Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Bis[μ_2-bis(diphenylphosphino)methane]-1:2κ^2P:P';2:3κ^2P:P'-dichlorido-1κCl,3κCl-*triangulo*-trigold(I) hexafluorophosphate

Edwin C. Constable, Catherine E. Housecroft,* Markus Neuburger, Silvia Schaffner and Ellen J. Shardlow

Department of Chemistry, University of Basel, Spitalstrasse 51, CH 4056 Basel, Switzerland
Correspondence e-mail: catherine.housecroft@unibas.ch

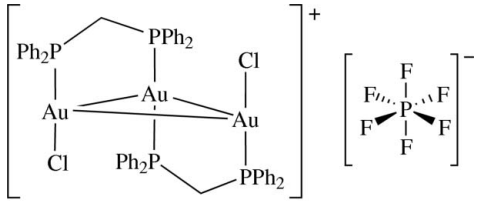
Received 16 May 2007; accepted 16 May 2007

Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.015 Å; disorder in main residue; R factor = 0.036; wR factor = 0.041; data-to-parameter ratio = 13.0.

In the title compound, $[Au_3Cl_2(C_{25}H_{22}P_2)_2](PF_6)$, the cation possesses a triangular Au_3 core [Au—Au distances 3.1525 (4), 3.2770 (4) and 3.1922 (4) Å], two sides of which are bridged by dppm ligands [dppm = bis(diphenylphosphino)methane]. One phenyl group is disordered over two positions in a 0.65:0.35 ratio. The structure of the cation is compared with those in three other salts reported previously.

Related literature

For related literature, see: Lin *et al.* (1994); Mendizabal *et al.* (2003); Pyykkö (2002, 2004); Shardlow (2007); Usón *et al.* (1983); Zhang *et al.* (2005).



Experimental

Crystal data

$[Au_3Cl_2(C_{25}H_{22}P_2)_2](PF_6)$
M_r = 1575.56
Triclinic, $P\overline{1}$
a = 9.6740 (1) Å
b = 15.4549 (2) Å
c = 18.9003 (3) Å
α = 105.9872 (8)°
β = 101.5928 (7)°
γ = 101.6696 (8)°
V = 2559.58 (6) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 8.89 mm^{-1}
T = 173 K
0.11 × 0.09 × 0.09 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997)
T_{min} = 0.38, T_{max} = 0.45
23737 measured reflections
12197 independent reflections
8452 reflections with $I > 3\sigma(I)$
R_{int} = 0.026

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.041
S = 1.11
8452 reflections
651 parameters
144 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 2.95 e Å^{-3}
$\Delta\rho_{min}$ = −4.06 e Å^{-3}

Table 1
Bond parameters (Å, °) for the trigold unit of (I) in different salts.

(I) is the $[Au_3Cl_2(C_{25}H_{22}P_2)_2]^+$ cation.

Compound	(I)(PF_6)	(I)[$AuCl(C_6F_5)_3$]	(I)Cl·EtOH	(I)(ClO_4)
Au1—Au2	3.1525 (4)	3.1645	3.076 (1)	3.0883 (8)
Au2—Au3	3.2770 (4)	3.0663	3.076 (1)	3.1738 (6)
Au1—Au3	3.1922 (4)	3.6784	3.729 (1)	3.4500 (8)
Au2—Au1—Au3	62.190 (9)	72.35	74.61 (3)	66.85 (2)
Au1—Au2—Au3	59.499 (9)	52.59	52.70 (2)	57.76 (1)
Au1—Au3—Au2	58.311 (9)	55.06	52.70 (2)	55.39 (1)
Reference	This work	Usón *et al.* (1983)	Lin *et al.* (1994)	Zhang *et al.* (2005)

Table 2
Hydrogen bonds (Å, °) in the title compound, involving PF_6^- anions.

Interaction	D—H	H···A	D···A	D—H···A
C10—H101···F4^{i}	0.96	2.43	3.22 (1)	140
C12—H121···F1^{ii}	0.96	2.42	3.35 (1)	162
C13—H131···F1^{ii}	0.96	2.47	3.38 (1)	159
C15—H151···F6^{ii}	0.96	2.38	3.29 (1)	157
C49—H491···F1^{iii}	0.96	2.56	3.28 (2)	132
C48—H481···F5^{iii}	0.96	2.67	3.42 (2)	136
C46—H461···F3	0.96	2.74	3.42 (2)	128
C46—H461···F5	0.96	2.68	3.45 (1)	137
C38—H382···F2	0.96	2.60	3.30 (1)	129
C31—H311···F2	0.96	2.40	3.26 (1)	149
C38—H382···F5	0.96	2.70	3.66 (1)	174
C33—H331···F4	0.96	2.68	3.46 (1)	135

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $x, 1+y, z$; (iii) $1-x, -y, -z$.

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *CRYSTALS*.

The authors thank the Swiss National Science Foundation and the University of Basel for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2371).

 © 2007 International Union of Crystallography doi:10.1107/S160053680702421X

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 291–294. Copenhagen: Munksgaard.

Lin, I. V. B., Hwang, J. M., Feng, D.-F., Cheng, M. C. & Wang, Y. (1994). *Inorg. Chem.* **33**, 3467–3472.

Mendizabal, F., Pyykkö, P. & Runeberg, N. (2003). *Chem. Phys. Lett.* **370**, 733–740.

Nonius (2001). *COLLECT*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Pyykkö, P. (2002). *Angew. Chem. Int. Ed.* **41**, 3573–3578.

Pyykkö, P. (2004). *Angew. Chem. Int. Ed.* **43**, 4412–4456.

Shardlow, E. J. (2007). PhD Thesis, University of Basel.

Usón, R., Laguna, A., Laguna, M., Fernandez, E., Villacampa, M. D., Jones, P. G. & Sheldrick, G. M. (1983). *J. Chem. Soc. Dalton Trans.* pp. 1679–1685.

