Synthesis of Group 1B Sandwich Cluster Compounds with $[Pt_3(\mu\text{-}CO)_3(PPh_3)_3]$ and the Structural Characterisation of $[M\{Pt_3(\mu\text{-}CO)_3(PPh_3)_3\}_2]PF_6$ (M = Au or Cu) by Single-crystal *X*-Ray Techniques†

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Sandwich cluster compounds of the type $[M\{Pt_3(\mu\text{-}CO)_3(PPh_3)_3\}_2]PF_6$ [M = Cu (**1a**) or Au (**1b**)], where the Group 1B metal is co-ordinated simultaneously to two planar $[Pt_3(\mu\text{-}CO)_3(PPh_3)_3]$ *triangulo* rings, have been synthesised from $[Pt_3(\mu\text{-}CO)_3(PPh_3)_4]$ and either $[Cu(MeCN)_4]PF_6$ or $[Au(L)Cl]$ (L = CO or Me_2S) in the presence of an excess of $TlPF_6$. Complexes (**1a**) and (**1b**) are both dark red crystalline solids and are isomorphous. They have been characterised using $^{31}P\text{-}\{^1H\}$ n.m.r. and single-crystal *X*-ray techniques.

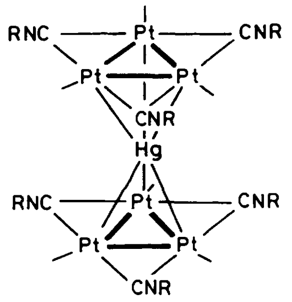
Sandwich cluster compounds $[M\{Pt_3(\mu\text{-}CO)_3(PPh_3)_3\}_2]PF_6$ [M = Cu (**1a**) or Au (**1b**)] have been obtained from reaction of $[Pt_3(\mu\text{-}CO)_3(PPh_3)_4]$ with either $[Cu(MeCN)_4]PF_6$ or $[Au(L)Cl]$ (L = CO or Me_2S) in the presence of excess $TlPF_6$. A number of related cluster compounds have been synthesised previously in which two platinum triangular units are co-ordinated to a heterometal atom in a 'sandwich' fashion. Yamamoto *et al.*[1] have characterised the compound $[Hg\{Pt_3(\mu\text{-}CNC_6H_3Me_2\text{-}2,6)_3(CNC_6H_3Me_2\text{-}2,6)_3\}_2]$ (**2**), a neutral complex formed during the Na–Hg reduction of $[Pt(CNC_6H_3Me_2\text{-}2,6)_2Cl_2]$ in the presence of excess 2,6-xylyl isocyanide, together with the homometallic cluster $[Pt_7(CNC_6H_3Me_2\text{-}2,6)_{12}]$.[2] Both compounds are unusual in containing isocyanides as the only ligand. Venanzi and co-workers[3] have synthesised the compound $[Hg_2\{Pt_3(\mu\text{-}CO)_3(PPhPr^i_2)_3\}_2]$ (**3**) which is also a neutral complex, formed from the triangular platinum cluster $[Pt_3(\mu\text{-}CO)_3(PPhPr^i_2)_3]$ by reaction with metallic mercury. This compound contains a Hg_2 unit sandwiched between two platinum triangles which may also be considered as derived from two $[Pt_3Hg(\mu\text{-}CO)_3(PPhPr^i_2)_3]$ clusters linked by a long Hg–Hg bond. Most recently, Venanzi and co-workers[4] have reported the cationic complex $[Ag\{Pt_3(\mu\text{-}CO)_3(PPr^i_3)_3\}_2]^+$ (**4**) which they prepared by adding excess AgO_3SCF_3 to a solution of the triangular cluster $[Pt_3(\mu\text{-}CO)_3(PPr^i_3)_3]$, but they were unable to synthesise the corresponding gold compound by this route.

We report here the syntheses and *X*-ray structure analyses of the first sandwich compounds of this type linked by Cu^I and Au^I atoms.

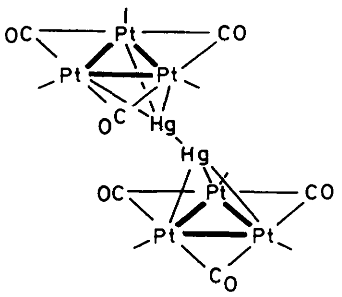
Results and Discussion

Our initial attempts to synthesise sandwich cluster compounds from $[Pt_3(\mu\text{-}CO)_3\{P(C_6H_{11})_3\}_3]$ and gold(I) complexes failed because the gold complexes abstracted phosphine from the cluster.[5] Venanzi and co-workers[4] had encountered similar difficulties with $[Pt_3(\mu\text{-}CO)_3(PPr^i_3)_3]$, although they had successfully synthesised the corresponding silver sandwich compound. Our use of $[Pt_3(\mu\text{-}CO)_3(PPh_3)_4]$,[6] which has an additional and labile phosphine ligand co-ordinated to the *triangulo* cluster, as a starting material for the synthesis of this type of sandwich compound, proved successful, leading to the formation of Au^I and Cu^I compounds of this type.

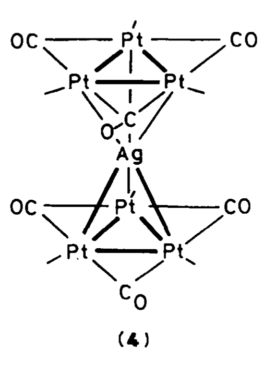
When equimolar amounts of $[Pt_3(\mu\text{-}CO)_3(PPh_3)_4]$ and either $[Au(CO)Cl]$ or $[Au(Me_2S)Cl]$ were stirred together in



(**2**); R = $C_6H_3Me_2$-2,6



(**3**)



(**4**)

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† Bis[1,2; 2,3; 1,3-tri-μ-carbonyl-1,2,3-tris(triphenylphosphine)triplatinio]-gold(I) (6 *Pt–Pt*) (6 *Au–Pt*) hexafluorophosphate and -copper(I) (6 *Pt–Pt*) (6 *Cu–Pt*) hexafluorophosphate respectively.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Selected bond lengths (Å) for $[M\{Pt_3(\mu\text{-}CO)_3(PPh_3)_3\}_2]PF_6$ [M = Cu (**1a**) or Au (**1b**)]

