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Synthesis of 2,4,6-tris(trifluoromethyl)phenyl complexes of gold and thallium

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Abstract

Reaction of [AuCl(AsPh$_3$)] with [LiFmes] (Fmes = 2,4,6-tris(trifluoromethyl)phenyl) leads to the gold(I) complex [Au(Fmes)(AsPh$_3$)], which can be used as precursor to other gold(I) complexes by displacement of AsPh$_3$. Thus, treatment with diphosphines leads to mono- or dinuclear gold(I) complexes, namely [Au(Fmes)(dppm)], [Au(dppe)$_2$][Au(Fmes)$_2$] or [{Au(Fmes)}$_2$(μ-P–P)] (P–P: bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe)). X-ray diffraction studies of [{Au(Fmes)}$_2$(μ-P–P)] show the expected *trans*-conformation for dppe but an unexpected *gauche* conformation for the dppm derivative. There are no short gold–gold contacts. The ionic nature of [Au(dppe)$_2$][Au(Fmes)$_2$] was also established by X-ray methods. Reaction of TlCl$_3$ with [LiFmes] affords [Tl(Fmes)$_3$], which does not react further with gold(I) derivatives to give gold(III) derivatives.

Keywords: Gold; Thallium; Diphosphine; Fluoroaryl

1. Introduction

The organometallic chemistry of gold has been developed with two principal types of ligand: ylides or pentafluorophenyl groups [1]. Both kinds of complexes are much more stable than the corresponding derivatives with conventional alkyl or aryl ligands. The higher stability of pentafluorophenyl derivatives has been attributed to two factors: (a) the high electronegativity of the ligand, which can produce some ionic character in the gold–carbon bond and some π back-donation from gold to carbon; and (b) the relative bulkiness of the ligand. The 2,4,6-tris(trifluoromethyl)phenyl ligand (Fmes) is a closely related ligand that is less electronegative (although still highly electron-withdrawing) but has a higher steric demand than the pentafluorophenyl group. These properties have been exploited to stabilise complexes of main group elements or transition metals with low oxidation states or low coordination numbers [2]. Recently, Espinet et al. have described some gold(I) and gold(III) derivatives of Fmes [3].

In this paper we report the synthesis and structural characterisation of some gold and thallium complexes with the tris(trifluoromethyl)phenyl ligand. We have also determined the crystal structure of the gold(I) complexes [Au(dppe)$_2$][Au(Fmes)$_2$], {Au(Fmes)}$_2$(μ-dppm) and {Au(Fmes)}$_2$(μ-dppe).

2. Results and discussion

2.1. Synthesis and characterisation

The reaction of lithium 2,4,6-tris(trifluoromethyl)-phenyl, prepared in situ, with [AuCl(AsPh$_3$)] (molar ratio 2:1) leads to the gold(I) complex [Au(Fmes)-(AsPh$_3$)] (**1**). This derivative is a precursor to other tris(trifluoromethyl)phenylgold(I) complexes, by dis-

