Synthesis and Characterization of Gold Adducts of $[M(tppme)(P_3)]$ [M = Co, Rh, or Ir; tppme = 1,1,1-tris(diphenylphosphinomethyl)ethane]. *X*-Ray Crystal Structures of $[Au\{M(tppme)(P_3)\}_2]PF_6$ (M = Co, Rh, or Ir) *

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Treatment of a dichloromethane solution of $[M(tppme)(P_3)]$ [M = Co, Rh, or Ir; tppme = 1,1,1-tris(diphenylphosphinomethyl)ethane] with the complexes $[AuCl(PR_3)]$ (R = Me or Ph) and $[Au_2Cl_2\{Ph_2P(CH_2)_nPPh_2\}]$ (*n* = 1 or 2) in the presence of $TlPF_6$ invariably affords the compounds $[Au\{M(tppme)(P_3)\}_2]PF_6\cdot$solvent (M = Co, Rh, or Ir). *X*-Ray crystallographic analyses of the three isomorphous compounds showed that the gold atom is bound to two pairs of phosphorus atoms belonging to the P_3 units of two $[M(tppme)(P_3)]$ fragments; the gold atom has a co-ordination geometry intermediate between tetrahedral and square planar. The unexpected elimination of the phosphane ligand from the gold fragments and the lengthening of the P–P bonds in which insertion of gold occurs are indicative of significant interaction between the gold atom and the MP_3 clusters.

The controlled reaction of complexes in which Group 1B metals are stabilized by a unidentate phosphine $[MCl(PR_3)]$ (M = Cu, Ag,[1] or Au;[2] R = alkyl or aryl) or ligated by bidentate phosphines $[Au_2Cl_2\{Ph_2P(CH_2)_nPPh_2\}]$ (*n* = 1 or 2)[3,4] gives with transition-metal carbonyl anions higher-nuclearity heteronuclear carbonyl clusters in good yield. Previous results have shown that osmium and ruthenium carbonyl anions add one monometal $[Au(PR_3)]^+$ species on an edge[5,6] or a triangular face[7] of the metal polyhedron. In the latter event the faces of the resulting tetrahedral AuM_3 moiety may be further capped by one[8] or two[9] $[Au(PR_3)]^+$ species. Pairs of Group 1B metals ligated by diphosphines also add to cluster anions yielding higher-nuclearity metal clusters which are significantly distorted from idealized geometries, mainly due to the constraints induced by the two gold atoms spanned by the diphosphine.[10] A common feature to the above results is that on formation of the heterometallic cluster no dissociation of the phosphine is observed unless fission of the metal–phosphorus bond is produced by appropriate reagents.[11] An example of spontaneous gold–phosphorus bond cleavage by a metallaborane cluster anion has recently been reported; however such cleavage, yielding a fused metallaborane cluster, only occurred for gold bound to $PMePh_2$ or PMe_2Ph.[12]

We have investigated the reactivity of gold complexes with uni- and bi-dentate phosphines toward the neutral compounds $[M(tppme)(P_3)]$ (M = Co, Rh, or Ir) which have a pseudo-tetrahedral core formed by three unsubstituted phosphorus atoms and one cobalt group metal, stabilized by the tripod tridentate tppme ligand [tppme = 1,1,1-tris(diphenylphosphinomethyl)ethane]. The polarized MP_3 core exhibits distinct reactivity; it interacts with electrophilic organic reagents and transition metal–ligand fragments through one P,[13] a P–P edge,[14] or the P_3 triangular face.[15]

Experimental

All reactions and manipulations were performed under an atmosphere of dry oxygen-free nitrogen. Solvents were freshly distilled under nitrogen from the appropriate drying agents immediately before use. The ^{31}P-$\{^1H\}$ n.m.r. spectra were measured on a Varian VXR 300 (at 121.4 MHz) spectrometer. Phosphorus-31 positive chemical shifts are to high frequency relative to 85% H_3PO_4 external standard at 0.0 p.p.m. Established methods were used to prepare $[AuCl(PR_3)]$ (R = Me or Ph), $[Au_2Cl_2\{Ph_2P(CH_2)_nPPh_2\}]$[16] (*n* = 1 or 2), and $[M(tppme)(P_3)]$ [M = Co,[17] Rh, or Ir[18]]. All the compounds were collected on a sintered-glass frit, in a closed system, and washed with benzene and light petroleum (b.p. 40—70 °C) in turn before being dried under a stream of nitrogen.

