changes occur. It also seems that the substitution of a chloride ion for a water molecule leaves the structure relatively unchanged. It should be noted that all the structures should be known. Averaging of the 2- and 1-hydrate energy changes gives an average enthalpy of reaction of 56·5 kJ mol^{-1}, close to what is observed for the vaporization of water. The entropy change appears to be more sensitive and should be the main criterion.

Evidence indicates that the major change in structure occurs in the formation of the 1-hydrate. The data are more compatible with a water molecule acting as a link between two adjacent Co^{II} ions than with the replacement of a water molecule by a chloride ion, or the formation of chloride linkages with the remaining water molecule relegated to the outer co-ordination sphere. The formation of anhydrous $CoCl_2$ is thus merely the exchange of a linking water molecule by a linking chloride ion.

The distorted octahedral structure is retained by all the hydrates indicating the retention of structure and the favouring of a co-ordination number of six. The chloride linkage is favoured when the water is absent and is retained practically unchanged from the 2-hydrate to the anhydrous compound.

We thank Dr. S. D. Christian for discussions, Dr. H. W. Joy for help with the computer programme, and the University of Oklahoma for a grant.

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Crystal and Molecular Structure of Tri-iodoheptakis(tri-*p*-fluorophenylphosphine)undecagold

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The crystal and molecular structure and the absolute configuration of the title compound have been determined from three-dimensional *X*-ray data collected by counter methods, and refined by least squares to *R* 0·034 for 1959 independent reflections. The crystals are in space-group *R*3, with unit-cell dimensions *a* = 15·96(2) Å, α = 108·4(1)°, and *Z* = 1. The molecular unit possesses C_3 symmetry. The metal-atom cluster derives from a centred icosahedron, in which one triangular face has been substituted by a single gold atom. Au–Au Interactions are: mean centre-to-periphery 2·68 Å, peripheral distances 2·836(4)—3·187(3) Å, mean 2·98 Å. There are three independent classes of Au–P bonds, in the range 2·21(1)—2·29(1) Å. The Au–I distances are 2·600(5) Å. The packing is discussed with reference to the disordered structure of $\mathrm{Au_{11}I_3[P(\textit{p}\text{-}ClC_6H_4)_3]_7}$.

THE methods of preparation and the properties of several gold cluster compounds have been reported,[1] and the crystal structures of $\mathrm{Au_{11}(SCN)_3(PPh_3)_7}$ (I),[2] and $\mathrm{Au_{11}I_3[P(\textit{p}\text{-}ClC_6H_4)_3]_7}$ (II) [3] have been determined.

Compound (I) is heavily disordered in the solid [2] and the crystals of compound (II) are also disordered, though to a lesser extent.[3] Essentially the same metal-atom cluster is present in the two complexes; the main novelty in the Au_{11} moiety is the presence of a ten-co-ordinate gold atom bonded only to other metal atoms, which are distributed at the apices of a polyhedron closely related to the icosahedron.[3]

The stereochemistry and, perhaps, the stoicheiometry too of this family of complexes is probably determined not only by electronics but also by crowding of the bulky phosphine ligands. In order to elucidate this role of the ligands, the structure determination of an ordered species seemed to be necessary. Since a noticeable thermal diffuse scattering (TDS) was present in the diffraction pattern of compound (II), we assumed it to be an indication of disorder, and all crystal species considered for a complete structural analysis [3] were examined in this respect. Finally, we made a complete structural investigation into $\mathrm{Au_{11}I_3[P(\textit{p}\text{-}FC_6H_4)_3]_7}$, (III), whose crystals did not exhibit any noticeable TDS.

EXPERIMENTAL

Crystal Data.—$C_{126}H_{84}Au_{11}F_{21}I_3P_7$, M = 4761·2, Trigonal. Hexagonal triple cell: a = 25·90(2) Å, c = 16·79(2) Å, systematic absences for $-h + k + l \neq 3n$; rhombohedral primitive cell: a = 15·96(2) Å, α = 108·4(1)°. U = 3250 Å^3, D_m = 2·44(2) (by flotation), Z = 1, D_c = 2·432, and $F(000)$ = 2162 for the primitive cell. Possible space-groups $R3$ and $R\bar{3}$. $R3$ (No. 146) Is confirmed on the basis of the vector map.

Cell parameters were determined by precession photographs and refined on a PAILRED diffractometer by the ω-lag method.[4] Mo-K_α Radiation, λ = 0·70930; μ(Mo-K_α) = 136·5 cm^{-1}.

Intensity Measurements.—The sample used for data collection measured 0·51 mm along the trigonal axis, and 0·24 × 0·24 mm in the perpendicular plane. The crystal was mounted along the direction of maximum elongation on a PAILRED linear equi-inclination diffractometer. The Mo radiation was monochromatised on a silicon single crystal cut normally to {111}, so that the radiation incident

[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] M. McPartlin, R. Mason, and L. Malatesta, *Chem. Comm.*, 1969, 334.

[3] V. G. Albano, P. L. Bellon, M. Manassero, and M. Sansoni, *Chem. Comm.*, 1970, 1210.

