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Structural Studies of Steric Effects in Phosphine Complexes. 10.[1] Crystal and Molecular Structure of Bis(trimesitylphosphine)silver(I) Hexafluorophosphate[2]

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The crystal and molecular structure of bis(trimesitylphosphine)silver(I) hexafluorophosphate $[Ag(P(mesityl)_3)_2]^+PF_6^-$ have been determined. Crystals are trigonal, space group $P3_121$ (D_3^4 No. 152), with a = 15.378 (2) Å, c = 19.945 (4) Å, and 3 formula units in the unit cell. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations with three-dimensional diffractometer data to a final discrepancy index $R_F = 0.070$ for 922 reflections with $I > 3\sigma(I)$. This is the first structure determination of a two-coordinate silver cation with phosphine ligands. Both cation and anion lie on separate crystallographic twofold axes, the anion being additionally disordered over two sites. In the cation, the bulk of the $P(mes)_3$ (mes = mesityl) ligands ensures an almost linear P–Ag–P moiety (179.4°), a regular propeller conformation with dihedral angles between the Ag–P–C and mesityl planes in the 45–51° range, a relatively long Ag–P distance 2.461 (6) Å and irregular angles at phosphorus (Ag–P–C 107.3–109.3 (9)°, C–P–C 108–113(1)°). Cone angle calculations are made for the $P(mes)_3$ ligand (θ = 203°).

Introduction

The concept of a "ligand profile",[3] which provides accurate values of maximum cone angles,[4] has been of particular assistance to us in providing a quantitative description of the bulkiness of phosphine ligands. It has been suggested[5,6] that trimesitylphosphine, with a predicted cone angle θ of 212° is the bulkiest known phosphine; this has been qualitatively demonstrated by its facile metalation with palladium(II) and platinum(II)[7] and more quantitatively in a mercury environment[8] where the cone angle was determined to be 208°. The recent synthesis[9] of $[Ag(P(mes)_3)_2]^+PF_6^-$(I) has allowed us to study the $P(mes)_3$ ligand in a crowded environment and also to rectify the dearth of structural data on two-coordinate silver(I) phosphine complexes.

Experimental Section

Crystallographic Measurements. Recrystallization of $[Ag(P(mes)_3)_2]\cdot PF_6$ from dichloromethane/hexane yielded colorless transparent needles.

Crystal data: $C_{54}H_{66}AgF_6P_3$; M_r = 1029.9; trigonal; a = 15.378 (2), c = 19.945 (4) Å; V = 4084.6 Å^3; D_m = 1.27 g cm^{-3} (by flotation in aqueous $ZnCl_2$ solution), D_c = 1.25 g cm^{-3}; Z = 3; $F(000)$ = 1605; Mo Kα radiation; λ = 0.71069; μ(Mo Kα) = 32.1 cm^{-1}. The Laue symmetry of the intensities is $\bar{3}m$ and together with the systematic absences ($00l$ absent if $l \neq 3n$) allow the space group to be $P3_121$ or $P3_112$ or their enantiomorphic relations $P3_221$ or $P3_212$. The analysis revealed that the true space group was either $P3_121$ or its enantiomer $P3_221$, but we were unable to decide between them (vide infra). $P3_121$ was chosen for the analysis.

Unit cell dimensions and space group information were obtained from Weissenberg and precession photographs. The lattice parameters were refined by a least-squares treatment of the diffractometer setting angles of 12 strong reflections. Three-dimensional intensity data for reflections $+h,+k,+l$ with $2° < 2\theta < 40°$ were collected on a computer-controlled Hilger–Watts four-circle diffractometer using monochromated Mo Kα radiation and the θ–2θ scan technique in our usual way.[10] There was some crystal decomposition during data collection, and this was corrected for by appropriate scaling. Data were corrected for Lorentz and polarization factors, and of the 1420 independent reflections measured, 922 with $I > 3\sigma(I)$ were labelled "observed" and used in the structure solution and refinement.