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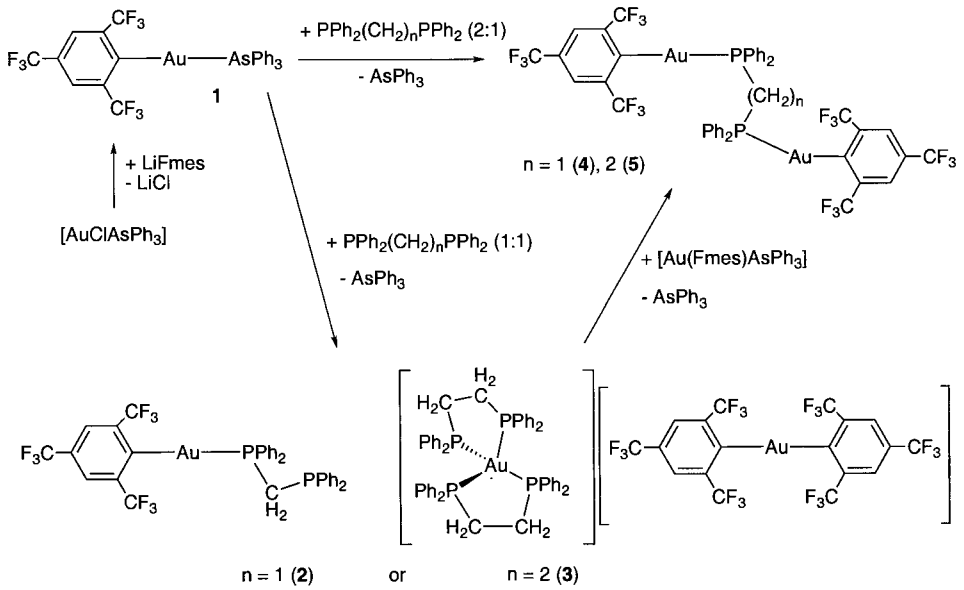
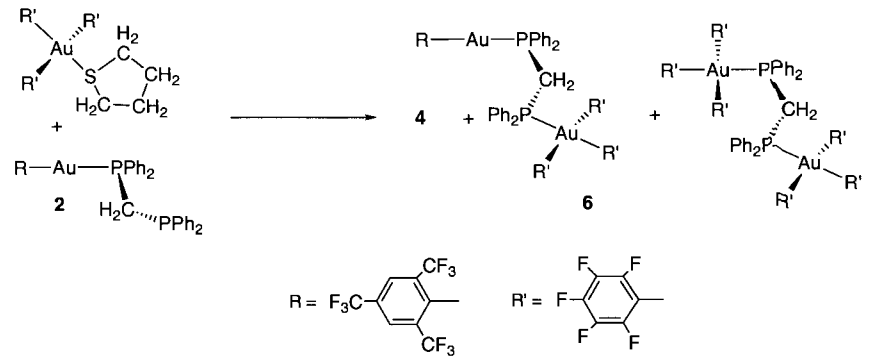
placement of the triphenylarsine ligand (Scheme 1). Complex **1** reacts with diphosphines in a 1:1 molar ratio to give gold(I) derivatives [Au(Fmes)(dppm)] (**2**) or $[Au(dppe)_2][Au(Fmes)_2]$ (**3**). The latter has been prepared as the tetraalkylammonium salt in [3]. We were not able to isolate complex **2** as a solid and we therefore, describe only its spectroscopic data. Complex **2** is highly soluble in hexane and an oily solid is obtained even at low temperature; this derivative can be prepared from the precursor [Au(Fmes)(tht)] (described in Ref. [3]) but again an oily solid was obtained. The reaction of complex **1** with diphosphines in a 2:1 molar ratio affords the dinuclear gold(I) derivatives **4**–**5**, which can be also synthesised by addition of complex **1** to an in situ solution of complexes **2**–**3**. These derivatives are air- and moisture-stable white solids at room temperature.

The ^{1}H-NMR spectra show the Fmes protons as singlets at ca. 8 ppm, and also signals from the triphenylarsine or diphosphine ligands. The ^{19}F-NMR spectra show the pattern arising from one Fmes group, a singlet at ca. −60 ppm for the *ortho*-CF_3 and another at ca. −63 ppm for the *para*-CF_3. The $^{31}P\{^1H\}$-NMR spectra of complexes **4** and **5** show a singlet at 31.6 and 40.2 ppm, respectively. The $^{31}P\{^1H\}$-NMR spectrum of complex **2** shows two broad resonances at 32 and −22 ppm, which at −55 °C are seen as doublets. The values of the chemical shifts and the presence of P–P coupling imply that the diphosphine dppm is monocoordinated to one Au(Fmes) unit, with its second phosphine 'arm' free, at least at low temperature. The $^{31}P\{^1H\}$-NMR spectrum of complex **3** shows only one signal, at ca. 15 ppm. The LSIMS mass spectra show the peaks corresponding to $[M\text{-Fmes}]^+$ at m/z (% abundance) = 503(100), 581(60), 1059(100), 1073(60), for **1**, **2**, **4**, and **5** respectively; in the LSIMS mass spectrum of complex **3**, the peak from the cation $[Au(dppe)_2]^+$ is observed at 993(65%).

In order to obtain dinuclear gold(I)–gold(III) complexes containing both pentafluorophenyl and Fmes



Scheme 1.



Scheme 2.