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

on the crystal was the Mo-K_α doublet, free from subharmonics. A total of 3793 hexagonal-indexed reflections were collected in the layers $hk0$—13 with $\sin\theta/\lambda < 0{\cdot}58$ Å^{-1}; only a few reflections, outside this region, were significantly above background. Each integrated intensity was measured by an ω-scan at a rate of 0·5° min^{-1}, and two backgrounds were counted for 1 min each, at the extreme points of the scan range. The intensities of a few zero-level reflections were measured at regular intervals during the whole period of data collection; no significant changes in the scattering power of the sample were observed. The transmission factors, in the range 0·101—0·176, were computed by the method of ref. 5, by use of a sampling of 8^3 points. The absorption corrected intensities were reduced to F_o values by correction for Lorentz and polarisation effects. The partial polarisation of the incident beam, due to the presence of the monochromator, has been taken into account.[6] No correction for extinction has been introduced, since no significant effects were observed. After removing the intensities with $\sigma(I)/I > 0{\cdot}25$, and averaging the symmetry-equivalent reflections, 1959 independent experimental structure amplitudes were obtained, which were re-indexed in terms of the rhombohedral lattice.

TABLE 1

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

	10^4x	10^4y	10^4z	$10^4\beta_{11}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{22}$	$10^4\beta_{23}$	$10^4\beta_{33}$
Au(1)	0	0	0	28(1)	25(2)	25(2)	28(1)	25(2)	28(1)
Au(2)	−1548(1)	−1548(1)	−1548(1)	38(1)	17(2)	17(2)	38(1)	17(2)	38(1)
Au(3)	−1319(1)	482(1)	−979(1)	38(0)	48(1)	28(1)	47(1)	47(1)	44(1)
Au(4)	513(1)	865(1)	−1099(1)	54(0)	46(1)	54(1)	47(0)	52(1)	43(0)
Au(5)	786(1)	1982(1)	856(1)	40(0)	20(1)	24(1)	26(0)	20(1)	39(0)
I	1052(2)	1560(2)	−2215(2)	88(2)	89((3)	98(3)	103(2)	119(3)	68(2)
P(2)	−2865(10)	−2865(10)	−2865(10)	63(8)	82(19)	82(19)	63(8)	82(19)	63(8)
P(3)	−2473(6)	942(6)	−1661(6)	40(6)	43(10)	11(10)	43(5)	45(10)	49(6)
P(5)	1311(6)	3664(6)	1486(6)	43(6)	34(10)	19(10)	40(5)	35(10)	45(6)
				B/Å^2					
F(2)	−5860(21)	−5010(21)	−1850(21)	9·1(6)					
F(31)	−1757(21)	2456(21)	−4433(21)	9·6(6)					
F(32)	−2560(19)	4182(18)	1379(19)	7·7(5)					
F(33)	−6635(17)	−2230(17)	−3847(17)	6·9(5)					
F(51)	594(20)	5085(19)	4983(19)	8·2(6)					
F(52)	−515(19)	4783(19)	−1565(19)	8·1(6)					
F(53)	5676(16)	6066(16)	3275(16)	5·7(4)					

* The atomic parameters in Tables 1—3 are referred to the rhombohedral cell obverse to the hexagonal cell shown in Figure 2 (see ref. 10, vol. 1, p. 20). † The β_{ij} 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(21)—(26)	−4516(12)	−4091(12)	−2359(12)	−160·8(1·1)	−44·6(8)	117·5(1·0)	4·8(3)
C(311)—(316)	−2056(13)	1820(13)	−3108(13)	138·7(9)	9·7(8)	−31·8(8)	4·6(3)
C(321)—(326)	−2563(13)	2654(13)	−30(13)	−122·7(1·0)	−33·7(7)	8·0(9)	4·9(3)
C(331)—(336)	−4730(12)	−791(12)	−2889(12)	43·3(1·1)	−45·5(8)	−84·8(1·0)	4·6(3)
C(511)—(516)	906(12)	4458(12)	3345(12)	−56·2(9)	18·7(7)	−110·0(8)	4·6(3)
C(521)—(526)	334(13)	4298(13)	−125(13)	69·6(1·3)	−41·7(8)	145·2(1·3)	5·5(4)
C(531)—(536)	3663(11)	4973(11)	2379(11)	−153·8(8)	−18·0(8)	−73·0(6)	4·1(3)

* X, Y, Z (all $\times 10^4$) and α, β, γ, are as defined in ref. 12.

Solution and Refinement of the Structure.—The vector map has been interpreted in terms of an Au_{11} cluster, similar to those previously reported,[2,3] in the non-centrosymmetrical space-group $R3$. The cell origin was fixed in the central gold atom of the cluster (see description of the structure). The positions of iodine and phosphorus atoms were found from a difference-Fourier map. Preliminary least-squares refinement of the $Au_{11}I_3P_7$ moiety led to R 0·09. The seven independent p-FC_6 groups, treated as planar rigid bodies of known geometry, were subsequently located by means of a trial-and-error procedure previously described.[7] The complete refinement was carried out by full-matrix least-squares, the minimized function 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 stages of refinement, A was 40·0, B −0·13, and C 7×10^{-4}, in order to obtain a reasonably constant distribution of the weighted mean quadratic error as a function of $\sin\theta/\lambda$ and F_o. The gold, iodine, and phosphorus atoms were assigned with anisotropic thermal factors, and the fluorine atoms with isotropic ones. A mean overall isotropic factor was assigned to each of the seven C_6 groups, treated as rigid bodies of D_{6h} symmetry, with C–C distances of 1·392 Å. The space-group being polar, two enantiomorphous models were refined (see the packing description). For both models complete convergence was observed after four cycles, none of the parameter shifts being $> 0{\cdot}3\sigma$. The final reliability indices were: for model (1) (see later, Figure 2) R 0·034, $R' = \{\Sigma w(F_o - k|F_c|)^2/\Sigma wF_o^2\}^{1/2}$ 0·041; for the enantiomorphous model (2) R 0·037 and R' 0·044. The absolute configuration of the crystal structure corresponds to

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

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

[7] V. G. Albano, P. L. Bellon, F. Pompa, and V. Scatturin, *Ist. Lombardo Rend. Sci.*, 1966, *A*, **100**, 337.