Table I. Final Fractional Coordinates (Ag and P, $\times 10^4$; others, $\times 10^3$) and Isotropic Thermal Parameters (U_{iso}, Å^2 $\times$ 10^3) with Estimated Standard Deviations in Parentheses

atom	x/a	y/b	z/c	U_{iso}
Ag	4734 (2)	0	3333	
P(1)	5268 (6)	1086 (5)	2335 (3)	
C(11)	571 (2)	236 (2)	2621 (9)	37 (6)
C(12)	514 (2)	251 (2)	308 (1)	45 (6)
C(121)	403 (2)	172 (2)	325 (1)	50 (6)
C(13)	549 (2)	347 (2)	337 (1)	66 (7)
C(14)	644 (2)	428 (2)	327 (1)	49 (6)
C(141)	683 (2)	526 (2)	361 (1)	69 (7)
C(15)	704 (2)	414 (2)	280 (1)	67 (7)
C(16)	668 (2)	317 (2)	246 (1)	65 (7)
C(161)	735 (2)	320 (2)	188 (1)	65 (7)
C(21)	625 (2)	96 (2)	188 (1)	62 (7)
C(22)	703 (2)	99 (2)	231 (1)	64 (7)
C(221)	720 (2)	130 (2)	305 (1)	80 (7)
C(23)	776 (2)	79 (2)	205 (1)	73 (8)
C(24)	769 (2)	54 (2)	135 (2)	91 (9)
C(241)	856 (3)	31 (3)	103 (2)	129 (11)
C(25)	697 (2)	50 (2)	96 (1)	78 (8)
C(26)	623 (2)	74 (2)	121 (1)	66 (7)
C(261)	556 (2)	76 (2)	70 (1)	73 (8)
C(31)	419 (2)	70 (2)	181 (1)	52 (6)
C(32)	348 (2)	−36 (2)	171 (1)	54 (7)
C(321)	380 (2)	−112 (2)	193 (1)	62 (7)
C(33)	253 (2)	−74 (2)	141 (1)	74 (8)
C(34)	226 (2)	−7 (2)	117 (1)	71 (8)
C(341)	127 (3)	−40 (3)	83 (2)	109 (10)
C(35)	295 (2)	103 (2)	122 (1)	78 (8)
C(36)	392 (2)	139 (2)	150 (1)	69 (8)
C(361)	458 (2)	253 (2)	146 (1)	67 (7)
P(2)	0	6338 (8)	1667	
F(1)	−116 (1)	575 (2)	150 (0)	
F(21)	−26 (3)	649 (4)	243 (2)	
F(22)	28 (4)	581 (4)	235 (2)	
F(31)	6 (4)	732 (3)	192 (2)	
F(41)	5 (3)	540 (3)	198 (2)	

Structure Solution and Refinement

With 3 formula units in the cell, both cation and anion must be on twofold axes in all possible space groups. The Ag···Ag vector distributions are quite different for $P3_121$ and $P3_112$, and it proved a simple matter to determine that only space group $P3_121$ (or its enantiomer $P3_221$) would fit the Patterson vector map. Coordinates for the Ag and P atoms were then determined and the remaining nonhydrogen atoms located from a subsequent three-dimensional Fourier synthesis. Four of the fluorines of the PF_6 anion were disordered equally over two sites and this was allowed for in the calculations. Refinement[11] by full-matrix, least-squares methods with

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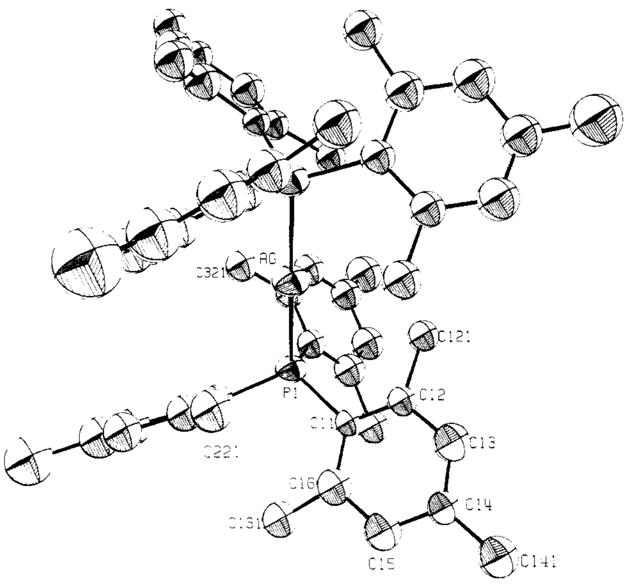

Figure 1. View of the $[Ag(P(mes)_3)_2]^+$ ion. The numbering scheme of ring 1 is shown; the other rings 2 and 3 are numbered similarly.