Zhang, T.-L., Qin, Y. & Meng, X.-G. (2005). *Acta Cryst.* E**61**, m2588–m2589.

supplementary materials

Acta Cryst. (2007). E**63**, m1698-m1699 [**doi:10.1107/S160053680702421X**]

Bis[μ$_2$-bis(diphenylphosphino)methane]-1:2κ^2*P*:*P*';2:3κ^2*P*:*P*'-dichlorido-1κ*Cl*,3κ*Cl*-*triangulo*-trigold(I) hexafluorophosphate

E. C. Constable, C. E. Housecroft, M. Neuburger, S. Schaffner and E. J. Shardlow

Comment

The structure of [**I**]$^+$ has been determined in several salts (Usón *et al.*, 1983, Lin *et al.*, 1994; Zhang *et al.*, 2005) and exhibits a V-shaped cluster of gold(I) centres. The structure of the cation in [**I**][PF_6] is shown in Fig. 1; with the exception of the bond parameters for the Au_3 unit, bond distances and angles are similar to those previously reported. One phenyl ring (atoms C89—C94 and C39—C44) is disordered over two positions with 0.65 (3) and 0.35 (3) occupancies. The three gold atoms in [**I**][PF_6] form a near equilateral triangle with Au—Au—Au bond angles in the range 58.311 (9) to 62.190 (9)^o. The two shorter edges are bridged by dppm ligands, one above and one below the triangle. This ligand disposition and the orientation of the two chloro ligands resembles those observed for [**I**]$^+$ in the chloro (Lin *et al.*, 1994), the perchlorate (Zhang, *et al.*, 2005) and the chlorotris(pentafluorophenyl)gold(III) (Usón *et al.*, 1983) salts. The principal difference between the structures arises in the aurophilic interactions (Pyykkö, 2002; Pyykkö, 2004) in the trigold unit (Table 1). The atom numbering for all structures in Table 1 is as defined in Fig. 1. No e.s.d.'s are available for atom positions in [**I**][$AuCl(C_6F_5)_3$]. It has been reported that the strength of an aurophilic interaction is comparable to that of a typical hydrogen bond (Pyykkö, 2004), and the coexistence of gold···gold contacts and hydrogen-bonded interactions and their role in crystal engineering has been discussed (Mendizabal *et al.*, 2003). Hydrogen bonding involving $[PF_6]^-$ anions in [**I**][PF_6] is extensive (Fig. 2 and Table 2) and we conclude that the geometry of the Au_3 cluster in salts containing [**I**]$^+$ responds to the influence of the hydrogen-bonded interactions in the lattice.

Experimental

ClAu(μ-dppm)AuCl was prepared by a literature method (Lin *et al.*, 1994). Crystals of [**I**][PF_6] were obtained serendipidously from a crude reaction mixture (CH_2Cl_2) containing ClAu(μ-dppm)AuCl to which an excess of NH_4PF_6 had been added (Shardlow, 2007).

Refinement

All H atoms were treated as riding models, with C—H = 0.96 Å and U_{iso}(H) = 1.2U_{eq}(C). Restraints have been used to control the behaviour of the disordered phenyl ring and the PF_6. C—C and P—F distances have been restrained to their common means respectively. Moreover U-values of bonded atoms in these two structural fragments have been restrained to be similar.

Figures

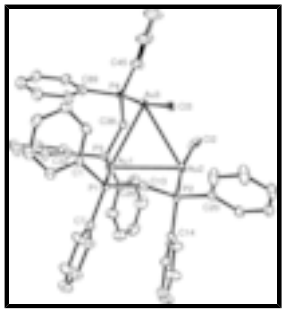


Fig. 1. The molecular structure of $[\mathbf{I}]^+$ in $[\mathbf{I}][PF_6]$ with displacement ellipsoids drawn at the 20% probability level. H atoms are omitted for clarity. One phenyl ring is disordered and only the major occupancies C89—C94 are shown.

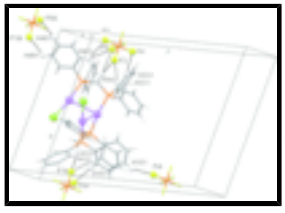


Fig. 2. Hydrogen-bonds in $[\mathbf{I}][PF_6]$ involving $[PF_6]^-$ anions. Symmetry codes: i = 1 − *x*, 1 − *y*, 1 − *z*; ii = *x*, 1 + *y*, *z*; iii = 1 − *x*, −*y*, −*z*.

Bis[μ$_2$-bis(diphenylphosphino)methane]- 1:2κ^2*P*:*P*';2:3κ^2*P*:*P*'- dichlorido-1κ*Cl*,3κ*Cl*-trigold(I) hexafluorophosphate

Crystal data

$[Au_3Cl_2(C_{25}H_{22}P_2)_2](PF_6)$	$Z = 2$
$M_r = 1575.56$	$F_{000} = 1488$
Triclinic, $P\overline{1}$	$D_x = 2.044$ Mg m^{-3}
Hall symbol: -P 1	Mo *K*α radiation λ = 0.71073 Å
a = 9.6740 (1) Å	Cell parameters from 12197 reflections
b = 15.4549 (2) Å	θ = 1–28º
c = 18.9003 (3) Å	μ = 8.89 mm^{-1}
α = 105.9872 (8)º	*T* = 173 K
β = 101.5928 (7)º	Plate, colourless
γ = 101.6696 (8)º	0.11 × 0.09 × 0.09 mm
V = 2559.58 (6) Å^3	

Data collection

Nonius KappaCCD diffractometer	8452 reflections with $I > 3\sigma(I)$
Monochromator: graphite	$R_{int} = 0.026$
T = 173 K	$\theta_{max} = 27.9$º
φ and ω scans	$\theta_{min} = 1.2$º
Absorption correction: multi-scan DENZO and SCALEPACK (Otwinowski & Minor, 1997)	*h* = −12→12
$T_{min} = 0.38$, $T_{max} = 0.45$	*k* = −20→20

23737 measured reflections	$l = -24 \rightarrow 24$
12197 independent reflections	

Refinement

Refinement on F	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.036$	Method, part 1, Chebychev polynomial, (Watkin, 1994, *P*rince, 1982) [*w*eight] = 1.0/[A_0*T_0(x) + A_1*T_1(x) ··· + A_{n-1}]*T_{n-1}(x)] where A_i are the Chebychev coefficients listed below and x = *F* /*F*max Method = Robust Weighting (*P*rince, 1982) W = [*w*eight] * [1-(delta*F*/6*sigma*F*)^2]^2 A_i are: 0.371 0.154 0.134 *P*rince, E. (1982). Mathematical Techniques in Crystallography and Materials Science. Ne*w* York: Springer-Verlag. Watkin, D. (1994). *Acta Cryst.* A**50**, 411–437.
$wR(F^2) = 0.041$	$(\Delta/\sigma)_{max} = 0.002$
$S = 1.11$	$\Delta\rho_{max} = 2.95$ e Å^{-3}
8452 reflections	$\Delta\rho_{min} = -4.06$ e Å^{-3}
651 parameters	Extinction correction: Larson (1970), Equation 22
144 restraints	Extinction coefficient: 25 (4)
Primary atom site location: structure-invariant direct methods	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Au1	0.53079 (3)	0.538005 (18)	0.269126 (16)	0.0384	
Au2	0.85524 (3)	0.612438 (19)	0.263223 (16)	0.0381	
Au3	0.60667 (3)	0.46319 (3)	0.110429 (16)	0.0481	
Cl2	0.9497 (2)	0.48182 (12)	0.24667 (14)	0.0622	
Cl3	0.67207 (17)	0.59597 (13)	0.07330 (9)	0.0404	
P1	0.47840 (18)	0.67473 (12)	0.26160 (10)	0.0343	
P2	0.80771 (18)	0.75229 (12)	0.28655 (10)	0.0345	
P3	0.54834 (19)	0.40221 (12)	0.29448 (10)	0.0345	
P4	0.5357 (2)	0.32487 (17)	0.12760 (11)	0.0492	
P5	0.6289 (3)	0.05910 (16)	0.26952 (18)	0.0699	
C1	0.3153 (7)	0.6553 (5)	0.1858 (4)	0.0389	
C2	0.3099 (9)	0.6066 (7)	0.1109 (5)	0.0567	
C3	0.1877 (10)	0.5902 (8)	0.0515 (5)	0.0658	
C4	0.0678 (9)	0.6204 (8)	0.0683 (6)	0.0633	
C5	0.0711 (11)	0.6654 (10)	0.1405 (7)	0.0874	
C6	0.1937 (10)	0.6830 (8)	0.2002 (6)	0.0708	
C7	0.4504 (8)	0.7439 (5)	0.3493 (4)	0.0423	
C8	0.4398 (14)	0.7087 (8)	0.4077 (6)	0.0763	
C9	0.4172 (17)	0.7641 (11)	0.4753 (7)	0.0966	
C10	0.4015 (14)	0.8493 (9)	0.4824 (6)	0.0813	