	(**1a**)	(**1b**)
Pt(1)-Pt(2)	2.650(2)	2.683(1)
Pt(1)-Pt(3)	2.648(2)	2.683(1)
Pt(2)-Pt(3)	2.651(2)	2.683(1)
Pt(1)-M	2.605(4)	2.729(1)
Pt(2)-M	2.598(2)	2.731(1)
Pt(3)-M	2.598(3)	2.725(1)
Pt(1)-P(1)	2.241(8)	2.242(4)
Pt(2)-P(2)	2.235(10)	2.249(5)
Pt(3)-P(3)	2.242(8)	2.250(4)
Pt(1)-C(1)	2.08(3)	2.053(18)
Pt(1)-C(2)	2.03(3)	2.051(15)
Pt(2)-C(2)	2.05(3)	2.086(15)
Pt(2)-C(3)	2.19(4)	2.054(17)
Pt(3)-C(1)	2.15(3)	2.041(16)
Pt(3)-C(3)	2.15(4)	2.126(17)
P(1)-C(111)	1.81(3)	1.828(13)
P(1)-C(121)	1.773(12)	1.789(11)
P(1)-C(131)	1.793(10)	1.808(11)
P(2)-C(211)	1.813(10)	1.802(10)
P(2)-C(221)	1.813(11)	1.824(10)
P(2)-C(231)	1.753(10)	1.807(12)
P(3)-C(311)	1.833(12)	1.822(12)
P(3)-C(321)	1.797(10)	1.807(10)
P(3)-C(331)	1.785(12)	1.809(12)
C(1)-O(1)	1.12(4)	1.189(24)
C(2)-O(2)	1.20(4)	1.174(19)
C(3)-O(3)	1.08(5)	1.123(21)
P(4)-F(1)	1.728(1)	1.530(23)
P(4)-F(2)	1.541(1)	1.542(15)
P(4)-F(3)	1.523(1)	1.523(21)

In this and subsequent Tables the e.s.d.s are in parentheses.

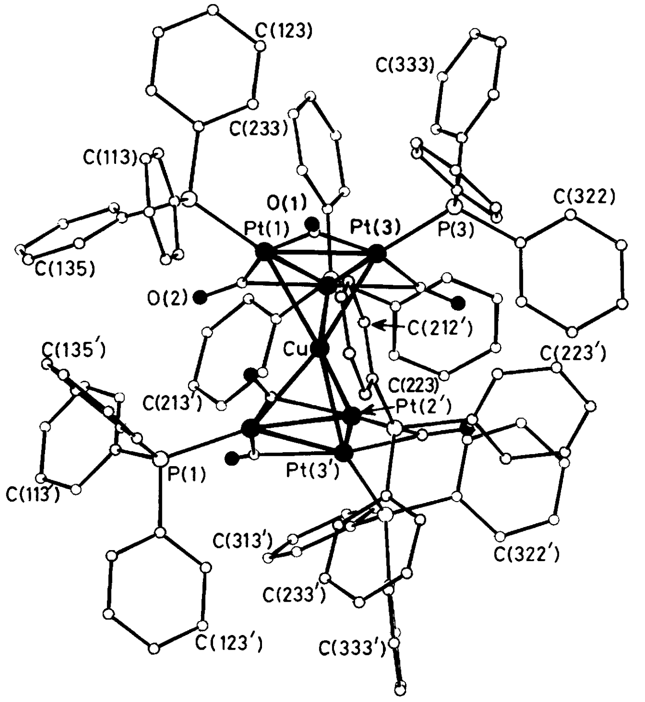

Figure 1. The structure of the cationic sandwich complex $[Cu\{Pt_3(\mu\text{-}CO)_3(PPh_3)_3\}_2]^+$ (**1a**) showing the atomic numbering scheme; the numbers for the C atoms of the phenyl rings run consecutively from the atom bonded to phosphorus

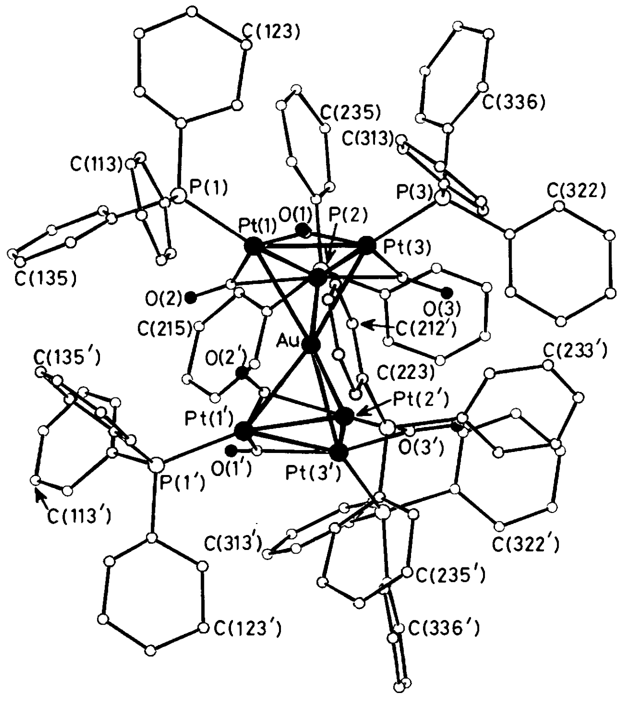

Figure 2. The structure of the cationic sandwich complex $[Au\{Pt_3(\mu\text{-}CO)_3(PPh_3)_3\}_2]^+$ (**1b**) showing the atomic numbering scheme; the numbers for the C atoms of the phenyl rings run consecutively from the atom bonded to phosphorus

benzene together with an excess of $TlPF_6$, a dark red precipitate was formed. Recrystallisation of this solid from CH_2Cl_2–hexane gave deep red crystals of $[Au\{Pt_3(\mu\text{-}CO)_3(PPh_3)_3\}_2]PF_6$ (**1b**) in *ca.* 86% yield. The i.r. spectrum of (**1b**) (Nujol mull) showed a single carbonyl stretching mode at 1 833 cm^{-1}, which is consistent with the presence of a C_3 axis in the molecule.[7] The corresponding copper complex $[Cu\{Pt_3(\mu\text{-}CO)_3(PPh_3)_3\}_2]PF_6$ (**1a**) was synthesised from $[Pt_3(\mu\text{-}CO)_3(PPh_3)_4]$ and $[Cu(MeCN)_4]PF_6$ in benzene, in *ca.* 80% yield. This compound also shows a single carbonyl stretching mode at 1 837 cm^{-1}.