Synthesis of the Compounds.—$[Au\{Co(tppme)(P_3)\}_2]PF_6$ (**1**). The compounds $[AuCl(PPh_3)]$ (0.14 g, 0.3 mmol) and $TlPF_6$ (0.1 g, 0.3 mmol) dissolved in dichloromethane–tetrahydrofuran (1 : 1) (30 cm^3) were added to a dichloromethane solution (40 cm^3) of $[Co(tppme)(P_3)]$ (0.47 g, 0.6 mmol) and the mixture was stirred at room temperature for 3 h. The resulting suspension was filtered and benzene was added. Red crystals of $[Au\{Co(tppme)(P_3)\}_2]PF_6$ (**1**) were obtained by slow concentration. The crude compound does not need further purification, although it can be recrystallized from dichloromethane and benzene (yield 80%). Crystals used for *X*-ray work (see below) contained dichloromethane and benzene solvate molecules (Found: C, 54.4; H, 4.5; Co, 5.4; P, 18.8. $C_{96}H_{92.5}AuClCo_2F_6P_{13}$ requires C, 54.6; H, 4.4; Co, 5.6; P, 19.0%). The same procedure was used to obtain the rhodium (**2**) (orange, yield 83%) (Found: C, 52.1; H, 4.3; Au, 8.6. $C_{96}H_{92.5}AuClF_6P_{13}Rh_2$ requires C, 52.4; H, 4.2; Au, 8.9%) and iridium (**3**) (yellow, yield 85%) (Found: C, 48.1; H, 4.0. $C_{94.25}H_{90.5}AuCl_{0.5}F_6Ir_2P_{13}$ requires C, 48.4; H, 3.9%) derivatives and to react $[M(tppme)(P_3)]$ (M = Co, Rh, or Ir) with $[AuCl(PMe_3)]$ and $[Au_2Cl_2\{Ph_2P(CH_2)_nPPh_2\}]$ (*n* = 1 or 2).

Crystal Structure Determinations.—The structures of the three isomorphous compounds $[Au\{Co(tppme)(P_3)\}_2]PF_6\cdot 2.25C_6H_6\cdot 0.5CH_2Cl_2$ (**1**), $[Au\{Rh(tppme)(P_3)\}_2]PF_6\cdot 2.25C_6H_6\cdot 0.5CH_2Cl_2$ (**2**), and, $[Au\{Ir(tppme)(P_3)\}_2]PF_6\cdot 2C_6H_6\cdot$

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Summary of crystal data, intensity collection, and structure refinement *

Compound	**(1)**	**(2)**	**(3)**
Formula	$C_{96}H_{92.5}AuClCo_2F_6P_{13}$	$C_{96}H_{92.5}AuClF_6P_{13}Rh_2$	$C_{94.25}H_{90.5}AuCl_{0.5}F_6Ir_2P_{13}$
M	2 113.24	2 201.19	2 339.01
Crystal size (mm)	0.35 × 0.30 × 0.20	0.40 × 0.30 × 0.25	0.40 × 0.40 × 0.35
a/Å	17.607(14)	17.666(3)	17.684(9)
b/Å	18.163(19)	18.320(4)	18.267(9)
c/Å	30.557(7)	30.615(5)	30.451(4)
β/°	103.82(5)	103.11(2)	103.36(7)
U/Å^3	9 489(12)	9 650(3)	9 570(7)
D_c/g cm^{-3}	1.479	1.515	1.623
μ(Mo-K_α)/cm^{-1}	21.81	21.39	45.70
Data collection range, θ/°	2.5—18	2.5—21	2.5—21
Reflections collected	6 530	10 360	10 280
Reflections used [$I > 3\sigma(I)$]	2 237	6 882	4 297
No. of variables	233	328	329
g in $w^{-1} = \sigma^2(F_o) + gF_o^2$	0.0005	0.001	0
Δ/σ	0.2	0.1	0.1
R, R'	0.077, 0.085	0.058, 0.066	0.063, 0.062

* Details common to all three structures: crystal system, monoclinic; space group, $P2_1/n$; $Z = 4$; temperature, 20 ± 2 °C; radiation, Mo-K_α (λ = 0.710 69 Å, graphite monochromator); scan mode, ω—2θ; scan width, 1.00 + 0.34 tanθ; scan speed, depending upon reflection; reflections collected, hkl, $\bar{h}kl$; Δ/σ = maximum shift/error ratio in final least-squares cycle; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$.