C11	0.4133 (10)	0.8847 (7)	0.4253 (5)	0.0635	
C12	0.4375 (9)	0.8335 (6)	0.3588 (4)	0.0482	
C13	0.6236 (7)	0.7503 (5)	0.2395 (4)	0.0362	
C14	0.8397 (8)	0.8099 (5)	0.3875 (4)	0.0394	
C15	0.8084 (8)	0.8944 (5)	0.4164 (5)	0.0474	
C16	0.8355 (9)	0.9362 (6)	0.4939 (5)	0.0586	
C17	0.8992 (15)	0.8984 (8)	0.5447 (6)	0.0783	
C18	0.930 (2)	0.8157 (10)	0.5176 (7)	0.1188	
C19	0.9010 (18)	0.7708 (8)	0.4398 (6)	0.0928	
C20	0.9235 (8)	0.8334 (5)	0.2544 (4)	0.0394	
C21	0.8744 (10)	0.8529 (9)	0.1886 (7)	0.0788	
C22	0.9696 (13)	0.9104 (10)	0.1641 (8)	0.0935	
C23	1.1131 (11)	0.9483 (7)	0.2048 (7)	0.0700	
C24	1.1642 (9)	0.9310 (6)	0.2719 (6)	0.0569	
C25	1.0690 (9)	0.8736 (6)	0.2964 (5)	0.0493	
C26	0.6729 (8)	0.4262 (5)	0.3875 (4)	0.0445	
C27	0.6617 (13)	0.4984 (8)	0.4482 (5)	0.0743	
C28	0.7438 (16)	0.5169 (12)	0.5207 (6)	0.1015	
C29	0.8367 (15)	0.4635 (12)	0.5355 (6)	0.0980	
C30	0.8541 (14)	0.3944 (10)	0.4760 (7)	0.0902	
C31	0.7710 (11)	0.3747 (7)	0.4016 (5)	0.0657	
C32	0.3757 (8)	0.3331 (5)	0.2981 (4)	0.0377	
C33	0.3741 (9)	0.2537 (5)	0.3186 (5)	0.0482	
C34	0.2439 (11)	0.1979 (6)	0.3189 (6)	0.0586	
C35	0.1145 (10)	0.2204 (6)	0.3007 (6)	0.0607	
C36	0.1152 (10)	0.3006 (7)	0.2817 (6)	0.0645	
C37	0.2461 (9)	0.3584 (6)	0.2815 (5)	0.0533	
C38	0.6086 (8)	0.3223 (5)	0.2235 (4)	0.0405	
C45	0.5879 (11)	0.2338 (7)	0.0645 (5)	0.0639	
C46	0.6316 (12)	0.1662 (8)	0.0864 (6)	0.0724	
C47	0.6587 (16)	0.0918 (8)	0.0301 (9)	0.0979	
C48	0.6431 (18)	0.0947 (9)	−0.0425 (8)	0.0984	
C49	0.606 (2)	0.1659 (13)	−0.0636 (8)	0.1303	
C50	0.5781 (17)	0.2351 (10)	−0.0100 (6)	0.0999	
C39	0.344 (4)	0.255 (4)	0.102 (3)	0.0886	0.35 (3)
C40	0.299 (3)	0.165 (3)	0.107 (2)	0.0911	0.35 (3)
C41	0.149 (2)	0.117 (3)	0.085 (2)	0.0986	0.35 (3)
C42	0.045 (3)	0.162 (3)	0.061 (3)	0.1050	0.35 (3)
C43	0.090 (3)	0.252 (3)	0.057 (3)	0.1094	0.35 (3)
C44	0.240 (3)	0.298 (4)	0.076 (3)	0.1023	0.35 (3)
C89	0.3386 (16)	0.2954 (10)	0.1095 (10)	0.0497	0.65 (3)
C90	0.2670 (16)	0.2046 (11)	0.1045 (10)	0.0634	0.65 (3)
C91	0.1153 (16)	0.1797 (14)	0.0948 (11)	0.0816	0.65 (3)
C92	0.0366 (17)	0.2456 (14)	0.0896 (11)	0.0852	0.65 (3)
C93	0.1088 (13)	0.3366 (14)	0.0955 (9)	0.0733	0.65 (3)
C94	0.2601 (13)	0.3617 (13)	0.1047 (8)	0.0579	0.65 (3)
F1	0.5384 (9)	−0.0466 (4)	0.2460 (5)	0.1087	
F2	0.7181 (10)	0.1628 (4)	0.2882 (7)	0.1579	
F3	0.6891 (10)	0.0284 (6)	0.1969 (5)	0.1189	

