SHELXL*97 (Sheldrick, 1997); molecular graphics: *NRCVAX*96, *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 2002); software used to prepare material for publication: *NRCVAX*96, *SHELXL*97 and *PRPCIF*97 (Ferguson, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1552). Services for accessing these data are described at the back of the journal.

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