Synthesis and interconversions of digold(I), tetragold(I), digold(II), gold(I)–gold(III) and digold(III) complexes of fluorine-substituted aryl carbanions†

Martin A. Bennett,[a] Suresh K. Bhargava,*[b] Nedaossadat Mirzadeh,[b] Steven H. Privér,[b] Jörg Wagler[a] and Anthony C. Willis[a]

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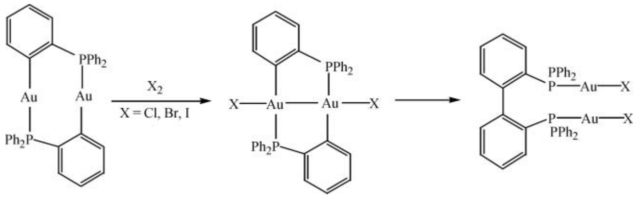
Treatment of [AuXL] (X = Br, L = $AsPh_3$; X = Cl, L = tht) with the lithium or trimethyltin derivatives of the carbanions $[2\text{-}C_6F_4PPh_2]^-$ and $[C_6H_3\text{-}n\text{-}F\text{-}2\text{-}PPh_2]^-$ (n = 5, 6) gives digold(I) complexes $[Au_2(\mu\text{-carbanion})_2]$ (carbanion = $2\text{-}C_6F_4PPh_2$ **2**, $C_6H_3\text{-}5\text{-}F\text{-}2\text{-}PPh_2$ **3**, $C_6H_3\text{-}6\text{-}F\text{-}2\text{-}PPh_2$ **4**) which, like their $2\text{-}C_6H_4PPh_2$ counterpart, undergo oxidative addition with halogens X_2 (X = Cl, Br, I) to give the corresponding, metal-metal bonded digold(II) complexes $[Au_2X_2(\mu\text{-carbanion})_2]$ (carbanion = $2\text{-}C_6F_4PPh_2$, X = Cl **5**, Br **8**, I **11**; carbanion = $C_6H_3\text{-}5\text{-}F\text{-}2\text{-}PPh_2$, X = Cl **6**, Br **9**, I **12**; carbanion = $C_6H_3\text{-}6\text{-}F\text{-}2\text{-}PPh_2$, X = Cl **7**, Br **10**, I **13**). In the case of $2\text{-}C_6F_4PPh_2$ and $C_6H_3\text{-}6\text{-}F\text{-}2\text{-}PPh_2$, the dihalodigold(II) complexes rearrange on heating to isomeric gold(I)–gold(III) complexes $[XAu^I(\mu\text{-}P,C\text{-carbanion})(\kappa^2\text{-}P,C\text{-carbanion})Au^{III}X]$ (carbanion = $2\text{-}C_6F_4PPh_2$, X = Cl **25**, Br **26**, I **27**; carbanion = $C_6H_3\text{-}6\text{-}F\text{-}2\text{-}PPh_2$, X = Cl **28**, Br **29**, I **30**), in which one of the carbanions chelates to the gold(III) atom. This isomerisation is similar to, but occurs more slowly than, that in the corresponding $C_6H_3\text{-}6\text{-}Me\text{-}2\text{-}PPh_2$ system. The Au_2X_2 complexes **6**, **9** and **12**, on the other hand, rearrange on heating *via* C–C coupling to give digold(I) complexes of the corresponding 2,2′-biphenyldiylbis-(diphenylphosphine), $[Au_2X_2(2,2'\text{-}Ph_2P\text{-}5\text{-}F\text{-}C_6H_3C_6H_3\text{-}5\text{-}F\text{-}PPh_2)]$ (X = Cl **32**, Br **33**, I **34**), this behaviour resembling that of the $2\text{-}C_6H_4PPh_2$ and $C_6H_3\text{-}5\text{-}Me\text{-}2\text{-}PPh_2$ systems. Since the C–C coupling probably occurs *via* undetected gold(I)–gold(III) intermediates, the presence of a 6-fluoro substituent is evidently sufficient to suppress the reductive eliminations, possibly because of an electronic effect that strengthens the gold(III)-aryl bond. Anation of **5** or **8** gives the bis(oxyanion)digold(II) complexes $[Au_2Y_2(\mu\text{-}2\text{-}C_6F_4PPh_2)_2]$ (Y = OAc **14**, ONO_2 **15**, OBz **16**, O_2CCF_3 **17** and OTf **20**), which do not isomerise to the corresponding gold(I)–gold(III) complexes $[YAu(\mu\text{-}2\text{-}C_6F_4PPh_2)(\kappa^2\text{-}2\text{-}C_6F_4PPh_2)AuY]$ on heating, though the latter [Y = OAc **35**, ONO_2 **36**, OBz **37**, O_2CCF_3 **38**] can be made by anation of **25–27**. Reaction of the bis(benzoato)digold(II) complex **16** with dimethylzinc gives a dimethyl gold(I)–gold(III) complex, $[Au^I(\mu\text{-}2\text{-}C_6F_4PPh_2)_2Au^{III}(CH_3)_2]$ **19**, in which both $2\text{-}C_6F_4PPh_2$ groups are bridging. In contrast, the corresponding reaction of **16** with C_6F_5Li gives a digold(II) complex $[Au^{II}_2(C_6F_5)_2(\mu\text{-}2\text{-}C_6F_4PPh_2)_2]$ **18**, which on heating isomerises to a gold(I)–gold(III) complex, $[(C_6F_5)Au^I(\mu\text{-}2\text{-}C_6F_4PPh_2)(\kappa^2\text{-}2\text{-}C_6F_4PPh_2)Au^{III}(C_6F_5)]$ **31**, analogous to **25–27**. The bis(triflato)digold(II) complex **20** is reduced by methanol or cyclohexanol in CH_2Cl_2 to a tetranuclear gold(I) complex $[Au_4(\mu\text{-}2\text{-}C_6F_4PPh_2)_4]$ **21** in which the four carbanions bridge a square array of metal atoms, as shown by a single-crystal X-ray diffraction study. The corresponding tetramers $[Au_4(\mu\text{-}C_6H_3\text{-}n\text{-}F\text{-}2\text{-}PPh_2)_4]$ (n = 5 **22**, 6 **23**) are formed as minor by-products in the preparation of dimers **3** and **4**; the tetramers do not interconvert readily with, and are not in equilibrium with, the corresponding dimers **2–4**. Addition of an excess of chlorine or bromine (X_2) to the digold(II) complexes **5** and **8**, and to their gold(I)–gold(III) isomers **25** and **26**, gives isomeric digold(III) complexes $[Au_2X_4(\mu\text{-}2\text{-}C_6F_4PPh_2)_2]$ (X = Cl **39**, Br **40**) and $[X_3Au(\mu\text{-}2\text{-}C_6F_4PPh_2)AuX(\kappa^2\text{-}2\text{-}C_6F_4PPh_2)]$ (X = Cl **41**, Br **42**), respectively. The structures of the digold(I) complexes **2**, **4** and **32**, the digold(II) complexes **5–11** and **14–18**, the gold(I)–gold(III) complexes **19**, **25**, **35** and **38**, the tetragold(I) complexes **21** and **22**, and the digold(III) complexes **41** and **42**, have been determined by single-crystal X-ray diffraction. In the digold(II) ($5d^9$–$5d^9$) series, there is a systematic lengthening, and presumably weakening, of the Au–Au distance in the range 2.5012(4)–2.5885(2) Å with increasing *trans*-influence of the axial ligand, in the order X = ONO_2 < O_2CCF_3 < OBz < Cl < Br < I < C_6F_5. The strength of the Au–Au interaction is probably the main factor that determines whether the digold(II) compounds isomerise to gold(I)–gold(III). The gold-gold separations in the digold(I) and gold(I)–gold(III) complexes are in the range 2.8–3.6 Å suggestive of aurophilic interactions, but these are probably absent in the digold(III) compounds (Au···Au separation *ca.* 5.8 Å). Attempted recrystallisation of complex **10** gave a trinuclear gold(II)–gold(II)–gold(I) complex, $[Au_3Br_2(\mu\text{-}C_6H_3\text{-}6\text{-}F\text{-}2\text{-}PPh_2)_3]$ **24**, which consists of the expected digold(II) framework in which one of the axial bromide ligands has been replaced by a σ-carbon bonded $(C_6H_3\text{-}6\text{-}F\text{-}2\text{-}PPh_2)Au^IBr$ fragment.