$0.25CH_2Cl_2$ (**3**) were investigated in order to detect possible effects on bonding of Au to the MP_3 cluster (M = Co, Rh, or Ir) in the parent [M(tppme)(P_3)] complex, due to changes in the nature of the M metal atom. An Enraf–Nonius CAD4 diffractometer and Mo-K_α radiation (λ = 0.710 69 Å) were used for all operations. Details of the crystal data, intensity collection procedures, and structure refinement are collected in Table 1. Lattice constants were determined by least-squares refinements of the angular settings of 24 reflections with 2θ in the ranges 20—22 (**1**), 24—34 (**2**), and 20—24° (**3**). The intensities of three standard reflections measured periodically revealed an appreciable steady decrease (30% overall) for (**3**) and a smaller one (7%) for compound (**2**), the crystal of which was coated with paraffin, but no decrease for (**1**). On the other hand, data collection for (**1**), which provided poorly diffracting material, had to be restricted to comparatively low θ values, due to rapid attenuation of the intensities with increasing θ. After correction for the decay, for compounds (**2**) and (**3**), intensity data were corrected for Lorentz and polarization effects. Empirical absorption corrections were applied.[19] The principal computer programs used in the crystallographic calculations, performed on an IBM 4361, are given in refs. 20—22. Scattering factors for the neutral atoms and the anomalous dispersion corrections for the metal atoms were from ref. 23.

The structure of the rhodium derivative was solved by a combination of direct and heavy-atom methods. The structures of the other two compounds were refined using as initial values for the co-ordinates of atoms not belonging to the solvate molecules those from the structure of the rhodium derivative. The function $\Sigma w(|F_o| - |F_c|)^2$ was minimized in the least-squares refinements. In the final cycles for compounds (**2**) and (**3**) the metal atoms were assigned anisotropic thermal parameters whereas all other atoms were assigned isotropic thermal parameters (overall values for the solvate molecules). In the case of (**1**), due to the scarcity and poor quality of data, only the Au atom was refined anisotropically, whereas the Co, P, and F atoms were assigned individual isotropic thermal parameters, and all C atoms were refined using a set of 12 overall thermal parameters. In particular, only four thermal parameters were used for the C atoms of all phenyl rings, their assignments depending on the positions of the atoms in the rings. Phenyl rings in all structures were refined as rigid groups with idealized geometry and H atoms, in the cation as well as in the solvate molecules, were introduced in calculated positions, with C–H 1.00 Å and $U_H = 1.2\ U_C$.

The presence and nature of solvent molecules in the lattice of (**2**) were revealed by ΔF maps. Population parameters for the three benzene molecules in the asymmetric unit (two being in general positions, refined as rigid bodies; the third one, hereafter referred to as benzene 3, lying close to an inversion centre) and for one dichloromethane molecule were assigned taking into account the peak heights from ΔF maps and the results of least-squares refinements in which different sets of occupancy factors were used for the solvate molecules. The set finally chosen produced a comparatively low R value and overall thermal parameters for the solvent molecules or the benzene 3 fragment which were substantially in agreement with each other and were moderately larger than the mean of the thermal parameters obtained for atoms of the small PF_6^- anion. Reasonable agreement with the elemental analysis data was also obtained. Further details of the solvent model for complex (**2**) are given in Table 2. The same values of the population parameters as for (**2**) were found to be suitable for the solvent in (**1**); however, refinements for the solvent in the latter compound were performed in separate cycles from the rest of the structure, applying a damping factor and constraints on the two C–C bonds of benzene 3 and on the C–Cl bonds of CH_2Cl_2 (more details are given in the Supplementary data). For complex (**3**), following similar procedures to those described for (**2**), smaller occupancy factors than in the other structures were found for one of the benzene molecules and for CH_2Cl_2. This may have been caused by the appreciable decomposition undergone by the crystal of (**3**). The benzene 3 fragment and the CH_2Cl_2 molecule of (**3**) were refined separately from the rest of the structure applying a constraint to the C–Cl bonds. The final R values appear in Table 1. Atomic co-ordinates for (**2**) are given in Table 2 and selected values of bond lengths and angles for the three compounds in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises non-hydrogen atom co-ordinates for (**1**) and (**3**), H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