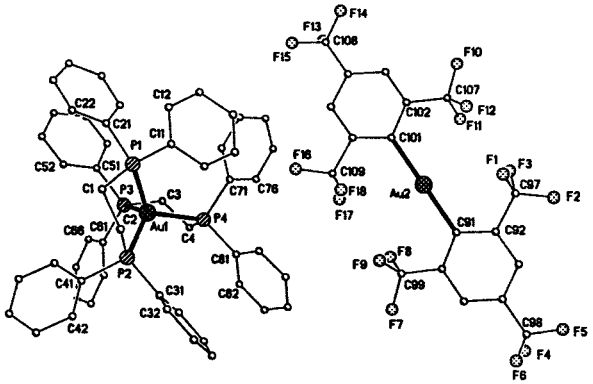


Fig. 1. Molecular structure of complex **3** showing the atom-numbering scheme. All H atoms have been omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for complex **3**

Bond lengths			
Au(1)–P(2)	2.3908(6)	C(1)–C(2)	1.529(3)
Au(1)–P(3)	2.3941(7)	C(3)–C(4)	1.538(4)
Au(1)–P(1)	2.4038(6)	Au(2)–C(101)	2.054(2)
Au(1)–P(4)	2.4092(6)	Au(2)–C(91)	2.065(2)
Bond angles			
P(2)–Au(1)–P(3)	126.63(2)	P(3)–Au(1)–P(4)	85.70(2)
P(2)–Au(1)–P(1)	86.38(2)	P(1)–Au(1)–P(4)	125.06(2)
P(3)–Au(1)–P(1)	117.33(2)	C(101)–Au(2)–C(91)	179.58(9)
P(2)–Au(1)–P(4)	120.43(2)		

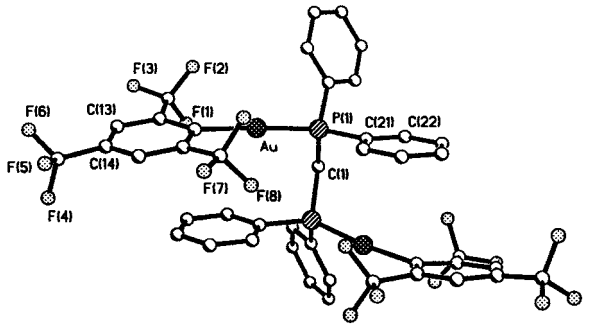


Fig. 2. Molecular structure of complex **4** showing the atom-numbering scheme. All H atoms have been omitted for clarity.

ligands, the reaction of complex **2** with $[Au(C_6F_5)_3(tht)]$ has been carried out (Scheme 2). The process however leads to a mixture of three dinuclear complexes: the expected mixed derivative **6** accompanied by two symmetrical complexes containing two Au(Fmes) or two $Au(C_6F_5)_3$ units (in a 3.4:1:1 molar ratio), as shown by the NMR spectra (Section 3).

The reaction of complex **2** with silver perchlorate (in the molar ratio 2:1) leads to a mixture which mainly contains complex **4** and $[Ag_2(OClO_3)_2(dppm)_3]$, instead of gold(I)–silver(I) complexes as described for the similar derivative [Au(mesityl)(dppm)] (mesityl = 2,4,6-tris(-methyl)phenyl) [4].

Treatment of $TlCl_3$ with a freshly prepared [LiFmes] solution (molar ratio 1:4) affords complex **7** $[Tl(Fmes)_3]$ as a white solid, the first thallium complex containing this ligand. The IR spectrum does not show any Tl–Cl absorption. A unique type of Fmes ligand is seen in the ^{1}H- and ^{19}F-NMR spectra, and all the resonances are strongly coupled to thallium, as reported for pentafluorophenylthallium derivatives [5] but in contrast to thallium 2,4,6-tris(trifluoromethyl)phenoxide, where no Tl–H or Tl–F couplings were reported [6]. The parent peak of the LSIMS mass spectrum corresponds to $[M - Fmes]^+$ at 767. To obtain gold(III) complexes by aryl oxidative transfer from thallium to gold, a well-known method with $[TlCl(C_6F_5)_2]$, or at least to transfer Fmes to gold [7], we proceeded to treat derivative **7** with $[Au(C_6F_5)(tht)]$, but there was no reaction after several days; under refluxing conditions, the gold(I) complex decomposed without reaction.

2.2. Crystal structures

In order to determine the molecular structure of complex **3**, we have carried out an X-ray diffraction analysis. Complex **3** is an ionic complex, namely $[Au(dppe)_2][Au(Fmes)_2]$, as shown in Fig. 1, with selected bonds and angles in Table 1. The synthesis and structure of the tetrabutylammonium salt of the same anion was recently described by some of us [3]. The structure of the anion in **3** is with one exception closely similar to that in Ref. [3] (where a more detailed discussion will be found), with a C–Au–C angle of 179.58(9)°, Au–C bond lengths of 2.054(2) and 2.065(2) Å, and narrow ring angles at the *ipso* C atoms (113.9, 113.3(2)°; this is a common feature of aryl complexes of coinage and related metals [3]). Similar values are observed in derivatives **4** and **5** (see below). The exception concerns the angle between the two aryl ligand planes, which is 27° in Ref. [3] but only 19° in **3**.

