An Octahedral Gold Cluster: Crystal and Molecular Structure of Hexakis-[tris-(*p*-tolyl)phosphine]-*octahedro*-hexagold Bis(tetraphenylborate)

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The crystal and molecular structure of the title compound has been determined from three-dimensional *X*-ray data collected by counter methods and refined by least-squares to *R* 0·052 from 3501 independent reflections. Crystals are triclinic, space group $P\bar{1}$, with unit cell dimensions $a = 17{\cdot}48(2)$, $b = 19{\cdot}02(2)$, $c = 13{\cdot}81(1)$ Å, $\alpha = 101{\cdot}1(1)$, $\beta = 94{\cdot}2(1)$, $\gamma = 116{\cdot}4(1)°$, $Z = 1$. The hexanuclear dication is a centrosymmetric octahedron significantly distorted. Two mutually opposite faces have edges ranging from 2·932(2) to 2·990(2), the remaining edges ranging from 3·043(2) to 3·091(2) Å. The overall mean Au–Au distance, 3·019 Å, is longer than the corresponding values in Au_{11} and Au_9 clusters. These long distances do not arise from non-bonding repulsions between adjacent ligands.

A PECULIARITY of gold is that it gives very unusual cluster compounds.[1] Besides the centred undecagold [2] and enneagold [3] clusters, whose structures have been reported, novel species of a lower molecular complexity have been prepared,[4] which are being presently characterized.

We now report the structure of a yellow species obtained in a low yield (a few crystals in a preparation, perhaps *ca.* 0·5 mg) as a by-product of the synthesis of a novel cluster compound. This latter is a red salt whose structure is still uncertain because of a very heavy disorder in the solid.

Owing to the minute yield obtained for the yellow compound and since preliminary photographs taken on one crystal showed the typical transform of a cluster of some complexity we decided to complete a structural analysis even though it was not possible to perform the customary sequence of physicochemical characterization. This characterization will be reported when a suitable route has been devized to obtain an appreciable amount of the complex.

EXPERIMENTAL

Crystal Data.—$[C_{126}H_{126}Au_6P_6][C_{24}H_{20}B]_2$, $M = 3643{\cdot}5$, Triclinic, $a = 17{\cdot}48(2)$, $b = 19{\cdot}02(2)$, $c = 13{\cdot}81(1)$ Å, $\alpha = 101{\cdot}1(1)$, $\beta = 94{\cdot}2(1)$, $\gamma = 116{\cdot}4(1)°$, $U = 3912$ Å^3, $D_m = 1{\cdot}56(3)$ (by flotation), $Z = 1$, $D_c = 1{\cdot}546$, $F(000) = 1784$ e. Space group $P\bar{1}$. Mo-K_α radiation, $\lambda = 0{\cdot}70930$ Å; μ(Mo-K_α) = 58·9 cm^{-1}.

Cell parameters were determined by precession photographs and refined on a PAILRED diffractometer by the ω-lag method.[5]

Intensity Measurements.—The molybdenum radiation was monochromatized on a highly oriented graphite crystal. Data were collected on a PAILRED equi-inclination diffractometer. The samples used in the data collection suffered from a relatively high mosaic dispersion (half-height spread: 0·4—0·6°) which had the consequence of partially overlapping adjacent reflections at relatively low equi-inclination angles. For this reason three crystals were mounted along the three cell axes and the diffracted intensities were collected up to the maximum feasible equi-inclination angle. Hence, for crystal (I), mounted along *b*, reflections were collected from layers *h*0—7*l*, for crystal (II) mounted along *c*, for *hk*0—3, and for crystal (III) mounted along *a*, for 0—4*kl*. For the three samples the collection was kept within sin θ/λ 0·53, since no noticeable reflections were observed outside this limit. For the three samples, each integrated intensity was measured by ω-scan at a rate of 1° min^{-1} and two backgrounds were counted for 20 s each at the extreme points of the scan range. Transmission factors, evaluated by the method of ref. 6 in 8^3 crystal points, had the following ranges: 0·27—0·44 for crystal (I), 0·45—0·50 for crystal (II), and 0·27—0·43 for crystal (III). The absorption-free intensities were corrected for Lorentz and polarization effects and for the effect of the partial polarization of the monochromatic beam.[7] No extinction correction was applied since no significant effects were observed. The three data sets were finally put on the same scale with the method of ref. 8; 3501 independent experimental structure amplitudes were obtained having $\sigma(I)/I < 0{\cdot}25$.