TABLE 3

Positional parameters ($\times 10^4$) of group atoms *

	x	y	z
C(21)	−3803(19)	−3613(17)	−2600(18)
C(22)	−3958(20)	−3058(12)	−1848(17)
C(23)	−4669(16)	−3535(16)	−1606(15)
C(24)	−5228(19)	−4567(17)	−2114(18)
C(25)	−5072(20)	−5122(12)	−2867(17)
C(26)	−4360(16)	−4645(16)	−3110(15)
C(311)	−2209(21)	1491(19)	−2434(18)
C(312)	−1699(19)	1172(18)	−2921(19)
C(313)	−1544(18)	1502(18)	−3595(18)
C(314)	−1901(21)	2151(19)	−3780(18)
C(315)	−2410(19)	2467(18)	−3293(19)
C(316)	−2565(18)	2137(18)	−2620(18)
C(321)	−2564(19)	1889(18)	−753(16)
C(322)	−1681(15)	2595(20)	107(18)
C(323)	−1680(14)	3359(15)	832(14)
C(324)	−2563(19)	3420(18)	695(16)
C(325)	−3443(15)	2714(20)	−165(18)
C(326)	−3444(14)	1949(15)	−890(14)
C(331)	−3745(14)	−51(20)	−2390(17)
C(332)	−4068(15)	−680(19)	−1999(14)
C(333)	−5052(18)	−1419(17)	−2496(17)
C(334)	−5712(14)	−1529(20)	−3384(17)
C(335)	−5389(15)	−898(19)	−3777(14)
C(336)	−4405(18)	−161(17)	−3280(17)
C(511)	1083(17)	4137(17)	2531(15)
C(512)	394(15)	3457(12)	2649(15)
C(513)	216(16)	3777(15)	3465(17)
C(514)	728(17)	4779(17)	4161(15)
C(515)	1418(15)	5459(12)	4040(15)
C(516)	1596(16)	5137(15)	3227(17)
C(521)	755(29)	4043(24)	599(17)
C(522)	464(19)	4783(18)	835(14)
C(523)	43(25)	5039(21)	111(19)
C(524)	−87(29)	4553(24)	−847(17)
C(525)	203(19)	3812(18)	−1082(14)
C(526)	625(25)	3556(21)	−360(19)
C(531)	2635(11)	4412(16)	1944(16)
C(532)	3258(15)	4096(13)	2438(17)
C(533)	4286(14)	4658(16)	2872(16)
C(534)	4691(11)	5534(16)	2814(16)
C(535)	4068(15)	5849(13)	2319(17)
C(536)	3040(14)	5289(16)	1885(16)

* Atom C(*ijk*) belongs to ring *j*, bonded to P(*i*); C(*ij*1) is bonded to P(*i*), and C(*ij*4) is in *para* to it; *j* is redundant for the single independent phenyl ring bonded to P(2).

model (1) at a statistical level of confidence higher than 99·5%.[8] The atomic scattering factors used in the least-squares and structure-factor computations were taken from ref. 9, and real and imaginary contributions to the anomalous scattering for gold, iodine, and phosphorus from ref. 10. A final difference-Fourier map, computed on the basis of model (1), had no signals exceeding 0·5 eÅ^{-3}. Table 1 reports the position and thermal co-ordinates of the independent atoms, Table 2 the rigid group parameters of the C_6 groups, and Table 3 the derived parameters of all carbon atoms. The final list of computed and observed structure-factor moduli for the rhombohedral cell is listed in Supplementary Publication No. SUP 20378 (2 pp., 1 microfiche).*

Computations.—All computations were carried out on a UNIVAC 1108 computer. For absorption correction a local programme was used, in which the directions of primary and diffracted beams are evaluated as recently described.[11] Counter data reduction, the trial-and-error procedure of ref. 7, and statistical analysis 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 in the 1966 ' International World List of Crystallographic Programs ' were used for Fourier analysis, structure-factor, and least-squares calculations; Johnson's ORTEP was used for thermal ellipsoid plotting, and a programme by Domenicano and Vaciago for computation of the molecular parameters.