The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of (**1b**) in CD_2Cl_2 shows the characteristic features of a symmetrical $[Pt_3X_3(PR_3)_3]$ triangular unit, but the lines are quite broad and at room temperature long-range couplings between the two Pt_3 triangles could not be distinguished.[7,8]

Single-crystal *X*-ray diffraction studies of (**1a**) and (**1b**) established the structures shown in Figures 1 and 2 respectively. Selected intramolecular bond lengths and angles are summarised in Table 1 and 2. Each of the $[M\{Pt_3(\mu\text{-}CO)_3(PPh_3)\}_2]^+$ cations has a crystallographically imposed two-fold rotation axis, which passes through the Group 1B metal atom and relates the two Pt_3 triangles. The two structures are very similar with the six platinum atoms in each defining a structure intermediate between a trigonal prism and an octahedron. The Pt–Pt distances in (**1a**) are equal within experimental error [2.648(2)—2.650(2) Å] and in (**1b**) all three Pt–Pt lengths have the same value, 2.683(1) Å, being significantly longer than those in (**1a**). These distances lie in the range observed for 42e triangular cluster compounds, 2.65—2.75 Å, but are shorter than those usually observed in 44e triangular clusters, 2.86—2.90 Å.[9] The theoretical reason for this geometric observation has been discussed in some detail previously.[8] The equivalence of the Pt–Pt bonds within each of the compounds (**1a**) and (**1b**)

Table 2. Selected bond angles (°) for $[M\{Pt_3(\mu\text{-}CO)_3(PPh_3)_3\}_2]PF_6$ [M = Cu (**1a**) or Au (**1b**)]