Solution and Refinement of the Structure.—The vector map has been interpreted in terms of a metal-atom cluster lying around a centre of symmetry. After preliminary refinement of the positional and thermal parameters of the gold atoms, the co-ordinates of all non-hydrogen atoms were found from a difference-Fourier map. The refinement was carried out by full-matrix least-squares, the function minimized being $\Sigma w(F_o - k|F_c|)^2$. Weights were assigned according to the formula $w = 1/(A + BF_o + CF_o^2)$ where, in the final cycles, *A* was 66·0, *B* 0·95, and *C* −0·027 in order to obtain a reasonably constant distribution of the weighted mean quadratic error as a function of sin θ/λ and of F_o. The nine independent *p*-tolyl groups of the cation and the four phenyl rings of the anion were treated as rigid bodies of known geometry: the C–C distances were all assumed to be 1·392 Å (except H_3C–C, 1·510 Å), and all C–C–C angles 120°. For each group a mean overall isotropic factor was refined. The final reliability indices were:

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[1] L. Malatesta, L. Naldini, G. Simonetta, and F. Cariati, *Chem. Comm.*, 1965, 212; *Co-ordination Chem. Rev.*, 1966, **1**, 255; *Inorg. Chim. Acta*, 1967, **1**, pp. 34, 315; F. Cariati and L. Naldini, *ibid.*, 1971, **5**, 172.

[2] (*a*) M. McPartlin, R. Mason, and L. Malatesta, *Chem. Comm.*, 1969, 334; (*b*) V. G. Albano, P. L. Bellon, M. Manassero, and M. Sansoni, *ibid.*, 1970, 1210; (*c*) P .L. Bellon, M. Manassero, and M. Sansoni, *J.C.S. Dalton*, 1972, 1481.

[3] P. L. Bellon, F. Cariati, M. Manassero, L. Naldini, and M. Sansoni, *Chem. Comm.*, 1971, 1423.

[4] L. Naldini, personal communication.

[5] J. Hornstra, Report No. 4021, N. V. Philips Gloeilampen Fabrik, Eindhoven, Netherlands, 1965.

[6] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1957, **10**, 180.

[7] W. L. Bond, *Acta Cryst.*, 1959, **12**, 375.

[8] W. C. Hamilton, J. S. Rollett, and R. A. Sparks, *Acta Cryst.*, 1965, **18**, 129.

R 0·052 and R' 0·065 $\{R' = [\Sigma w(F_o - k|F_c|)^2/\Sigma w F_o^2]^{1/2}\}$. Atomic scattering factors were taken from ref. 9 and the real and imaginary contributions to the anomalous scattering of gold and phosphorus from ref. 10. A difference-Fourier map, computed on the basis of the final co-ordinates had no peak $>$0·4 eÅ^{-3}, apart from one peak of *ca.* 2 eÅ^{-3} at the centre of the cluster. Positional co-ordinates and thermal parameters of the atoms treated individually are given in Table 1; Table 2 reports the same parameters for thirteen rigid groups, and the derived parameters for all carbon atoms are listed in Table 3. The final list of computed and observed structure factor moduli in electrons is given in Supplementary Publication No. SUP 20764 (4 pp, 1 microfiche).*

TABLE 1 [a, b]