Introduction

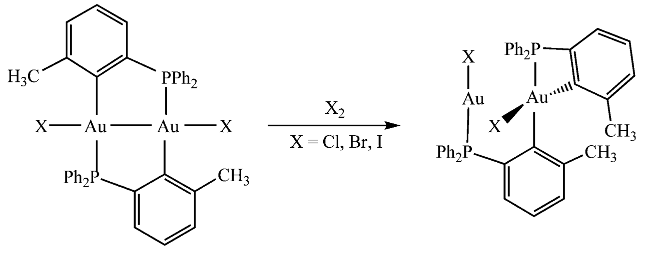
The bifunctional carbanion $[2\text{-}C_6H_4PPh_2]^-$ commonly behaves as a chelating ligand (κ^2-*P*,*C*) with the d-block elements, forming four-membered ring systems.[1] There are also well-established examples of complexes of Au,[2,3] Pt,[4,5] Pd,[6,7] and Rh[8–10] containing bridging $2\text{-}C_6H_4PPh_2$ and, particularly in the case of Pd, of interconversion between the two modes. Although most complexes of $2\text{-}C_6H_4PPh_2$ have been obtained by C–H activation (*ortho*-metallation) of coordinated triphenylphosphine, oxidative addition of the C–Br bond of $2\text{-}BrC_6H_4PPh_2$ to a low-valent metal centre and *trans*-metallation from reagents such as $2\text{-}LiC_6H_4PPh_2$ have proved to be useful alternatives in cases where *ortho*-metallation fails.[1]

Trans-metallation of $2\text{-}LiC_6H_4PPh_2$ with $[AuBr(PEt_3)]$ gives the digold(I) complex $[Au_2(\mu\text{-}2\text{-}C_6H_4PPh_2)_2]$ **1**, in which each $5d^{10}$ metal atom is linearly coordinated.[2,3] Complex **1** undergoes oxidative addition of halogens (X_2) to give the symmetrical, metal–metal bonded digold(II) ($5d^9$–$5d^9$) species $[Au_2X_2(\mu\text{-}2\text{-}C_6H_4PPh_2)_2]$, which rearrange by reductive elimination of the metallated aryl groups to give *P*-bonded 2,2′-biphenyldiylbis(diphenylphosphine) complexes of digold(I) (Scheme 1).[3,11]



Scheme 1

The analogous dihalodigold(II) complexes containing methyl substituents *ortho* to the Au–C bonds do not undergo C–C coupling, even under forcing conditions, but rearrange rapidly, even below room temperature, to give digold(I,III) complexes in which one of the cyclometallated ligands is chelated to the gold(III) atom and the two gold(III)–carbon bonds are mutually *cis* (Scheme 2).[12] Although they have not been detected, analogous species are likely intermediates in the C–C coupling reaction shown in Scheme 1.



Scheme 2

Replacement of all the hydrogen atoms in an aromatic ring by the more electronegative fluorine tends to stabilise and strengthen metal–aryl bonds, possibly owing to the greater ionic–covalent resonance energy of the M–C bond.[13,14] An extensive chemistry of transition metal–pentafluorophenyl complexes has been developed, especially with the later d-block elements,[14] and a range of homoleptic species has also been prepared.[15] A recent example in gold chemistry is the isolation and structural characterization of $[Au_2(C_6F_5)_4(tht)_2]$ (tht = tetrahydrothiophene), which is the first example of an unbridged gold complex containing an $[Au_2]^{4+}$ core that contains no chelating ligands.[16] The stabilising effect of fluorine substitution has also enabled the preparation of the monomeric bis(chelate) complexes of nickel(II) and palladium(II), $[M(\kappa^2\text{-}2\text{-}C_6F_4PPh_2)_2]$,[17] the protio analogues of which are as yet unknown. With these results in mind, we undertook the preparation of $[Au_2(\mu\text{-}2\text{-}C_6F_4PPh_2)_2]$ **2** in order to compare its chemistry with that of **1**. We have also extended the work to prepare digold complexes containing the mono-fluoro substituted ligand fragments C_6H_3-*n*-F-2-PPh_2 (*n* = 5, 6) in order to determine the effect of the position of one fluorine substituent in the metallated aryl ring on the reactivity of the digold complexes.

Results

Digold(I) complexes

The dinuclear, cycloaurated complex $[Au_2(\mu\text{-}2\text{-}C_6F_4PPh_2)_2]$ **2** can be obtained similarly to $[Au_2(\mu\text{-}2\text{-}C_6H_4PPh_2)_2]$ **1** in 42–65% yield as a white, air- and moisture-stable solid by the reaction of $2\text{-}LiC_6F_4PPh_2$ with $[AuBr(AsPh_3)]$ or $[AuCl(tht)]$ (tht = tetrahydrothiophene); it was also formed from $[AuBr(PEt_3)]$ and the organolithium reagent but other, unidentified products were also present. Alternatively, complex **2** can be prepared in 85% yield by reaction of $[AuCl(tht)]$ with the organotin reagent $2\text{-}Me_3SnC_6F_4PPh_2$ in refluxing dichloromethane. The positive ion FAB-mass spectrum of **2** shows the expected parent-ion peak at *m*/*z* 1060 and the ^{31}P NMR spectrum shows a singlet at δ 42.7, *ca.* 7 ppm downfield from that of its protio analogue. Close examination of this peak indicated that it is a multiplet with poorly resolved P–F coupling. Analogously, reaction of 2-Li-4-$FC_6H_3PPh_2$ with $[AuBr(AsPh_3)]$ gives the cycloaurated digold(I) compound $[Au_2(\mu\text{-}C_6H_3\text{-}5\text{-}F\text{-}2\text{-}PPh_2)_2]$ **3** as a colourless solid in 55% yield. The ^{31}P NMR spectrum of this solid shows a triplet resonance at δ 36.1 due to **3**, although some preparations gave a mixture containing **3** as the major product together with a minor product that showed a triplet at δ 40.6 (see later). Reaction of 2-Me_3Sn-4-$FC_6H_3PPh_2$ with $[AuCl(tht)]$ gave the same two species.

The digold(I) complex $[Au_2(\mu\text{-}C_6H_3\text{-}6\text{-}F\text{-}2\text{-}PPh_2)_2]$ **4** can be prepared in 75% yield by heating 2-Me_3Sn-3-$FC_6H_3PPh_2$ with $[AuCl(tht)]$ in dichloromethane. The ^{31}P NMR spectrum of **4** shows a doublet of doublets at δ 39.0. Low temperature lithiation of (2-bromo-3-fluorophenyl)diphenylphosphine and subsequent reaction with $[AuBr(AsPh_3)]$ gave a colourless solid of the expected composition in 85% yield. The ^{31}P NMR spectrum of this solid contained a doublet of doublets at δ 39.0 and a doublet of multiplets at δ 41.1, the former peak always being the more intense (*ca.* 70%). All attempts to separate the species responsible for these

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[a] *Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia*
[b] *School of Applied Sciences (Applied Chemistry), RMIT University, GPO Box 2476V, Melbourne, Victoria 3001, Australia*

† Electronic supplementary information (ESI) available: complete experimental details along with Table S1 and Table S2 containing analytical data and crystal data for the gold complexes. CCDC reference numbers 725984 (**2**, monoclinic), 725985 (**5**), 725986 (**25**), 725987 (**8**), 725988 (**15**), 725989 (**11**), 725990 (**35**), 725991 (**2**, triclinic), 725992 (**36**), 725993 (**21**), 725994 (**19**), 725995 (**16**), 725996 (**41**), 725997 (**42**), 725998 (**4**), 725999 (**24**), 726000 (**28**), 726001 (**6**), 726002 (**32**), 726003 (**22**), 726004 (**33**), 726005 (**7**), 726006 (**18**), 726007 (**17**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b906769h

peaks were unsuccessful. As discussed below, the minor species obtained in the preparations of **3** and **4** appear to be tetramers, $[Au_4(\mu\text{-}C_6H_3\text{-}n\text{-}F\text{-}2\text{-}PPh_2)_4]$ (n = 5, 6).