Treatment of a dichloromethane solution of [M(tppme)(P_3)]

Table 2. Atomic co-ordinates (× 10^4) for $[Au\{Rh(tppme)(P_3)\}_2]PF_6{\cdot}2.25C_6H_6{\cdot}0.5CH_2Cl_2$, (**2**)*

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Au	716(1)	−87(1)	1 895(1)	C(71)	−1 891(4)	−2 129(4)	423(2)
Rh(1)	2 243(1)	1 400(1)	2 569(1)	C(72)	−1 137(4)	−2 344(4)	414(2)
Rh(2)	−1 446(1)	−723(1)	1 236(1)	C(73)	−989(4)	−3 065(4)	314(2)
P(1)	3 097(2)	1 448(2)	3 255(1)	C(74)	−1 594(4)	−3 571(4)	223(2)
P(2)	1 329(2)	1 961(2)	2 878(1)	C(75)	−2 348(4)	−3 356(4)	232(2)
P(3)	2 661(2)	2 498(2)	2 356(1)	C(76)	−2 496(4)	−2 635(4)	332(2)
P(4)	1 600(2)	921(2)	1 861(1)	C(81)	−1 786(3)	−769(3)	41(2)
P(5)	1 896(2)	150(2)	2 474(1)	C(82)	−1 170(3)	−279(3)	81(2)
P(6)	2 742(2)	510(2)	2 116(1)	C(83)	−1 006(3)	36(3)	−302(2)
P(7)	−486(2)	−684(2)	1 919(1)	C(84)	−1 458(3)	−139(3)	−725(2)
P(8)	−97(2)	−758(2)	1 244(1)	C(85)	−2 074(3)	−630(3)	−764(2)
P(9)	−520(2)	−1 680(2)	1 548(1)	C(86)	−2 238(3)	−945(3)	−381(2)
P(10)	−2 029(2)	−1 164(2)	543(1)	C(91)	−1 336(4)	1 071(3)	776(2)
P(11)	−1 909(2)	434(2)	1 027(1)	C(92)	−545(4)	1 137(3)	972(2)
P(12)	−2 556(2)	−963(2)	1 484(1)	C(93)	−88(4)	1 626(3)	795(2)
C(1)	2 585(6)	2 937(6)	3 250(4)	C(94)	−422(4)	2 049(3)	423(2)
C(2)	3 289(6)	2 415(6)	3 413(4)	C(95)	−1 213(4)	1 983(3)	227(2)
C(3)	1 800(6)	2 632(6)	3 302(4)	C(96)	−1 670(4)	1 494(3)	404(2)
C(4)	2 572(7)	3 212(7)	2 756(4)	C(101)	−2 147(4)	1 024(4)	1 467(3)
C(5)	2 744(7)	3 617(6)	3 554(4)	C(102)	−2 734(4)	1 548(4)	1 372(3)
C(6)	−3 332(7)	−326(7)	644(5)	C(103)	−2 853(4)	2 017(4)	1 710(3)
C(7)	−3 081(7)	−1 026(6)	432(4)	C(104)	−2 384(4)	1 961(4)	2 141(3)
C(8)	−2 819(7)	332(6)	601(4)	C(105)	−1 797(4)	1 437(4)	2 236(3)
C(9)	−3 369(7)	−457(7)	1 152(4)	C(106)	−1 679(4)	968(4)	1 898(3)
C(10)	−4 170(8)	−153(7)	388(5)	C(111)	−2 566(4)	−726(4)	2 067(3)
C(11)	4 066(4)	1 049(3)	3 318(2)	C(112)	−2 035(4)	−1 092(4)	2 403(3)
C(12)	4 123(4)	374(3)	3 117(2)	C(113)	−1 991(4)	−926(4)	2 853(3)
C(13)	4 850(4)	58(3)	3 143(2)	C(114)	−2 477(4)	−393(4)	2 967(3)
C(14)	5 521(4)	417(3)	3 371(2)	C(115)	−3 008(4)	−28(4)	2 631(3)
C(15)	5 464(4)	1 091(3)	3 572(2)	C(116)	−3 052(4)	−194(4)	2 181(3)
C(16)	4 737(4)	1 407(3)	3 546(2)	C(121)	−2 892(4)	−1 914(4)	1 468(2)
C(21)	2 797(4)	1 027(4)	3 736(3)	C(122)	−2 343(4)	−2 472(4)	1 504(2)