F4	0.5492 (12)	0.0834 (7)	0.3351 (4)	0.1344	
F5	0.4984 (6)	0.0786 (4)	0.2162 (3)	0.0704	
F6	0.7605 (10)	0.0398 (6)	0.3212 (6)	0.1499	
H21	0.3915	0.5840	0.1005	0.0717*	
H31	0.1854	0.5587	−0.0004	0.0781*	
H41	−0.0182	0.6086	0.0276	0.0734*	
H51	−0.0123	0.6858	0.1510	0.0966*	
H61	0.1944	0.7148	0.2517	0.0782*	
H81	0.4473	0.6464	0.4026	0.1033*	
H91	0.4133	0.7400	0.5168	0.1262*	
H101	0.3823	0.8854	0.5277	0.0960*	
H111	0.4046	0.9468	0.4311	0.0695*	
H121	0.4454	0.8602	0.3191	0.0552*	
H131	0.6143	0.8130	0.2550	0.0470*	
H132	0.6105	0.7285	0.1852	0.0470*	
H151	0.7677	0.9235	0.3816	0.0551*	
H161	0.8085	0.9933	0.5123	0.0658*	
H171	0.9218	0.9300	0.5990	0.0930*	
H181	0.9746	0.7874	0.5524	0.1198*	
H191	0.9218	0.7120	0.4214	0.1026*	
H211	0.7735	0.8264	0.1595	0.1034*	
H221	0.9342	0.9237	0.1182	0.1285*	
H231	1.1790	0.9870	0.1869	0.0929*	
H241	1.2648	0.9585	0.3012	0.0704*	
H251	1.1041	0.8615	0.3429	0.0615*	
H271	0.5956	0.5350	0.4385	0.0862*	
H281	0.7372	0.5673	0.5617	0.1114*	
H291	0.8896	0.4742	0.5872	0.1084*	
H301	0.9237	0.3601	0.4862	0.1109*	
H311	0.7811	0.3259	0.3604	0.0810*	
H331	0.4640	0.2374	0.3325	0.0622*	
H341	0.2438	0.1422	0.3322	0.0754*	
H351	0.0245	0.1809	0.3010	0.0743*	
H361	0.0249	0.3167	0.2685	0.0813*	
H371	0.2466	0.4152	0.2700	0.0702*	
H381	0.7138	0.3406	0.2363	0.0511*	
H382	0.5750	0.2598	0.2243	0.0511*	
H401	0.3690	0.1357	0.1249	0.1098*	0.3500
H411	0.1188	0.0558	0.0867	0.1190*	0.3500
H421	−0.0570	0.1309	0.0480	0.1274*	0.3500
H431	0.0196	0.2815	0.0402	0.1340*	0.3500
H441	0.2707	0.3555	0.0685	0.1281*	0.3500
H901	0.3210	0.1603	0.1076	0.0703*	0.6500
H911	0.0659	0.1184	0.0918	0.0888*	0.6500
H921	−0.0671	0.2282	0.0816	0.0984*	0.6500
H931	0.0546	0.3811	0.0930	0.0949*	0.6500
H941	0.3090	0.4226	0.1073	0.0807*	0.6500
H461	0.6447	0.1671	0.1384	0.0874*	
H471	0.6869	0.0411	0.0435	0.1149*	

H481	0.6592	0.0444	−0.0801	0.1092*
H491	0.5998	0.1677	−0.1146	0.1489*
H501	0.5512	0.2859	−0.0238	0.1136*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Au1	0.04197 (14)	0.03611 (14)	0.04576 (15)	0.01282 (11)	0.01474 (11)	0.02356 (12)
Au2	0.03584 (14)	0.03875 (15)	0.04292 (15)	0.01733 (11)	0.00944 (11)	0.01406 (11)
Au3	0.04596 (16)	0.0768 (2)	0.03611 (15)	0.02721 (14)	0.01776 (12)	0.02902 (14)
Cl2	0.0510 (10)	0.0267 (8)	0.0873 (15)	0.0177 (7)	−0.0229 (10)	0.0101 (9)
Cl3	0.0341 (7)	0.0638 (11)	0.0259 (7)	0.0151 (7)	0.0100 (6)	0.0163 (7)
P1	0.0354 (8)	0.0359 (9)	0.0400 (9)	0.0127 (7)	0.0165 (7)	0.0189 (7)
P2	0.0349 (8)	0.0363 (9)	0.0409 (9)	0.0138 (7)	0.0151 (7)	0.0195 (7)
P3	0.0400 (9)	0.0353 (9)	0.0338 (8)	0.0126 (7)	0.0107 (7)	0.0178 (7)
P4	0.0406 (10)	0.0726 (14)	0.0350 (9)	0.0115 (9)	0.0119 (8)	0.0203 (9)
P5	0.0814 (16)	0.0422 (12)	0.0975 (19)	0.0271 (11)	0.0226 (14)	0.0346 (12)
C1	0.034 (3)	0.038 (4)	0.048 (4)	0.008 (3)	0.014 (3)	0.018 (3)
C2	0.049 (4)	0.085 (6)	0.045 (4)	0.036 (4)	0.017 (4)	0.021 (4)
C3	0.054 (5)	0.102 (8)	0.039 (4)	0.024 (5)	0.012 (4)	0.019 (5)
C4	0.036 (4)	0.086 (7)	0.061 (5)	0.016 (4)	−0.001 (4)	0.025 (5)
C5	0.047 (5)	0.115 (9)	0.080 (7)	0.032 (6)	0.012 (5)	−0.004 (7)
C6	0.042 (4)	0.089 (7)	0.065 (6)	0.022 (5)	0.011 (4)	−0.001 (5)
C7	0.042 (4)	0.043 (4)	0.045 (4)	0.009 (3)	0.020 (3)	0.015 (3)
C8	0.113 (9)	0.079 (7)	0.066 (6)	0.038 (6)	0.056 (6)	0.039 (5)
C9	0.137 (11)	0.115 (10)	0.063 (7)	0.035 (9)	0.063 (7)	0.043 (7)
C10	0.096 (8)	0.090 (8)	0.054 (6)	0.025 (7)	0.035 (6)	0.008 (6)
C11	0.055 (5)	0.068 (6)	0.050 (5)	0.013 (4)	0.015 (4)	−0.004 (4)
C12	0.051 (4)	0.047 (4)	0.039 (4)	0.011 (3)	0.012 (3)	0.005 (3)
C13	0.039 (3)	0.035 (3)	0.043 (4)	0.014 (3)	0.017 (3)	0.020 (3)
C14	0.044 (4)	0.039 (4)	0.045 (4)	0.016 (3)	0.021 (3)	0.020 (3)
C15	0.044 (4)	0.037 (4)	0.055 (5)	0.008 (3)	0.010 (3)	0.010 (3)
C16	0.051 (5)	0.045 (4)	0.065 (6)	0.006 (4)	0.020 (4)	−0.003 (4)
C17	0.122 (9)	0.068 (6)	0.047 (5)	0.021 (6)	0.041 (6)	0.014 (5)
C18	0.25 (2)	0.095 (9)	0.051 (6)	0.098 (11)	0.052 (9)	0.034 (6)
C19	0.180 (13)	0.080 (7)	0.043 (5)	0.079 (8)	0.032 (7)	0.027 (5)
C20	0.038 (3)	0.039 (4)	0.048 (4)	0.014 (3)	0.018 (3)	0.018 (3)
C21	0.049 (5)	0.119 (9)	0.088 (7)	0.011 (5)	0.017 (5)	0.076 (7)
C22	0.066 (6)	0.141 (11)	0.113 (9)	0.023 (7)	0.039 (6)	0.095 (9)
C23	0.059 (5)	0.074 (6)	0.099 (8)	0.012 (5)	0.046 (5)	0.050 (6)
C24	0.050 (4)	0.045 (4)	0.081 (6)	0.011 (4)	0.031 (4)	0.020 (4)
C25	0.048 (4)	0.048 (4)	0.058 (5)	0.017 (3)	0.021 (4)	0.019 (4)
C26	0.049 (4)	0.048 (4)	0.036 (4)	0.006 (3)	0.009 (3)	0.022 (3)
C27	0.089 (7)	0.088 (7)	0.039 (5)	0.026 (6)	0.009 (5)	0.015 (5)
C28	0.096 (9)	0.143 (12)	0.040 (5)	0.009 (9)	0.008 (6)	0.016 (7)
C29	0.088 (8)	0.144 (12)	0.040 (5)	−0.008 (8)	−0.006 (5)	0.041 (7)
C30	0.084 (8)	0.123 (10)	0.070 (7)	0.034 (7)	−0.003 (6)	0.053 (7)
C31	0.067 (6)	0.080 (6)	0.056 (5)	0.023 (5)	0.005 (4)	0.036 (5)