Various salts of the cation have previously been subjected to crystal structure determination, seeking structure relationships with their reported antitumour activity in mice [8,9]. The gold centre is tetracoordinated with almost equal Au–P bond lengths of 2.3908(6)–2.4092(6) Å, similar to those reported in $[Au(dppe)_2]Cl$ [10] and $[Au(dppe)_2][SbF_6]$ [11]. The P–Au–P angles are 85.70(2) and 86.38(2)° for the bite angles and 117.33(2)–126.63(2)° for the others, cf. $[Au(dppe)_2]Cl$ 85.4(1)–129.6(1)° and $[Au(dppe)_2][SbF_6]$ 86.4(1)–130.6(1)°.

X-ray diffraction studies of complexes **4** and **5** were carried out to determine whether the bulkiness of the ligand affects the geometry of the molecule compared to other less hindered complexes. Fig. 2 shows the molecule of **4**, with selected bond lengths and angles in Table 2; it displays crystallographic twofold symmetry. The gold(I) centre displays an almost linear coordina-

tion, with a C–Au–P angle of 174.56(10)°. The ring angle at the *ipso* carbon is narrow, 114.8(3)°. There are no short gold–gold contacts, the intramolecular Au–Au distance being 7.041 Å and the shortest intermolecular more than 6.6 Å. The latter gold–gold distance can be rationalised in terms of the steric bulk of the Fmes ligand, which does not allow a *cis* conformation of the diphosphine; the observed torsion angle Au–P···P′–Au′ is −109° (*gauche*). This contrasts with other cases containing a single dppm bridge, where a *cis* conformation is preferred, leading to short gold–gold distances such as the 3.154(1) Å found in $[(AuPh)_2(\mu\text{-dppm})]$ [12], 3.251(1) Å in $[(AuMe)_2(\mu\text{-dppm})]$ [12], 3.3307(9) Å in $[(AuCC'Bu)_2(\mu\text{-dppm})]$ [13], 3.236(1) Å in $[\{Au(SeC(NH_2)_2)\}_2(\mu\text{-dppm})]Cl_2$ [14], 3.1680(3) Å in $[(AuSiPh_3)_2(\mu\text{-dppm})]$ [15], and 3.163(1) Å in $[\{Au(C_6F_5)\}_2(\mu\text{-dppm})]$ which also contains a fluorophenyl ligand [16]. Curiously the dinuclear gold(III) complex with a bridging dppm and 2,6-diphenylpyridine acting as tridentate C,N,C-donor ligand also shows a *cis* geometry, although in this case the π stacking of these ligands, which prefer to be parallel to each other, can favour this conformation [17]. An intermediate case is presented by the complex $[(AuCl)_2(\mu\text{-dppm})]$, which shows a gold–gold distance of 3.341(1) Å with a PAu···AuP torsion angle of 68° [18].

Table 2
Selected bond lengths (Å) and angles (°) for complex **4**

Bond lengths			
Au–C(11)	2.069(3)	P(1)–C(21)	1.835(4)
Au–P(1)	2.2844(9)	P(1)–C(1)	1.843(3)
P(1)–C(31)	1.821(4)		
Bond angles			
C(11)–Au–P(1)	174.56(10)	C(31)–P(1)–Au	112.80(12)
C(31)–P(1)–C(21)	105.73(17)	C(21)–P(1)–Au	116.09(13)
C(31)–P(1)–C(1)	103.15(18)	C(1)–P(1)–Au	111.85(8)
C(21)–P(1)–C(1)	106.16(14)	P(1) # 1–C(1)–P(1)	116.2

Symmetry transformation used to generate equivalent atoms: # 1, −x+1, y, −z+1/2.

