Crystal and Molecular Structure of Chloro(triphenyl phosphite)gold(I) †

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Crystals of [AuCl{P(OPh)$_3$}] are triclinic, space group $P\bar{1}$, with a = 9.539(6), b = 10.438(5), c = 9.634(5) Å, α = 82.27(3), β = 84.56(4), γ = 70.52(4)°, Z = 2. Least-squares refinement based on 1 931 reflection intensities has converged at R 0.052. The co-ordination at the gold atom is linear [Au–P 2.192(5) and Au–Cl 2.273(5) Å]. It is suggested that the shortening of the Au–P bond by 0.043 Å relative to that in chloro(triphenylphosphine)gold(I) is caused by the effect of the electronegative substituents at the phosphorus atom on its lone-pair orbital used to form the σ bond to the gold atom.

THE presence of electronegative substituents on a phosphine ligand in a metal complex is known to cause a decrease in the metal–phosphorus bond length compared to that in a corresponding aryl- or alkyl-phosphine complex.[1,2] This shortening has been ascribed to several different causes such as partial metal-to-ligand d_π–d_π back donation,[3,4] lower steric requirements [5] due to a smaller cone angle in fluorophosphines and phosphites,[6] and contraction of the phosphorus lone-pair donor orbital.[7]

In a recent report [5] of the crystal structures of *trans*-[Pd(NCS)$_2$(PPh$_3$)$_2$] and *trans*-[Pd(SCN)$_2${P(OPh)$_3$}$_2$] it was found that the Pd–P(phosphite) bond length was shorter than the Pd–P(phosphine) by 0.028 Å. The possible causes for this shortening were discussed and it was concluded that it was probably due to a combination of reduced non-bonded interactions due to the smaller cone angle of the phosphite ligands and the smaller mutual *trans*-bond-lengthening influence of the phosphite ligands. If this conclusion is of general applicability it can be tested by comparing the metal–phosphorus bond lengths in phosphine and phosphite complexes where there are no *cis* ligands, thus eliminating any steric effect, and with a common *trans* ligand, thus eliminating any difference in *trans* influence. A suitable pair of molecules for such a comparison are the linear complexes chloro(triphenylphosphine)gold(I) and chloro(triphenyl phosphite)gold(I). The structure of the former complex has recently been reported by Baenziger *et al.*[8] We now report the structure of the latter complex.

EXPERIMENTAL

Chloro(triphenyl phosphite)gold(I) was prepared by a method based on that of Kowala and Swan.[9] Triphenyl phosphite (0.65 g, 2.1 mmol) was added to tetrachloroauric(III) acid (0.50 g, 1.64 mmol) dissolved in water–ethanol (1 : 1, 10 cm^3) at 0 °C. The mixture was stirred whilst the temperature increased to room temperature and a cream precipitate was formed. This was recrystallised from hot ethanol by allowing the solution to cool slowly to 0 °C and the white needles were washed with diethyl ether and dried *in vacuo* (0.68 g, 76%), m.p. 106 °C (uncorrected), i.r. (Nujol mull) 347ms cm^{-1} ν(Au–Cl).

Crystal Data.—$C_{18}H_{15}AuClO_3P$, M = 542.8, Triclinic, a = 9.539(6), b = 10.438(5), c = 9.634(5) Å, α = 82.27(3), β = 84.56(4), γ = 70.52(4)°, U = 894.8 Å^3, Z = 2, D_c = 2.01 g cm^{-3}, $F(000)$ = 258. Mo-K_α radiation, μ = 87.4 cm^{-1}. Space group $P\bar{1}$.

The data crystal was a tapering needle of dimensions 0.4 × 0.2 × 0.12 mm with a triangular cross-section.

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† No reprints available.

[1] J. G. Verkade, *Co-ordination Chem. Rev.*, 1972, **9**, 1.

[2] A. Pidcock in ' Transition Metal Complexes of Phosphorus, Arsenic, and Antimony Ligands,' ed. C. A. McAuliffe, Macmillan, 1973.

[3] F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 1962, **84** 4432; F. A. Cotton, *Inorg. Chem.*, 1964, **3**, 702.

[4] R. J. Clark and M. A. Busch, *Accounts Chem. Res.*, 1973, **6**, 246.

[5] A. J. Carty, P. C. Chieh, N. J. Taylor, and Y. S. Wong, *J.C.S. Dalton*, 1976, 572.

[6] C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 2956.

[7] R. W. Rudolph and R. W. Parry, *J. Amer. Chem. Soc.*, 1967, **89**, 1621.