C(22)	2 578(4)	295(4)	3 692(3)	C(123)	−2 575(4)	−3 199(4)	1 509(2)
C(23)	2 360(4)	−67(4)	4 045(3)	C(124)	−3 356(4)	−3 368(4)	1 479(2)
C(24)	2 362(4)	304(4)	4 443(3)	C(125)	−3 904(4)	−2 810(4)	1 443(2)
C(25)	2 581(4)	1 036(4)	4 488(3)	C(126)	−3 672(4)	−2 083(4)	1 437(2)
C(26)	2 798(4)	1 398(4)	4 135(3)	P(13)	1 063(4)	3 116(4)	4 546(2)
C(31)	767(3)	1 348(3)	3 160(2)	F(1)	813(8)	2 296(8)	4 544(5)
C(32)	841(3)	1 316(3)	3 623(2)	F(2)	221(9)	3 341(9)	4 593(5)
C(33)	411(3)	808(3)	3 805(2)	F(3)	1 355(9)	3 907(9)	4 541(6)
C(34)	−92(3)	331(3)	3 524(2)	F(4)	1 896(9)	2 902(8)	4 477(5)
C(35)	−166(3)	363(3)	3 061(2)	F(5)	782(8)	3 152(8)	3 997(5)
C(36)	263(3)	872(3)	2 879(2)	F(6)	1 344(7)	3 074(7)	5 076(5)
C(41)	514(4)	2 467(3)	2 531(3)	C(131)	6 981(9)	4 804(8)	694(4)
C(42)	328(4)	2 380(3)	2 066(3)	C(132)	7 787(9)	4 717(8)	804(4)
C(43)	−323(4)	2 728(3)	1 807(3)	C(133)	8 110(9)	4 019(8)	848(4)
C(44)	−789(4)	3 164(3)	2 013(3)	C(134)	7 627(9)	3 407(8)	782(4)
C(45)	−603(4)	3 251(3)	2 478(3)	C(135)	6 822(9)	3 494(8)	672(4)
C(46)	48(4)	2 903(3)	2 737(3)	C(136)	6 499(9)	4 192(8)	628(4)
C(51)	2 148(4)	2 852(3)	1 810(3)	C(141)	4 626(8)	2 924(11)	68(7)
C(52)	2 284(4)	2 492(3)	1 433(3)	C(142)	4 575(8)	2 513(11)	444(7)
C(53)	1 896(4)	2 713(3)	1 005(3)	C(143)	4 396(8)	2 853(11)	816(7)
C(54)	1 373(4)	3 295(3)	953(3)	C(144)	4 269(8)	3 605(11)	811(7)
C(55)	1 238(4)	3 655(3)	1 329(3)	C(145)	4 321(8)	4 016(11)	436(7)
C(56)	1 626(4)	3 433(3)	1 758(3)	C(146)	4 499(8)	3 676(11)	64(7)
C(61)	3 663(4)	2 591(3)	2 298(2)	C(151)	9 597(13)	4 708(13)	−367(9)
C(62)	4 168(4)	1 996(3)	2 375(2)	C(152)	9 502(13)	4 439(12)	43(9)
C(63)	4 922(4)	2 065(3)	2 311(2)	C(153)	9 916(13)	4 758(12)	435(8)
C(64)	5 170(4)	2 729(3)	2 169(2)	C(161)	823(21)	4 995(20)	3 693(16)
C(65)	4 665(4)	3 324(3)	2 092(2)	Cl(1)	276(9)	4 774(9)	3 216(6)
C(66)	3 911(4)	3 255(3)	2 156(2)	Cl(2)	621(9)	5 860(9)	3 835(5)

* In this and following crystallographic tables estimated standard deviations in the least significant digit(s) are in parentheses. Atoms Au to C(126) belong to the complex cation, P(13) to F(6) to the anion. The other atoms, belonging to the solvate molecules, have the following occupancy factors: C(131)—C(136), 1.00; C(141)—C(146), 0.75; C(151)—C(153), 1.00; C(161)—Cl(2), 0.50.