Positional and thermal parameters of non-group atoms with estimated standard deviations in parentheses

	x	y	z	β_{11} or B/Å^2	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
Au(1)	3934(0)	4151(0)	5531(1)	38(0)	31(0)	33(1)	31(0)	38(1)	47(0)
Au(2)	5872(0)	4616(0)	5574(1)	39(0)	36(0)	26(1)	30(0)	23(1)	48(0)
Au(3)	5358(0)	5922(0)	6384(1)	42(0)	38(0)	21(1)	29(0)	12(1)	39(0)
P(1)	2764(5)	3313(4)	6113(6)	37(3)	29(5)	22(8)	31(3)	35(7)	44(5)
P(2)	6912(5)	4305(5)	6214(6)	40(3)	54(5)	24(8)	42(3)	47(7)	50(5)
P(3)	5763(5)	6981(5)	7787(6)	46(4)	37(6)	14(9)	37(3)	20(8)	51(5)
B	8449(35)	1346(31)	7633(42)	8·1(15)					

[a] All values × 10^4 except those of B. [b] β_{ij} values are coefficients of the form: $h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23}$.

TABLE 2 *

Rigid-group parameters and mean isotropic temperature factors of phenyl rings

	X	Y	Z	α/°	β/°	γ/°	B/Å^2
C(111)–C(117)	2848(9)	1566(10)	6750(13)	−65·9(6)	76·5(7)	−40·4(6)	6·3(4)
C(121)–C(127)	2467(9)	4461(9)	8369(12)	−124·7(7)	−0·5(7)	54·5(9)	6·5(4)
C(131)–C(137)	673(10)	2446(9)	4367(12)	137·4(6)	27·2(7)	83·5(7)	6·1(4)
C(211)–C(217)	8500(9)	6041(8)	8192(10)	−44·5(5)	−5·2(7)	160·7(7)	5·1(3)
C(221)–C(227)	6021(9)	2495(9)	7113(11)	−153·3(6)	43·8(8)	−162·5(6)	5·7(4)
C(231)–C(237)	8302(12)	4110(10)	4468(14)	41·6(7)	28·1(9)	121·4(8)	7·4(5)
C(311)–C(317)	4617(12)	8150(11)	7487(12)	174·4(7)	31·2(1·0)	59·6(7)	8·2(5)
C(321)–C(327)	5292(8)	6443(8)	10165(12)	−59·6(6)	9·8(7)	−32·2(7)	5·3(3)
C(331)–C(337)	8085(9)	8355(8)	8280(11)	−103·0(6)	80·4(6)	23·1(6)	5·7(3)
C(11)–C(16)	7785(15)	872(13)	9586(19)	−54·6(1·2)	−6·0(1·5)	−24·5(1·3)	10·7(7)
C(21)–C(26)	9294(14)	3220(14)	7916(19)	−12·1(1·2)	−63·3(1·3)	−167·5(1·3)	11·0(7)
C(31)–C(36)	9771(13)	778(10)	7023(13)	25·4(1·0)	−49·4(1·0)	56·2(1·0)	7·3(5)
C(41)–C(46)	6782(14)	490(15)	6072(19)	46·6(1·4)	−16·5(1·6)	−82·9(1·6)	12·3(8)

* X, Y, Z and α, β, γ as defined in *J. Chem. Soc.* (*A*), 1971, 2420; X, Y, and Z are × 10^4.

Computations.—All computations were carried out on a UNIVAC 1106 computer. For absorption correction a local programme was used in which the directions of primary and diffracted beams were evaluated as recently described.[11] Counter data reduction and statistical analyses for weighting schemes were based upon Fortran programmes written in our laboratory by M. Sansoni. In addition, local versions of entries Nos. 7528, 7531, 7532, and 7535 of the 1966 'International World List of Crystallographic Programs' were used for Fourier analysis, structure-factor, and least-squares calculations; Johnson's ORTEP for the drawings and a programme by Domenicano and Vaciago for computations of molecular parameters were used.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

Structural analysis has shown that the yellow solid is made up of $[Au_6\{P(p\text{-}MeC_6H_4)_3\}_6][BPh_4]_2$. The hexanuclear dication is an octahedron which lies around and possesses a crystallographic centre of symmetry; the anions occupy a general position. The ionic packing (Figure 1) is a consequence of normal van der Waals interactions; a survey of all non-bonding contacts reveals no unusually short distances. The overall conformation of the cation is shown in Figure 2, which also shows the atom numbering system used in the analysis. The anisotropic behaviour of the thermal ellipsoids of the Au_6P_6 moiety is shown in Figure 3.