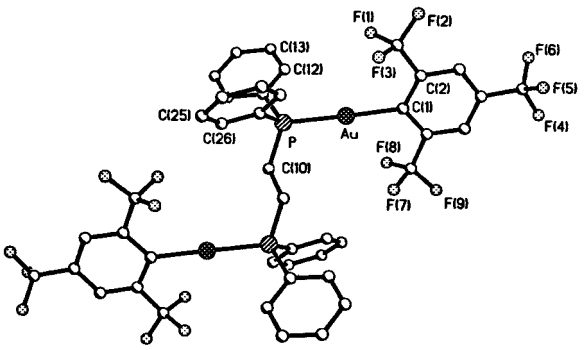


Fig. 3. Molecular structure of complex **5** showing the atom-numbering scheme. All H atoms have been omitted for clarity.

Table 3
Bond lengths (Å) and angles (°) for complex **5**

Bond lengths			
Au–C(1)	2.064(2)	P–C(10)	1.831(2)
Au–P	2.2804(6)	P–C(11)	1.813(2)
P–C(21)	1.813(2)		
Bond angles			
C(1)–Au–P	178.69(6)	C(11)–P–C(10)	104.99(9)
C(21)–P–C(11)	108.02(9)	C(21)–P–Au	113.68(7)
C(10)–P–Au	113.14(7)	C(11)–P–Au	112.18(7)
C(21)–P–C(10)	104.14(9)		

Symmetry transformations used to generate equivalent atoms: # 1: −x+2, −y+1, −z+1.

The Au–P distance of 2.2844(9) Å is slightly longer than those reported in $[(AuCC'Bu)_2(\mu\text{-dppm})]$ (2.266(2) and 2.268(2) Å) but appreciably shorter than in $[(AuSiPh_3)_2(\mu\text{-dppm})]$ (2.357(1) and 2.370(1) Å). The Au–P distance and the Au–C distance (2.069(3) Å) are similar to those in alkyl or aryl derivatives with a dppm bridge.

The crystal structure of complex **5** is shown in Fig. 3, with selected bond lengths and angles in Table 3. It displays inversion symmetry about the mid-point of the ethane C–C bond. The geometry around the gold atom is linear, C–Au–P 178.69(6)°, and the angle at the *ipso* C of Fmes is narrow at 115.0(2)°. The long intramolecular gold–gold distance (5.092 Å) is associated with the symmetry-imposed *trans* conformation of dppe, which is the commonest in complexes containing a single dppe bridge, as found in $[(AuS_2CNEt_2)_2(\mu\text{-dppe})]$ [19], $[(AuCl)_2(\mu\text{-dppe})]$ [20], $[(AuSePh)_2(\mu\text{-dppe})]$ [21], $[(AuS\text{-carborane})_2(\mu\text{-dppe})]$ (S-carborane is 1,2-dicarba-closo-dodecaborane-1-thiolate) [22], $[\{Au(Si(SiMe_3)_3)\}_2(\mu\text{-dppe})]$ [15] and the related derivative $[(AuMes)_2(\mu\text{-dppe})]$ (Mes = 2,4,6-tris(methyl)phenyl) [23]. To the best of our knowledge, the *cis*-conformation has only been reported in $[(AuCCPh)_2(\mu\text{-dppe})]$ (Au–Au distance of 3.153(2) Å) [24] and in a dinuclear gold(III) complex containing a dppe bridge and 2,6-diphenylpyridine acting as tridentate C,C,N-donor ligand, although as in the dppm derivate (see above) the π stacking of these ligands favours this conformation [17]. The shortest intermolecular Au–Au distance is more than 8 Å, in contrast to 3.0442(9) Å in $[(AuSePh)_2(\mu\text{-dppe})]$ (forming polymeric chains) and 3.189(1) Å in $[(AuCl)_2(\mu\text{-dppe})]$ (forming dimers). The Au–P and the Au–C bond lengths, 2.2804(6) and 2.064(2) Å respectively, are similar to those found in complex **4** and in $[(AuMes)_2(\mu\text{-dppe})]$.

In conclusion, we describe the synthesis of the first Fmes thallium complex and a new Fmes gold(I) precursor, from which fluoromesityl–phosphino–gold(I) complexes can be prepared. The high steric demand of this ligand leads to an unusual *gauche*-conformation in the dinuclear diphosphine complex $\{Au(Fmes)\}_2(\mu\text{-}PPh_2\text{-}$

CH_2PPh_2). We have shown that mononuclear complexes of the same stoichiometry [Au(Fmes)(P–P)] have different molecular structure depending on the diphosphine, [Au(Fmes)(dppm)] and $[Au(dppe)_2][Au(Fmes)_2]$.