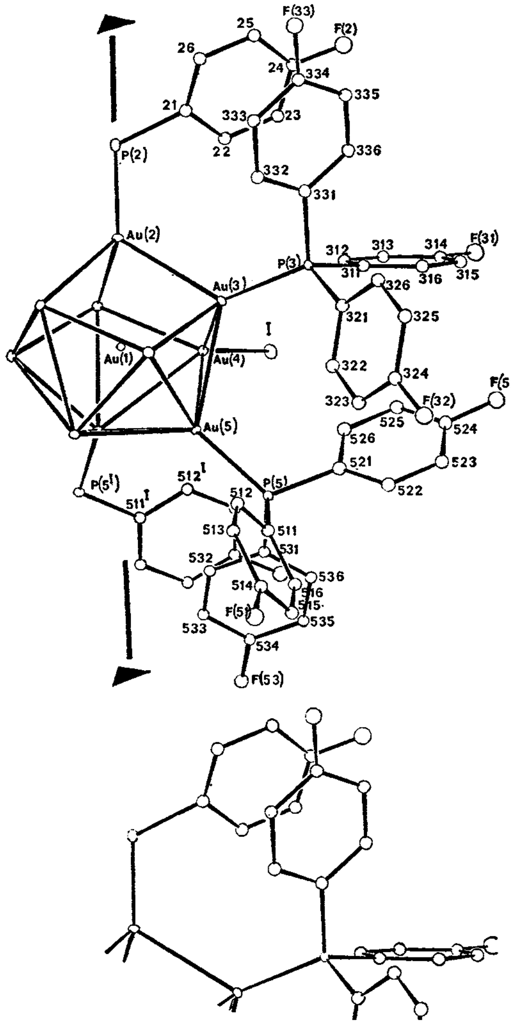

FIGURE 1 Stacking of molecules of $Au_{11}I_3[P(p\text{-}FC_6H_4)_3]_7$ along the three-fold axis. The symbols C for carbon atoms have been omitted for clarity

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

Overall Molecular Configuration and Packing.—The crystal consists of monomeric molecules $Au_{11}I_3[P(p\text{-}FC_6H_4)_3]_7$. An inspection of all non-bonding interactions within each molecule and between different molecules does not reveal unusually short contacts. The molecule possesses three-fold symmetry. Figure 1 shows the labelling scheme used.

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[8] W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502.

[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.

The planes of rings C(21)—(26) and C(331)—(336) are nearly parallel (Figure 1); the mean interplanar separation is 3·6 Å. Two more rings, C(531)—(536) and $C(511^{I})$—(516^{I}), behave in the same way, so that the molecule possesses six such pairs. These are further examples of the *quasi*-graphitic interactions between phenyl rings which we have reported in a number of complexes of triphenylphosphine (see ref. 12 and refs. therein). The molecular packing deserves a somewhat detailed description, in view of the fact that the present species is the first example of an ordered structure for these kinds of cluster compounds; such description will be referred to the hexagonal cell. The molecules stack along equivalent three-fold axes, at a repeat distance of *c*. In Figure 2, a projection down *c*, three such stacks are shown, which are shifted by *c*/3 with respect to one another. The fact that the present compound possesses very nearly the same *a* axis as compound (II) [25·90(2) *vs*. 25·40(2) Å], whereas the *c* axes are widely different [16·79(2) *vs*. 79·65(8) Å], implies that in both compounds the phosphine ligands possess essentially the same configuration in the radial direction, whereas the manner in which the molecules stack along *c* is different. This stacking involves, among others, the rings bonded to atom P(2), which are disordered in compound (II).[3] In the present structure, the head-to-tail sequence along the three-fold axis is determined by contacts between the *quasi*-graphitic ring pairs mentioned earlier; the interaction is shown in the lower part of Figure 1. The two independent pairs of rings are almost parallel; Figure 3 is a projection of the four $P(p\text{-}FC_6)$ moieties (two pairs, belonging to contacting molecules) on the plane of ring C(21)—(26). The two molecules come into contact through rings C(21)—(26) and C(531)—(536), whose planes are 3·2 Å apart. Atom F(53) of one molecule is almost exactly beneath atom C(24) of the other molecule (Figure 3). The $C\cdots F$ distance of 3·2 Å is exactly the sum of half the thickness of an aromatic ring, 1·85 Å, plus the van der Waals radius of fluorine, 1·35 Å.[13] It is probably impossible to attain this four-ring stacking when fluorine is substituted by chlorine, as occurs in compound (II), and this may be the reason why, in the latter, a disordered packing becomes stable.

