Preparation and Crystal Structure of the Four-co-ordinate Gold(I) Complex Chlorotris(triphenylphosphine)gold(I) *

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The reaction between stoicheiometric amounts of triphenylphosphine and chloro(triphenylphosphine)-gold(I) in acetonitrile leads to chlorotris(triphenylphosphine)gold(I). An *X*-ray structure determination [space group $P2_1/n$, a = 10.197(2), b = 33.586(6), c = 13.306(2) Å, β = 90.04(2)°, Z = 4, R' = 0.047 for 6 272 reflections] shows the presence of four-co-ordinate gold(I) with a long Au–Cl bond (2.710 Å). Related thermochemical and ^{31}P n.m.r. data are presented.

Four-co-ordination in gold(I) complexes was established in the solid state by an early, partial *X*-ray study of $[Au\{o\text{-}C_6H_4(AsEt_2)_2\}_2]^+I^-$.[1] In the last few years there has been considerable interest in confirming, or otherwise, the generally assumed four-co-ordination in complexes of the form AuL_4^+ or AuL_3X (L = neutral ligand, X = halide or pseudohalide). Although the singlet Mössbauer spectra of AuL_4^+ species at 4 K is consistent with regular tetrahedral co-ordination (L = PPh_3,[2] $PMePh_2$, and $AsPh_3$ [3]), *X*-ray investigation of three modifications of $[Au(PPh_3)_4]BF_4$ [4] revealed either trigonal co-ordination with an additional very distant ligand (Au ··· P 3.95 Å) or a disorder between trigonal and tetrahedral sites (site ratios 1 : 1 at room temperature, 1 : 7 at −150 °C). Tetrahedral co-ordination was first established for $[Au(PMePh_2)_4]^+$,[5] with crystallographic $\bar{4}$ symmetry, and since for $[Au(SbPh_3)_4]^+$,[6] with three independent cations of symmetry 3.

We have recently shown four-co-ordination in two modifications of the neutral complex $[Au(SCN)(PPh_3)_3]$,[7,8] in which there is some distortion towards $(Ph_3P)Au^+ \cdots SCN^-$ (Au–S 2.791, 2.93 Å). We now present the *X*-ray structure of the analogous chloro-complex $[AuCl(PPh_3)_3]$.

Results and Discussion

The reaction of stoicheiometric amounts of PPh_3 and $[AuCl(PPh_3)]$ in acetonitrile leads on evaporation to crystalline $[AuCl(PPh_3)_3]$ in the form of colourless square prisms. {The choice of solvent seems to be critical, since recrystallisation of the product from dichloromethane–light petroleum yielded colourless triclinic crystals (approximate cell constants a = 10.76, b = 13.03, c = 13.94 Å, α = 104.8, β = 106.2, γ = 103.6°) which rapidly lose solvent of crystallisation and which we formulate tentatively as $[AuCl(PPh_3)_2]\cdot xCH_2Cl_2$ on the basis of the cell volume U = 1 710 Å^3, *cf.* $[AuCl(PPh_3)_2]\cdot \frac{1}{2}C_6H_6$, U = 1 643 Å^3 (ref. 9).} The ^{31}P n.m.r. chemical shift of 14.9 p.p.m. {*cf.* $[AuCl(PPh_3)]$ 33.2 p.p.m., both relative to 85% H_3PO_4} is consistent with the order of shifts bis > mono > tris noted for $[Au(SCN)(PPh_3)_n]$.[10]