3. Experimental

3.1. General

All the reactions were carried out under an argon atmosphere at room temperature (r.t.). IR spectra were recorded on a Perkin–Elmer 883 spectrophotometer, over the range 4000–200 cm^{-1}, by using Nujol mulls between polyethylene sheets. ^1H-, ^{19}F- and $^{31}P\{^1H\}$-NMR spectra were recorded on a Bruker ARX 300 or GEMINI 2000 apparatus in $CDCl_3$ solutions (if no other solvent is stated); chemical shifts are quoted relative to $SiMe_4$ (external, ^1H), $CFCl_3$ (external, ^{19}F) and 85% H_3PO_4 (external, ^{31}P). C, H, N and S analyses were performed with a Perkin–Elmer 2400 microanalyser. Mass spectra were recorded on a VG Autospec using LSIMS technique (with Cs gun) and 3-nitrobenzyl alcohol as matrix. *Caution:* thallium compounds are highly toxic and must be handled with special care.

3.2. Preparation of [Au(Fmes)($AsPh_3$)] (1)

To a freshly prepared Et_2O solution of Li(Fmes) (Fmes = 1,3,5-tris(trifluoromethyl)phenyl; 0.6 mmol) [25] was added [$AuCl(AsPh_3)$] (0.162 g, 0.3 mmol) [26]. After stirring for 6 h, two drops of water were added to hydrolyse the excess of lithium derivative. The mixture was evaporated to dryness, then CH_2Cl_2 was added and the solution filtered through a Na_2SO_4 sinter. The clear solution was evaporated to ca. 1 ml, and addition of petroleum ether afforded **1** as a white solid. Yield of **1**: 155 mg, 66%. ^1H-NMR: δ 8.08 (s, 2H, Fmes), 7.6–7.3 (m, 15H, Ph). ^{19}F-NMR: δ −60.9 (s, $6F_o$), −63.51 (s, $3F_p$). Anal. Calc. for $C_{27}H_{17}AuAsF_9$: C, 41.35; H, 2.2. Found: C, 41.2; H, 2.0%. LSIMS (m/z, %, assignment): 503 (100, $[M-(Fmes)]^+$), 809 (45, $[Au(AsPh_3)_2]^+$).

3.3. Preparation of [Au(Fmes)(dppm)] (2)

To a deuterated $CHCl_3$ solution (1 ml) or CH_2Cl_2 solution (10 ml) of **1** (0.1 mmol, 78 mg) or [Au(Fmes)(tht)] (0.1 mmol, 57 mg) was added the diphosphine dppm (0.1 mmol, 38 mg). After stirring for 30 min, derivative **2** is formed, as seen in the NMR spectra. NMR data for complex **2**. ^1H-NMR: δ 8.05 (s, 2H, Fmes), 7.6–7.3 (m, 20H, Ph), 3.16 (br, 2H, CH_2–P). ^{19}F-NMR: δ −60.57 (s, $6F_o$), −63.44 (s, $3F_p$). $^{31}P\{^1H\}$-NMR: δ 32.0 (br, 1P), −22.1 (br, 1P); $^{31}P\{^1H\}$-NMR (−55 °C): δ 32.0 (d, $^2J(PP) = 105.9$ Hz, 1P), −22.1 (d, 1P). LSIMS (m/z, %, assignment): 581 (60, $[Au(dppm)]^+$), 862 (50, $[M]^+$), 965 (20, $[Au(dppm)_2]^+$), 1059 (100, $[Au_2(Fmes)(dppm)]^+$).

3.4. Preparation of [Au(dppe)$_2$][Au(Fmes)$_2$] (3)

To a CH_2Cl_2 solution (10 ml) of **1** (0.1 mmol, 78 mg) was added the diphosphine dppe (0.1 mmol, 40 mg). After stirring for 30 min, the solution was evaporated to ca. 1 ml. Addition of petroleum ether afforded complex **3** as a white solid. Yield of **3**: 48 mg, 55%. ^1H-NMR: δ 8.14 (s, 2H, Fmes), 7.6–7.4 (m, 20H, Ph), 2.47 (s, 4H, CH_2–P). ^{19}F-NMR: δ −60.42 (s, $6F_o$), −63.47 (s, $3F_p$). $^{31}P\{^1H\}$-NMR: δ 15.1 (br). Anal. Calc. for $C_{70}H_{52}Au_2F_{18}P_4$: C, 47.95; H, 3.0. Found: C, 47.7; H, 2.75%. LSIMS (m/z, %, assignment): 595 (100, $[Au(dppe)]^+$), 876 (90, $[Au(Fmes)(dppe)]^+$), 993 (65, $[Au(dppe)_2]^+$), 1073 (15, $[Au_2(Fmes)(dppe)]^+$).