C32	0.047 (4)	0.030 (3)	0.040 (4)	0.009 (3)	0.016 (3)	0.016 (3)
C33	0.058 (5)	0.036 (4)	0.061 (5)	0.018 (3)	0.024 (4)	0.024 (3)
C34	0.080 (6)	0.037 (4)	0.072 (6)	0.016 (4)	0.032 (5)	0.028 (4)
C35	0.060 (5)	0.056 (5)	0.070 (6)	0.005 (4)	0.029 (4)	0.026 (4)
C36	0.048 (5)	0.063 (6)	0.092 (7)	0.019 (4)	0.025 (5)	0.034 (5)
C37	0.047 (4)	0.053 (5)	0.075 (6)	0.020 (4)	0.025 (4)	0.034 (4)
C38	0.042 (4)	0.045 (4)	0.040 (4)	0.015 (3)	0.014 (3)	0.019 (3)
C45	0.070 (6)	0.051 (5)	0.055 (5)	−0.007 (4)	0.028 (4)	0.002 (4)
C46	0.082 (7)	0.069 (6)	0.067 (6)	0.006 (5)	0.047 (5)	0.015 (5)
C47	0.121 (10)	0.050 (6)	0.116 (10)	−0.002 (6)	0.071 (9)	0.007 (6)
C48	0.141 (12)	0.061 (7)	0.073 (8)	0.003 (7)	0.054 (8)	−0.012 (6)
C49	0.204 (19)	0.107 (12)	0.061 (8)	0.023 (12)	0.049 (10)	0.002 (8)
C50	0.139 (12)	0.105 (10)	0.040 (5)	0.023 (8)	0.029 (6)	0.004 (6)
C39	0.048 (13)	0.15 (3)	0.086 (16)	0.002 (14)	0.012 (11)	0.094 (19)
C40	0.045 (12)	0.15 (3)	0.094 (16)	−0.002 (13)	0.012 (11)	0.085 (18)
C41	0.047 (11)	0.16 (3)	0.103 (17)	−0.001 (13)	0.017 (12)	0.082 (19)
C42	0.052 (12)	0.17 (3)	0.109 (18)	0.001 (13)	0.011 (12)	0.091 (19)
C43	0.058 (12)	0.17 (3)	0.114 (19)	0.004 (14)	0.005 (13)	0.10 (2)
C44	0.058 (12)	0.16 (3)	0.106 (18)	0.010 (14)	0.010 (13)	0.10 (2)
C89	0.039 (6)	0.082 (8)	0.037 (6)	0.016 (6)	0.009 (5)	0.034 (7)
C90	0.050 (7)	0.076 (9)	0.048 (7)	−0.002 (7)	0.004 (6)	0.016 (7)
C91	0.055 (8)	0.099 (11)	0.067 (9)	−0.011 (7)	0.012 (7)	0.016 (8)
C92	0.050 (8)	0.132 (13)	0.063 (8)	0.006 (7)	0.013 (7)	0.031 (9)
C93	0.049 (6)	0.132 (13)	0.055 (8)	0.035 (7)	0.013 (6)	0.051 (8)
C94	0.041 (6)	0.123 (11)	0.039 (6)	0.044 (7)	0.019 (5)	0.049 (7)
F1	0.137 (6)	0.053 (3)	0.144 (6)	0.016 (4)	0.046 (5)	0.047 (4)
F2	0.123 (6)	0.054 (4)	0.228 (10)	−0.007 (4)	−0.063 (6)	0.043 (5)
F3	0.121 (6)	0.136 (6)	0.161 (7)	0.074 (5)	0.087 (5)	0.081 (6)
F4	0.206 (9)	0.155 (7)	0.073 (4)	0.103 (7)	0.045 (5)	0.041 (5)
F5	0.076 (3)	0.065 (3)	0.079 (4)	0.023 (3)	0.025 (3)	0.032 (3)
F6	0.141 (7)	0.109 (6)	0.187 (8)	0.051 (5)	−0.030 (6)	0.071 (6)

Geometric parameters (Å, °)

Au1—Au2	3.1525 (4)	C21—H211	0.960
Au1—Au3	3.1922 (4)	C22—C23	1.363 (16)
Au1—P1	2.3047 (16)	C22—H221	0.959
Au1—P3	2.3083 (16)	C23—C24	1.382 (14)
Au2—Au3	3.2770 (4)	C23—H231	0.961
Au2—Cl2	2.3496 (17)	C24—C25	1.385 (11)
Au2—P2	2.2441 (17)	C24—H241	0.960
Au3—Cl3	2.3560 (18)	C25—H251	0.960
Au3—P4	2.241 (2)	C26—C27	1.403 (13)
P1—C1	1.815 (7)	C26—C31	1.387 (12)
P1—C7	1.812 (7)	C27—C28	1.357 (15)
P1—C13	1.831 (7)	C27—H271	0.959
P2—C13	1.814 (7)	C28—C29	1.38 (2)
P2—C14	1.802 (7)	C28—H281	0.960
P2—C20	1.823 (7)	C29—C30	1.39 (2)