The present compound is the second example of an octahedral cluster for a Group IB metal. The first is represented by the copper hydride $[HCuPPh_3]_6$ described by Churchill *et al.*[12] Owing to the lack of chemical data on our compound, which is obtained in a similar way to that for the copper cluster, we could not rule out the presence in it of hydrido-ligands. However, this is rather improbable in view of the crystal stability. During data collection as well as during preparation and preliminary manipulation, the samples were absolutely stable in air. The formulation of the dication obtained from the crystallographic analysis yields a total of 76 e for the cluster. This number is surprisingly low when compared with the electronics of the hexanuclear carbonyl clusters [*e.g.* $Rh_6(CO)_{16}$ which possess 86 e]

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index, issue (items less than 10 pp. are supplied as full size copies).

[9] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[10] 'International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962.

[11] G. Ciani, M. Manassero, and M. Sansoni, *J. Appl. Cryst.*, 1971, **4**, 173.

[12] S. A. Bezman, M. R. Churchill, J. A. Osborn, and J. Wormald, *J. Amer. Chem. Soc.*, 1971, **93**, 2063; M. R. Churchill, S. A. Bezman, J. A. Osborn, and J. Wormald, *Inorg. Chem.*, 1972, **11**, 1818.

and also with that of the copper hydride (84 e), but is consistent with the electron systems of the Au_{11} and Au_9 clusters. In the latter, there are $12 + \frac{6}{11}$ and $12 + \frac{4}{9}$, *i.e. ca.* 12·5 e per gold atom, whereas in the present cation each gold atom possesses $12 + \frac{2}{3}$ e. In the Au_6 octahedron the *cis* Au–Au distances range from 2·932(2) to 3·091(2) Å, so that the geometry of the cluster departs significantly from O_h symmetry. The six crystallographically independent edges of the octahedron can be divided into two classes: two opposite faces, related by the inversion centre and defined by the apices Au(1), Au(2), and Au(3), have long edges of mean length 3·073 Å, whereas the remaining edges are shorter (mean 2·965 Å). Thus, the octahedron appears to be squeezed along a three-fold axis passing through the centres of the two larger faces. The deformation of the present cluster is the same as that observed in $H_6Cu_6(PPh_3)_6$;[12] interestingly enough, in both octahedra there is the same

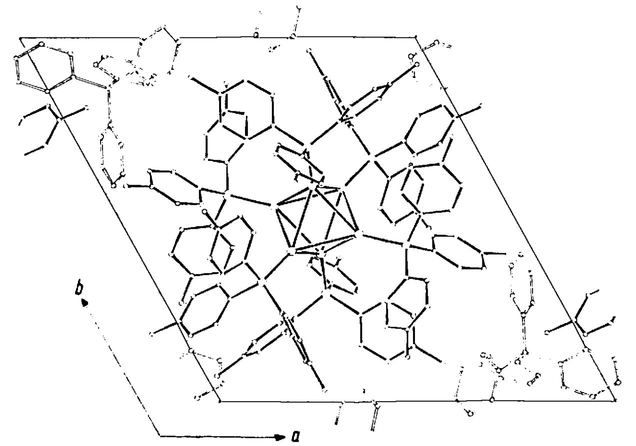

FIGURE 1 Ionic packing of $[Au_6\{P(p\text{-}MeC_6H_4)_3\}_6][BPh_4]_2$ as seen along the *c* axis. Axes *a* and *b* do not lie in the plane of Figure