[8] N. C. Baenziger, W. E. Bennett, and D. M. Soboroff, *Acta Cryst.*, 1976, **B32**, 962.

[9] C. Kowala and J. M. Swan, *Austral. J. Chem.*, 1966, **19**, 547.

Accurate cell parameters were derived from the setting angles of 12 reflections on a Hilger and Watts Y290 four-circle diffractometer (Mo-$K_{\alpha 1}$, λ 0.709 26 Å). The intensities of unique reflections with $\theta \leqslant 22°$ were measured by an ω—2θ step scan using Mo-K_α radiation (graphite crystal monochromator). Three standard reflections remeasured after every 100 reflections showed no significant variation. The 2 615 unique reflections measured were corrected for Lorentz and polarisation effects and at a later stage for absorption. The 1 931 reflections with $I > 3\sigma(I)$ were used in the structure analysis.

Structure Solution and Refinement.—The positions of all the non-hydrogen atoms were derived by the usual heavy-atom technique and refined by full-matrix least squares (Au, P, and Cl anisotropic) to a residual R 0.066. The data were then corrected for absorption. Hydrogen atoms were included at idealised positions (C–H 1.08 Å) with $U_{\text{iso.}}$ values equal to those of the carbon atoms to which they were attached. Continued refinement with hydrogen atoms held fixed and all the other atoms allowed to refine anisotropically converged at R 0.052, R' 0.072.* The largest shift to error was 0.1. In the final cycles of refinement an empirical weighting scheme was used, defined as $w = 1/(20 + |F| + 0.2|F|^2)$, and gave reasonably constant average values of $\omega\Delta^2$ as a function of $|F|$. Scattering factors for neutral atoms and dispersion corrections for Au, P, and Cl were taken from ref. 10. A final difference-Fourier synthesis had peaks of up to 1.5 eÅ^{-3} in the region of the gold atom but was elsewhere featureless. The structure solution and refinement was carried out using the '*X*-Ray' program system.[11] Final atom parameters are listed in Table 1. The anisotropic thermal parameters and the structure factors are in Supplementary Publication No. SUP 22042 (11 pp.).†

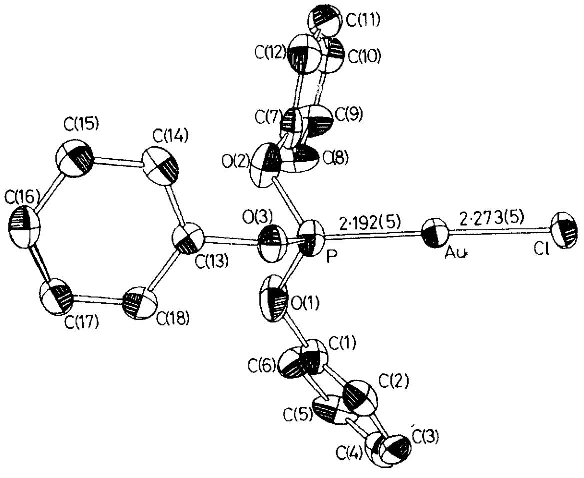
TABLE 1

Final atomic fractional co-ordinates ($\times 10^4$) with standard deviations in parentheses

	x	y	z
Au	1 125(1)	3 254(1)	1 012(1)
Cl	2 339(5)	3 749(5)	−1 029(5)
P	−0 009(6)	2 798(4)	3 011(5)
O(1)	0 760(18)	1 476(16)	3 976(16)
O(2)	−1 632(17)	2 615(15)	2 980(15)
O(3)	−0 451(13)	4 011(11)	3 915(11)
C(1)	2 288(21)	0 643(16)	3 750(18)
C(2)	3 356(29)	1 152(19)	3 487(21)
C(3)	4 785(30)	0 246(41)	3 264(28)
C(4)	4 983(31)	−1 088(33)	3 259(24)
C(5)	3 890(33)	−1 583(20)	3 562(28)
C(6)	2 421(22)	−0 655(20)	3 918(25)
C(7)	−1 951(22)	1 911(20)	2 001(18)
C(8)	−1 275(24)	0 532(21)	1 925(27)
C(9)	−1 747(28)	−0 107(23)	1 063(30)
C(10)	−2 806(28)	0 596(27)	0 162(25)
C(11)	−3 490(27)	1 921(29)	0 214(28)
C(12)	−3 134(28)	2 627(21)	1 139(26)
C(13)	−1 352(17)	4 159(14)	5 176(16)
C(14)	−2 768(24)	5 034(17)	5 080(18)
C(15)	−3 659(21)	5 311(17)	6 305(21)
C(16)	−3 058(24)	4 684(21)	7 556(19)
C(17)	−1 671(24)	3 844(21)	7 625(18)
C(18)	−0 768(20)	3 568(18)	6 416(19)

