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X-ray structural determination of a bulky phosphine complex: chloro{tris(2,4,6-trimethoxyphenyl)phosphine}gold(I), {AuCl[P(C₉H₁₁O₃)₃]}

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Abstract

The title compound, {AuCl[P($C_9H_{11}O_3$)_3]}, has three fold symmetry in the solid state. The Au–Cl and Au–P bond lengths are 2.294 and 2.255 Å, respectively, and the Au atom has nearly linear coordination geometry, with P–Au–Cl 176.03(9)°. The extreme bulkiness of the phosphine ligand is shown by the mean cone angle of 188° (based on O atoms defining the cone), though the cone angle is considerably smaller than 214° for trimesitylphosphine in the known analogous complex. The shorter Au–P bond distance than for Ag–P (2.379(1) Å) in the corresponding known silver chloride complex of tris(2,4,6-trimethoxyphenyl)phosphine tentatively supports an earlier conclusion that gold is smaller than silver. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Bulky phosphine; X-ray structure; Cone angle; Two-coordinate gold complex.

1. Introduction

Our long-standing interest in the steric effects of bulky phosphine ligands [1,2] led us some years ago to determine the crystal structure of chloro(trimesitylphosphine)gold(I) containing the bulkiest known phosphine [3]. Another related bulky phosphine, tris(2,4,6trimethoxyphenyl)phosphine, has garnered recent attention [4]. Since several crystallographic studies of mono tertiarylphosphine gold(I) chloride complexes have been reported [5–28] we undertook the structural determination of the title compound to provide a relative steric profile of tris(2,4,6-trimethoxyphenyl)phosphine, particularly as compared with other bulky phosphines.

2. Results and discussion

Chloro{tris(2,4,6 - trimethoxyphenyl)phosphine}gold-(I) (1) has approximate threefold symmetry in the solid

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state (Fig. 1). The dihedral angles between the aryl ring planes and the relevant Au–P–Cln1(n = 1, 2, 3) planes are 50.4(3), 56.7(3)and 15.3(3)° for planes C11–C16, C21–C26 and C31–C36, respectively. The three aryl



Fig. 1. A view of (1) with the atomic numbering scheme; displacement ellipsoids are drawn at the 30% probability level.

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Summary of dimensions (Å, °) for some chloro(monophosphine)gold(I) complexes

Structure	Au–Cl	Au–P	Cl–Au–P	Reference
[(MeO) ₃ C ₆ H ₂] ₃ PAuCl	2.294(2)	2.255(2)	176.03(9)	this work
(Mesityl) ₃ PAuCl	2.2716(19)	2.2634(15)	178.01(8)	[3]
Ph ₃ PAuCl	2.279(3)	2.235(3)	179.6(1)	[5]
(Cyclohexyl) ₃ PAuCl	2.279(5)	2.242(4)	177.0(2)	[7]
(Ethyl) ₃ PAuCl	2.305(8)	2.232(9)	178.5(3)	[9]
	2.306(8)	2.231(8)	178.9(3)	
Ph(Me ₂ C ₄ H ₂)PAuCl	2.288(2)	2.227(2)	176.1(1)	[10]
(o-Tolyl)3PAuCl	2.281(3)	2.243(2)	179.4(1)	[11]
(m-Tolyl)3PAuCl	2.288(2)	2.235(2)	175.1(1)	[12]
Ph(cyclohexyl) ₂ PAuCl	2.234(3)	2.234(2)	178.3(1)	[13]
Ph(anthracenyl) ₂ PAuCl	2.281	2.249	173.9	[14]
Ph ₂ (2-trimethylsiloxy)- PAuCl	2.285	2.229	177.3	[16]
Ph ₂ (trimethylsily- methyl)PAuCl	2.292	2.236	176.9	[20]
(Me ₂ N) ₃ PAuCl	2.289	2.222	177.9	[25]

rings of the bulky triarylphosphine ligand have very similar geometries. The P atom is displaced 0.18(1), 0.22(1) and 0.09(1) Å from the aromatic plane and the ortho methoxy O atoms are displaced in the opposite direction (e.g. O12 -0.04(1), O16 +0.09(1) A). There are also weak interactions between the Au atom and the three immediately adjacent methoxy oxygens (O32, O12 and O22, Au. O separations 2.922(1), 3.112(1) and 3.122(1) Å. Comparable values for the known analogous Ag complex are: 2.818(3), 3.038(3) and 3.140(3) A [4]. In the analogous trimesitylphosphine complex the significant Au-H interactions to the ortho methyl groups (mean contacts Au…C 3.229 Å and Au···H 2.40 Å) were characterized as 'remote agostic' [29]. Whether the same designation of an attractive interaction is applicable for (1) is not as clear from the structural data. All six ortho methoxy groups in (1) have their methyl groups oriented so that they are remote from the central P atom and are turned away from the Au atom. In the trimesitylphosphine complex the mean P–Cn1–Cn6 angle (117.3(6) A) (where n = 1, 2, 3) is 6.7° less than the mean P–Cn1–Cn2 angles $(124.0(6)^{\circ})$. Comparable angles in the present complex are 118.8(17) and 125.2(17)°, respectively. For the analogous 1:1 silver chloride and bromide complexes studied by Baker et al. [4], these angles follow the same trends. The mean Au-P-C angle and the mean C-P-C angle in (1) are 110.5(8) and 108.4(10)°, respectively; comparable values for the corresponding trimesitylphosphine complex are 107.6(2) and 111.2(3)°, attesting to the greater ortho interactions due to the larger steric bulk of the Pmes₃ ligand (see below). The comparable mean angles in the known silver chloride complex are identical to those found in (1) [4].