3.5. Preparation of [{Au(Fmes)}$_2$(μ-P–P)]; P–P = dppm (4), dppe (5)

These complexes can be prepared in two different ways: (a) To a 10 ml Et_2O solution of **1** (0.1 mmol, 78 mg) was added the diphosphine (0.05 mmol; dppm 19 mg, dppe 20 mg). After stirring for 1 h, the solution was concentrated to ca. 1 ml. Addition of petroleum ether afforded complexes **4**–**5** as white solids. (b) To a 5 ml Et_2O (or 1 ml $CDCl_3$) solution of **2** (0.05 mmol) or **3** (0.025 mmol; 44 mg) was added the corresponding amount of complex **1** (0.05 mmol; 39 mg). Then as stated in (a). Yield of **4**: 40 mg, 60%. ^1H-NMR: δ 7.88 (s, 4H, Fmes), 7.6–7.3 (m, 20H, Ph), 3.63 (t, $^2J(HP) = 10.2$ Hz, 2H, CH_2–P). ^{19}F-NMR: δ −60.60 (s, $6F_o$), −63.66 (s, $3F_p$). $^{31}P\{^1H\}$-NMR: δ 31.6 (s). Anal. Calc. for $C_{43}H_{26}Au_2F_{18}P_2$: C, 38.55; H, 1.95. Found: C, 38.25; H, 1.85. LSIMS (m/z, %, assignment): 581 (20, $[Au(dppm)]^+$), 1059 (100, $[Au_2(Fmes)(dppm)]^+$). Yield of **5**: 45 mg, 66%. ^1H-NMR: δ 8.10 (s, 4H, Fmes), 7.7–7.2 (m, 20H, Ph), 2.79 (s, 4H, CH_2–P); ^{19}F-NMR: δ −60.09 (s, $6F_o$), −63.24 (s, $3F_p$). $^{31}P\{^1H\}$-NMR: δ 40.2 (s). Anal. Calc. for $C_{44}H_{28}Au_2F_{18}P_2$: C, 39.0; H, 2.08. Found: C, 39.35; H, 2.4%. LSIMS (m/z, %, assignment): 595 (100, $[Au(dppe)]^+$), 1073 (60, $[Au_2(Fmes)(dppe)]^+$).

3.6. Reaction of [Au(Fmes)(dppm)] with [Au(C_6F_5)$_3$(tht)]

To a 10 ml Et_2O (or 1 ml $CDCl_3$) solution of **2** (0.05 mmol) was added [$Au(C_6F_5)_3$(tht)] (0.05 mmol; 39 mg) [27]. After stirring for 1 h, the solution was concentrated to ca. 1 ml. Addition of petroleum ether afforded a mixture of complexes [(Fmes)Au(μ-dppm)$Au(C_6F_5)_3$] (**6**), [{Au(Fmes)}$_2$(μ-dppm)] (**4**) and [{$Au(C_6F_5)_3$}$_2$(μ-dppm)] as white solids. NMR data for complex **6**: ^1H-NMR: δ 8.01 (s, 2H, Fmes), 7.6–7.3 (m, 20H, Ph), 3.42 (t, $^2J(HP) = 9.1$ Hz, 2H, CH_2–P). ^{19}F-NMR: δ

Table 4
Details of crystal data and structure refinement for complexes **3**, **4** and **5**