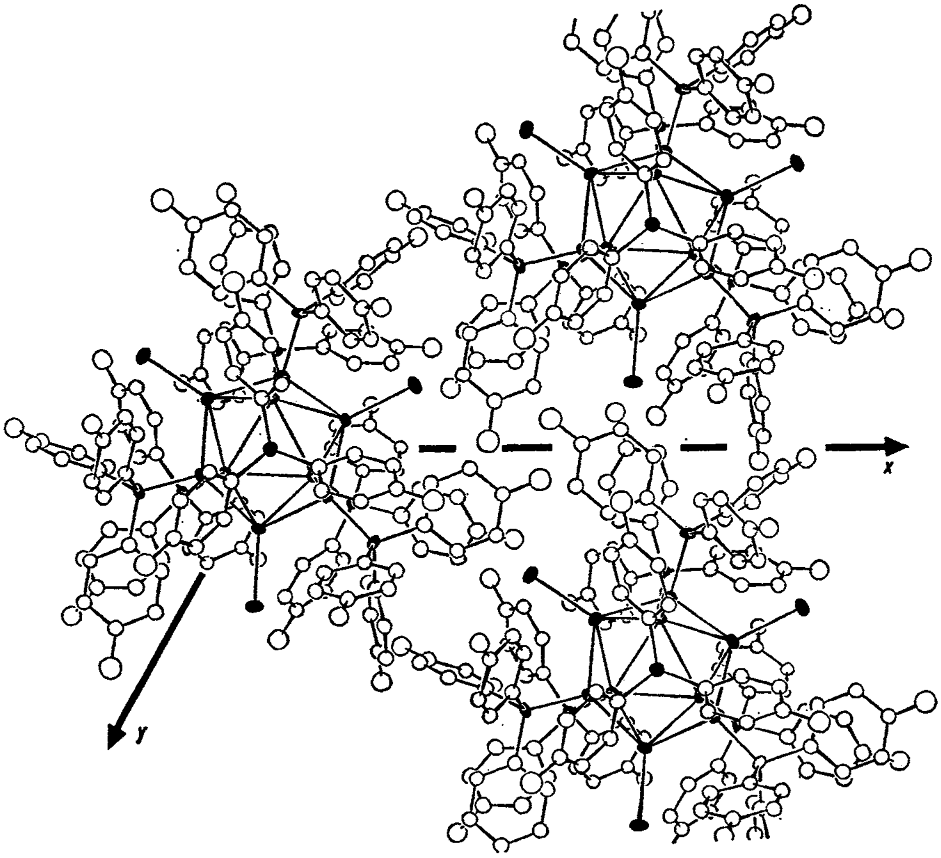

FIGURE 2 Absolute configuration of the crystal structure of $Au_{11}I_3[P(p\text{-}FC_6H_4)_3]_7$. The *x* and *y* axes have the same directions as the *a* and *b* axes of the hexagonal cell; *c* points downwards

The Metal Atom Cluster.—The whole cluster, an incomplete icosahedron in which one triangular face has been substituted by a single gold atom Au(2), possesses C_3 symmetry (ideally, C_{3v}); two views of it are shown in

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[12] V. G. Albano, P. L. Bellon, and M. Sansoni, *J. Chem. Soc.* (*A*), 1971, 2420.

[13] L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithaca, New York, 1960.

Figure 4. The eleven metal atoms fall into five non-equivalent classes exhibiting different co-ordination patterns as well as different co-ordination numbers: the central atom Au(1), which lies on the three-fold axis, is ten-co-ordinate, the apical atom Au(2), also on the three-fold axis, is five-co-ordinate, three Au(3) and three Au(4) atoms, which form an equatorial chair-like hexagon, are six-co-ordinate, and, finally, the three basal Au(5) atoms are seven-co-ordinate. The co-ordination polyhedron of the inner atom is bordered by ten triangular faces, and by three irregularly shaped squares sharing an apex in Au(2). Au(1) Is the first example of a metal atom whose co-ordination sphere is occupied exclusively by other metal atoms, in a discrete molecular compound. As mentioned in the introduction, it represents a novel peculiar species in the chemistry of co-ordination compounds; its high co-ordination number and its radius, smaller than that of the peripheral atoms, suggest to us that it be regarded as a different metallic species in the host icosahedral cage Au_{10}. Owing to the presence of two chemically different gold atom species, and to the fact that the icosahedron is a very common feature in intermetallic compounds, the whole Au_{11} unit can be referred to as an intermetallic cluster.

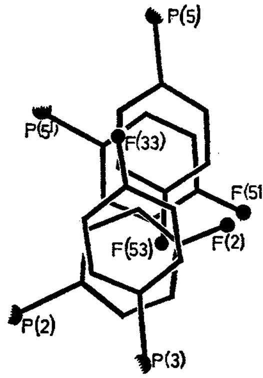

FIGURE 3 Stacking of two graphitic couples of phenyl rings, belonging to two different molecules