(M = Co, Rh, or Ir) with the complexes $[AuCl(PR_3)]$ (R = Me or Ph) or $[Au_2Cl_2\{Ph_2P(CH_2)_nPPh_2\}]$ (*n* = 1 or 2) in a 2:1 M:Au ratio in the presence of $TlPF_6$ affords compounds of formula $[Au\{M(tppme)(P_3)\}_2]PF_6$ [M = Co (**1**), Rh (**2**), or Ir (**3**)], in good yield. The compounds are air stable in the solid state and sparingly soluble in dichloromethane. The formation of (**1**)—(**3**) is invariably achieved also if the reaction is carried out in the presence of higher amounts of gold complexes with

Table 3. Selected bond distances (Å) and angles (°) for compounds (**1**)—(**3**)

	(**1**) (M = Co)	(**2**) (Rh)	(**3**) (Ir)		(**1**) (M = Co)	(**2**) (Rh)	(**3**) (Ir)
Au–P(4)	2.43(1)	2.436(3)	2.416(8)	P(4)–Au–P(5)	55.7(4)	56.5(1)	56.9(3)
Au–P(5)	2.49(1)	2.451(3)	2.453(8)	P(4)–Au–P(7)	157.9(3)	157.7(1)	158.2(3)
Au $\cdots$ P(6)	3.65(1)	3.656(2)	3.678(7)	P(4)–Au–P(8)	127.1(4)	126.7(1)	126.9(3)
Au–P(7)	2.39(1)	2.404(3)	2.422(8)	P(5)–Au–P(7)	133.3(4)	132.1(1)	130.4(3)
Au–P(8)	2.54(1)	2.500(3)	2.509(8)	P(5)–Au–P(8)	154.8(3)	154.8(1)	154.6(3)
Au $\cdots$ P(9)	3.65(1)	3.655(2)	3.654(8)	P(7)–Au–P(8)	55.7(4)	56.6(1)	57.5(3)
M(1)–P(1)	2.20(1)	2.295(3)	2.265(8)	P(1)–M(1)–P(2)	91.6(5)	89.0(1)	88.9(3)
M(1)–P(2)	2.18(1)	2.293(3)	2.289(8)	P(1)–M(1)–P(3)	94.8(4)	92.3(1)	90.9(3)
M(1)–P(3)	2.21(1)	2.288(3)	2.288(8)	P(2)–M(1)–P(3)	94.4(4)	91.6(1)	91.7(3)
M(1)–P(4)	2.28(1)	2.374(4)	2.372(9)	P(4)–M(1)–P(5)	60.7(4)	58.3(1)	58.5(3)
M(1)–P(5)	2.27(1)	2.371(3)	2 379(8)	P(4)–M(1)–P(6)	54.4(4)	52.6(1)	52.8(3)
M(1)–P(6)	2.32(1)	2.431(4)	2.457(9)	P(5)–M(1)–P(6)	55.6(4)	53.1(1)	54.1(3)
M(2)–P(7)	2.30(1)	2.375(4)	2.395(9)	P(7)–M(2)–P(8)	60.5(5)	58.5(1)	59.6(3)
M(2)–P(8)	2.28(1)	2.380(3)	2.378(7)	P(7)–M(2)–P(9)	54.8(4)	52.8(1)	52.3(3)
M(2)–P(9)	2.35(1)	2.439(4)	2.463(8)	P(8)–M(2)–P(9)	55.0(4)	52.8(1)	53.4(3)
M(2)–P(10)	2.17(1)	2.286(4)	2.280(9)	P(10)–M(2)–P(11)	92.6(5)	90.6(1)	89.0(3)
M(2)–P(11)	2.23(1)	2.310(3)	2.287(8)	P(10)–M(2)–P(12)	92.6(5)	90.1(1)	89.9(3)
M(2)–P(12)	2.18(1)	2.300(3)	2.282(8)	P(11)–M(2)–P(12)	92.6(4)	89.5(5)	89.0(3)
P(4)–P(5)	2.30(2)	2.313(5)	2.32(1)				
P(4)–P(6)	2.10(2)	2.129(5)	2.15(1)				
P(5)–P(6)	2.14(2)	2.149(5)	2.20(1)				
P(7)–P(8)	2.31(2)	2.325(5)	2.37(1)				
P(7)–P(9)	2.14(2)	2.143(5)	2.14(1)				
P(8)–P(9)	2.14(2)	2.142(5)	2.18(1)				