The structures of **2** and **4** have been established by single-crystal X-ray diffraction. They contain two linearly coordinated gold(I) atoms bridged by the carbanionic ligands in a head-to-tail arrangement similar to that in the corresponding complexes of $2\text{-}C_6H_4PPh_2$ and $C_6H_3\text{-}6\text{-}Me\text{-}2\text{-}PPh_2$.[2,12] The monoclinic form of **2** isolated from the reaction of $2\text{-}LiC_6F_4PPh_2$ with $[AuBr(AsPh_3)]$ is isomorphous and isostructural with **1** but the structure has an associated stacking fault. This problem was absent from a triclinic modification of **2** that crystallised from the reaction of the bis(benzoato) complex, $[Au_2(OBz)_2(\mu\text{-}2\text{-}C_6F_4PPh_2)_2]$, with methanol (see later). Its structure is shown in Fig. 1; selected bond distances and angles for the triclinic modification of **2** and for **4** are listed in Table 1. The corresponding parameters for the monoclinic modification of **2** do not differ significantly from those of the triclinic form. The Au···Au separations in **2** [2.8198(3) and 2.8187(3) Å for the two independent molecules] and in **4** [2.87624(14) Å] straddle those in **1** [2.8954(3) Å][2] and in $[Au_2(\mu\text{-}C_6H_3\text{-}6\text{-}Me\text{-}2\text{-}PPh_2)_2]$ [2.861(2) Å],[12] all being in the range of 2.5–3.3 Å believed to be typical of aurophilic interactions.[18] The Au–P and Au–C distances are similar to those in both $[Au(C_6F_5)(PPh_3)]$ [2.270(1) and 2.056(3) Å, respectively][19] and in **1** [2.300(1) Å and 2.056(3) Å, respectively].[2]

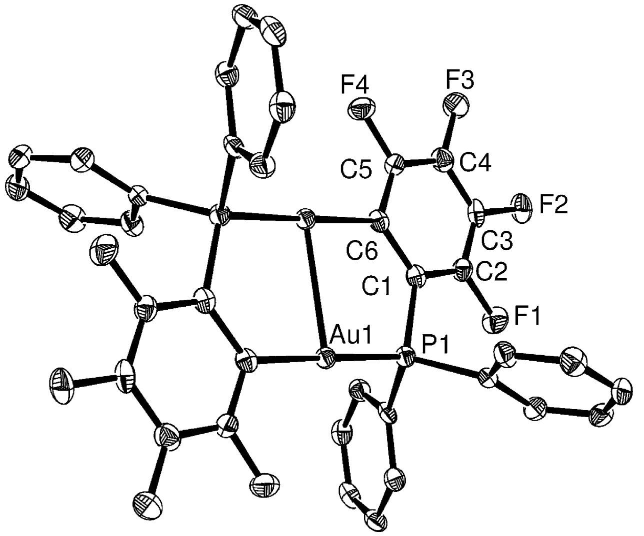


Fig. 1 Molecular structure of $[Au_2(\mu\text{-}2\text{-}C_6F_4PPh_2)_2]$ **2**. Ellipsoids show 50% probability levels and hydrogen atoms have been omitted for clarity. Only one molecule of the asymmetric unit is shown.

Table 1 Selected bond distances (Å) and angles (°) in the triclinic modification of $[Au_2(\mu\text{-}2\text{-}C_6F_4PPh_2)_2]$ **2** and $[Au_2(\mu\text{-}C_6H_3\text{-}6\text{-}F\text{-}2\text{-}PPh_2)_2]$ **4**

	2	**4**
Au···Au	2.8198(3), 2.8187(3)	2.87624(14)
Au–P	2.2803(10), 2.2831(10)	2.2987(5)
Au–C	2.058(4), 2.063(4)	2.061(2)
C–F	1.352 (av.)	1.367(3)
C–Au–P	178.54(10), 176.46(10)	174.62(6)
P–Au–Au	87.45(3), 86.54(3)	84.260(14)
C–Au–Au	93.66(11), 93.07(11)	94.01(6)

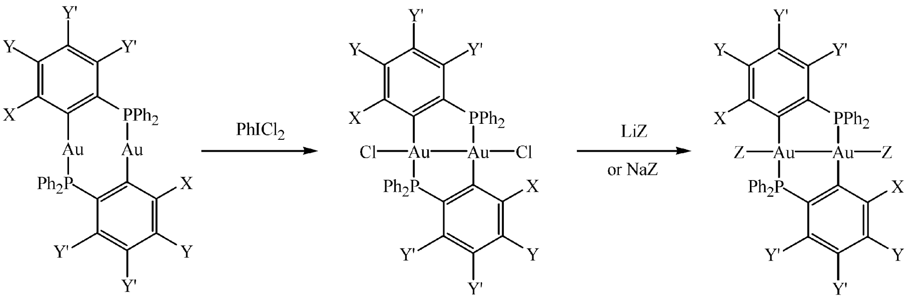
The Au–C bonds in $[Au_2(\mu\text{-}2\text{-}C_6F_4PPh_2)_2]$ **2** were not cleaved by two equivalents of concentrated HCl at room temperature, as shown by ^{31}P NMR spectroscopy. However, treatment of **2** with a large excess of concentrated HCl gave the monomeric Au(I) complex $[AuCl\{PPh_2(C_6F_4H)\}]$ as a colourless solid. Elemental analysis is consistent with the proposed formation and the ESI mass spectrum shows a peak at m/z 566, corresponding to the $[M]^+$ fragment. The ^1H NMR spectrum shows the expected multiplet at δ 6.8–7.7 due to the aromatic hydrogens, and the ^{31}P NMR spectrum shows a single resonance centred at δ 26.1, split into a doublet of 14.8 Hz, presumably due to coupling with an *ortho*-fluorine of the $(C_6F_4H)PPh_2$ group.

Digold(II) complexes

Like the digold(I) complexes which contain $2\text{-}C_6H_4PPh_2$ and $C_6H_3\text{-}6\text{-}Me\text{-}2\text{-}PPh_2$ as bridging ligands,[3,11,12] $[Au_2(\mu\text{-}2\text{-}C_6F_4PPh_2)_2]$ **2** and its mono-fluoro counterparts $[Au_2(\mu\text{-}C_6H_3\text{-}n\text{-}F\text{-}2\text{-}PPh_2)_2]$ [**3** (n = 5); **4** (n = 6)] react with $PhICl_2$ (acting as a source of Cl_2) at low temperature to give the yellow, metal–metal bonded dichlorodigold(II) complexes, $[Au_2Cl_2(\mu\text{-}2\text{-}C_6F_4PPh_2)_2]$ **5** and $[Au_2Cl_2(\mu\text{-}C_6H_3\text{-}n\text{-}F\text{-}2\text{-}PPh_2)_2]$ [**6** (n = 5); **7** (n = 6)], respectively, in *ca.* 85% yield. The corresponding orange dibromo [**8**; **9** (n = 5); **10** (n = 6)] and red diiodo [**11**; **12** (n = 5); **13** (n = 6)] complexes were prepared by treating dichloromethane solutions of **5–7** with an excess of the appropriate lithium or sodium salts in methanol (Scheme 3). Complexes **8** and **11** can also be made by oxidative addition reactions of **2** with Br_2 or I_2, respectively. Both methods for preparing the iodo complex **11** failed to give a pure product. The expected diiododigold(II) complex $[Au_2I_2(\mu\text{-}2\text{-}C_6F_4PPh_2)_2]$ was always the major product (*ca.* 80%), but there were also small amounts of unidentified products whose ^{31}P NMR chemical shifts appeared at δ 5 and 31. However, it was possible to select an X-ray quality crystal of **11** from the impure solid. In contrast with **1**, complex **2** does not undergo oxidative addition with dibenzoyl peroxide to give a bis(benzoato)digold(II) complex, nor does it react with methyl iodide.