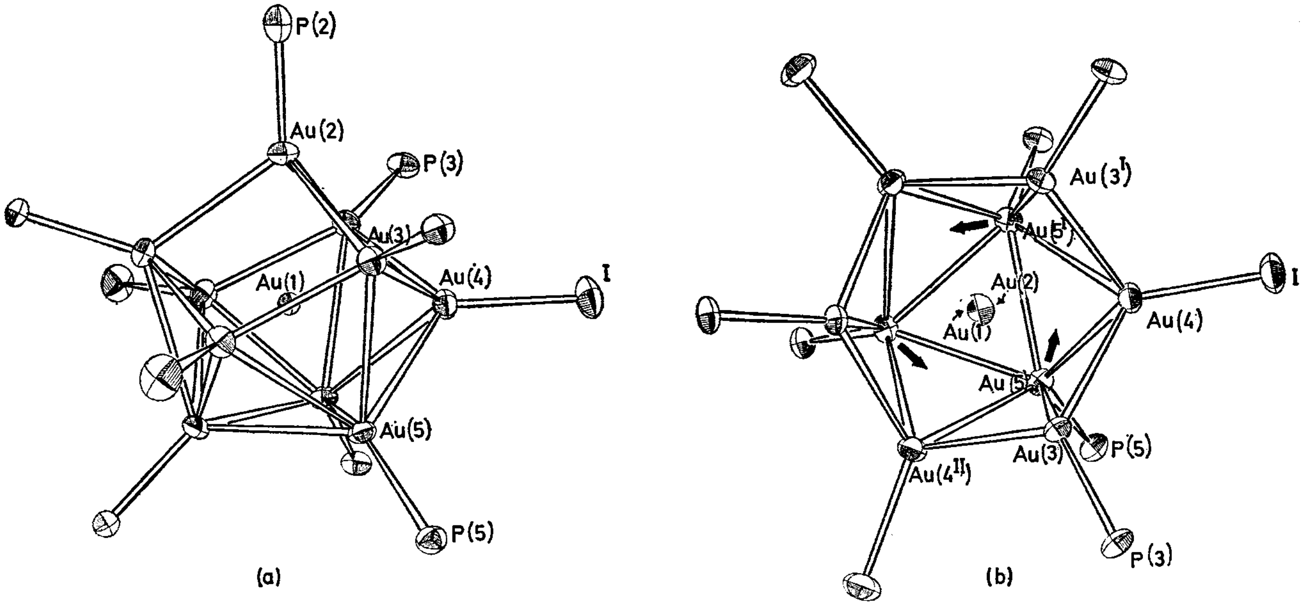

FIGURE 4 Two perspective views of the $Au_{11}I_3P_7$ moiety. The arrows in (*b*) show the displacement of the three basal Au(5) atoms from the positions which would be required by a C_{3v} symmetry

The mean of the ten centre-to-periphery Au–Au distances in the present structure is 2·68 Å, the same as in compound (II), and very nearly the same as in (I) (2·67 Å).[2] The nearest-neighbour distances on the surface of the cluster are rather scattered (2·84—3·19 Å); their mean value (2·98 Å) indicates the bonding character of the peripheral interactions. The centre-to-periphery and the peripheral mean distances are to be compared with the Au–Au distance of 2·884 Å in the metal.[14]

We have tentatively explained the smaller radius of Au(1) by assigning it the total oxidation number of the cluster (+3). This interpretation works well from the point of view of the effective atomic number of that atom, because it needs ten one-electron donors Au^0 to achieve the noble-gas configuration. This model was an alternative to that suggested by Mason *et al.* in their discussion of the structure of compound (I); the central atom is formally Au^0, and achieves the radon configuration through one-electron donation from seven $Au(PR_3)$ ligands.[2] However, the existence of a series of salts of the cations $Au_9(PR_3)_8{}^{3+}$, whose preparation and structures have been recently reported,[15] shows that there exists no simple rule governing the stoicheiometry of these compounds, based upon the effective atomic number of the inner atom. Au_9 Clusters possess a

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[14] W. B. Pearson, ' Lattice Spacings and Structures of Metals and Alloys,' Pergamon Press, London, 1957.

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

central gold atom which is bonded to eight Au(PR$_3$) units; these lie, once again, at the apices of an incomplete icosahedron. In the case of one-electron donation from peripheral Au^0 atoms only, the central atom in these cations achieves an effective atomic number of 84, either whether it is assigned with the oxidation number 0 or +3. So, before an electronic rule for these complexes can be established, further preparative and structural work seems to be needed.

Factors of stability of gold ' intermetallic ' clusters seem to be a set of molecular orbitals of nearly icosahedral symmetry, centred on the inner atom, and the bonding character of the peripheral interactions. The molecular complexity might depend to a large extent upon the crowding of phosphine ligands around the metal cluster; the role of this factor is clear if one considers that, when non-ligands anions are present instead of the ligand ones (*e.g.* PF_6^- instead of SCN^- or I^-), the cluster complexity goes from Au$_{11}$ to Au$_9$. If the steric repulsions between bulky ligands is limiting this complexity, then the possibility arises that a centred icosahedral unit Au$_{13}$ will be prepared, provided that suitable ligands are found.

In view of the role that peripheral Au–Au interactions may play in stabilizing the cluster, the wide dispersion of the length of the polyhedron edges (see Table 4) needs some discussion. The deformation which is responsible for such a spread is the lack in the icosahedron of one basal triangle. The triangle is substituted by the sole Au(2) atom, which is bonded to the three Au(3) atoms of the chair-like equatorial hexagon [Au(2)–Au(3) 2·942 Å]. As a result of these bonding interactions, the hexagon is raised as a whole with respect to Au(1), which lies approximately at the same level as atoms Au(4); the distances of the central atom from the planes defined by Au(3) and Au(4) atoms are 1·05 and 0·15 Å, respectively. Consequently, six out of the nine edges connecting the basal triangle [Au(5) atoms] to the equatorial atoms are lengthened with respect to all peripheral interactions.

A further deformation is the departure of the cluster from the C_{3v} symmetry, which is caused by the slight rotation of the basal triangle from its ideal position [see arrows in Figure 4 (b)]; this might happen either in order to minimize the length of three Au(4)–Au(5) edges, which become 2·873(2) Å long, or as a result of non-bonding interactions such as those which have been shown in the discussion of the molecular packing.

Metal–Ligand Interactions and the Ligands.—Each peripheral gold atom is bonded to one ligand; there are three equivalent Au–I and seven Au–P interactions, the latter divided into three different classes. All the Au(1)–Au(*i*)–L moieties are essentially linear, although their slight bending is statistically significant (see Table 4).

The Au–I bond length of 2·600(5) Å is the same as in the polymeric AuI.[16] A survey of the literature has not revealed the existence of further experimental Au–I bond lengths, apart from one which quotes an anomalously long bond of 3·35 Å.[17] The present value agrees with a number of Ir–I and Rh–I bond lengths (see ref. 18 and refs. therein).