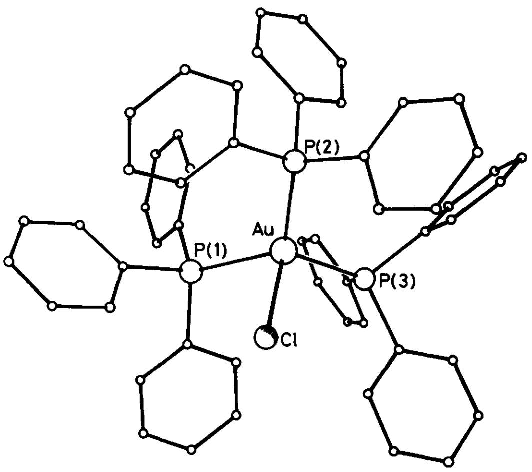

Figure. Molecular structure of $[AuCl(PPh_3)_3]$

The structure of $[AuCl(PPh_3)_3]$ was determined by *X*-ray crystallography. The Figure shows the molecule, which is four-co-ordinate with a long Au–Cl bond {2.710 Å; *cf.* 2.279 Å in $[AuCl(PPh_3)]$ [11] and 2.500 Å in $[AuCl(PPh_3)_2]$ [9]}. The Au–Cl bond length in this series of compounds appears to be more affected than the Au–P [2.235, 2.331(av.), 2.410(av.) Å for the mono-, bis-, and tris-phosphine complex respectively] by increase in co-ordination number. The compound $[AuCl(PPh_3)_3]$ may be considered, like the two modifications of $[Au(SCN)(PPh_3)_3]$,[7,8] to lie between ideal three- and four-co-ordination; its Au–P bonds are longer than those of $[Au(PPh_3)_3]^+$ [2.384 (av.),[12] 2.373 (av.) Å [13] in two different salts] but shorter than those of $[Au(PMePh_2)_4]^+$ (2.449 Å [5]). Similarities in the geometries of the $[AuX(PPh_3)_3]$ compounds are the Au–P bond lengths [2.410 (av.) for X = Cl; 2.40 and 2.41 Å for X = SCN] and the distance of the gold atom to the P_3 mean plane (0.39 for X = Cl; 0.38 and 0.40 Å for X = SCN; *cf.* 0.8 Å for an ideal tetrahedron with bond lengths 2.4 Å).

Experimental

Phosphorus-31 n.m.r. spectra were recorded on an FT-NMR JEOL FX90Q spectrometer at room temperature.

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* *Supplementary data available* (No. SUP 23377, 51 pp.): observed and calculated structure factors, thermal parameters, H co-ordinates. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Non-S.I. unit employed: 1 cal = 4.184 J.

Table 1. Atomic co-ordinates (× 10^4) for $[AuCl(PPh_3)_3]$

	x	y	z
Au	2 788(1)	1 126(1)	2 234(1)
P(1)	2 208(2)	1 109(1)	553(1)
P(2)	1 941(2)	625(1)	3 438(1)
P(3)	3 150(2)	1 773(1)	3 031(1)
Cl	5 165(2)	795(1)	1 961(2)
C(12)	3 457(4)	447(1)	−243(4)
C(13)	3 535	86	−756
C(14)	2 403	−89	−1 147
C(15)	1 192	98	−1 024
C(16)	1 114	460	−511
C(11)	2 246	634	−120
C(22)	−432(5)	1 137(1)	982(3)
C(23)	−1 748	1 227	807
C(24)	−2 101	1 459	−20
C(25)	−1 138	1 600	−672
C(26)	178	1 510	−498
C(21)	531	1 278	329
C(32)	3 783(5)	1 309(1)	−1 158(4)
C(33)	4 628	1 562	−1 677
C(34)	4 948	1 933	−1 276
C(35)	4 422	2 051	−356
C(36)	3 577	1 798	164
C(31)	3 258	1 427	−237
C(42)	2 452(5)	23(1)	2 059(3)
C(43)	2 486	−369	1 716
C(44)	2 037	−677	2 330
C(45)	1 553	−592	3 287
C(46)	1 519	−200	3 630
C(41)	1 968	108	3 016
C(52)	2 066(4)	546(2)	5 557(4)
C(53)	2 751	490	6 454
C(54)	4 116	462	6 444
C(55)	4 796	490	5 538
C(56)	4 111	546	4 641
C(51)	2 746	573	4 650
C(62)	−20(4)	1 117(1)	4 127(4)
C(63)	−1 310	1 243	4 264
C(64)	−2 349	994	4 004
C(65)	−2 098	617	3 606
C(66)	−807	490	3 469
C(61)	232	740	3 729
C(72)	3 170(5)	1 552(1)	5 022(4)
C(73)	2 825	1 568	6 036
C(74)	1 949	1 858	6 373
C(75)	1 417	2 131	5 697
C(76)	1 761	2 115	4 684
C(71)	2 638	1 825	4 346
C(82)	966(5)	2 089(1)	2 069(4)
C(83)	265	2 371	1 518
C(84)	849	2 733	1 268
C(85)	2 133	2 813	1 568
C(86)	2 833	2 531	2 120
C(81)	2 250	2 169	2 370
C(92)	5 147(4)	2 277(1)	3 739(4)
C(93)	6 425	2 425	3 758
C(94)	7 318	2 259	3 136
C(95)	7 057	1 945	2 495
C(96)	5 779	1 798	2 476
C(91)	4 824	1 963	3 098