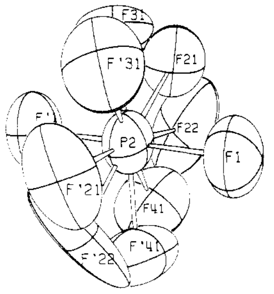

Figure 2. View of the disordered PF_6^- ion.

anisotropic[12] thermal parameters for Ag, P, and F and isotropic thermal parameters for the carbon atoms reduced *R* to 0.0699, and $R_{wF} = (\sum w\Delta^2/\sum wF_o^2)^{1/2} = 0.073$. The weights used in the refinement were derived from the counting statistics with $w = 1/(\sigma^2F + 0.003F^2)$. The scattering factors used in the structure factor calculations were taken from ref 13 and 14. A final difference map showed a number of maxima in positions consistent with some of the protons bonded to the mesityl rings but no clear evidence for the methyl protons. Anomalous dispersion calculations[15] were then made to try to distinguish between space groups $P3_121$ and $P3_221$, but no significant difference in the *R* factor was obtained.

The final fractional coordinates with standard deviations from the last cycle of refinement are listed in Table I and refer to space group $P3_121$. Table II contains details of ion geometry and Table III has mean plane equations and displacements. Listings of observed and calculated structure amplitudes, anisotropic thermal parameters, bond lengths and angles not given in Table II, and Table III are available.[16] The structure of the bis(trimesitylphosphine)silver(I) cation and the hexafluorophosphate anion, with our numbering scheme, are shown in Figures 1 and 2, respectively. Figure 3 is a stereoview of the crystal structure prepared with the aid of ORTEP.[17]

Discussion

The crystal structure (Figure 3) contains discrete well-resolved cations and anions located on independent twofold crystallographic axes.

Table II. Selected Interatomic Distances (Å) and Angles (Deg) with Estimated Standard Deviations in Parentheses

(a) Bond Distances[a]

Ag-P(1)	2.461 (6)	P(2)-F(1)	1.58 (2)
P(1)-C(11)	1.82 (2)	P(2)-F(21)	1.61 (3)
P(1)-C(21)	1.86 (3)	P(2)-F(22)	1.54 (4)
P(1)-C(31)	1.80 (3)	P(2)-F(31)	1.56 (3)
		P(2)-F(41)	1.60 (4)

(b) Bond Angles[b]

P(1)-Ag-P(1)$^{\mathrm{I}}$[c]	179.4 (5)	P(1)-C(21)-C(26)	125 (2)
Ag-P(1)-C(11)	107.2 (7)	C(21)-C(22)-C(221)	126 (2)
Ag-P(1)-C(21)	109.3 (9)	C(221)-C(22)-C(23)	113 (2)
Ag-P(1)-C(31)	108.2 (9)	C(23)-C(24)-C(241)	118 (3)
C(11)-P(1)-C(21)	113 (1)	C(241)-C(24)-C(25)	120 (3)
C(11)-P(1)-C(31)	108 (1)	C(21)-C(26)-C(261)	126 (3)
C(21)-P(1)-C(31)	110 (1)	C(25)-C(26)-C(261)	116 (2)
P(1)-C(11)-C(12)	118 (2)	P(1)-C(31)-C(32)	119 (2)
P(1)-C(11)-C(16)	121 (2)	P(1)-C(31)-C(36)	124 (2)
C(11)-C(12)-C(121)	124 (2)	C(31)-C(32)-C(321)	118 (2)
C(121)-C(12)-C(13)	114 (2)	C(321)-C(32)-C(33)	118 (2)
C(13)-C(14)-C(141)	124 (2)	C(33)-C(34)-C(341)	122 (3)
C(141)-C(14)-C(15)	119 (2)	C(341)-C(34)-C(35)	117 (3)
C(11)-C(16)-C(161)	127 (2)	C(31)-C(36)-C(361)	126 (2)
C(15)-C(16)-C(161)	114 (2)	C(35)-C(36)-C(361)	114 (2)
P(1)-C(21)-C(22)	115 (2)		

(c) Torsion Angles

C(11)-P(1)-P(1)$^{\mathrm{I}}$-C(11)$^{\mathrm{I}}$	159	C(21)-P(1)-P(1)$^{\mathrm{I}}$-C(21)$^{\mathrm{I}}$	45
C(11)-P(1)-P(1)$^{\mathrm{I}}$-C(21)$^{\mathrm{I}}$	−78	C(21)-P(1)-P(1)$^{\mathrm{I}}$-C(31)$^{\mathrm{I}}$	166
C(11)-P(1)-P(1)$^{\mathrm{I}}$-C(31)$^{\mathrm{I}}$	42	C(31)-P(1)-P(1)$^{\mathrm{I}}$-C(31)$^{\mathrm{I}}$	−74