P3—C26	1.814 (7)	C29—H291	0.960
P3—C32	1.817 (7)	C30—C31	1.387 (14)
P3—C38	1.832 (7)	C30—H301	0.960
P4—C38	1.822 (7)	C31—H311	0.960
P4—C45	1.806 (10)	C32—C33	1.382 (9)
P4—C39	1.84 (4)	C32—C37	1.390 (10)
P4—C89	1.806 (15)	C33—C34	1.378 (12)
P5—F1	1.579 (6)	C33—H331	0.960
P5—F2	1.563 (6)	C34—C35	1.369 (13)
P5—F3	1.588 (7)	C34—H341	0.960
P5—F4	1.586 (7)	C35—C36	1.381 (13)
P5—F5	1.584 (5)	C35—H351	0.960
P5—F6	1.574 (6)	C36—C37	1.396 (12)
C1—C2	1.393 (11)	C36—H361	0.960
C1—C6	1.382 (11)	C37—H371	0.960
C2—C3	1.383 (12)	C38—H381	0.960
C2—H21	0.959	C38—H382	0.960
C3—C4	1.395 (13)	C45—C46	1.338 (16)
C3—H31	0.960	C45—C50	1.398 (15)
C4—C5	1.342 (15)	C46—C47	1.443 (15)
C4—H41	0.960	C46—H461	0.960
C5—C6	1.383 (14)	C47—C48	1.36 (2)
C5—H51	0.960	C47—H471	0.960
C6—H61	0.960	C48—C49	1.36 (2)
C7—C8	1.372 (12)	C48—H481	0.960
C7—C12	1.380 (11)	C49—C50	1.37 (2)
C8—C9	1.414 (15)	C49—H491	0.961
C8—H81	0.960	C50—H501	0.960
C9—C10	1.329 (18)	C39—C40	1.403 (10)
C9—H91	0.961	C39—C44	1.402 (10)
C10—C11	1.350 (16)	C40—C41	1.401 (10)
C10—H101	0.960	C40—H401	0.944
C11—C12	1.381 (11)	C41—C42	1.401 (10)
C11—H111	0.959	C41—H411	0.946
C12—H121	0.960	C42—C43	1.401 (10)
C13—H131	0.960	C42—H421	0.958
C13—H132	0.960	C43—C44	1.403 (10)
C14—C15	1.389 (10)	C43—H431	0.946
C14—C19	1.390 (12)	C44—H441	0.937
C15—C16	1.374 (12)	C89—C90	1.401 (9)
C15—H151	0.959	C89—C94	1.404 (9)
C16—C17	1.363 (15)	C90—C91	1.400 (9)
C16—H161	0.964	C90—H901	0.949
C17—C18	1.356 (16)	C91—C92	1.402 (10)
C17—H171	0.965	C91—H911	0.951
C18—C19	1.383 (14)	C92—C93	1.400 (9)
C18—H181	0.964	C92—H921	0.953
C19—H191	0.957	C93—C94	1.399 (9)
C20—C21	1.373 (12)	C93—H931	0.951

C20—C25	1.387 (11)	C94—H941	0.948
C21—C22	1.386 (13)		
Au2—Au1—Au3	62.191 (9)	C14—C19—C18	120.5 (9)
Au2—Au1—P1	91.42 (4)	C14—C19—H191	119.2
Au3—Au1—P1	101.01 (4)	C18—C19—H191	120.3
Au2—Au1—P3	99.15 (4)	P2—C20—C21	122.8 (6)
Au3—Au1—P3	90.65 (4)	P2—C20—C25	118.3 (6)
P1—Au1—P3	167.01 (6)	C21—C20—C25	118.9 (7)
Au1—Au2—Au3	59.499 (9)	C20—C21—C22	120.4 (9)
Au1—Au2—Cl2	104.90 (6)	C20—C21—H211	119.8
Au3—Au2—Cl2	79.66 (5)	C22—C21—H211	119.8
Au1—Au2—P2	84.86 (4)	C21—C22—C23	120.4 (10)
Au3—Au2—P2	108.81 (5)	C21—C22—H221	119.8
Cl2—Au2—P2	169.64 (7)	C23—C22—H221	119.8
Au1—Au3—Au2	58.311 (9)	C22—C23—C24	120.1 (8)
Au1—Au3—Cl3	105.39 (4)	C22—C23—H231	120.0
Au2—Au3—Cl3	77.12 (4)	C24—C23—H231	119.9
Au1—Au3—P4	82.19 (5)	C23—C24—C25	119.4 (8)
Au2—Au3—P4	110.30 (5)	C23—C24—H241	120.3
Cl3—Au3—P4	171.67 (7)	C25—C24—H241	120.3
Au1—P1—C1	113.1 (2)	C20—C25—C24	120.7 (8)
Au1—P1—C7	112.9 (2)	C20—C25—H251	119.7
C1—P1—C7	106.5 (3)	C24—C25—H251	119.6
Au1—P1—C13	112.6 (2)	P3—C26—C27	116.6 (7)
C1—P1—C13	104.1 (3)	P3—C26—C31	123.8 (7)
C7—P1—C13	106.9 (3)	C27—C26—C31	119.5 (8)
Au2—P2—C13	115.4 (2)	C26—C27—C28	120.5 (11)
Au2—P2—C14	111.4 (2)	C26—C27—H271	119.8
C13—P2—C14	107.5 (3)	C28—C27—H271	119.7
Au2—P2—C20	113.2 (2)	C27—C28—C29	120.2 (13)
C13—P2—C20	103.1 (3)	C27—C28—H281	120.0
C14—P2—C20	105.5 (3)	C29—C28—H281	119.8
Au1—P3—C26	111.9 (3)	C28—C29—C30	120.2 (10)
Au1—P3—C32	113.3 (2)	C28—C29—H291	119.8
C26—P3—C32	104.4 (3)	C30—C29—H291	120.0
Au1—P3—C38	113.9 (2)	C29—C30—C31	120.1 (11)
C26—P3—C38	107.6 (4)	C29—C30—H301	119.9
C32—P3—C38	105.1 (3)	C31—C30—H301	119.9
Au3—P4—C38	115.6 (3)	C30—C31—C26	119.3 (10)
Au3—P4—C45	112.1 (3)	C30—C31—H311	120.4
C38—P4—C45	105.3 (4)	C26—C31—H311	120.3
Au3—P4—C39	124.8 (11)	P3—C32—C33	118.9 (6)
C38—P4—C39	102.2 (12)	P3—C32—C37	121.7 (5)
C45—P4—C39	93.3 (18)	C33—C32—C37	119.4 (7)
Au3—P4—C89	107.3 (5)	C32—C33—C34	120.2 (7)
C38—P4—C89	106.4 (6)	C32—C33—H331	119.9
C45—P4—C89	110.0 (6)	C34—C33—H331	119.9
F1—P5—F2	176.9 (6)	C33—C34—C35	121.1 (7)
F1—P5—F3	87.3 (5)	C33—C34—H341	119.5