	(**1a**)	(**1b**)		(**1a**)	(**1b**)
Pt(3)–Pt(1)–Pt(2)	60.0(1)	60.0(1)	C(111)–P(1)–Pt(1)	113.4(9)	112.7(4)
M–Pt(1)–Pt(2)	59.2(1)	60.6(1)	C(121)–P(1)–Pt(1)	112(1)	113.4(5)
M–Pt(1)–Pt(3)	59.3(1)	60.5(1)	C(121)–P(1)–C(111)	106(1)	106.6(6)
P(1)–Pt(1)–Pt(2)	145.8(3)	145.3(1)	C(131)–P(1)–Pt(1)	116.8(7)	115.8(4)
P(1)–Pt(1)–Pt(3)	140.1(2)	140.4(1)	C(131)–P(1)–C(111)	104(1)	103.6(6)
P(1)–Pt(1)–M	148.7(3)	147.5(1)	C(131)–P(1)–C(121)	103(1)	103.6(7)
C(1)–Pt(1)–Pt(2)	112.3(9)	108.8(4)	C(211)–P(2)–Pt(2)	114.4(8)	113.5(4)
C(1)–Pt(1)–Pt(3)	52.4(9)	48.9(5)	C(221)–P(2)–Pt(2)	115(1)	115.5(4)
C(1)–Pt(1)–M	82.3(8)	80.7(4)	C(221)–P(2)–C(211)	102(1)	103.6(5)
C(1)–Pt(1)–P(1)	95.2(9)	98.7(4)	C(231)–P(2)–Pt(2)	113(1)	113.3(5)
C(2)–Pt(1)–Pt(2)	49.8(8)	50.1(4)	C(231)–P(2)–C(211)	106(1)	106.7(6)
C(2)–Pt(1)–Pt(3)	109.8(8)	110.1(4)	C(231)–P(2)–C(221)	104(1)	103.1(6)
C(2)–Pt(1)–M	82.4(8)	82.4(4)	C(311)–P(3)–Pt(3)	116.5(8)	116.0(4)
C(2)–Pt(1)–P(1)	103.5(8)	103.1(4)	C(321)–P(3)–Pt(3)	113.4(8)	112.9(4)
C(2)–Pt(1)–C(1)	161(1)	158.1(6)	C(321)–P(3)–C(311)	104(1)	103.5(6)
Pt(1)–M–Pt(1)	109.2(2)	112.3(1)	C(331)–P(3)–Pt(3)	112(1)	112.7(5)
Pt(3)–Pt(2)–Pt(1)	59.9(1)	60.0(1)	C(331)–P(3)–C(311)	103(1)	103.7(6)
M–Pt(2)–Pt(1)	59.5(1)	60.5(1)	C(331)–P(3)–C(321)	106(1)	107.1(6)
M–Pt(2)–Pt(3)	59.3(1)	60.4(1)	Pt(3)–C(1)–Pt(1)	77(1)	81.9(7)
P(2)–Pt(2)–Pt(1)	139.9(2)	140.2(1)	O(1)–C(1)–Pt(1)	146(3)	139(1)
P(2)–Pt(2)–Pt(3)	145.4(2)	145.7(1)	O(1)–C(1)–Pt(3)	136(3)	139(1)
P(2)–Pt(2)–M	149.2(2)	147.4(1)	Pt(3)–C(3)–Pt(2)	75(2)	79.8(6)
C(3)–Pt(2)–Pt(1)	111(1)	111.1(5)	O(3)–C(3)–Pt(2)	136(3)	143(1)
C(3)–Pt(2)–Pt(3)	52(1)	51.3(5)	O(3)–C(3)–Pt(3)	146(4)	137(2)
C(3)–Pt(2)–M	83(1)	82.2(6)	Pt(2)–C(2)–Pt(1)	81(1)	80.9(5)
C(3)–Pt(2)–P(2)	102(1)	102.7(6)	O(2)–C(2)–Pt(1)	139(2)	139(1)
C(2)–Pt(2)–Pt(1)	49.1(8)	49.0(4)	O(2)–C(2)–Pt(2)	139(2)	139(1)
C(2)–Pt(1)–Pt(3)	109.0(8)	108.9(4)	C(112)–C(111)–P(1)	123(2)	121.9(9)
C(2)–Pt(2)–M	82.2(9)	81.8(5)	C(116)–C(111)–P(1)	117(2)	118.0(7)
C(2)–Pt(2)–P(2)	97.5(9)	97.8(5)	C(122)–C(121)–P(1)	118(1)	118(1)
C(2)–Pt(2)–C(3)	160(1)	159.3(7)	C(126)–C(121)–P(1)	122(2)	122(1)
Pt(2)–Pt(3)–Pt(1)	60.0(1)	60.0(1)	C(132)–C(131)–P(1)	118(1)	119.0(9)
M–Pt(3)–Pt(1)	59.5(1)	60.6(1)	C(136)–C(131)–P(1)	122(2)	121(1)
M–Pt(3)–Pt(2)	59.3(1)	60.7(1)	C(212)–C(211)–P(2)	117(2)	117.6(9)
P(3)–Pt(3)–Pt(1)	145.6(2)	145.5(1)	C(216)–C(211)–P(2)	123(1)	122.4(8)
P(3)–Pt(3)–Pt(2)	140.0(3)	140.1(1)	C(222)–C(221)–P(2)	121(2)	120.3(7)
P(3)–Pt(3)–M	148.8(3)	147.3(1)	C(226)–C(221)–P(2)	119(2)	119.7(7)
C(1)–Pt(3)–Pt(1)	50.1(9)	49.3(5)	C(232)–C(231)–P(2)	116(2)	118(1)
C(1)–Pt(3)–Pt(2)	109.9(9)	109.1(5)	C(236)–C(231)–P(2)	124(2)	121.9(9)
C(1)–Pt(3)–M	81.2(7)	81.0(4)	C(312)–C(311)–P(3)	119(2)	118.1(9)
C(1)–Pt(3)–P(3)	104.1(8)	104.5(4)	C(316)–C(311)–P(3)	120(2)	121.8(8)
C(3)–Pt(3)–Pt(1)	113(1)	108.8(5)	C(322)–C(321)–P(3)	123(2)	122.4(8)
C(3)–Pt(3)–Pt(2)	53(1)	48.9(5)	C(326)–C(321)–P(3)	117(1)	117.5(7)
C(3)–Pt(3)–M	84.0(9)	81.1(4)	C(332)–C(331)–P(3)	119(2)	119.5(8)
C(3)–Pt(3)–P(3)	94(1)	98.3(4)	C(336)–C(331)–P(3)	121(2)	120(1)
C(3)–Pt(3)–C(1)	162(1)	157.0(6)	F(2)–P(4)–F(1)	94.6(1)	91(1)
Pt(3)–M–Pt(3)	135.2(3)	136.1(1)	F(3)–P(4)–F(1)	83.4(1)	89(1)
Pt(2)–M–Pt(1)	61.2(1)	58.9(1)	F(3)–P(4)–F(2)	88.4(1)	89(1)
Pt(3)–M–Pt(1)	61.2(1)	58.9(1)	F(1)–P(4)–F(1)	180.0	180.0
Pt(3)–M–Pt(2)	61.4(1)	58.9(1)	F(2)–P(4)–F(2)	180.0	180.0
			F(3)–P(4)–F(3)	180.0	180.0

contrasts with the observed structures of (**3**) and (**4**) where in both cases one Pt–Pt length is shorter than the other two.[3,4]

The mean Pt–Cu distance in (**1a**) is 2.600(3) Å and the mean Pt–Au distance in (**1b**) is 2.728(1) Å. The latter is slightly shorter than the Pt–Au distances found in the following tetrahedral Pt_3Au cluster compounds: $[Pt_3Au(CO)_3\{P(C_6H_{11})\}_4]^+$ [2.758(5) Å],[10] $[Pt_3Au(CO)_2(SO_2)\{P(C_6H_{11})_3\}_4]^+$ [2.758(5) Å],[11] $[Pt_3Au(\mu\text{-}Cl)(SO_2)_2\{P(C_6H_{11})_3\}_3\{P(C_6H_4F\text{-}p)_3\}]$ [2.769(1) Å],[11] and the trigonal bipyrimidal Pt_3Au_2 cluster compound $[Pt_3Au_2(\mu\text{-}Cl)(SO_2)_2\{P(C_6H_{11})_3\}_3\{P(C_6H_4F\text{-}p)_3\}_2]$ [2.785(2) Å].[12]

In (**1a**) and (**1b**) the opposite triangular metal planes are parallel to within 0.12 and 0.06° respectively. The distances between the centroids of the Pt_3 planes in the copper and gold sandwich clusters are 4.270 [(**1a**)] and 4.492 Å [(**1b**)] which reflects the difference of 0.127 Å in the mean Pt–M separations. The two triangles in each structure are twisted from an eclipsed D_{3h} conformation by similar angles of 21.5 [(**1a**)] and 22.3° [(**1b**)], Figure 3. In the analogous Hg complex $[Hg\{Pt_3(\mu\text{-}CNC_6H_3Me_2\text{-}2,6)_3(CNC_6H_3Me_2\text{-}2,6)_3\}_2]$ (**2**) the two Pt_3 triangles are twisted by 11.0° from the eclipsed conformation.[2] This relatively small twist angle may be related to the greater length of the Pt–Hg bonds which results in the greater Pt_3 triangle separation in (**2**) of 4.95 Å. However, this simple steric argument is not consistent with the observation that in the cationic Ag^I sandwich $[Ag\{Pt_3(\mu\text{-}CO)_3(PPr^i_3)_3\}_2]^+$ (**4**) an exactly staggered conformation (twist angle of 60°) is adopted,[4] although the separation of the Pt_3 triangles (judged by the Pt–Ag lengths) is greater than in either (**1a**) or (**1b**) potentially allowing a more eclipsed conformation. Theoretical studies have indicated that in clusters with layers of platinum triangles the rotational barriers are very small and the observed solid-