(d) Shorter Intra- and Interion Contacts

Ag...C(121)	3.34	C(161)...C(221)	3.66
Ag...C(221)	3.33	C(221)...C(221)$^{\mathrm{I}}$	3.63
Ag...C(321)	3.22	C(221)...C(361)$^{\mathrm{II}}$	3.62
C(121)...C(321)$^{\mathrm{I}}$	3.59	C(261)...C(321)	3.72
C(121)...C(361)	3.73	C(321)...C(361)$^{\mathrm{III}}$	3.45
C(141)...C(161)$^{\mathrm{II}}$	3.61		

[a] Benzene $C(sp^2)$-$C(sp^2)$ bond lengths are in the range 1.33 (3)-1.48 (3) Å, with a mean value 1.42 (3) Å. $C(sp^2)$-$C(sp^3)$ bond lengths are in the range 1.46 (3)-1.67 (5) Å, with a mean value 1.53 (4) Å. Full details are given in the supplementary material. [b] The C-C-C angles within the benzene ring are in the range 116 (2)-123 (2)°, with a mean value 120°. The cis F-P-F angles of the disordered PF_6 anion are in the range 84 (2)-97 (2)°. Full details are given in the supplementary material. [c] The superscripts refer to the following equivalent positions: I $x-y, -y, {}^2/_3-z$; II $1-y, x-y, {}^1/_3+z$; III $1-x, y-x, {}^1/_3-z$.

In the cations the Ag–P distance is 2.461 (6) Å. There are no two-coordinate Ag–P systems available for comparison, but data are available for a number of three- and four-coordinate Ag(I) complexes. For three-coordinate silver, Ag–P distances of 2.411 (3) and 2.449 (2) Å have been reported for $[AgP(OMe)_3NO_3]_2$[18a] and $[Ag(PPh_2Et)_2]_2[Ni(S_2C_2(CN)_2)_2]$,[18b] respectively. Some typical values of Ag–P distances in tetrahedral complexes are 2.379 (3), 2.402 (5), 2.470 (2), and 2.479 (5) Å, found for the complexes $[Ag\ PPh_3Cl]_4$,[19a] $[AgPEt_3Br]_4$,[19b] $[Ag(PPh_3)_2Cl]_2$,[19c] and $[Ag(PPh_3)_2NCS]_2$,[19d] respectively. In the chairlike form of $[AgPPh_3I]_4$, trigonally coordinated Ag has Ag–P distances of 2.430 (3) Å and tetrahedrally coordinated Ag has Ag–P distances of 2.454 (3) Å.[20] The Ag–P bond distance based upon the sum of tetrahedral covalent radii is calculated to be 2.44 Å.[21] It might be anticipated that the Ag–P distance in I would be shorter

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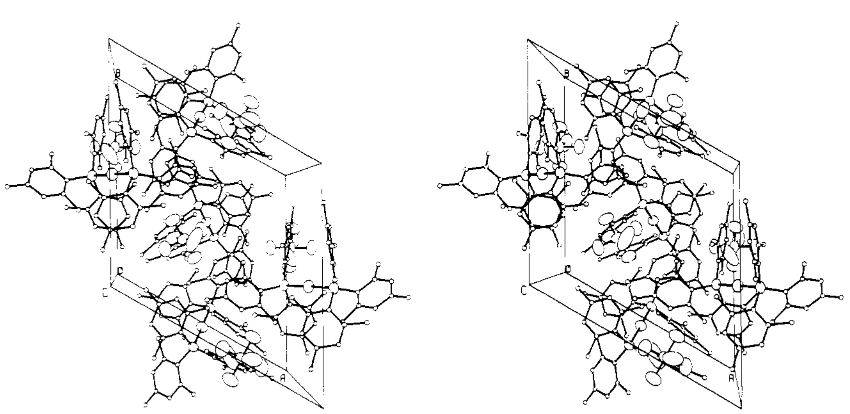

Figure 3. Stereoview of the crystal structure of $[Ag(P(mes)_3)_2]^+PF_6^-$. For clarity, only one form of the disordered PF_6^- ion is shown.

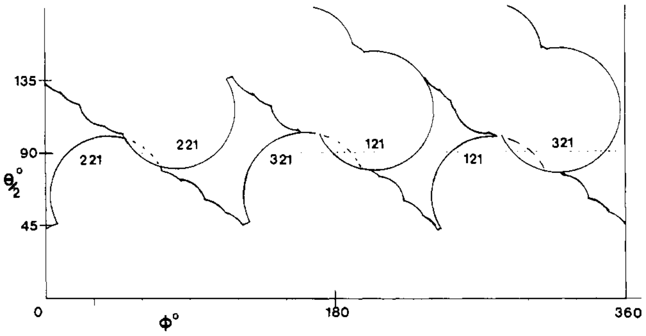

Figure 4. Ligand profile plot of the $P(mesityl)_3$ group in $[Ag(P(mes)_3)_2]^+$. For details see ref 3. The numbers at the curves identify the *o*-methyl carbon atoms.