F2—P5—F3	90.0 (7)	C35—C34—H341	119.4
F1—P5—F4	88.3 (5)	C34—C35—C36	119.2 (8)
F2—P5—F4	94.3 (7)	C34—C35—H351	120.4
F3—P5—F4	173.0 (6)	C36—C35—H351	120.4
F1—P5—F5	90.2 (4)	C35—C36—C37	120.6 (8)
F2—P5—F5	88.3 (4)	C35—C36—H361	119.8
F3—P5—F5	87.7 (4)	C37—C36—H361	119.7
F4—P5—F5	86.9 (4)	C36—C37—C32	119.4 (7)
F1—P5—F6	90.2 (5)	C36—C37—H371	120.3
F2—P5—F6	91.3 (5)	C32—C37—H371	120.3
F3—P5—F6	91.1 (6)	P3—C38—P4	111.3 (4)
F4—P5—F6	94.3 (6)	P3—C38—H381	109.0
F5—P5—F6	178.8 (6)	P4—C38—H381	109.0
P1—C1—C2	118.7 (5)	P3—C38—H382	109.0
P1—C1—C6	122.4 (6)	P4—C38—H382	109.0
C2—C1—C6	118.8 (7)	H381—C38—H382	109.5
C1—C2—C3	120.6 (7)	P4—C45—C46	122.4 (7)
C1—C2—H21	119.7	P4—C45—C50	117.2 (10)
C3—C2—H21	119.7	C46—C45—C50	120.4 (10)
C2—C3—C4	118.7 (8)	C45—C46—C47	118.4 (11)
C2—C3—H31	120.6	C45—C46—H461	120.8
C4—C3—H31	120.7	C47—C46—H461	120.8
C3—C4—C5	120.9 (8)	C46—C47—C48	118.8 (13)
C3—C4—H41	119.5	C46—C47—H471	120.6
C5—C4—H41	119.6	C48—C47—H471	120.6
C4—C5—C6	120.6 (9)	C47—C48—C49	122.7 (11)
C4—C5—H51	119.7	C47—C48—H481	118.6
C6—C5—H51	119.6	C49—C48—H481	118.7
C5—C6—C1	120.2 (9)	C48—C49—C50	117.8 (13)
C5—C6—H61	119.9	C48—C49—H491	121.1
C1—C6—H61	119.8	C50—C49—H491	121.1
P1—C7—C8	121.1 (7)	C45—C50—C49	121.8 (15)
P1—C7—C12	120.8 (6)	C45—C50—H501	119.1
C8—C7—C12	118.0 (8)	C49—C50—H501	119.1
C7—C8—C9	119.9 (10)	P4—C39—C40	125 (2)
C7—C8—H81	120.0	P4—C39—C44	114 (2)
C9—C8—H81	120.1	C40—C39—C44	120 (3)
C8—C9—C10	120.9 (10)	C39—C40—C41	120 (3)
C8—C9—H91	119.6	C39—C40—H401	120.0
C10—C9—H91	119.5	C41—C40—H401	119.6
C9—C10—C11	119.4 (9)	C40—C41—C42	119 (3)
C9—C10—H101	120.3	C40—C41—H411	120.3
C11—C10—H101	120.3	C42—C41—H411	120.5
C10—C11—C12	121.6 (10)	C41—C42—C43	121 (3)
C10—C11—H111	119.2	C41—C42—H421	119.7
C12—C11—H111	119.2	C43—C42—H421	119.8
C11—C12—C7	120.2 (8)	C42—C43—C44	120 (3)
C11—C12—H121	120.0	C42—C43—H431	120.0
C7—C12—H121	119.9	C44—C43—H431	119.7

P1—C13—P2	114.0 (3)	C43—C44—C39	119 (3)
P1—C13—H131	108.4	C43—C44—H441	120.4
P2—C13—H131	108.3	C39—C44—H441	120.2
P1—C13—H132	108.4	P4—C89—C90	117.3 (9)
P2—C13—H132	108.3	P4—C89—C94	121.7 (10)
H131—C13—H132	109.5	C90—C89—C94	120.9 (13)
P2—C14—C15	122.5 (6)	C89—C90—C91	119.7 (14)
P2—C14—C19	119.9 (6)	C89—C90—H901	120.2
C15—C14—C19	117.6 (7)	C91—C90—H901	120.2
C14—C15—C16	120.5 (8)	C90—C91—C92	119.6 (15)
C14—C15—H151	119.3	C90—C91—H911	120.2
C16—C15—H151	120.2	C92—C91—H911	120.2
C15—C16—C17	121.3 (8)	C91—C92—C93	120.6 (15)
C15—C16—H161	118.8	C91—C92—H921	119.7
C17—C16—H161	119.8	C93—C92—H921	119.7
C16—C17—C18	119.0 (9)	C92—C93—C94	120.0 (14)
C16—C17—H171	120.4	C92—C93—H931	119.9
C18—C17—H171	120.6	C94—C93—H931	120.1
C17—C18—C19	121.0 (11)	C89—C94—C93	119.2 (14)
C17—C18—H181	120.4	C89—C94—H941	120.5
C19—C18—H181	118.5	C93—C94—H941	120.3

Bond parameters (Å, °) for the trigold unit of $(I)^+$ in different salts

Compound	(I)[PF_6]	(I)[$AuCl(C_6F_5)_3$]	(I)Cl·EtOH	(I)[ClO_4]
Au1-Au2	3.1525 (4)	3.1645	3.076 (1)	3.0883 (8)
Au2-Au3	3.2770 (4)	3.0663	3.076 (1)	3.1738 (6)
Au1-Au3	3.1922 (4)	3.6784	3.729 (1)	3.4500 (8)
Au2-Au1-Au3	62.190 (9)	72.35	74.61 (3)	66.85 (2)
Au1-Au2-Au3	59.499 (9)	52.59	52.70 (2)	57.76 (1)
Au1-Au3-Au2	58.311 (9)	55.06	52.70 (2)	55.39 (1)
Reference	This work	Usón *et al.*, 1983	Lin *et al.*, 1994	Zhang *et al.*, 2005

Hydrogen bonds (Å, °) in (I)[PF_6] involving $[PF_6]^-$ anions. Symmetry codes are defined in Fig. 2

Interaction	D—H	H···A	D···A	D—H···A
C10-H101···F4^{i}	0.96	2.43	3.22 (1)	140
C12-H121···F1^{ii}	0.96	2.42	3.35 (1)	162
C13-H131···F1^{ii}	0.96	2.47	3.38 (1)	159
C15-H151···F6^{ii}	0.96	2.38	3.29 (1)	157
C49-H491···F1^{iii}	0.96	2.56	3.28 (2)	132
C48-H481···F5^{iii}	0.96	2.67	3.42 (2)	136
C46-H461···F3	0.96	2.74	3.42 (2)	128
C46-H461···F5	0.96	2.68	3.45 (1)	137
C38-H382···F2	0.96	2.60	3.30 (1)	129
C31-H311···F2	0.96	2.40	3.26 (1)	149
C38-H382···F5	0.96	2.70	3.66 (1)	174