The ^{31}P NMR spectra of the dihalodigold(II) complexes **5–13** each show a single resonance in the region δ −18 to 2, at higher frequency than those of the digold(I) complexes (Table 2); the shielding increases in the order I > Br > Cl. The resonances are *ca.* 5 ppm further upfield than those of the corresponding digold(II) compounds of $2\text{-}C_6H_4PPh_2$, whereas the reverse order holds for the digold(I) compounds. The far-IR spectra of **5** and **8** show bands due to gold-halide stretching vibrations at 288 and 199 cm^{-1}, respectively, which are similar to those observed for $[Au_2X_2(\mu\text{-}2\text{-}C_6H_4PPh_2)_2]$ (X = Cl, 278 cm^{-1}; X = Br, 190 cm^{-1})[3] and for the digold(II) bis(ylide) complexes $[Au_2X_2\{\mu\text{-}(CH_2)_2PPh_2\}_2]$ (X = Cl, 293 cm^{-1}; Br, 220 cm^{-1}.[20]

The structures of the dichloro complexes **5–7**, of the dibromo complex **8**, and of the diiodo complex **11** have been determined by single-crystal X-ray diffraction analysis. The molecular structure of **5** is shown in Fig. 2 and selected bond lengths and angles for these and other digold(II) complexes of $2\text{-}C_6F_4PPh_2$ (see later) and $C_6H_3\text{-}n\text{-}F\text{-}2\text{-}PPh_2$ (n = 5, 6) are listed in Table 3. The structures are derived from those of the digold(I) precursors by addition of a pair of halogen atoms along the Au–Au axis, thus



X = F, Y = F, Y' = F **2**
X = H, Y = F, Y' = H **3**
X = F, Y = H, Y' = H **4**

X = F, Y = F, Y' = F **5**
X = H, Y = F, Y' = H **6**
X = F, Y = H, Y' = H **7**

X = F, Y = F, Y' = F, Z = Br **8**; Z = I **11**
X = H, Y = F, Y' = H, Z = Br **9**; Z = I **12**
X = F, Y = H, Y' = H, Z = Br **10**; Z = I **13**

Scheme 3

Table 2 ^{31}P NMR data for the digold(I) and digold(II) complexes of 2-$C_6F_4PPh_2$, C_6H_3-*n*-F-2-PPh_2 (*n* = 5, 6) and 2-$C_6H_4PPh_2$

Compound	$\delta_P(C_6D_6)$	Multiplicity	Coupling/Hz	Corresponding values in the 2-$C_6H_4PPh_2$ series
[Au_2(μ-2-$C_6F_4PPh_2)_2$] **2**	42.7	br s		36.4
[Au_2(μ-C_6H_3-5-F-2-$PPh_2)_2$] **3**	36.0	t	5.2	
[Au_2(μ-C_6H_3-6-F-2-$PPh_2)_2$] **4**	39.0	dd	1.2, 2.4	
[Au_2Cl_2(μ-2-$C_6F_4PPh_2)_2$] **5**	−2.3	br s		1.3
[Au_2Cl_2(μ-C_6H_3-5-F-2-$PPh_2)_2$] **6**	1.7	t	6.0	
[Au_2Cl_2(μ-C_6H_3-6-F-2-$PPh_2)_2$] **7**	0.8	t	5.0	
[Au_2Br_2(μ-2-$C_6F_4PPh_2)_2$] **8**	−8.3	br s		−4.6
[Au_2Br_2(μ-C_6H_3-5-F-2-$PPh_2)_2$] **9**	−3.4	t	6.0	
[Au_2Br_2(μ-C_6H_3-6-F-2-$PPh_2)_2$] **10**	−4.2	t	4.6	
[Au_2I_2(μ-2-$C_6F_4PPh_2)_2$] **11**	−17.2	s		−12.7
[Au_2I_2(μ-C_6H_3-5-F-2-$PPh_2)_2$] **12**	−11.6	t	5.0	
[Au_2I_2(μ-C_6H_3-6-F-2-$PPh_2)_2$] **13**	−12.0	t	4.0	
[$Au_2(OAc)_2$(μ-2-$C_6F_4PPh_2)_2$] **14**	−1.3	br s		4.1
[$Au_2(ONO_2)_2$(μ-2-$C_6F_4PPh_2)_2$] **15**	−0.1	br s		5.4
[$Au_2(OBz)_2$(μ-2-$C_6F_4PPh_2)_2$] **16**	−0.1	br s		4.3
[$Au^{II}_2(O_2CCF_3)_2$(μ-2-$C_6F_4PPh_2)_2$] **17**	−0.05	br s		
[$Au^{II}_2(C_6F_5)_2$(μ-2-$C_6F_4PPh_2)_2$] **18**	−9.6	br s		
[$Au^{II}_2(OTf)_2$(μ-2-$C_6F_4PPh_2)_2$] **20**	3.1	s		

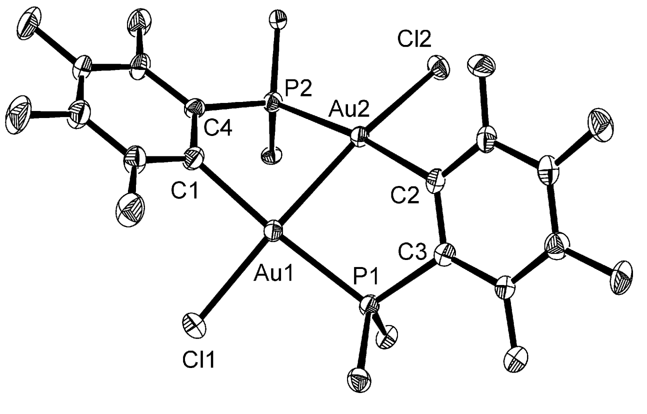


Fig. 2 Molecular structure of [$Au_2^{II}Cl_2$(μ-2-$C_6F_4PPh_2)_2$] **5**. Ellipsoids show 30% probability levels and only one molecule of the asymmetric unit is shown. Hydrogen atoms and solvent molecules have been omitted for clarity. The phenyl rings of the PPh_2 groups only show the *ipso* carbons.

completing close to square planar coordination about each gold atom. The Au–Au separations are *ca.* 0.3 Å shorter than those in the parent digold(I) compounds, consistent with the presence of a gold(II)–gold(II) ($5d^9$–$5d^9$) single bond, and, for [Au_2X_2(2-$C_6F_4PPh_2)_2$], they decrease in the order X = I > Br > Cl. The Au–Au distance in the diiodide **11** [2.5685(2) Å] is slightly shorter than that in its 2-$C_6H_4PPh_2$ counterpart [2.5898(6) Å, 2.5960(7) Å for two independent molecules[11]], although the Au–I distances in the two molecules [2.6778(4), 2.6747(4) Å for the former; 2.669 Å (average) for the latter] are almost identical. The Au–Cl distances in **5** [2.3615(18), 2.3749(17) Å; 2.3685(18), 2.3628(17) Å for two independent molecules], **6** [2.3828(9), 2.3646(10) Å] and **7** [2.3673(15), 2.3715(16) Å; 2.3650(15), 2.3612(18) Å for two independent molecules] are similar to those observed in the digold(II) bis(ylide) complex [$Au_2Cl_2\{(CH_2)_2PPh_2\}_2$] [2.388(8) Å].[21] The Cl–Au–Au angles in the $C_6F_4PPh_2$ complexes **5**, **8** and **11** deviate by 10–13° from the expected 180°; those in **7** deviate more (*ca.* 10 °) than those in **6** (*ca.* 5°), perhaps to accommodate the *ortho*-fluorine substituents.

Metathesis reactions of **5** with silver acetate, nitrate, benzoate or trifluoroacetate gave the expected digold(II) complexes [Au_2Y_2(μ-2-$C_6F_4PPh_2)_2$] [Y = OAc (**14**), ONO_2 (**15**), OBz (**16**), O_2CCF_3 (**17**)], all of which show singlet resonances in the region of δ 0 in their ^{31}P NMR spectra (see Table 2). The IR spectrum of the acetato complex **14**, recorded as a KBr disc, shows strong bands at 1630 and 1588 cm^{-1} due to *ν*(C=O) and 1300 cm^{-1}

due to ν(C=O). The IR spectrum of the nitrato complex **15** exhibits strong N–O stretching bands at 1250 and 1510 cm^{-1} due to symmetric and asymmetric $\nu(NO_2)$ stretching bands, respectively. These separations are typical of unidentate acetato and nitrato complexes, respectively.[22] The structures of **15–17** have been solved by X-ray diffraction studies and confirm the unidentate binding mode of the axial ligands. Selected bond lengths and angles for **15–17** are collected in Table 3.