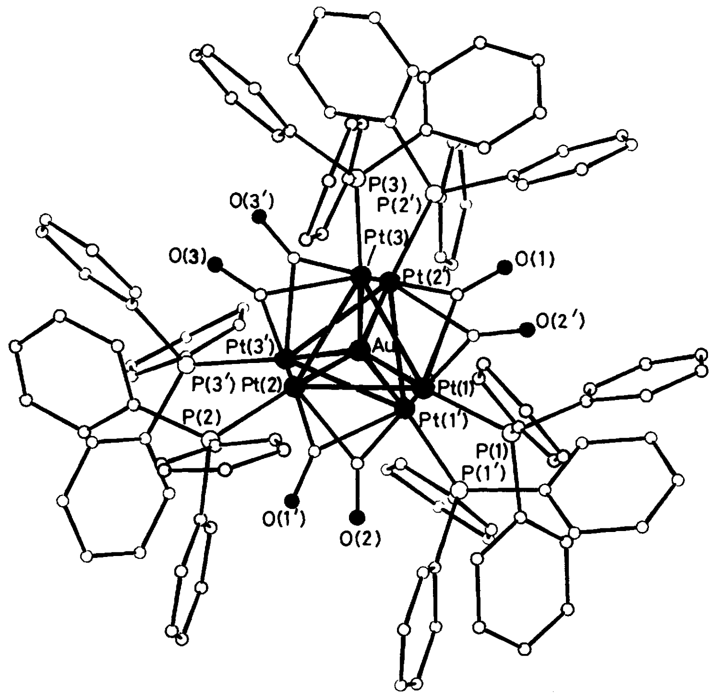

Figure 3. A view of the cation (**1b**) showing the virtual C_3 symmetry present in the clusters $[M\{Pt_3(\mu\text{-}CO)_3(PPh_3)_3\}_2]^+$

state conformation could be influenced by crystal-packing effects.[9]

The bridging CO ligands are symmetrically co-ordinated around the platinum triangles with Pt–C distances in the ranges 2.03(3)—2.19(4) Å for (**1a**) and 2.041(16)—2.126(17) Å for (**1b**). The Pt–P distances are in the ranges 2.235(10)—2.242(8) Å for (**1a**) and 2.242(4)—2.250(4) Å for (**1b**). The carbonyls are displaced from the planes of the three metal atoms and towards the central Group 1B metal atom with mean deviations of the O atoms from the Pt_3 planes being 0.28 [(**1a**)] and 0.33 Å [(**1b**)]. The phosphine ligands are also displaced from the plane of the Pt_3 plane, but in this instance away from the central atom, with mean P atom deviations from the plane of −0.88 for (**1a**) and −0.86 Å for (**1b**). The mean angle between the Pt–P vectors and the Pt_3 planes [−14.91 in (**1a**) and −14.83° in (**1b**)] is markedly greater than that of the Pt–C vectors [2.35 in (**1a**) and 2.37° in (**1b**)] in both compounds. Displacement of the carbonyl and organophosphine ligands from the Pt_3 plane in similar directions were also observed in the related silver compound (**4**).[4]

The bonding in the sandwich compounds of the type described in this paper and in (**2**), (**3**), and (**4**) has been discussed previously.[9,13] The primary bonding interactions result from the overlap of the Pt_3 ring orbitals of a_1 symmetry and the $(n + 1)s$ valence orbital of the Group 1B metal atom. A three-centre orbital interaction results and in $[M\{Pt_3(\mu\text{-}CO)_3(PR_3)_3\}_2]^+$ (M = Cu, Ag, or Au), which have a total of 94 valence electrons only the most stable in-phase combination is occupied. In $[Hg\{Pt_3(\mu\text{-}CNR)_3(CNR)_3\}_2]$, (**2**), which has a total of 96 valence electrons an additional orbital of a_2'' symmetry is occupied, which is localised predominantly on the Pt_3 triangles.

Experimental

The reactions were routinely carried out using Schlenk-line techniques under an atmosphere of pure dry N_2 and using dry oxygen-free solvents. Microanalyses (C, H, and N) were carried out by Mr. M. Gascoyne and his staff of this laboratory. Infrared spectra were recorded on a Perkin-Elmer 1710 Fourier-transform i.r. spectrometer as Nujol mulls between KBr discs and calibrated using polystyrene film. Unless otherwise stated, proton decoupled ^{31}P and ^{195}Pt n.m.r. spectra were recorded in deuteriated solvents on a Bruker AM250 spectrometer operating at 101.26 and 53.77 MHz respectively. Chemical shifts were referenced externally to aqueous solutions of trimethyl phosphate and $Na_2[PtCl_6]$ respectively. Chemical shifts were taken as positive to high frequency of the reference. Computer simulations of the n.m.r. spectra were carried out using a program developed by Professor R. K. Harris, then of the University of East Anglia, and adopted for use on the Oxford University VAX system by Dr. A. E. Derome.

Synthesis of $[Au\{Pt_3(\mu\text{-}CO)_3(PPh_3)_3\}_2]PF_6$, (**1b**).—(*a*) *Using* $[Au(Me_2S)Cl]$. $[Pt_3(\mu\text{-}CO)_3(PPh_3)_4]\cdot C_6H_6$ (0.24 g, 0.13 mmol) was dissolved in benzene (30 cm^3) and $TlPF_6$ (0.15 g, 0.43 mmol) added with stirring followed by $[Au(Me_2S)Cl]$ (0.04 g, 0.14 mmol). After 15 min, a dark red solid gradually precipitated as the solution became colourless. The solid was filtered off and extracted with CH_2Cl_2. Addition of hexane gave, on standing, deep red crystals of $[Au\{Pt_3(\mu\text{-}CO)_3(PPh_3)_3\}_2]PF_6$. Yield: 0.20 g (88%).