TABLE 4

Selected intramolecular distances and angles *

(*a*) Distances (Å)

Au(1)–Au(2)	2·600(2)	P(2)–C(21)	1·85(3)
Au(1)–Au(3)	2·680(3)	P(3)–C(311)	1·80(3)
Au(1)–Au(4)	2·718(3)	P(3)–C(321)	1·81(3)
Au(1)–Au(5)	2·671(2)	P(3)–C(331)	1·82(2)
Au(2)–Au(3)	2·942(4)	P(5)–C(511)	1·80(3)
Au(3)–Au(4)	2·876(4)	P(5)–C(521)	1·80(3)
Au(3)–Au(4^{II})	2·836(4)	P(5)–C(531)	1·82(2)
Au(3)–Au(5)	3·145(2)	F(2)–C(24)	1·30(5)
Au(4)–Au(5)	2·873(3)	F(31)–C(314)	1·33(5)
Au(4)–Au(5^{I})	3·187(3)	F(32)–C(324)	1·35(4)
Au(5)–Au(5^{I})	3·011(4)	F(33)–C(334)	1·31(3)
Au(2)–P(2)	2·211(10)	F(51)–C(514)	1·36(4)
Au(3)–P(3)	2·283(12)	F(52)–C(524)	1·36(5)
Au(4)–I	2·600(5)	F(53)–C(534)	1·33(3)
Au(5)–P(5)	2·295(10)		

(*b*) Angles (°)

Au(2)–Au(1)–Au(3)	67·7(1)	Au(4)–Au(5^{I})–Au(5)	55·2(1)
Au(2)–Au(1)–Au(4)	93·3(1)	Au(5)–Au(5^{I})–Au(5^{II})	60
Au(3)–Au(1)–Au(4)	64·4(1)	Au(1)–Au(2)–P(2)	180
Au(3)–Au(1)–Au(4^{II})	63·4(1)	Au(1)–Au(3)–P(3)	176·3(3)
Au(3)–Au(1)–Au(5)	72·0(1)	Au(1)–Au(4)–I	174·5(1)
Au(4)–Au(1)–Au(5)	64·4(1)	Au(1)–Au(5)–P(5)	174·2(3)
Au(4)–Au(1)–Au(5^{I})	72·5(1)	Au(2)–P(2)–C(21)	115(1)
Au(5)–Au(1)–Au(5^{I})	68·6(1)	Au(3)–P(3)–C(311)	113(1)
Au(3)–Au(2)–Au(3^{I})	93·8(1)	Au(3)–P(3)–C(321)	114(1)
Au(2)–Au(3)–Au(4)	83·3(1)	Au(3)–P(3)–C(331)	115(1)
Au(2)–Au(3)–Au(4^{II})	84·1(1)	Au(5)–P(5)–C(511)	112(1)
Au(3)–Au(4)–Au(3^{I})	97·5(1)	Au(5)–P(5)–C(521)	114(1)
Au(3)–Au(4)–Au(5)	66·3(1)	Au(5)–P(5)–C(531)	115(1)
Au(3)–Au(5)–Au(4)	56·9(1)	P(2)–C(21)–C(24)	174(2)
Au(4)–Au(3)–Au(5)	56·8(1)	P(3)–C(311)–C(314)	174(1)
Au(3)–Au(4^{II})–Au(5)	62·6(1)	P(3)–C(321)–C(324)	176(2)
Au(3)–Au(5)–Au(4^{II})	53·2(1)	P(3)–C(331)–C(334)	176(2)
Au(4^{II})–Au(3)–Au(5)	64·1(1)	P(5)–C(511)–C(514)	177(2)
Au(4)–Au(5)–Au(5^{I})	65·5(1)	P(5)–C(521)–C(524)	177(2)
Au(5)–Au(4)–Au(5^{I})	59·3(1)	P(5)–C(531)–C(534)	179(2)

* Superior roman numerals indicate atoms belong to the asymmetric units: I *y*, *z*, *x*, and II *z*, *x*, *y*.

The Au(2)–P(2) distance is shorter than the corresponding ones involving Au(3) and Au(5) [2·21(1) *vs.* 2·29(1) Å]. The lower value reflects the smaller coordination number of Au(2) with respect to all the other metal atoms in the cluster; Au(2) also exhibits the shortest centre-to-periphery interaction. These Au–P bond lengths compare well with 2·27(1) Å found in Au(CN)(PPh$_3$),[19] and with 2·25(1) Å in W(π-C$_5$H$_5$)(CO)$_3$Au(PPh$_3$).[20] The phosphine ligand bonded to Au(2) possesses C_3 symmetry, P(2) being on a special position. Two crystal structures of species containing phosphine ligands lying on three-fold axes have been reported by us;[3,21] in both cases, in fact, the PPh$_3$ group was disordered. In the present structure no

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evidences of disorder have been noticed during the refinement (*i.e.* anomalously high thermal factors) nor in the final difference-Fourier map. A comparison of the bonding parameters within the three crystallographically independent phosphine ligands shows that the former is not peculiar in any respect (see Table 4).

All the phenyl rings of the molecule are linearly bonded to the P atoms, the deviations of $P(i)-C(ij1)-C(ij4)$ angles from 180° being practically insignificant. The mean P–C bond length is 1·82 Å, and all individual distances agree with this value within 1σ. The same is true for the seven independent C–F interactions, the mean of which (1·33 Å) is identical with the value found for fluorinated aromatic hydrocarbons.[22] The C–F distances found here are the results of a refinement in which the fluorine atoms have been treated as individual atoms, whereas the carbon atoms have been constrained into rigid bodies of assumed geometry. Therefore, the normal distribution of these distances around the expected mean may be taken as a further indication that the constraint imposed on the phenyl rings (D_{6h} symmetry, C–C 1·392 Å) is fully adequate from a statistical point of view.