TABLE 3

Positional parameters (× 10^3) of group carbon atoms

	x	*y*	*z*		*x*	*y*	*z*
C(111)	283(2)	245(1)	646(2)	C(313)	515(1)	885(1)	794(2)
C(112)	277(1)	182(1)	568(1)	C(314)	429(1)	845(1)	743(1)
C(113)	278(1)	114(1)	590(1)	C(315)	390(1)	762(1)	699(2)
C(114)	286(1)	109(1)	691(1)	C(316)	436(2)	719(1)	708(2)
C(115)	292(1)	171(1)	769(1)	C(317)	379(2)	892(2)	733(2)
C(116)	290(1)	239(1)	746(2)	C(321)	552(2)	674(1)	900(1)
C(117)	287(3)	35(1)	715(2)	C(322)	581(1)	623(1)	929(2)
C(121)	261(2)	389(1)	724(2)	C(323)	563(1)	599(1)	1019(2)
C(122)	324(1)	469(2)	768(2)	C(324)	517(1)	628(1)	1080(1)
C(123)	312(1)	513(1)	855(1)	C(325)	488(1)	680(1)	1050(2)
C(124)	239(1)	477(1)	898(2)	C(326)	506(2)	703(1)	960(2)
C(125)	176(1)	397(1)	854(2)	C(327)	498(2)	603(2)	1177(2)
C(126)	188(2)	353(1)	767(2)	C(331)	693(1)	769(1)	806(2)
C(127)	227(2)	525(2)	993(2)	C(332)	736(1)	781(1)	734(1)
C(131)	171(1)	285(2)	519(2)	C(333)	825(1)	832(1)	741(1)
C(132)	162(1)	323(1)	446(2)	C(334)	871(1)	871(1)	840(1)
C(133)	82(1)	292(1)	382(2)	C(335)	828(1)	859(1)	922(1)
C(134)	11(1)	223(1)	392(1)	C(336)	739(1)	808(1)	905(2)
C(135)	20(1)	184(1)	466(2)	C(337)	968(1)	927(2)	859(2)
C(136)	100(1)	215(2)	530(2)	C(11)	810(2)	110(2)	873(2)
C(137)	−75(1)	189(2)	323(2)	C(12)	844(2)	71(2)	925(3)
C(211)	771(1)	516(1)	723(1)	C(13)	812(2)	48(2)	1011(3)
C(212)	749(1)	575(1)	769(2)	C(14)	747(2)	64(2)	1044(2)
C(213)	810(1)	643(1)	842(1)	C(15)	712(2)	103(2)	992(3)
C(214)	893(1)	652(1)	871(1)	C(16)	745(2)	126(2)	906(3)
C(215)	914(1)	593(1)	826(1)	C(21)	891(3)	239(1)	782(2)
C(216)	854(1)	525(1)	752(2)	C(22)	889(2)	290(2)	869(2)
C(217)	958(2)	726(1)	951(2)	C(23)	928(3)	373(2)	879(2)
C(221)	647(2)	341(1)	667(2)	C(24)	968(3)	405(1)	802(2)
C(222)	565(2)	277(1)	620(1)	C(25)	970(2)	354(2)	715(2)
C(223)	531(1)	207(1)	655(2)	C(26)	931(3)	271(2)	705(2)
C(224)	578(1)	200(1)	735(1)	C(31)	917(2)	103(2)	732(2)
C(225)	660(1)	263(1)	782(1)	C(32)	1001(2)	143(1)	787(2)
C(226)	694(1)	334(1)	747(2)	C(33)	1061(1)	118(2)	757(2)
C(227)	541(2)	124(1)	773(2)	C(34)	1038(2)	53(2)	673(2)
C(231)	753(2)	414(2)	527(2)	C(35)	953(2)	13(1)	618(2)
C(232)	770(2)	457(2)	453(2)	C(36)	893(1)	38(2)	647(2)
C(233)	830(1)	455(1)	391(2)	C(41)	753(2)	87(3)	681(3)
C(234)	872(1)	409(1)	403(2)	C(42)	695(3)	6(3)	670(3)
C(235)	855(2)	366(1)	478(2)	C(43)	620(3)	−32(2)	587(3)
C(236)	796(1)	368(2)	540(2)	C(44)	603(2)	10(3)	533(3)
C(237)	936(2)	407(2)	336(2)	C(45)	661(3)	92(3)	544(3)
C(311)	521(2)	759(2)	760(2)	C(46)	736(3)	130(2)	618(3)
C(312)	561(1)	842(2)	803(2)				

Atom C(*ijk*) belongs to ring *j*, bonded to P(*i*): C(*ij*1) is bonded to P(*i*); C(*ij*4), *para* to C(*ij*1), is bonded to C(*ij*7). For rings bonded to the boron atom, *i* is redundant.