(*b*) *Using* $[Au(CO)Cl]$. The same product was obtained on reacting $[Pt_3(\mu\text{-}CO)_3(PPh_3)_4]$ (0.23 g, 0.13 mmol) with $[Au(CO)Cl]$ (0.04 g, 0.13 mmol) in the presence of $TlPF_6$ (0.14 g, 0.40 mmol) according to the same procedure as above. Yield: 0.18 g (82%) (Found: C, 41.6; H, 2.9; Au, 6.3; Pt, 34.0. $C_{114}H_{90}AuF_6O_6P_7Pt_6$ requires C, 42.1; H, 2.8; Au, 6.1; Pt, 36.0%). I.r. (cm^{-1}): ν(CO) 1 833vs, $\nu(PF_6)$ 838s. $^{31}P\text{-}\{^1H\}$ n.m.r. in CD_2Cl_2 solution: $\delta(^{31}P)$ 31.9 p.p.m. Single crystals were grown for *X*-ray diffraction by slow diffusion of diethyl ether into an acetone solution.

Table 3. Fractional atomic co-ordinates for $[M\{Pt_3(\mu\text{-}CO)_3(PPh_3)_3\}_2]PF_6$ [M = Cu (**1a**) or Au (**1b**)]

	(**1a**)			(**1b**)		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Pt(1)	−0.037 82(2)	0.152 04(2)	0.168 73(2)	−0.039 66(2)	0.151 08(4)	0.164 73(3)
Pt(2)	0.027 32(2)	0.282 98(2)	0.168 84(2)	0.026 63(2)	0.282 54(4)	0.164 74(3)
Pt(3)	−0.070 69(2)	0.315 07(2)	0.168 80(2)	−0.072 17(2)	0.316 25(4)	0.164 79(3)
M	0.000 00	0.250 46(7)	0.250 00	0.000 00	0.249 98(6)	0.250 00
P(1)	−0.068 3(3)	0.021 5(3)	0.135 3(2)	−0.070 0(2)	0.021 1(3)	0.131 4(2)
P(2)	0.090 3(3)	0.319 0(3)	0.134 7(3)	0.090 6(2)	0.318 0(3)	0.131 7(2)
P(3)	−0.137 4(3)	0.409 3(3)	0.135 0(4)	−0.138 7(2)	0.411 0(3)	0.131 6(2)
C(1)	−0.110 1(7)	0.194 7(6)	0.174 2(7)	−0.109 2(6)	0.201 8(10)	0.169 4(7)
O(1)	−0.148 9(5)	0.175 1(9)	0.178 7(9)	−0.148 5(5)	0.177 6(8)	0.176 8(5)
C(2)	0.039 3(5)	0.150 7(9)	0.171 5(5)	0.038 4(5)	0.148 2(9)	0.168 1(6)
O(2)	0.075 3(5)	0.099 9(9)	0.178 3(9)	0.073 8(5)	0.098 7(8)	0.178 0(5)
C(3)	−0.010 0(7)	0.409 6(7)	0.172 0(7)	−0.007 6(6)	0.400 7(11)	0.169 2(7)
O(3)	0.003 4(5)	0.476 4(7)	0.180 8(7)	0.001 7(5)	0.417 6(8)	0.177 0(5)
C(111)	−0.118 5(8)	−0.022 8(15)	0.159 7(8)	−0.119 4(4)	−0.024 2(7)	0.157 3(4)
C(112)	−0.162 3(8)	−0.069 3(15)	0.128 7(8)	−0.162 5(4)	−0.072 5(7)	0.127 5(4)
C(113)	−0.197 1(8)	−0.108 9(15)	0.150 7(8)	−0.197 2(4)	−0.111 1(7)	0.149 6(4)
C(114)	−0.188 0(8)	−0.102 1(15)	0.203 7(8)	−0.188 8(4)	−0.101 4(7)	0.201 4(4)
C(115)	−0.144 2(8)	−0.055 6(15)	0.234 7(8)	−0.145 7(4)	−0.053 1(7)	0.231 2(4)
C(116)	−0.109 4(8)	−0.016 0(15)	0.212 7(8)	−0.111 0(4)	−0.014 5(7)	0.209 2(4)
C(121)	−0.097 9(9)	0.024 9(17)	0.067 2(7)	−0.100 0(5)	0.023 3(9)	0.064 0(4)
C(122)	−0.116 2(9)	0.105 2(17)	0.044 4(7)	−0.117 0(5)	0.103 2(9)	0.040 7(4)
C(123)	−0.140 9(9)	0.110 7(17)	−0.008 9(7)	−0.141 2(5)	0.107 6(9)	−0.011 8(4)
C(124)	−0.147 5(9)	0.035 9(17)	−0.039 3(7)	−0.148 4(5)	0.032 0(9)	−0.041 0(4)
C(125)	−0.129 2(9)	−0.044 4(17)	−0.016 5(7)	−0.131 4(5)	−0.047 9(9)	−0.017 7(4)
C(126)	−0.104 4(9)	−0.049 9(17)	0.036 8(7)	−0.107 2(5)	−0.052 3(9)	0.034 8(4)
C(131)	−0.020 2(7)	−0.064 2(12)	0.144 5(7)	−0.021 1(4)	−0.064 3(7)	0.141 7(5)
C(132)	0.017 9(7)	−0.057 3(12)	0.119 6(7)	0.018 1(4)	−0.057 9(7)	0.118 6(5)
C(133)	0.057 1(7)	−0.121 0(12)	0.127 3(7)	0.057 8(4)	−0.120 9(7)	0.127 8(5)
C(134)	0.058 3(7)	−0.191 6(12)	0.159 8(7)	0.058 2(4)	−0.190 5(7)	0.160 1(5)
C(135)	0.020 2(7)	−0.198 5(12)	0.184 6(7)	0.019 0(4)	−0.196 9(7)	0.183 3(5)