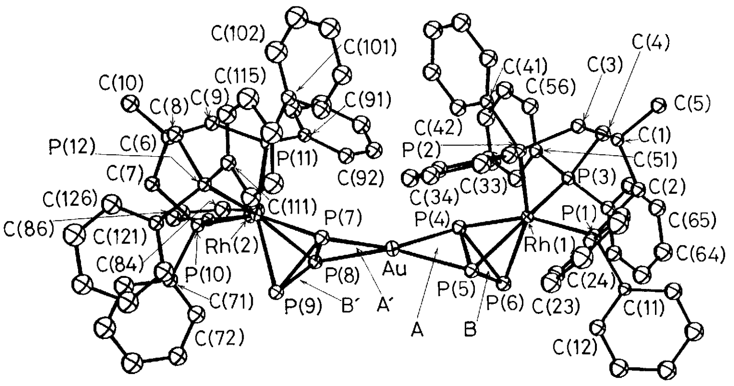

Figure. View of the $[Au\{Rh(tppme)(P_3)\}_2]^+$ cation with 20% probability ellipsoids. Two carbon atoms are identified for each phenyl ring. The A and A′ planes are respectively defined by atoms Au, P(4), P(5), and Au, P(7), P(8); planes B and B′ by P(4), P(5), P(6), and P(7), P(8), P(9)

respect to the above stoicheiometry, or even in the presence of a ten-fold excess of unidentate ligand (PPh_3 or PMe_3). Such results point to interaction of the $[Au(PR_3)]^+$ or $[Au_2\{PPh_2(CH_2)_nPPh_2\}]^{2+}$ cation with the MP_3 core, followed by labilization of the phosphane ligand and formation of (**1**), (**2**), or (**3**) through the co-ordination of a second [M(tppme)(P_3)] complex. Such labilization appears to be significant for it is not affected by the basicity of the unidentate phosphine or by the stabilization of two gold ions by the bidentate ligands. The synthesis of these compounds provides a drastic departure from the general routes to neutral gold(I)–phosphine cluster derivatives. There are also differences with respect to the reaction of the metallaborane $[Fe_4(CO)_{12}BH]^-$ anion with $[Au(PR_3)]^+$ species, where gold–phosphorus bond cleavage only occurs for $PR_2R' = PMePh_2$ or PMe_2Ph.[12]

The structures of the three compounds consist of $[Au\{M(tppme)(P_3)\}_2]^+$ trimetal cations [M = Co (**1**), Rh (**2**), or Ir (**3**)] and PF_6^- anions. Moreover, there are interposed benzene and dichloromethane solvate molecules in the lattice. The overall geometry of the complex cation (Figure) is similar for the three compounds, with the gold atom bridging between the two [M(tppme)(P_3)] units. The Au atom is linked to two unsubstituted P atoms from the P_3 group of each unit. With two quite small (55—57°) and four large (> 126°) P–Au–P angles the gold environment is intermediate between planar and elongated tetrahedral. With reference to the labelling given in the Figure, the dihedral angles between the A and A′ planes, each defined by Au and one pair of connected P atoms, are 51.5(4) (**1**), 51.1(1) (**2**), and 50.4(3)° (**3**). The angles between the A and B, or A′ and B′ planes, where B and B′ are the planes of the triangular P_3 units, are all in the range 133—135°. It is noteworthy that such values are close to those (127—131°) already found for the hinge angles formed by ML_2 or CPh_2 units upon insertion into a bond of a P_2S or As_2S unit bound to a metal atom.[24–26] The spread of bond lengths for the soft Au–P bonds in the three compounds [the largest, 2.39(1)—2.54(1) Å, being found for (**1**)] may be caused by packing forces in the lattice; this is also suggested by the fact that the longest bond in the gold environment is the same [Au–P(8)] in each structure. The two P–P bonds of each cation into which