Reaction of the bis(benzoato) complex **16** with C_6F_5Li gave the bis(pentafluorophenyl)digold(II) complex $[Au_2(C_6F_5)_2(\mu\text{-}2\text{-}C_6F_4PPh_2)_2]$ **18**. This complex shows a singlet resonance in its ^{31}P NMR spectrum at δ −9.6, *i.e.*, *ca.* 3 ppm more shielded than that of the analogous 2-$C_6H_4PPh_2$ compound,[23] in line with the trend noted above. The X-ray structure of **18** is similar to that of the other digold(II) compounds, but the Au–Au separation [2.5885(2) Å] is distinctly greater. It is, however, less than that observed in the 2-$C_6H_4PPh_2$ analogue [2.6139(4) Å][23] and in the bis(ylide) complexes $[Au_2Y_2\{\mu\text{-}(CH_2)_2PPh_2\}_2]$ [2.677(1) Å: Y = C_6F_5; 2.676(1) Å: Y = CF_3].[24] The Au–C_6F_5 distances in **18** [2.129(4), 2.124(4) Å] are similar to those in the bis(ylide)bis(pentafluorophenyl) complex [2.145(8)–2.164(7) Å].[24]

Attempts to prepare a digold(II) dimethyl derivative by treatment of **5** with methyllithium gave only mixtures of unidentified species with complex ^{31}P NMR spectra. The reaction of **16** with dimethylzinc also did not yield the hoped-for product, but gave cleanly the heterovalent, digold(I,III) dimethyl compound $[Au^I(\mu\text{-}2\text{-}C_6F_4PPh_2)_2Au^{III}(CH_3)_2]$ **19**, which may be formed by isomerisation of the homovalent compound. This behaviour is similar to that found in the 2-$C_6H_4PPh_2$ series.[23] The ^{1}H NMR spectrum of **19** shows a doublet at δ 0.56 ($^3J_{P\text{-}H}$ = 2 Hz) due to Au–CH_3 and the ^{31}P NMR spectrum contains two broad peaks at δ 20 and 36 ($W_{1/2}$ *ca.* 50 Hz) arising from inequivalent phosphorus atoms. The unsymmetrical structure implied by these data has been confirmed by single-crystal X-ray diffraction and is shown in Fig. 3. The two 2-$C_6F_4PPh_2$ groups bridge the gold atoms in a head-to-tail arrangement, the separation between the metal atoms [2.85632(16) Å] being greater than that in the digold(II) dihalides but significantly shorter than that in $[Au^I(\mu\text{-}2\text{-}C_6H_4PPh_2)_2Au^{III}(CH_3)_2]$ [2.8874(4) Å].[23] The methyl groups on the planar-coordinated gold(III) atom are mutually *trans*, and the

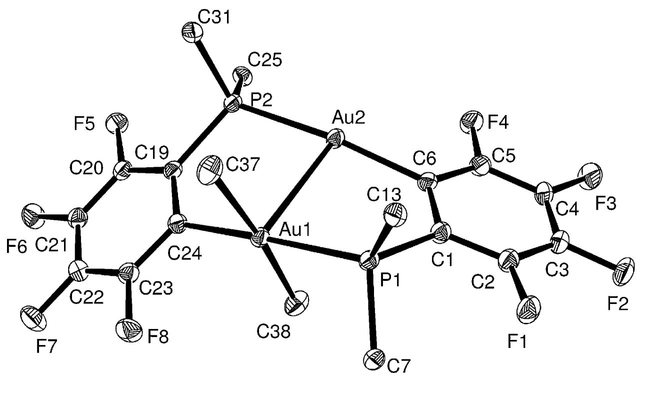


Fig. 3 Molecular structure of $[Au^I(\mu\text{-}2\text{-}C_6F_4PPh_2)_2Au^{III}(CH_3)_2]$ **19**. Ellipsoids show 50% probability levels and hydrogen atoms have been omitted for clarity. Only the *ipso* carbons of the phenyl groups attached to the phosphorus atoms are shown.

Table 3 Selected bond lengths (Å) and angles (°) for digold(II) complexes of 2-$C_6F_4PPh_2$ and C_6H_3-*n*-F-2-PPh_2 (*n* = 5, 6)[a]

	5a	**5b**	**6**	**7a**	**7b**	**8a**	**8b**
Au–Au	2.5416(4)	2.5330(4)	2.56223(19)	2.5390(3)	2.5494(3)	2.5510(3)	2.5411(3)
Au–P	2.3290(17), 2.3378(17)	2.3358(18), 2.3347(17)	2.3331(9), 2.3327(10)	2.3381(15), 2.3429(16)	2.3313(15), 2.3383(16)	2.3329(13), 2.3396(12)	2.3392(13), 2.3349(12)
Au–C	2.072(7), 2.067(7)	2.076(7), 2.082(6)	2.073(4), 2.066(4)	2.075(6), 2.067(6)	2.064(6), 2.068(6)	2.066(5), 2.064(5)	2.072(5), 2.070(5)
Au–X	2.3615(18), 2.3749(17)	2.3685(18), 2.3628(17)	2.3828(9), 2.3646(10)	2.3650(15), 2.3612(18)	2.3673(15), 2.3715(16)	2.4878(6), 2.4968(6)	2.4915(6), 2.4844(5)
C–Au–P	175.3(2), 172.9(2)	173.93(18), 170.9(2)	174.20(11), 176.53(11)	173.13(18), 173.31(18)	174.47(18), 172.48(18)	175.13(15), 173.09(15)	173.60(14), 171.28(14)
P–Au–Au	85.76(5), 83.08(4)	84.85(4), 82.09(4)	82.95(2), 84.29(2)	84.22(4), 82.91(4)	83.74(4), 82.79(4)	85.36(3), 82.77(3)	84.11(3), 81.84(3)
C–Au–Au	90.3(2), 90.09(19)	89.09(18), 90.39(19)	91.97(10), 92.29(10)	89.07(18), 90.62(17)	90.06(17), 91.04(17)	90.10(15), 90.44(14)	89.50(14), 90.69(13)

	11	**15**	**16**	**17a**	**17b**	**18**
Au–Au	2.5685(2)	2.5012(4)	2.52120(11)	2.5093(2)	2.5048(2)	2.5885(2)
Au–P	2.3398(12), 2.3441(12)	2.348(2), 2.348(2)	2.3356(6), 2.3380(6)	2.3384(12), 2.3394(12)	2.3455(11), 2.3437(12)	2.3243(11), 2.3301(12)
Au–C	2.062(5), 2.075(4)	2.077(9), 2.056(9)	2.063(2), 2.075(2)	2.077(4), 2.071(5)	2.069(4), 2.081(4)	2.071(4), 2.074(4)
Au–X	2.6778(4), 2.6747(4)	2.132(6), 2.164(6)	2.1116(15), 2.1002(15)	2.108(4), 2.110(4)	2.097(4), 2.129(3)	2.129(4), 2.124(4)
C–Au–P	173.29(13), 174.17(13)	171.5(2), 173.3(3)	173.81(6), 171.00(6)	172.74(13), 170.93(15)	171.48(14), 171.19(13)	172.05(12), 172.54(12)
P–Au–Au	84.50(3), 85.09(3)	83.00(6), 84.67(6)	84.815(14), 82.433(14)	83.91(3), 82.21(3)	84.03(3), 83.67(3)	82.96(3), 81.91(3)
C–Au–Au	88.98(13), 89.11(12)	88.9(2), 88.6(2)	89.20(6), 88.61(6)	88.85(13), 88.85(15)	87.45(13), 87.52(13)	89.21(11), 90.98(11)

[a] (**a**) and (**b**) refer to independent molecules in the unit cell. X = Cl in **5a**, **5b**, **6**, **7a** and **7b**; Br in **8a** and **8b**; I in **11**; O in **15**, **16**, **17a** and **17b**; C atom of the C_6F_5 group in **18**.