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Reactions of Tin Halides with $\{(\pi\text{-Dienyl})Fe(CO)_2\}_2$ Compounds

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The products of the reactions of $\{(\pi\text{-dienyl})Fe(CO)_2\}_2$ with SnX_2 (dienyl = C_5H_5, MeC_5H_4, or C_9H_7; X = F, Cl, Br, or I) may be $\{(\pi\text{-dienyl})Fe(CO)_2X\}$, $\{(\pi\text{-dienyl})Fe(CO)_2SnX_3\}$, $\{(\pi\text{-dienyl})Fe(CO)_2\}_2SnX_2$, or $\{(\pi\text{-dienyl})Fe(CO)_2\}_3SnX$ depending on X, the reaction conditions, and the mole ratio of reactants. It is suggested that when X = F or Cl, the insertion of SnX_2 into the Fe–Fe bonds takes place largely in one step giving the $\{(\pi\text{-dienyl})Fe(CO)_2\}_2SnX_2$ derivatives. However, when X = Br or I, the dimers are first converted to a mixture of $\{(\pi\text{-dienyl})Fe(CO)_2X\}$ and $\{(\pi\text{-dienyl})Fe(CO)_2SnX_3\}$. The second of these reacts further with excess dimer to give the ' insertion ' products. The reactions of $\{(\pi\text{-dienyl})'Fe(CO)_2\}_2$ with $\{(\pi\text{-dienyl})Fe(CO)_2SnX_3\}$ or $\{(\pi\text{-dienyl})Fe(CO)_2\}_2SnX_2$ may be used to prepare $\{(\pi\text{-dienyl})Fe(CO)_2\}\{(\pi\text{-dienyl})'Fe(CO)_2\}SnX_2$ and $\{(\pi\text{-dienyl})Fe(CO)_2\}_2\{(\pi\text{-dienyl})'Fe(CO)_2\}SnX$ respectively. The tin(IV) halides, with the exception of the fluoride, react readily with the dimers to give a similar variety of products.

THE oxidative addition of a wide variety of mono- and poly-nuclear metal carbonyl complexes to tin(II) halides provides a useful synthetic route to compounds containing tin(IV)–transition metal bonds.[1] Of particular interest are the reactions of $\{(\pi\text{-dienyl})Fe(CO)_2\}_2$ with SnX_2 (dienyl = C_5H_5; X = Cl, Br, or I) in refluxing methanol or tetrahydrofuran which have been reported to give $\{(\pi\text{-dienyl})Fe(CO)_2\}_2SnX_2$ derivatives as the sole products.[2,3] Kinetic studies of the reactions where X = Cl and Br have been described.[4]

Thus these reactions appeared to be straightforward, but we now report that this is not the case. They give $\{(\pi\text{-dienyl})Fe(CO)_2X\}$, $\{(\pi\text{-dienyl})Fe(CO)_2SnX_3\}$, $\{(\pi\text{-dienyl})Fe(CO)_2\}_2SnX_2$, or $\{(\pi\text{-dienyl})Fe(CO)_2\}_3SnX$ {dienyl = C_5H_5, MeC_5H_4, or C_9H_7 (indenyl); X = F, Cl, Br, or I} depending on the reaction conditions, the mole ratio of reactants, and the halogen X. Although the (π-dienyl) ligand does not influence the course of the reactions, it does affect their rates.

These are the first such reactions of tin(II) fluoride which have been reported. Many of the other compounds are new, particularly the $\{(\pi\text{-dienyl})Fe(CO)_2\}_3SnX$ derivatives of which the only other example is $\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_3SnPh$,[5] and the mixed $\{(\pi\text{-dienyl})Fe(CO)_2\}\{(\pi\text{-dienyl})'Fe(CO)_2\}SnX_2$ and $\{(\pi\text{-dienyl})Fe(CO)_2\}_2\{(\pi\text{-dienyl})'Fe(CO)_2\}SnCl$ complexes which have no precedent and which would probably be difficult to prepare by other methods.

The tin(IV) halides, except the fluoride which is inert, react readily with $\{(\pi\text{-dienyl})Fe(CO)_2\}_2$ to give a mixture of $\{(\pi\text{-dienyl})Fe(CO)_2X\}$ and $\{(\pi\text{-dienyl})Fe(CO)_2SnX_3\}$ complexes as has previously been shown for $\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2$ and SnX_4 (X = Cl, Br, or I).[6] However, when more strenuous conditions and an excess of the dimer is used, the $\{(\pi\text{-dienyl})Fe(CO)_2\}_2SnX_2$ and $\{(\pi\text{-dienyl})Fe(CO)_2\}_3SnCl$ derivatives are obtained.

EXPERIMENTAL

All chemicals were purchased except for $\{(\pi\text{-}C_9H_7)Fe(CO)_2\}_2$ which was prepared by the method of Hallam and Pauson.[7]

The reactions were carried out under an atmosphere of nitrogen in methanol, butanol, 100—120° petrol, benzene, xylene, or tetrahydrofuran solution using *ca.* 0·002 mol of

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