Table 2. Bond lengths (Å) and angles (°)

Au−P(1)	2.431(2)	Au−P(2)	2.404(2)
Au−P(3)	2.395(2)	Au−Cl	2.710(2)
C(11)−P(1)	1.830(5)	C(21)−P(1)	1.826(5)
C(31)−P(1)	1.840(5)	C(41)−P(2)	1.825(5)
C(51)−P(2)	1.818(5)	C(61)−P(2)	1.827(5)
C(71)−P(3)	1.835(6)	C(81)−P(3)	1.840(5)
C(91)−P(3)	1.825(5)		
P(1)−Au−P(2)	119.6(1)	P(1)−Au−P(3)	116.1(1)
P(2)−Au−P(3)	116.6(1)	P(1)−Au−Cl	92.0(1)
P(2)−Au−Cl	98.3(1)	P(3)−Au−Cl	107.7(1)
Au−P(1)−C(11)	119.3(2)	Au−P(1)−C(21)	112.2(2)
C(11)−P(1)−C(21)	102.3(2)	Au−P(1)−C(31)	113.5(2)
C(11)−P(1)−C(31)	102.3(2)	C(21)−P(1)−C(31)	105.8(2)
Au−P(2)−C(41)	118.1(2)	Au−P(2)−C(51)	116.8(2)
C(41)−P(2)−C(51)	100.1(2)	Au−P(2)−C(61)	109.0(2)
C(41)−P(2)−C(61)	106.4(2)	C(51)−P(2)−C(61)	105.2(2)
Au−P(3)−C(71)	114.7(2)	Au−P(3)−C(81)	113.0(2)
C(71)−P(3)−C(81)	104.1(2)	Au−P(3)−C(91)	118.8(2)
C(71)−P(3)−C(91)	100.7(2)	C(81)−P(3)−C(91)	103.6(2)

Preparation of $[AuCl(PPh_3)_3]$.—Triphenylphosphine (3.4 mmol) and $[AuCl(PPh_3)]$ (1.7 mmol) were dissolved in acetonitrile. On evaporation of the solvent, the product was obtained in crystalline form (Found: C, 63.25; H, 4.60. $C_{54}H_{45}AuClP_3$ requires C, 63.65; H, 4.40%). As many as three moles of PPh_3 may be added to $[AuCl(PPh_3)]$ stepwise or all at once; the one-step reaction liberates 23(2) kcal mol^{-1} Au, the alternative stepwise reactions 11.3(0.9), 8.1(0.8), and 4.3(0.5) kcal mol^{-1} respectively [all measurements in EtOH–CH_2Cl_2 (4 : 1)].

Crystal Data.—$C_{54}H_{45}AuClP_3$, $M = 1\,019.3$. Monoclinic, $P2_1/n$, $a = 10.197(2)$, $b = 33.586(6)$, $c = 13.306(2)$ Å, $\beta = 90.04(2)°$, $U = 4\,557$ Å^3, $Z = 4$, $D_c = 1.49$ g cm^{-3}, $F(000) = 2\,040$, Mo-K_α radiation ($\lambda = 0.710\,69$ Å), $\mu = 3.4$ cm^{-1}.

8 448 Profile-fitted [14] intensities from a crystal of size 0.4 × 0.2 × 0.2 mm were recorded in the range $7 < 2\theta < 50°$ on a Stoe four-circle diffractometer. After Lorentz, polarisation, and absorption corrections, averaging equivalents gave 7 984 unique reflections, 6 272 of which with $F > 4\sigma(F)$ were used for all calculations (performed with the program system SHELXTL written by G. M. S.). Despite the closeness of β to 90°, the Laue symmetry was clearly no higher than $2/m$. Cell constants were obtained from 2θ values of 48 strong reflections in the range $21 < 2\theta < 24°$.

The structure was solved by the heavy-atom method and refined to R 0.052, R' 0.047 {weighting scheme $w^{-1} = [\sigma^2(F) + 0.000\,15\,F^2]$}. Phenyl rings were refined as rigid groups with C–C 1.395, C–H 0.96 Å, all angles 120°, all atoms isotropic, $U(H) = 1.2U(C)$. A final difference map showed no peaks larger than 1 e Å^{-3}. Final atomic co-ordinates and bond lengths and angles are presented in Tables 1 and 2 respectively.

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