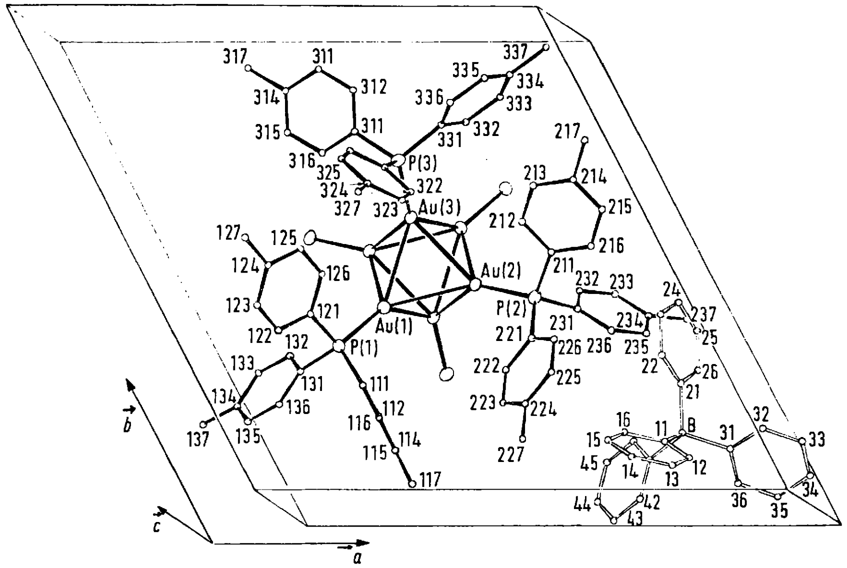

FIGURE 2 The overall conformation of the cation and the atomic numbering system used

difference between the (mean) long and short edges: 0·108 Å in the gold cation *vs.* 0·113 Å in the neutral hydride. In the copper cluster, however, the mean short edge, 2·542 Å, is equivalent to the Cu–Cu distance in the metal (2·556 Å), whereas in the present compound the short edge (2·965 Å) is longer than the distance in the metal (2·884 Å). The overall mean of six independent Au–Au distances (3·02 Å) is longer than the corresponding means taken on the peripheral interactions only, in the centred Au_{11} and Au_9 clusters (2·98 and 2·81 Å, respectively).*

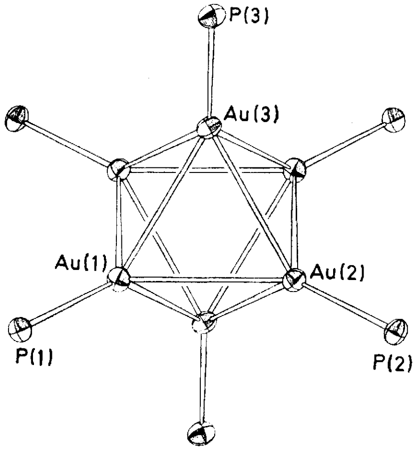

FIGURE 3 View of the thermal ellipsoids in the Au_6P_6 moiety

In a preliminary communication dealing with the present structure[13] we tentatively interpreted these long Au–Au interactions by assigning a pair of electrons to an antibonding cluster orbital. A detailed interpretation of the electron system of this cluster is on schedule but, even at this stage, it can be stated that these long distances are not caused by non-bonding repulsions. This is shown by the lack of severe deformations in the angles Au(*trans*) · · · Au–P (none of which is less than 175°) and in the conformational angles of the phosphine groups, Au–P–C and C–P–C. which do not appear particularly to be strained (see Table 4). Moreover, if the ligand repulsions were the cause of lengthening of the octahedral edges, a more dramatic effect would occur in the copper cluster, which also has six phosphine groups apically bonded to a smaller octahedron. The displacement of the phosphorus atoms from the true apical positions (probably a consequence of the inter-ring repulsions) is much greater in the copper complex than in the present one. This is better appreciated if, instead of comparing complicated patterns of deformation in M(*cis*)–M–P and M(*trans*) · · · M–P angles, the distances of the P atoms from the equatorial planes in both octahedra are considered.† In the copper hydride the majority of these distances are between 0·2 and 0·4 Å whereas in the present cation all are well below 0·2 Å (see Table 5).