than the Ag–P distances mentioned above on the grounds that it is a two-coordinate species whereas the others are of higher coordination. That the observed length in I is comparable with or greater than these distances may be taken as evidence for some bond length extension associated with intramolecular overcrowding between mesityl groups on opposing ligands. The P–Ag–P angle is essentially linear (179.4°), any large deviation from linearity being precluded by the bulk of the mesityl systems. The mean bond lengths P–C 1.83 (2), aromatic C–C 1.41 (3), and $C(sp^2)-CH_3$ 1.53 (4) Å are in agreement with those reported for the free trimesitylphosphine[6] and for $[HgP(mes)_3(NO_3)_2]_2$.[8] The dimensions of the disordered PF_6 anion (P–F 1.54–1.60 (4) Å) are in accord with values usually found for this group.[22]

The $P(mes)_3$ ligand adopts a fairly regular propeller conformation (Figures 1 and 3) with dihedral angles between the appropriate Ag–P–C and mesityl planes in the range 45–50°. These values are similar to those found in the free ligand (44°) and in $[HgP(mes)_3(NO_3)_2]_2$ (45–49°).[8] The propeller conformation results in three *o*-methyl groups, C(121), C(221), and C(321), being adjacent to Ag and Ag···C distances of 3.34, 3.33 and 3.22(4) Å, respectively; the remaining three *o*-methyl groups, (C(161), C(261), C(361)) also suffer from overcrowding because the conformation adopted position these atoms above an adjacent aromatic ring carbon atom bonded to phosphorus (C···C(methyl) 2.98, 3.02, 2.96 (4) Å). As a result of these repulsions, the P atoms are displaced to one side of the relevant aromatic ring plane (0.24–0.32 Å) and the *o*-methyl group are displaced in the opposite direction (0.07–0.25 Å) away from the Ag atom. Relief from overcrowding is also afforded by angle bending. Thus five of the six (P)C–C–C(methyl) angles are greater than 120° in the range of 124–127 (2)°; the angle at the remaining *o*-methyl group (C(31)–C(32)–C(321)) is 118 (2)°, but it is not possible to attach any significance to this because of the relatively large standard deviations. The *p*-methyl groups do not suffer from any intramolecular crowding and lie in the appropriate ring plane to within the accuracy of the analysis. The conformation adopted by the phosphines in the molecule deviates from a fully staggered $C_3P-Ag-PC_3$ atom system by an average of 17°, presumably to accommodate methyl···methyl intramolecular contacts.

In $[HgP(mes)_3(NO_3)_2]_2$,[8] where there is no repulsion between $P(mes)_3$ groups, the mean Hg–P–C (105.4 (4)°) and mean C–P–C angles (113.2 (5)°) reflect the overcrowding *within* the $P(mes)_3$ moiety. In $[Ag(P(mes)_3)_2]^+$ where there is, in addition, repulsion *between* $P(mes)_3$ groups, the Ag–P–C (107.3–109.3 (9)°) and C–P–C (108–113 (1)°) angles are irregular and do not show the same marked differences as was found in $[HgP(mes)_3(NO_3)_2]_2$.

So that the maximum cone angle θ of the $P(mes)_3$ moiety could be determined, a ligand profile diagram[3] was prepared (Figure 4) from the coordinates of Table I. Maximum semi-cone angles ($\theta/2$) are 100.0, 101.0, and 102.7°, leading to a mean cone angle θ of 203 (2)°. This is smaller than the value predicted from models (212°)[4,23] and while being smaller, as expected, than the 208 (1)° found for $P(mes)_3$ in the slightly less sterically demanding $[HgP(mes)_3(NO_3)_2]_2$[8], the difference may not be truly significant. By contrast, there are large variations in cone angles in $P(Cy)_3$ (19°) and $P(o\text{-tol})_3$ (15°) moieties as they are subjected to steric stress.

Structural studies of $P(mes)_3$ and $As(mes)_3$ in other environments are under way.

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Registry No. I, 73907-76-3.

Supplementary Material Available: Listings of bond lengths and angles, anisotropic thermal parameters, observed and calculated structure factors, and mean plane data, Table III (12 pages). Ordering information is given on any current masthead page.

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[23] If CPK models had a hydrogen van der Waals radius of 1.20 Å (as used in X-ray analysis) instead of 1.00 Å, the Tolman "model cone angles" would increase by up to 9°.