Table 4. Phosphorus-31 n.m.r. data for the compounds

		δ*/p.p.m.	
Compound	θ/°C	P(tppme)	P(P_3)
(1)	Ambient	37.56 (3, br)	−246.42 (3, br)
(2)	Ambient	23.72 [3, br, d, ^1J(P–Rh) 138 Hz]	−233.98 (3, br)
	−90	23.45 [3, br, d, ^1J(P–Rh) 138 Hz]	−218.41 (2, br), −261.22 (1, br)
(3)	Ambient	−8.32 (3, br)	−271.54 (3, br)
	−90	−8.00 (3, br)	−256.70 (2, br), −299.40 (1, br)

* Hydrogen-1 decoupled; measured in CD_2Cl_2 solution. Chemical shifts positive to high field of 85% H_3PO_4 (external): br = broad, d = doublet.

insertion by the Au atom occurs lengthen significantly (by 8%, in the mean) with respect to the other bonds of the P_3 groups, although such lengthening is definitely smaller than those caused by insertions of different metal–ligand systems into a heteroatomic bond of an E_2S (E = P[25] or As[24]) ring. Also at variance with previous results,[24,25] the M–P bond of each MP_3 unit lying opposite the perturbed P–P bond is slightly lengthened with respect to the other two M–P bonds of the same unit. No other important effects on the geometry of the [M(tppme)(P_3)] fragments, due to bonding by gold, are observed, neither are there major effects accompanying changes in the nature of the metal atom. The latter result, which could not definitely be predicted at the outset, may lessen the interest in comparisons between the three structures. However, the understanding of geometrical features of the gold insertion is improved by the availability of structural data on the three compounds.

All the compounds exhibit in their $^{31}P-\{^1H\}$ n.m.r. spectra at room temperature the PF_6^- multiplet with the expected shift (145.4 p.p.m.) and two broad resonances, well separated, having a 1:1 intensity ratio (Table 4). The lower-field signals are assigned to the phosphorus atoms of the tppme ligand and the higher-field ones to the unsubstituted phosphorus atoms, as the corresponding chemical shifts are not significantly different from those found for the parent [M(tppme)(P_3)] (M = Co, Rh, or Ir) compounds.[27] The tppme resonance of the rhodium derivative is resolved into two broad signals having a coupling constant (138 Hz) in the usual range for $^1J(P_{tppme}–Rh)$. As the equivalence on the n.m.r. time-scale of the P_{tppme} and of the P_{P3} signals is inconsistent with the structures in the solid state, variable-temperature $^{31}P-\{^1H\}$ spectra were recorded for the rhodium **(2)** and iridium **(3)** compounds whose signals are not affected by metal-atom quadrupole moments. For both compounds the resonance of the tppme ligand remains substantially unchanged down to the lowest temperature reached (−90 °C). The resonance due to the unsubstituted P atoms remains unchanged down to −80 °C, but on lowering the temperature further it is resolved into two broad signals centred at −218.41 and −261.22 p.p.m. **(2)** and −256.70 and −299.40 p.p.m. **(3)**, having a 2:1 intensity ratio. Although it is not possible to freeze the fluxional processes completely, even at −90 °C, the presence of two signals is suggestive of inequivalence between the phosphorus atoms bound to gold, on the one hand, and the others in the P_3 units, on the other hand. The [M(tppme)(P_3)] compounds and the isoelectronic [Co(tppme)(P_2X)]BF_4 (X = S or Se)[28] undergo dynamic processes in solution, even at low temperatures, which cause equivalence of the three P atoms of the tppme ligand as well as of those in the cyclic units (P_3 or P_2X). This is probably due to rotation of the cyclic unit with respect to the metal–tppme fragment as no low-energy pathways for direct scrambling of phosphorus ligands have been reported. Although such processes should also occur in the present compounds, they are not sufficient to account for the equivalence of the P_3 phosphorus atoms at > −80 °C which is only consistent with the Au atom undergoing rapid motion over the sets of positions in the P_3 rings.

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