Au–CH_3 bond lengths [2.117(3), 2.125(3) Å] are similar to those in the 2-$C_6H_4PPh_2$ analogue and in [$Au(CH_3)_3(PPh_3)$].[25]

Attempts to cleave selectively one of the Au–CH_3 bonds of **19** with HCl or CF_3SO_3H were unsuccessful. There was no reaction between **19** and one equiv. of HCl, even after 2 d; with CF_3SO_3H (one equiv.) some reduction to the digold(I) precursor **2** occurred; there were also peaks at δ 40.5, 43.7 and 45.7 in the ^{31}P NMR spectrum, the last of which may be due to the tetrameric gold(I) complex (see later).

Reduction of the digold(II) complexes

Compounds **5** and **8** are readily reduced to **2** by treatment with zinc powder. Attempts to prepare a difluorodigold(II) complex by treatment of dichloromethane solutions of **5** or **8** with AgF also resulted in reduction to the digold(I) complex **2**, as confirmed by the ^{31}P NMR spectra of the solutions and comparison of the crystallographic parameters of the isolated solid with those of **2** (monoclinic modification). A similar result attended the attempted recrystallisation of the bis(benzoato) complex **16** with methanol, and a plausible equation for this reduction is shown in eqn (1).

$$\begin{aligned}&Au_2(OBz)_2(\mu\text{-}2\text{-}C_6F_4PPh_2)_2 + CH_3OH \rightarrow \\ &Au_2(\mu\text{-}2\text{-}C_6F_4PPh_2)_2 + CH_2O + 2\ BzOH \qquad (1)\end{aligned}$$

In agreement with this suggestion, replacement of methanol by cyclohexanol gave complex **2**, together with cyclohexanone, which was detected by its characteristic IR band at 1703 cm^{-1}. An attempt to prepare a bis(alkoxo)digold(II) complex by treatment of **5** with CF_3CH_2OH/KOH caused immediate reduction to **2**.

Even in the absence of alcohols, complex **16** also decomposed cleanly, though more slowly, to **2** on heating in dichloromethane or benzene over a period of hours. We did not attempt to identify the organic products in these reactions. The corresponding 2-$C_6H_4PPh_2$ complex behaves similarly, but the reaction is slower and other unidentified products are formed.

The nitrato complex **15** decomposed on heating in toluene to 70 °C, but in this case complex **2** was not formed. The resulting ^{31}P NMR spectrum showed two main signals at δ 39.3 and 65.2, but the species responsible for these peaks were not identified; the latter may be due to a phosphine oxide that had been formed as a result of oxidation by NO_3^-.

Treatment of a dichloromethane solution of **5** with an excess of silver triflate gave a precipitate of silver chloride and the solution changed colour from yellow to orange. Work up gave an orange solid whose ^{31}P NMR spectrum showed a singlet at δ 3.1, consistent with the formation of the symmetrical bis(triflato)digold(II) complex [$Au_2(OTf)_2(\mu\text{-}2\text{-}C_6F_4PPh_2)_2$] **20**. As expected, **20** reacted with LiBr to give the dibromo complex **8** quantitatively, as shown by ^{31}P NMR spectroscopy. However, attempts to recrystallise **20** from dichloromethane–methanol gave a colourless solid, the elemental analysis of which was consistent with the empirical formula $C_6F_4PPh_2Au$. This was shown by X-ray crystallography to be a novel tetranuclear gold(I) complex, [$Au_4(\mu\text{-}2\text{-}C_6F_4PPh_2)_4$] **21**, the structure of which is shown in Fig. 4. It consists of four gold atoms arranged in a square, bridged by four 2-$C_6F_4PPh_2$ groups in an alternate up/down arrangement, the coordination about each metal atom being close to linear. By symmetry, the asymmetric unit of the structure consists of one quarter of the macrocycle. The Au···Au separation between neighbouring atoms is 3.12972(16) Å, compared with 2.8201(4) Å in **2**, consistent with a weaker aurophilic interaction in the tetramer. However, the Au–P [2.2882(7) Å] and Au–C [2.056(3) Å] bond lengths are similar to those in **2**. Compound **21** showed a singlet at δ 45.7 in its ^{31}P NMR spectrum, *i.e.*, 3 ppm less shielded than that of **2**; there is a peak at *m*/*z* 2121 due to the $[M + H]^+$ ion in its ESI-mass spectrum.

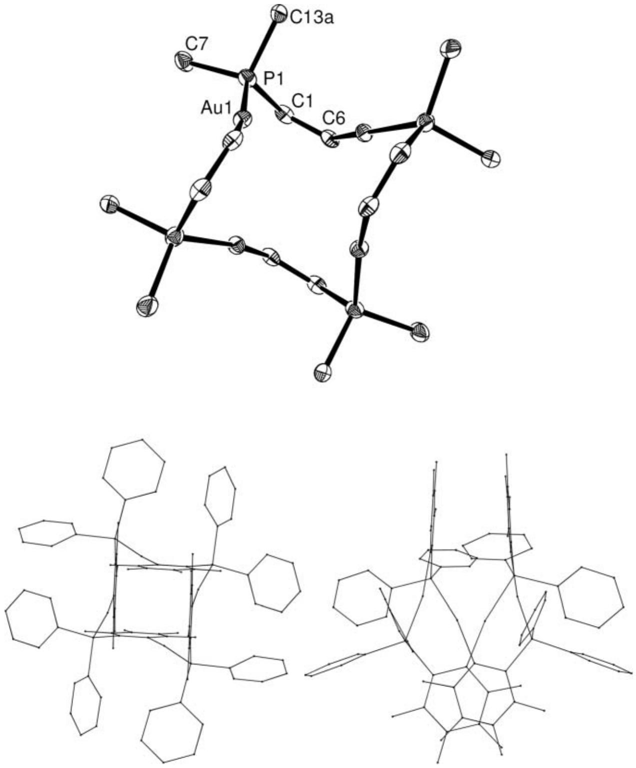


Fig. 4 Top: Molecular structure of [$Au_4(\mu\text{-}2\text{-}C_6F_4PPh_2)_4$] **21**. Ellipsoids show 30% probability levels. Hydrogen atoms, solvent molecules and disordered components have been omitted for clarity. Only the *ipso* carbons of the phenyl groups attached to the phosphorus atoms and the two carbon atoms of the C_6F_4 ring that form the macrocycle are shown; Bottom: Stick plots showing two different views of **21**. Selected bond distances (Å) in **21**: Au···Au 3.12972(16), Au–P 2.2882(7), Au–C 2.056(3).

The unexpected discovery of the tetramer **21** in the 2-$C_6F_4PPh_2$ system suggested that the minor resonance at δ 36.1 occasionally observed in samples of [$Au_2(\mu\text{-}C_6H_3\text{-}5\text{-}F\text{-}2\text{-}PPh_2)_2$] **3** (see above) might be due to the corresponding tetranuclear species [$Au_4(\mu\text{-}C_6H_3\text{-}5\text{-}F\text{-}2\text{-}PPh_2)_4$] **22**. Similarly, the resonances at δ 39.0 and 41.0 in the corresponding 6-fluoro product could be assigned to the dinuclear complex **4** and its tetranuclear form, [$Au_4(\mu\text{-}C_6H_3\text{-}6\text{-}F\text{-}2\text{-}PPh_2)_4$] **23**, respectively. In both cases, the peaks due to the putative tetramers are 2–4 ppm to low field of those of the dimers, as is true for the corresponding 2-$C_6F_4PPh_2$ compounds **2** and **21**. In agreement, the ESI-mass spectra of the mixtures, in each case, showed the expected $[M + H]^+$ peaks due to dimer and tetramer.

A solution of a sample of **3** in dichloromethane, the ^{31}P NMR spectrum of which contained no peak at δ 40.6, deposited a single crystal that, unexpectedly, proved to be the tetranuclear complex [$Au_4(\mu\text{-}C_6H_3\text{-}5\text{-}F\text{-}2\text{-}PPh_2)_4$] **22**. The molecular structure is shown in Fig. 5. It is not clear whether **3** had dimerised to **22** during the crystallisation or whether the original solution had contained an undetectably small amount of **22** that crystallised preferentially.