The Au-Cl bond length (2.294(2) Å) and P-Au-Cl

bond angle $(176.03(9)^\circ)$ in (1) are comparable with those reported in other structural studies of species containing the R_3P -Au-Cl fragment (R_3P = triaryl- or trialkyl-phosphine). For comparison, relevant Au-Cl and Au-P bond lengths and P-Au-Cl angles for some selected structures of this type, revealed in a search of the Cambridge Structural Database [30], are shown in Table 1. The Au-P bond length of 2.255(2) Å (1) is slightly less than the Au-P bond distance in chlorotrimesitylphosphine (2.2634(15) Å), but comparable to those found in Cy₃PAuCl (2.242(4) Å) and (otolyl)₃PAuCl (2.243(2) Å). The Ag-P bond distance in previously reported chloro{tris[trimethoxyphenyl)phosphine]}silver(I) is 2.379(1) Å and a weak Ag. O interaction of 2.818(3) Å gives rise to a P-Ag-Cl angle of 175.0(1)° [4]. This longer distance for the Ag–P bond compared to the Au-P one in the present complex is in keeping with the recent conclusion that gold is smaller than silver based on a structural comparison of the analogous bis(trimesitylphosphine) cations [31]. However, since our much earlier structural analysis of the [Ag(Pmes₃)₂] cation indicated that significant intramolecular steric distortions occur within that cation [32], the recent conclusion based on comparing the $[M(Pmes_3)_2]$ cations is clearly flawed. Our present comparison of the analogous L-M-Cl complexes provides more valid evidence for the conclusion that gold is indeed smaller than silver. However, the presence of other intramolecular interactions which are still significant in the present complex (such as the Au…O interactions) suggests that caution should still be exercised in making such a conclusion, i.e. a definitive study should involve a smaller phosphine.

In order to quantify the relative bulkiness of the tris(2,4,6-trimethoxyphenyl)phosphine and trimesitylphosphine ligands, we calculated the cone angles of these ligands from the crystallographic data for the two analogous gold complexes. By calculating semi-cone angles ($\theta/2$) using the 'ligand-profile' concept [1] with C–H at 1.08 Å, resultant average cone angles [2] of 188° and 214° were obtained for tris(2,4,6-trimethoxyphenyl)phosphine and trimesitylphosphine, respectively. The smaller estimated steric size of the former ligand is commensurate with the folding back of the methoxy groups and the observed structural data for the title complex.

3. Experimental

3.1. Compound synthesis and NMR spectral data

The compound was synthesized by stirring tris(2,4,6-trimethoxyphenyl)phosphine with (dimethylsulfide)-

Table 1

gold(I) chloride in dichloromethane at room temperature for about 5 h. The yield of 1 was 90%. The colorless crystals were obtained from chloroform-toluene mixture on slow evaporation. The melting point is 503 K (dec). Spectral data: ³¹P-NMR (CDCl₃): -32.9. ¹H-NMR (CDCl₃): 3.53 (s, 18H, OCH₃); 3.78 (s, 9H, OCH₃); 6.02 (d, 4 Hz, 6H, phenyl) ppm.

3.2. Crystal data and data collection parameters

C₂₇H₃₃AuClO₉P, M = 764.92, Tetragonal, a = 15.3343(9), c = 12.3291(11) Å, U = 2899.1(3) Å³, T = 294 K, space group P4₃, graphic monochromated Mo K α radiation, $\lambda = 0.71073$ Å, Z = 4, $D_{calc} = 1.753$ Mg m⁻³, F(000) = 1512, colourless crystals with dimensions $0.43 \times 0.25 \times 0.22$ mm, $\mu = 5.275$ mm⁻¹, CAD4 diffractometer, θ range for data collection 2–27°, 3331 unique reflections measured, 2562 with $I > 2\sigma(I)$.

3.3. Structure solution and refinement

The structure was solved by Patterson methods and refined full-matrix least-squares on F_o^2 , using the program SHELXL-93 [33]. All data used were corrected for Lorentz-polarization factors, and for absorption (Gaussian integration, NRCVAX [34]). The hydrogen atoms were included in idealized positions as riding atoms. Final *R*-factors were R = 0.0291, wR = 0.0556 for observed data and R = 0.0569 and wR = 0.0603 for all data.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre, CCDC No. 141601 for compound 1. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc. cam.ac.uk).

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