DISCUSSION

The molecular conformation and atom-numbering scheme are shown in the Figure. The hydrogen-atom numbering follows that of the carbon atoms to which they are attached. Bond lengths and angles in the complex are listed in Table 3. There are no intermolecular contacts significantly shorter than the sum of the relevant van der Waals' radii,[12] the shortest being Au $\cdots$ H(9)($\bar{x},\bar{y},\bar{z}$) at 3.09 Å; the shortest intramolecular contact to a phenyl-ring hydrogen is Au $\cdots$ H(2) at 3.02 Å. The co-ordination at the gold atom is closely linear [P–Au–Cl 178.5(2)°]. The gold–chlorine distance [2.273(5) Å] is similar to that [2.279(3) Å] in [AuCl(PPh$_3$)].[8] A lower *trans* influence of phosphite compared to phosphine ligands for platinum(II) complexes has been suggested[13] based on the M–Cl (*trans* to P) stretching frequencies in the i.r. spectra. A similar effect is seen in linear gold(I) complexes where ν(Au–Cl)



Perspective view of the molecule

TABLE 2

Calculated positions for hydrogen atoms ($\times 10^4$) and their isotropic thermal parameters ($\times 10^3$)

	x	y	z	$U_{\text{iso.}}$/Å^2
H(2)	3 144	2 241	3 439	92
H(3)	5 725	0 620	3 102	114
H(4)	6 083	−1 770	2 996	110
H(5)	4 074	−2 660	3 547	104
H(6)	1 499	−1 014	4 298	102
H(8)	−0 357	−0 035	2 577	105
H(9)	−1 272	−1 203	1 077	116
H(10)	−3 105	0 076	−0 606	108
H(11)	−4 360	2 641	−0 504	114
H(12)	−3 740	3 694	1 205	101
H(14)	−3 195	5 508	4 069	77
H(15)	−4 793	5 999	6 272	81
H(16)	−3 736	4 882	8 517	88
H(17)	−1 240	3 368	8 634	84
H(18)	0 373	2 898	6 466	74

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* $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, $R' = [\Sigma\omega(||F_o| - |F_c||)^2/\Sigma\omega|F_o|^2]^{\frac{1}{2}}$.

† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

[10] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104; D. T. Cromer, *ibid.*, p. 17; R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[11] '*X*-Ray' system, Technical Report TR 72–192, Computer Science Center, University of Maryland, July 1973. Version of June 1974 as implemented at the Atlas Computer Laboratory, Chilton, Berkshire.

[12] J. E. Huheey, 'Inorganic Chemistry,' Harper and Row, 1975, pp. 184—185 and refs. therein.

[13] M. J. Church and M. J. Mays, *J. Chem. Soc.* (*A*), 1968, 3074.

is at 329 and 347 cm^{-1} in the triphenylphosphine[14] and in the triphenyl phosphite complexes, although the observed difference in the Au–Cl bond lengths of 0.006 Å is not statistically significant. The conformation of the triphenyl phosphite ligand is similar to that observed in other complexes[5,15,16] and the pattern of bond angles at the phosphorus with one O–P–O angle of 107° and the other two O–P–O angles of 99° has also been observed elsewhere. Of the P–O bond lengths, that for P–O(2) is slightly longer than the other two and is associated with a relatively short O(2)–C(7) bond, otherwise they are unexceptional.