C(136)	−0.019 1(7)	−0.134 8(12)	0.177 0(7)	−0.020 6(4)	−0.133 8(7)	0.174 1(5)
C(211)	0.151 4(7)	0.257 3(15)	0.159 8(8)	0.150 5(3)	0.255 5(7)	0.157 5(4)
C(212)	0.169 6(7)	0.241 0(15)	0.212 8(8)	0.167 2(3)	0.237 7(7)	0.209 4(4)
C(213)	0.217 2(7)	0.196 2(15)	0.235 0(8)	0.214 5(3)	0.192 8(7)	0.231 7(4)
C(214)	0.246 7(7)	0.167 7(15)	0.204 1(8)	0.245 1(3)	0.165 7(7)	0.202 2(4)
C(215)	0.228 6(7)	0.184 0(15)	0.151 1(8)	0.228 4(3)	0.183 5(7)	0.150 3(4)
C(216)	0.180 9(7)	0.228 8(15)	0.129 0(8)	0.181 2(3)	0.228 4(7)	0.127 9(4)
C(221)	0.113 6(10)	0.430 8(13)	0.145 4(10)	0.113 5(4)	0.430 5(6)	0.141 4(4)
C(222)	0.164 5(10)	0.450 6(13)	0.178 3(10)	0.164 5(4)	0.449 5(6)	0.173 5(4)
C(223)	0.181 2(10)	0.537 3(13)	0.186 0(10)	0.180 8(4)	0.535 9(6)	0.182 9(4)
C(224)	0.147 0(10)	0.604 1(13)	0.160 7(10)	0.146 1(4)	0.603 2(6)	0.160 3(4)
C(225)	0.096 1(10)	0.584 2(13)	0.127 8(10)	0.095 2(4)	0.584 1(6)	0.128 2(4)
C(226)	0.079 4(10)	0.497 6(13)	0.120 2(10)	0.078 9(4)	0.497 8(6)	0.118 7(4)
C(231)	0.070 1(10)	0.307 7(17)	0.067 4(8)	0.070 6(5)	0.305 8(9)	0.063 5(4)
C(232)	0.028 7(10)	0.249 2(17)	0.046 0(8)	0.027 9(5)	0.251 0(9)	0.040 4(4)
C(233)	0.012 4(10)	0.231 1(17)	−0.006 7(8)	0.011 4(5)	0.238 8(9)	−0.012 1(4)
C(234)	0.037 5(10)	0.271 6(17)	−0.038 2(8)	0.037 7(5)	0.281 3(9)	−0.041 4(4)
C(235)	0.079 0(10)	0.330 1(17)	−0.016 9(8)	0.080 4(5)	0.336 1(9)	−0.018 2(4)
C(236)	0.095 3(10)	0.348 2(17)	0.035 9(8)	0.096 8(5)	0.348 3(9)	0.034 3(4)
C(311)	−0.201 2(8)	0.383 2(15)	0.144 0(8)	−0.201 4(4)	0.385 8(7)	0.141 6(5)
C(312)	−0.228 6(8)	0.308 3(15)	0.121 2(8)	−0.228 3(4)	0.310 9(7)	0.119 0(5)
C(313)	−0.275 1(8)	0.284 2(15)	0.130 7(8)	−0.274 6(4)	0.285 8(7)	0.128 5(5)
C(314)	−0.294 3(8)	0.335 1(15)	0.163 0(8)	−0.293 9(4)	0.335 6(7)	0.160 6(5)
C(315)	−0.267 0(8)	0.410 0(15)	0.185 9(8)	−0.267 0(4)	0.410 5(7)	0.183 2(5)
C(316)	−0.220 4(8)	0.434 1(15)	0.176 4(8)	−0.220 7(4)	0.435 6(7)	0.173 7(5)
C(321)	−0.122 9(9)	0.518 1(12)	0.159 9(8)	−0.123 6(4)	0.519 4(6)	0.157 3(4)
C(322)	−0.139 8(9)	0.592 1(12)	0.129 3(8)	−0.140 5(4)	0.593 9(6)	0.127 9(4)
C(323)	−0.130 7(9)	0.674 8(12)	0.151 6(8)	−0.130 9(4)	0.675 9(6)	0.150 5(4)
C(324)	−0.104 7(9)	0.683 7(12)	0.204 5(8)	−0.104 3(4)	0.683 4(6)	0.202 5(4)
C(325)	−0.087 8(9)	0.609 7(12)	0.235 1(8)	−0.087 4(4)	0.609 0(6)	0.231 8(4)
C(326)	−0.096 9(9)	0.527 0(12)	0.212 8(8)	−0.097 0(4)	0.526 9(6)	0.209 3(4)
C(331)	−0.154 6(10)	0.418 2(18)	0.066 5(8)	−0.156 3(5)	0.420 2(8)	0.063 3(4)
C(332)	−0.116 0(10)	0.398 1(18)	0.043 7(8)	−0.120 0(5)	0.394 6(8)	0.039 4(4)
C(333)	−0.127 7(10)	0.406 4(18)	−0.009 6(8)	−0.132 7(5)	0.402 9(8)	−0.013 1(4)
C(334)	−0.177 9(10)	0.434 9(18)	−0.040 0(8)	−0.181 8(5)	0.436 9(8)	−0.041 7(4)
C(335)	−0.216 4(10)	0.455 0(18)	−0.017 2(8)	−0.218 1(5)	0.462 5(8)	−0.017 7(4)
C(336)	−0.204 7(10)	0.446 6(18)	0.036 0(8)	−0.205 3(5)	0.454 2(8)	0.034 7(4)
P(4)	0.750 00	0.250 00	0.500 00	0.750 00	0.250 00	0.500 00
F(1)	0.619 6(8)	0.276 0(13)	0.466 8(8)	0.770 9(8)	0.309 8(13)	0.466 8(8)
F(2)	0.074 9(6)	0.162 4(14)	0.466 5(8)	0.806 7(6)	0.229 7(14)	0.534 7(8)
F(3)	0.077 48(8)	0.169 8(12)	0.463 0(8)	0.753 4(8)	0.173 4(12)	0.466 4(8)