The mean Au–P distances (Table 4) are 2·29 Å which compares well with the corresponding distances found in $[Au_{11}I_3P(p\text{-}FC_6H_4)_3]_7$ and with a number of similar interactions (see ref. 2*c* and refs. therein). The nine independent P–C bond lengths appear to be rather scattered; their mean, excluding the P(1)–C(131) bond, which is rather high [1·89(2) Å], is 1·822 to be compared

TABLE 4

Selected intramolecular distances (Å) and angles (°)

Au(1)–Au(2)	3·091(2)	Au(1)–Au(3)–Au(2′)	57·7(1)
Au(1)–Au(3)	3·084(1)	Au(2′)–Au(1)–Au(3)	59·5(1)
Au(2)–Au(3)	3·043(2)	Au(1′)–Au(2)–Au(3)	59·6(1)
Au(1)–Au(2′)	2·932(2)	Au(1′)–Au(3)–Au(2)	58·3(1)
Au(1)–Au(3′)	2·972(2)	Au(2)–Au(1′)–Au(3)	62·1(1)
Au(2)–Au(3′)	2·990(2)	Au(1′)–Au(2′)–Au(3)	58·5(1)
		Au(1′)–Au(3)–Au(2′)	62·5(1)
Au(1) · · · Au(1′)	4·277(2)	Au(2′)–Au(1′)–Au(3′)	59·1(1)
Au(2) · · · Au(2′)	4·249(2)	Au(1)–Au(2)–Au(1′)	90·4(1)
Au(3) · · · Au(3′)	4·290(2)	Au(2)–Au(1)–Au(2′)	89·6(1)
		Au(1)–Au(3)–Au(1′)	89·8(1)
Au(1)–Au(2)–Au(3)	60·4(1)	Au(3)–Au(1)–Au(3′)	90·2(1)
Au(1)–Au(3)–Au(2)	60·6(1)	Au(2)–Au(3)–Au(2′)	89·4(1)
Au(2)–Au(1)–Au(3)	59·1(1)	Au(3)–Au(2)–Au(3′)	90·6(1)
Au(1)–Au(2′)–Au(3)	62·8(1)		
Au(1)–P(1)	2·274(8)	P(2)–Au(2)–Au(1)	140·3(2)
Au(2)–P(2)	2·311(11)	P(2)–Au(2)–Au(3)	132·6(2)
Au(3)–P(3)	2·293(8)	P(2)–Au(2)–Au(1′)	129·1(2)
		P(2)–Au(2)–Au(3′)	136·5(2)
P(1)–Au(1)–Au(1′)	175·9(3)	P(3)–Au(3)–Au(3′)	175·1(2)
P(1)–Au(1)–Au(2)	140·1(3)	P(3)–Au(3)–Au(1)	139·6(2)
P(1)–Au(1)–Au(3)	133·7(2)	P(3)–Au(3)–Au(2)	138·4(3)
P(1)–Au(1)–Au(2′)	130·3(3)	P(3)–Au(3)–Au(1′)	130·4(2)
P(1)–Au(1)–Au(3′)	135·9(2)	P(3)–Au(3)–Au(2′)	131·9(3)
P(2)–Au(2)–Au(2′)	175·4(2)		
P(1)–C(111)	1·85(3)	C(111)–P(1)–C(121)	107·2(14)
P(1)–C(121)	1·82(3)	C(111)–P(1)–C(131)	105·0(13)
P(1)–C(131)	1·89(2)	C(121)–P(1)–C(131)	104·9(13)
P(2)–C(211)	1·83(2)	C(211)–P(2)–C(221)	109·7(10)
P(2)–C(221)	1·79(2)	C(211)–P(2)–C(231)	104·7(11)
P(2)–C(231)	1·81(3)	C(221)–P(2)–C(231)	106·0(16)
P(3)–C(311)	1·84(4)	C(311)–P(3)–C(321)	103·7(14)
P(3)–C(321)	1·82(2)	C(311)–P(3)–C(331)	105·6(13)
P(3)–C(331)	1·84(2)	C(321)–P(3)–C(331)	104·4(11)
		P(1)–C(111)–C(114)	177·1(13)
Au(1)–P(1)–C(111)	115·4(12)	P(1)–C(121)–C(124)	179·3(18)
Au(1)–P(1)–C(121)	109·3(8)	P(1)–C(131)–C(134)	176·4(15)
Au(1)–P(1)–C(131)	114·2(8)	P(2)–C(211)–C(214)	176·3(13)
Au(2)–P(2)–C(211)	110·4(9)	P(2)–C(221)–C(224)	179·2(15)
Au(2)–P(2)–C(221)	113·2(10)	P(2)–C(231)–C(234)	171·0(12)
Au(2)–P(2)–C(231)	112·3(12)	P(3)–C(311)–C(314)	175·2(15)
Au(3)–P(3)–C(311)	110·6(8)	P(3)–C(321)–C(324)	175·8(16)
Au(3)–P(3)–C(321)	117·9(8)	P(3)–C(331)–C(334)	177·2(14)
Au(3)–P(3)–C(331)	113·5(5)		
B–C(11)	1·72(7)	C(11) · · · C(31)	2·79(5)
B–C(21)	1·73(6)	C(11) · · · C(41)	2·61(5)
B–C(31)	1·66(8)	C(21) · · · C(31)	2·78(5)
B–C(41)	1·65(6)	C(21) · · · C(41)	2·79(5)
C(11) · · · C(21)	2·80(5)	C(31) · · · C(41)	2·76(5)