C33-H331···F4	0.96	2.68	3.46 (1)	135

Fig. 1

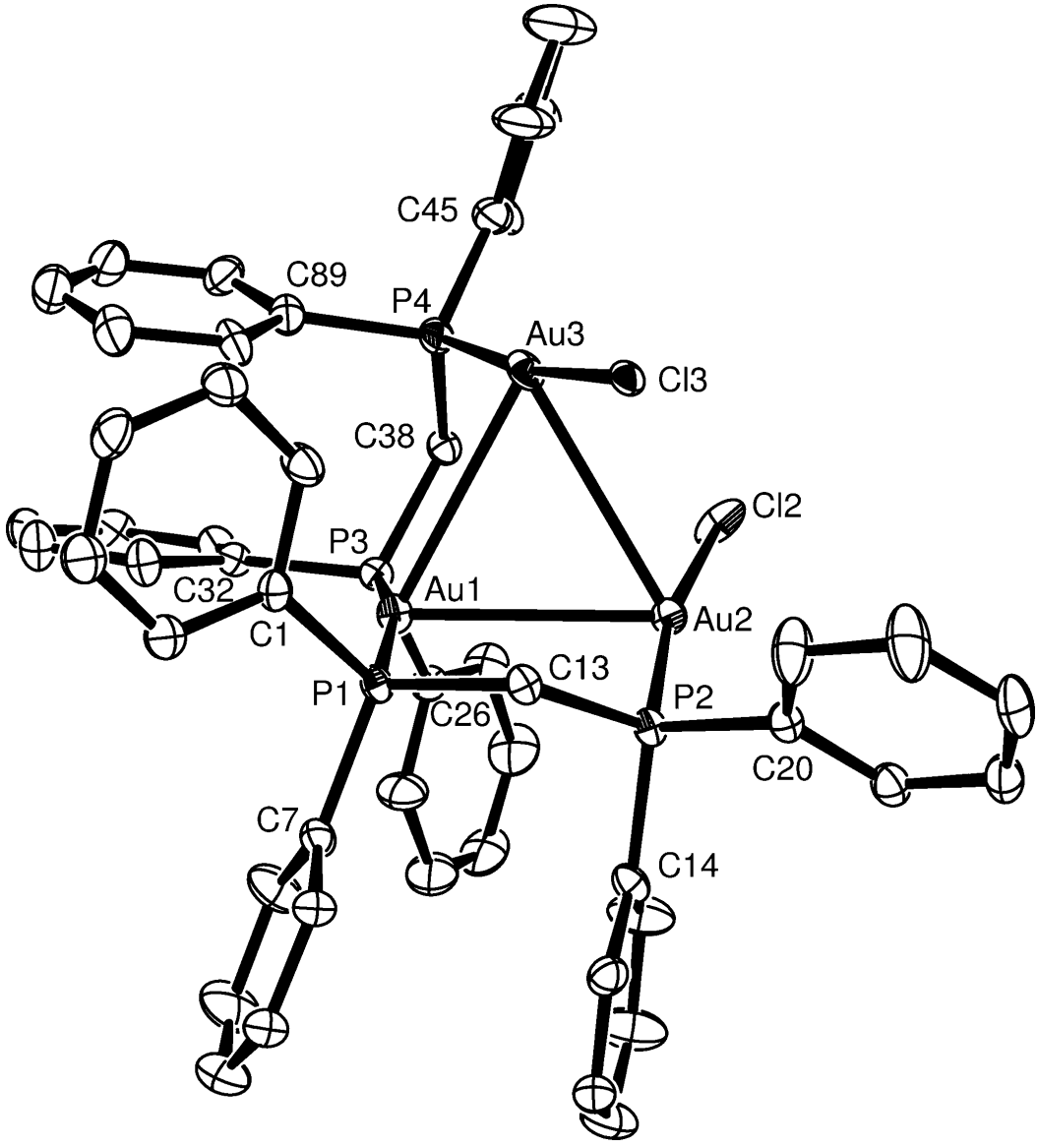
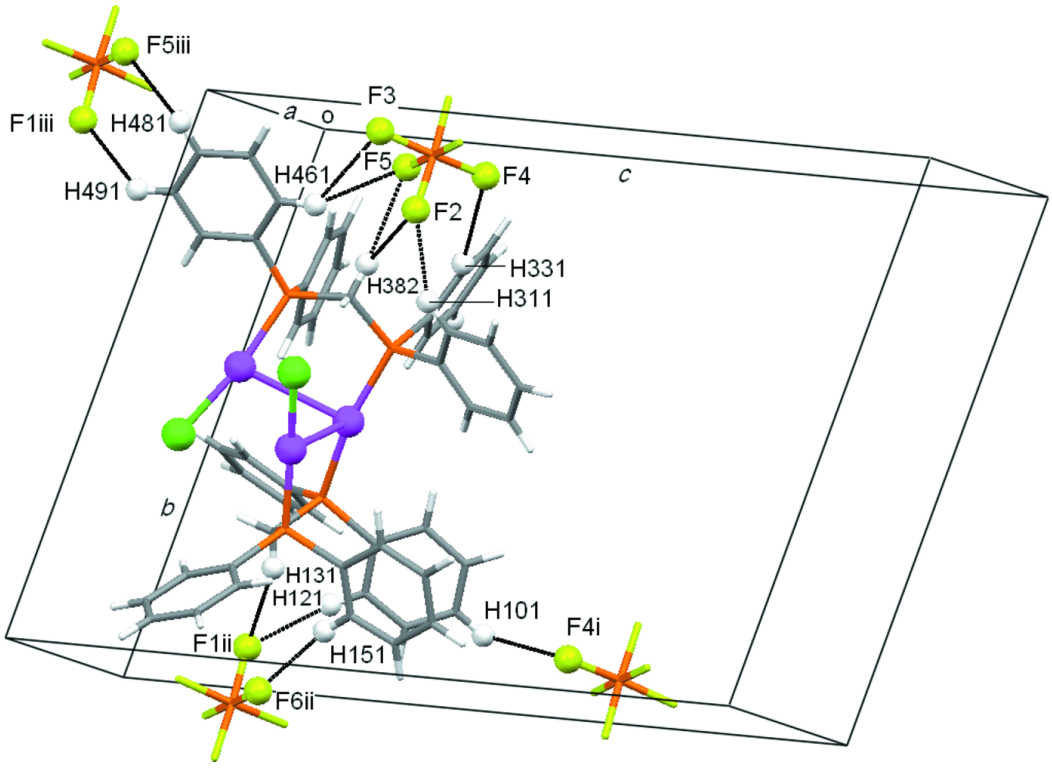


Fig. 2


F5iii
F1iii
H481
H491
F3
a
o
H461
F5
F4
c
F2
H331
H382
H311
b
H131
H121
H101
F4i
F1ii
H151
F6ii