TABLE 3

Interatomic distances (Å) and angles (°) with standard deviations in parentheses

(*a*) Bonds			
Au–Cl	2.273(5)	C(6)–C(1)	1.31(3)
Au–P	2.192(5)	C(7)–C(8)	1.38(3)
P–O(1)	1.554(15)	C(8)–C(9)	1.33(4)
P–O(2)	1.626(18)	C(9)–C(10)	1.35(4)
P–O(3)	1.553(13)	C(10)–C(11)	1.32(14)
O(1)–C(1)	1.44(2)	C(11)–C(12)	1.36(4)
O(2)–C(7)	1.38(3)	C(12)–C(7)	1.40(3)
O(3)–C(13)	1.41(2)	C(13)–C(14)	1.36(2)
C(1)–C(2)	1.29(4)	C(14)–C(15)	1.39(3)
C(2)–C(3)	1.39(3)	C(15)–C(16)	1.37(3)
C(3)–C(4)	1.34(5)	C(16)–C(17)	1.32(3)
C(4)–C(5)	1.30(5)	C(17)–C(18)	1.38(3)
C(5)–C(6)	1.45(3)	C(18)–C(13)	1.35(2)
(*b*) Angles			
Cl–Au–P	178.5(2)	C(4)–C(5)–C(6)	119(2)
Au–P–O(1)	119.1(6)	C(5)–C(6)–C(1)	116(2)
Au–P–O(2)	118.4(6)	C(12)–C(7)–C(8)	119(2)
Au–P–O(3)	111.5(5)	C(7)–C(8)–C(9)	120(2)
O(1)–P–O(2)	98.9(9)	C(8)–C(9)–C(10)	121(2)
O(1)–P–O(3)	107.4(8)	C(9)–C(10)–C(11)	120(3)
O(2)–P–O(3)	99.0(7)	C(10)–C(11)–C(12)	122(2)
P–O(1)–C(1)	123(1)	C(11)–C(12)–C(7)	117(2)
P–O(2)–C(7)	122(1)	C(18)–C(13)–C(14)	122(1)
P–O(3)–C(13)	128(1)	C(13)–C(14)–C(15)	119(2)
C(2)–C(1)–C(6)	126(2)	C(14)–C(15)–C(16)	118(2)
C(1)–C(2)–C(3)	117(2)	C(15)–C(16)–C(17)	122(2)
C(2)–C(3)–C(4)	119(3)	C(16)–C(17)–C(18)	121(2)
C(3)–C(4)–C(5)	122(2)	C(17)–C(18)–C(13)	118(2)

A comparison of the gold–phosphorus bond lengths [2.235(3) and 2.192(5) Å] in the two complexes [AuCl(PPh$_3$)] and [AuCl{P(OPh)$_3$}] shows that the Au–P bond in the phosphite complex is 0.043 Å shorter than that in the phosphine complex.* This cannot be due to steric effects or *trans* influence and, as it is of the same order of magnitude as the bond-length shortening in the palladium complexes described by Carty *et al.*,[5] we think it extremely unlikely that their conclusions as to the cause of the shortenings in the palladium complexes are correct. Other possible causes of the Au–P bond-length shortening in the gold phosphite complex are d_π–d_π back bonding, a change in hybridisation at the phosphorus, or a purely σ-bond shortening caused by the electronegative substituents.

There is considerable controversy concerning the extent of transition-metal–phosphine π bonding, but it has been suggested[17] that in platinum(II) complexes of alkyl- or aryl-phosphines the amount of d_π–d_π back bonding is minimal. However in the case of phosphite or fluorophosphine complexes it has been suggested[3,4] that the electronegative substituents on the phosphorus reduce the size and energy of the empty d_π orbitals on the phosphorus to a sufficient extent to allow d_π–d_π back bonding and thus reduce the metal–phosphorus bond length by a synergic effect. In order to test this hypothesis it is necessary to compare metal–phosphine and -phosphite bond lengths in a situation where there is no possibility of π bonding by the metal. In spite of earlier arguments[18] invoking hyperconjugation in borane adducts of phosphine, it seems more likely that there are only σ bonds involved and that boron adducts provide a non-π-bonding system for comparison purposes. The only report we have been able to find in the literature of the structure of a boron–phosphite adduct is of $PCH_2(OMe)(OCHMe)_2 \cdot BH_3$ where the boron–phosphorus bond length is 1.879(17) Å.[19] This may be compared with the B–P bond lengths of 1.935(9) Å in $Ph_3P \cdot B_2H_4 \cdot PPh_3$[20] and 1.901(7) Å in $PMe_3 \cdot BH_3$.[21] Thus the shortening of the boron–phosphite compared to the boron–phosphine bond averages 0.04 Å and the similarity of this value to that observed in the gold complexes suggests that there is no appreciable contribution to bond lengths by π bonding in the gold complexes. Although this argument relies on only one boron–phosphite complex, it is reinforced by evidence on the related trifluorophosphine–boron complexes where the reported B–P bond lengths are 1.848(28) in $B_2H_4(PF_3)_2$,[22] 1.836(12) in $PF_3 \cdot BH_3$,[23] and 1.825(15) Å in $PF_3 \cdot B_4F_6$.[24] Although in PF_3 complexes part of the B–P bond-length shortening may be due to hybridisation changes at the phosphorus, there still remains a further shortening which is analogous to that in the phosphite complex. It is interesting to note that, as discussed earlier by Bryan and Kuczkowski,[21] this shortening of the B–P bond is not accompanied by an increase in bond strength; rather the reverse is true, militating against a π-bonding interpretation.