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* If the mean Au–Au distance in Au_{11} and Au_9 clusters is taken on both centre-to-periphery and peripheral interactions, the resulting values are lower.

† The metal octahedra in both complexes exhibit closely related distortions. After averaging the lengths of opposite edges in the non-centrosymmetric Cu cluster, we have compared the patterns of edges meeting to each apex. This has allowed an ' atom-by-atom ' correspondence to be established in the two clusters. The correspondence, used in Table 5, is: Au(1) ≡ Cu(5) [or Cu(3)]; Au(2) ≡ Cu(6) [or Cu(1)]; and Au(3) ≡ Cu(2) [or Cu(4)].

[13] P. L. Bellon, M. Manassero, L. Naldini, and M. Sansoni, *J.C.S. Chem. Comm.*, 1972, 1035.

TABLE 5

A comparison of the deviations (Å) of phosphorus atoms from the equatorial planes in $[Au_6L_6]^{2+}$ and in $Cu_6H_6L_6$

Plane defined by:	
Au(1), Au(2), Au(1′), Au(2′)	Cu(1), Cu(3), Cu(5), Cu(6)
P(1) ±0·0846, P(2) ±0·0922	P(5) −0·026, P(3) 0·135, (P6) −0·320, P(1) −0·255
Plane defined by:	
Au(1), Au(3), Au(1′), Au(3′)	Cu(2), Cu(3), Cu(4), Cu(5)
P(1) ±0·1328, P(3) ±0·1182	P(5) 0·079, P(3) 0·274, P(2) 0·002, P(4) −0·215
Plane defined by:	
Au(2), Au(3), Au(2′), Au(3′)	Cu(1), Cu(2), Cu(4), Cu(6)
P(2) ±0·1606, P(3) ±0·1461	P(6) −0·345, P(1) −0·374, P(2) 0·298, P(4) −0·044

with 1·823 Å in triphenylphosphine itself. The distances and angles in the tetraphenylborate anion have relatively high estimated standard deviations. Although the B–C distances are systematically higher than those found in a recent structural report (see ref. 14), the difference is not statistically significant.

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[14] R. J. Sime, R. P. Dodge, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, 1971, **10**, 537.