Synthesis of $[Cu\{Pt_3(\mu\text{-}CO)_3(PPh_3)_3\}_2]PF_6$, **(1a)**. Contact between the product and metal implements (*e.g.* spatula) was avoided in this synthesis since decomposition had been a problem in early attempts. $[Pt_3(\mu\text{-}CO)_3(PPh_3)_4]\cdot C_6H_6$ (0.40 g, 0.22 mmol) was dissolved in benzene (30 cm^3) and $[Cu(MeCN)_4]PF_6$ (0.08 g, 0.21 mmol) added with stirring. During the course of an hour a deep red precipitate was formed as the solution became almost colourless. The solid was filtered off and extracted into CH_2Cl_2. Slow addition of diethyl ether gave deep red crystals of $[Cu\{Pt_3(\mu\text{-}CO)_3(PPh_3)_3\}_2]PF_6$. Yield; 0.28 g (81%) (Found: C, 43.6; H, 3.0; Cu, 2.1. $C_{114}H_{90}CuF_6O_6P_7Pt_6$ requires C, 43.9; H, 2.8; Cu, 2.0%). *X*-Ray microanalysis confirmed that the Pt:Cu atom ratio was 6:1. I.r. (cm^{-1}): ν(CO) 1 837vs, $\nu(PF_6)$ 839s. Single crystals were grown for *X*-ray diffraction by slow diffusion of diethyl ether into a CH_2Cl_2 solution.

Reaction of $[Pt_3(\mu\text{-}CO)_3\{P(C_6H_{11})_3\}_3]$ *with* [Au(CO)Cl].—$[Pt_3(\mu\text{-}CO)_3\{P(C_6H_{11})_3\}_3]\cdot C_6H_6$ (0.30 g, 0.19 mmol) was dissolved in benzene (25 cm^3). $TlPF_6$ (0.10 g, 0.29 mmol) and [Au(CO)Cl] (25 mg, 0.10 mmol) were added and the solution stirred for 12 h during which time it darkened considerably. The solvent was removed *in vacuo* and the residue extracted into CH_2Cl_2. Addition of ethanol gave, on standing at −20 °C, bright red crystals of $[Pt_3Au(\mu\text{-}CO)_3\{P(C_6H_{11})_3\}_4]PF_6$. Yield: 0.14 g (35% based on Pt) (Found: C, 42.6; H, 5.9. $C_{75}H_{132}AuF_6O_3P_5Pt_3$ requires C, 42.2; H, 6.2%). $^{31}P\text{-}\{^1H\}$ N.m.r. in CD_3Cl_2 solution: $\delta(^{31}P)$ 51.8 (3 P), 82.4 (1 P) p.p.m. (lit.[11] 51.9, 82.7 p.p.m.).

X-*Ray Structure Analyses.*—*Crystal data for* **(1a)**. $C_{114}H_{90}CuF_6O_6P_7Pt_6$, M = 3 118.54, monoclinic, space group $C2/c$, a = 26.583(3), b = 15.331(2), c = 27.366(3) Å, β = 108.56(2) °, U = 10 554 Å^3, $F(000)$ = 5 852, $\mu(\text{Mo-}K_\alpha)$ = 79.42 cm^{-1}, Z = 4, D_c = 1.96 g cm^{-3}.

Crystal data for **(1b)**. $C_{114}H_{90}AuF_6O_6P_7Pt_6$, M = 3 252.22, monoclinic, space group $C2/c$, a = 26.637(3), b = 15.371(2), c = 27.821(3) Å, β = 108.73(2)°, U = 10 788 Å^3, $F(000)$ = 7 452, $\mu(\text{Mo-}K_\alpha)$ = 155.05 cm^{-1}, Z = 4, D_c = 2.00 g cm^{-3}.

The methods of data collection, data processing, and absorption correction used for compounds **(1a)** and **(1b)** are similar to those described previously.[14] The crystals selected for data collection had dimensions 0.44 × 0.48 × 0.21 mm [**(1a)**] and 0.24 × 0.24 × 0.16 mm [**(1b)**]. A scan width of 0.8° was used to collect data in the θ range 3—25° for both crystals. 360 Azimuthal scan data for **(1a)** and 432 for **(1b)** were used in absorption correction and relative transmission factors varied from 1.000 to 0.810 for **(1a)** and 1.000 to 0.903 for **(1b)**. Equivalent reflections were merged to give 5 998 data for **(1a)** and 5 050 data for **(1b)** with $I/\sigma(I) \geqslant 3.0$.

Structure solution and refinement.[15] For **(1b)** the three independent platinum atoms and the gold atom were found from a Patterson synthesis. The structure of **(1a)** was assumed to be isomorphous with **(1b)** from the close relationships in the unit-cell dimensions and systematic absences. The metal positions from **(1b)** were therefore used as a starting set in the solution of **(1a)**. The remaining non-hydrogen atoms were found from subsequent difference Fourier syntheses, after several cycles of refinement of metal atom parameters. Blocked full-matrix least-squares refinement of the atomic positional and thermal parameters converged at final R and R' values of 0.0443 and 0.0442 respectively for **(1a)** and 0.0484 and 0.0464 respectively for **(1b)**. The phenyl rings were treated as rigid hexagons (C–C = 1.395 Å) and the hydrogen atoms were included in the structure factor calculations at calculated positions (C–H = 1.08 Å) with fixed thermal parameters of 0.08 Å^2. Anisotropic thermal parameters were assigned to the metals, phosphorus, and fluorine atoms during the final cycles of least-squares refinement for both **(1a)** and **(1b)**. Fractional atomic co-ordinates are given in Table 3.

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