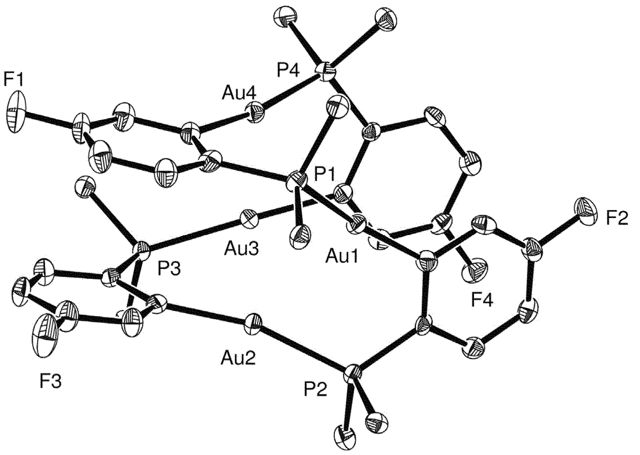


Fig. 5 Molecular structure of [$Au_4(\mu\text{-}C_6H_3\text{-}5\text{-}F\text{-}2\text{-}PPh_2)_4$] **22**. Ellipsoids show 50% probability levels. Hydrogen atoms and solvent molecules have been omitted for clarity. Only the *ipso* carbons of the PPh_2 groups are shown. Selected bond distances (Å) in **22**: Au···Au 3.1412 (av.), Au–P 2.2972 (av.), Au–C 2.055 (av.).

The Au–P and Au–C distances of the two compounds are similar. The Au···Au separations range between 3.0468(3) and 3.2984(3) Å, the average value (3.141 Å) being slightly greater than that in **21**.

In an attempt to generate the tetramer **23**, [$Au_2(\mu\text{-}C_6H_3\text{-}6\text{-}F\text{-}2\text{-}PPh_2)_2$] **4** was heated in toluene at 75 °C. After 4 h, a small peak appeared at δ 42.2 assignable to **23** but further heating produced numerous peaks in the range δ 42–47, and **4** was still present.

Formation of a trinuclear gold complex

Although solutions of the dibromo complex [$Au_2Br_2(\mu\text{-}C_6H_3\text{-}6\text{-}F\text{-}2\text{-}PPh_2)_2$] **10** appeared to be pure by ^{31}P NMR spectroscopy, attempts to grow a single crystal gave unexpectedly a trinuclear complex of empirical formula $Au_3Br_2(C_6H_3\text{-}6\text{-}F\text{-}2\text{-}PPh_2)_3$ **24**. The structure, shown in Fig. 6, consists of the expected digold(II) framework in which one of the axial bromide ligands has been replaced by a σ-bonded ($6\text{-}FC_6H_3\text{-}2\text{-}PPh_2$)AuBr fragment, which is folded around to give a gold-gold separation, Au(2)–Au(3), of 3.0432(3) Å, probably as a consequence of aurophilic interaction; this is significantly greater than the separation, Au(1)–Au(2) of 2.6065(3) Å, between the gold atoms that are bridged by two $6\text{-}FC_6H_3\text{-}2\text{-}PPh_2$ ligands. The Au–Br bond length, Au(3)–Br(2), of 2.4181(6) Å in the linear ($6\text{-}FC_6H_3\text{-}2\text{-}PPh_2$)$Au^IBr$ fragment is similar to that reported for [$AuBr(PPh_3)$],[26] but is significantly shorter than that in the planar Au–Au–Br unit [Au(1)–Br(1) = 2.56131(6) Å]; this distance, and the Au(1)–Au(2) distance, are both longer than their counterparts in [$Au_2Br_2(\mu\text{-}2\text{-}C_6F_4PPh_2)_2$] **8** [*d*(Au–Au) = 2.5510(3) and 2.5411(3) Å for the two independent molecules; *d*(Au–Br) = 2.4968(6), 2.4878(6) Å and 2.4915(6), 2.4844(5) Å for the two independent molecules], perhaps a reflection of the *trans*-bond weakening influence of the σ-aryl ligand.

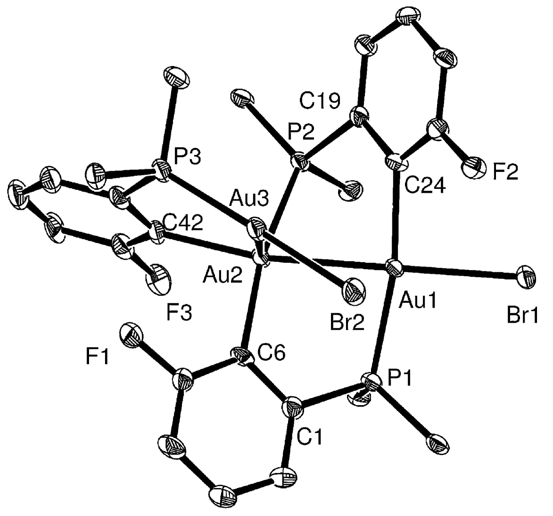


Fig. 6 Molecular structure of **24**. Ellipsoids show 50% probability levels. Hydrogen atoms and solvent molecules have been omitted. Only the *ipso* carbons of the PPh_2 groups are shown for clarity.

Empirically, the composition of **24** corresponds to one molecule of the digold(II) complex **10** and half a molecule of the digold(I) complex **4**. Presumably the sample of **10** either contained a small amount, or decomposed in solution to give a small amount, of complex **4**, which then mono-arylated **10** to give the trinuclear complex, according to eqn (2):

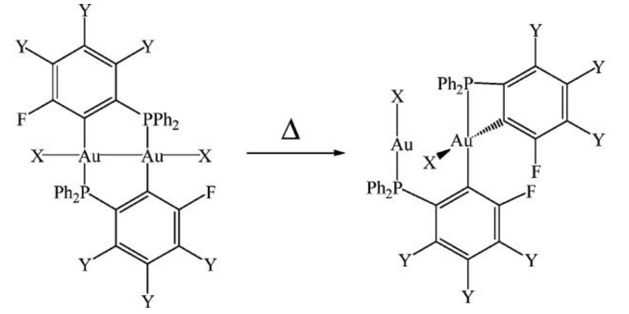
$$\begin{gathered}2\,[Au_2Br_2(\mu\text{-}C_6H_3\text{-}6\text{-}F\text{-}2\text{-}PPh_2)_2] + \\ [Au_2(\mu\text{-}C_6H_3\text{-}6\text{-}F\text{-}2\text{-}PPh_2)_2] \rightarrow 2 \\ [\{Au_2Br(\mu\text{-}C_6H_3\text{-}6\text{-}F\text{-}2\text{-}PPh_2)_2\}(C_6H_3\text{-}6\text{-}F\text{-}2\text{-}PPh_2)AuBr]\end{gathered} \quad (2)$$

The ^{31}P NMR spectrum of a solution containing a mixture of **10** and **4** in a 2 : 1 mole ratio showed three small peaks at δ −4.5, −3.5 and 38.1, the first two of which can be assigned to the inequivalent phosphorus atoms of the digold(II) unit of **24**, while the last is due to the phosphorus atom on gold(I). The remaining peaks (*ca.* 90% of the total) represented the starting materials, the gold(I)–gold(III) isomerisation product of **10** (see below), and some unidentified species. Attempts to isolate or detect analogues of complex **24** containing $2\text{-}C_6F_4PPh_2$ or $C_6H_3\text{-}5\text{-}F\text{-}PPh_2$ failed.