Compound	**3**	**4**	**5**
Empirical formula	$C_{70}H_{52}Au_2F_{18}P_4$	$C_{43}H_{26}Au_2F_{18}P_2$	$C_{44}H_{28}Au_2F_{18}P_2$
Formula weight	1752.93	1340.51	1354.54
Temperature (K)	143(2)	173(2)	143(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$	$P2_1/c$
a (Å)	12.038(2)	21.2598(6)	11.4503(14)
b (Å)	13.803(2)	8.6920(2)	9.3155(10)
c (Å)	20.239(4)	24.9461(6)	20.643(2)
α (°)	92.257(6)	90	90
β (°)	99.150(6)	114.704(3)	96.279(3)
γ (°)	99.978(6)	90	90
V (Å^3)	3262.3(10)	4187.90(18)	2188.6(4)
Z	2	4	2
D_{calc} (Mg m^{-3})	1.785	2.126	2.055
Absorption coefficient (mm^{-1})	4.684	7.188	6.878
$F(000)$	1704	2536	1284
Crystal habit	Colourless tablet	Colourless prism, cut	Colourless wedge
Crystal size (mm)	$0.29 \times 0.24 \times 0.16$	$0.7 \times 0.4 \times 0.3$	$0.27 \times 0.14 \times 0.10$
Diffractometer	Bruker SMART 1000 CCD	Siemens SMART CCD	Bruker SMART 1000 CCD
Theta range for data collection (°)	1.02–30.03	1.80–28.27	1.79–30.00
Index ranges	$-16 \le h \le 16$, $-19 \le k \le 19$, $-28 \le l \le 28$	$-28 \le h \le 22$, $-11 \le k \le 11$, $-23 \le l \le 33$	$-15 \le h \le 16$, $-13 \le k \le 13$, $-29 \le l \le 29$
Reflections collected	60970	13649	25278
Independent reflections	18 974 [$R_{int} = 0.0413$]	5146 [$R_{int} = 0.0306$]	6368 [$R_{int} = 0.0265$]
Max/min transmission	0.862 and 0.670	0.928 and 0.428	0.945 and 0.600
Data/restraints/parameters	18974/220/847	5146/69/294	6368/249/298
Goodness-of-fit on F^2	0.963	1.052	1.012
R_1 [$I > 2\sigma(I)$]	0.0230	0.0304	0.0181
wR_2 (all data)	0.0490	0.0736	0.0444
Largest difference peak and hole (e Å^{-3})	1.023 and −0.974	1.869 and −2.801	0.908 and −0.989

−60.50 (s, $6F_o$, CF_3), −63.64 (s, $3F_p$, CF_3), −120.68 (m, $4F_o$, C_6F_5), −122.75 (m, $2F_o$, C_6F_5), −156.79 (t, $1F_p$, C_6F_5), −157.94 (m, $2F_p$, C_6F_5), −160.95 (m, $2F_m$, C_6F_5), −161.88 (m, $4F_m$, C_6F_5). $^{31}P\{^1H\}$-NMR: δ 28.0 (d, $^2J(PP) = 17.7$ Hz, 1P, *trans* to Fmes), 10.7 (m, 1P).

3.7. Preparation of [Tl(Fmes)$_3$] (7)

To a freshly prepared Et_2O solution of [Li(Fmes)] (Fmes = 1,3,5-tris(trifluoromethyl)phenyl; 1.6 mmol) was added $TlCl_3$ (125 mg, 0.4 mmol). After stirring overnight, two drops of water were added to hydrolyse the excess of lithium derivative. The mixture was dried to dryness, then CH_2Cl_2 was added and filtered through a Na_2SO_4 sinter. The clear solution was evaporated to ca. 1 ml and the addition of petroleum ether afforded **7** as a white solid. Yield of **7**: 168 mg, 40%. ^{1}H-NMR: δ 8.25 (d, $^4J(^{203,205}Tl–H) = 99.1$ Hz, Fmes). ^{19}F-NMR: δ −61.64 (d, $^4J(^{203,205}Tl–F) = 70.4$ Hz, $6F_o$), −64.04 (d, $^6J(^{203,205}Tl–F) = 22.8$ Hz, $3F_p$). Anal. Calc. for $C_{27}H_6F_{27}Tl$: C, 30.95; H, 0.6. Found: C, 30.75; H, 0.8%. LSIMS (m/z, %, assignment): 767 (100, $[M - (Fmes)]^+$).

3.8. Crystal structure determination of complexes 3, 4 and 5

Colourless crystals were obtained from slow diffusion of petroleum ether 40–60 into a CH_2Cl_2 solution of the appropriate complex. Crystal data and details of data collection and structure refinement are given in Table 4. Data were measured on SMART area detectors. Absorption corrections were based on multiple scans (program SADABS). The structures were refined anisotropically on F^2 (program SHELXL-97 [28]) using a system of restraints (to light atom U values and local ring symmetry). H atoms were included using a riding model.

4. Supplementary material

Complete X-ray data (excluding structure factors) for complexes **3**, **4** and **5** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 153822–153824. Copies can be obtained free of charge from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-

1123-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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