If there is any contribution to the bond-length difference from a change in hybridisation of the donor orbital

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* A similar short Au–P bond of 2.19 Å has been reported for the complex [AuCl(PCl$_3$)] (G. J. Arai, *Rec. Trav. chim.*, 1962, **81**, 307). However, this bond length should be treated with caution since the atom co-ordinates were not refined and to quote bond lengths to two decimal places may be misleading.

[14] G. E. Coates and C. Parkin, *J. Chem. Soc.*, 1963, 421.

[15] H. S. Preston, J. M. Stewart, H. J. Plastas, and S. O. Grim, *Inorg. Chem.*, 1972, **11**, 161.

[16] H. J. Plastas, J. M. Stewart, and S. O. Grim, *Inorg. Chem.*, 1973, **12**, 265.

[17] J. F. Nixon and A. Pidcock, *Ann. Rev. N.M.R. Spectroscopy*, 1969, **2**, 346.

[18] T. McAllister and H. Mackle, *Trans. Faraday Soc.*, 1969, **1**, 734.

[19] J. Rogers, D. W. White, and J. G. Verkade, *J. Chem. Soc.* (*A*), 1971, 77.

[20] W. Van Doorne, A. W. Cordes, and G. W. Hunt, *Inorg. Chem.*, 1973, **12**, 1686.

[21] P. S. Bryan and R. L. Kuczkowski, *Inorg. Chem.*, 1972, **11**, 553.

[22] E. R. Lory, R. F. Porter, and S. H. Bauer, *Inorg. Chem.*, 1971, **10**, 1072.

[23] R. L. Kuczkowski and D. R. Lide, *J. Chem. Phys.*, 1967, **46**, 357.

[24] B. G. DeBoer, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, 1969, **8**, 836.

of the phosphorus the extent can be estimated from the relative angles subtended by the substituents on the phosphorus. In the linear gold complexes [AuCl(PPh$_3$)] and [AuCl{P(OPh)$_3$}] the relative average angles are C–P–C 105.1, Au–P–C 113.5, O–P–O 101.8, and Au–P–O 116.3°. One can make an order-of-magnitude estimate of the effective difference in covalent radius of the phosphorus by making two assumptions: first that the orbitals used for the σ bonds by the phosphorus are s and p hybrids of the form $s + \lambda p$ directed along the bond axes;[25] secondly that the effective covalent radius of phosphorus varies with hybridisation in a way comparable to that of carbon.[26] The theoretical reduction in covalent radius of the phosphorus lone pair from phosphine to phosphite due to the change in hybridisation is then calculated as <0.01 Å, which is much too small to explain the observed difference in Au–P bond lengths.

A remaining possibility is contraction of the phosphorus-donor orbital in the phosphite ligand.[7] The argument here is that the electronegative substituents on the phosphorus increase its effective nuclear charge and that this causes the lone pair to be pulled in towards the nucleus, hence causing a shortening of the metal–phosphite bond by a purely σ-bond effect. It might be expected that any increase in effective nuclear charge would decrease all the bond lengths to substituent atoms on the phosphorus. Although such a trend is not universal, it can for instance be seen in the series of phosphorus(V) compounds PMe$_2$F$_3$, PMeF$_4$, and PF$_5$ where for the equatorial bonds the P–C distances are 1.798 and 1.780 Å and the P–F distances are 1.553, 1.543, and 1.534 Å respectively,[27] a similar trend being observed for the axial bonds. In addition we would expect that in metal phosphine complexes the phosphorus–metal bond would be more sensitive to an increase in effective nuclear charge since, unlike the other bonds, it involves a formal charge separation, P$^+$–M$^-$, across the bond. Whilst there is no positive proof of this type of effect in the gold complexes, it does explain the relative bond lengths in the phosphine and phosphite complexes of both gold and boron and in default of a better explanation we tentatively suggest it as the cause.

If one accepts that the difference of *ca.* 0.04 Å in metal–phosphorus bond lengths between phosphine and phosphite complexes is an intrinsic σ-bond effect of the ligand, it follows that, in other transition-metal phosphine and phosphite complexes, only in situations involving bond-length shortenings greater than this should one start to invoke steric or π-bonding influences.

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[25] C. A. Coulson, 'Valence,' Oxford University Press, 1961, ch. 8.

[26] 'Molecular Structures and Dimensions,' Crystallographic Data Centre, Cambridge, 1972, vol. A1.

[27] L. S. Bartell and K. W. Hansen, *Inorg. Chem.*, 1965, **4**, 1777.