Isomerisation of the digold(II) complexes

When heated to 70 °C for 3–5 h, toluene solutions of the dihalodigold(II) complexes [$Au_2X_2(\mu\text{-}2\text{-}C_6F_4PPh_2)_2$] and [$Au_2X_2(\mu\text{-}C_6H_3\text{-}6\text{-}F\text{-}2\text{-}PPh_2)_2$] (X = Cl, Br, I) become colourless. From these solutions, almost colourless solids of general formula [$XAu(\mu\text{-}2\text{-}C_6F_4PPh_2)(\kappa^2\text{-}2\text{-}C_6F_4PPh_2)AuX$] [X = Cl (**25**), Br (**26**), I (**27**)] or [$XAu(\mu\text{-}2\text{-}C_6H_3\text{-}6\text{-}F\text{-}2\text{-}PPh_2)(\kappa^2\text{-}C_6H_3\text{-}6\text{-}F\text{-}2\text{-}PPh_2)AuX$] [X = Cl, **28**; Br, **29**; I, **30**] can be isolated in high yields (Scheme 4). The digold(I,III) dibromide and digold(I,III) diiodide can also prepared by the reaction of **25** or **28** with NaBr and NaI, respectively. In contrast to the behaviour of the [$Au_2X_2(\mu\text{-}2\text{-}C_6H_4PPh_2)_2$] complexes (X = Cl, Br, I) (Scheme 1), there was no evidence for the formation of C–C coupled products.[3,11,12]

The ^{31}P NMR spectra of **25–30** show a pair of equally intense singlets in the regions of +40 and −80 ppm; the chemical shift of the latter resonance is typical of a phosphorus atom in a four-membered chelate ring.[27] Similar isomerisations also occur in the 6-methyl series (Scheme 2), although much more rapidly. The mass spectra of **25–28** show a peak corresponding to the [M − halide]$^+$ fragment and the far-IR spectra of **25** and **26** contain strong bands due to $\nu(Au^I\text{–}X)$ at 325 and 239 cm^{-1}, respectively. Weaker bands tentatively assigned to $\nu(Au^{III}\text{–}X)$ appear at 238 cm^{-1} (**25**) and



Y = F; X = Cl **5**, Br **8**, I **11**

Y = H; X = Cl **7**, Br **10**, I **13**

Y = F; X = Cl **25**, Br **26**, I **27**

Y = H; X = Cl **28**, Br **29**, I **30**

Scheme 4

184 cm^{-1} (**26**). The observed IR bands are characteristic of tertiary phosphine–gold halide complexes.[28,29]

The bis(pentafluorophenyl) complex **18** also isomerises on heating in toluene or in CH_2Cl_2–C_6D_6 to the corresponding gold(I)–gold(III) complex **31**, which was isolated as a pale yellow solid that showed a pair of multiplets at δ 50 and −62.5 in its ^{31}P NMR spectrum. This behaviour differs from that of the corresponding 2-$C_6H_4PPh_2$ complex, which rearranges predominantly by C–C coupling to the biphenyldiyl product, $[Au_2(C_6F_5)_2(\mu\text{-}2,2'\text{-}Ph_2PC_6H_4C_6H_4PPh_2)]$, together with a small amount of the zwitterionic complex $[(C_6F_5)_2Au^{III}(\mu\text{-}2\text{-}C_6H_4PPh_2)_2Au^I]$.[23]

The structures of **25** and **28** have been confirmed by single-crystal X-ray diffraction and the structure of **25** is shown in Fig. 7; selected bond distances and angles for **25** and **28** are listed in Table 4. Complexes **25** and **28** each contain an Au(III) atom, coordinated by $C_6F_4PPh_2$ or C_6H_3-6-F-2-PPh_2, respectively, in a four-membered chelate ring and a chloride ligand, and an Au(I) atom linearly coordinated by chloride and a phosphorus atom of the bridging 2-$C_6F_4PPh_2$ or C_6H_3-6-F-2-PPh_2 group. The angle subtended at the Au(III) atom by the four-membered ring [**25**, 69.11(17)°; **28**, 68.18(9)°] is typical for transition metal complexes containing *ortho*-metallated PPh_3.[1] The Au–Au separations of 3.0916(3) Å (**25**) and 3.5922(2) Å (**28**) are similar to those in the structurally similar compounds of the 6-methyl series, *viz.*, $[YAu^I(\mu\text{-}2\text{-}Ph_2PC_6H_3\text{-}6\text{-}Me)Au^{III}Y(\kappa^2\text{-}C_6H_3\text{-}6\text{-}Me\text{-}2\text{-}PPh_2)]$ (Y = I, C_6F_5).[12,27] and are consistent with a weak aurophilic interaction between the metal atoms.

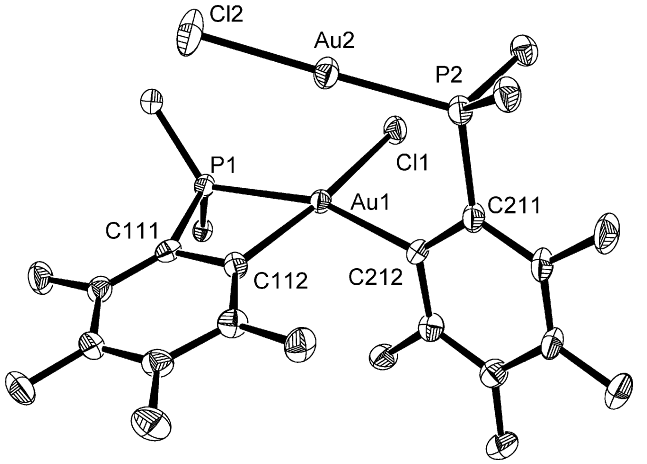


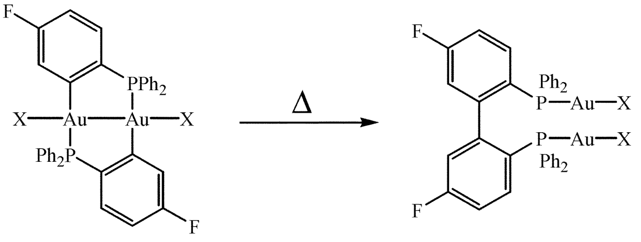
Fig. 7 Molecular structure of $[ClAu(\mu\text{-}2\text{-}C_6F_4PPh_2)(\kappa^2\text{-}2\text{-}C_6F_4PPh_2)AuCl]$ (**25**). Ellipsoids show 30% probability levels. Hydrogen atoms and solvent molecules have been omitted for clarity. The phenyl rings of the PPh_2 groups only show the *ipso* carbons.

Table 4 Selected bond distances (Å) and angles (°) in **25**, **28**, **35** and **36**[a]

	25	28	35	36
Au(1)–Au(2)	3.0916(3)	3.5922(2)	3.0279(3)	3.0426(4)
Au(1)–P(1)	2.3474(14)	2.3710(8)	2.3527(13)	2.375(2)
Au(2)–P(2)	2.2351(13)	2.2256(8)	2.2200(13)	2.214(2)
Au(1)–C(212)	2.076(5)	2.074(3)	2.088(5)	2.084(8)
Au(1)–C(112)	2.044(6)	2.027(3)	2.013(6)	2.005(9)
Au(1)–X(1)	2.3418(14)	2.3473(7)	2.041(3)	2.086(7)
Au(2)–X(2)	2.2805(15)	2.3004(8)	2.037(4)	2.090(6)
X(1)–Au(1)–C(112)	169.82(17)	168.36(9)	174.8(6)	173.2(3)
C(212)–Au(1)–C(112)	97.1(2)	97.66(12)	99.1(6)	95.7(4)
X(1)–Au(1)–P(1)	100.87(5)	101.67(3)	104.92(11)	108.9(2)
Au(1)–P(1)–C(111)	83.1(2)	83.07(11)	81.4(6)	82.0(3)
X(1)–Au(1)–C(212)	92.31(16)	93.11(8)	85.95(17)	85.4(4)
P(1)–Au(1)–C(212)	162.31(16)	163.96(8)	166.39(14)	162.0(3)
P(1)–Au(1)–C(112)	69.11(17)	68.18(9)	69.9(6)	68.8(3)
X(2)–Au(2)–P(2)	176.35(7)	170.94(3)	174.64(15)	178.97(18)

[a] X = Cl in **25** and **28**, O in **35** and **36**.

In contrast to the behaviour of the 6-fluoro substituted complexes, the corresponding 5-fluoro compounds $[Au_2X_2(\mu\text{-}C_6H_3\text{-}5\text{-}F\text{-}2\text{-}PPh_2)_2]$ (X = Cl, **6**; Br, **9**; I, **12**) undergo C–C coupling on heating or exposure to light to give P-bonded biphenyldiyldigold(I) species $[Au_2X_2(2,2'\text{-}Ph_2P\text{-}5\text{-}F\text{-}C_6H_3C_6H_3\text{-}5\text{-}F\text{-}PPh_2)]$ (X = Cl, **32**; Br, **33**; I, **34**) (Scheme 5). This behaviour parallels that of the gold complexes containing the ligands 2-$C_6H_4PPh_2$[3] and C_6H_3-5-Me-2-PPh_2.[3,11,12]



X = Cl, **6**; Br, **9**, I, **12**

X = Cl, **32**; Br, **33**, I, **34**

Scheme 5

The ESI-mass spectra of **32–34** each show a peak corresponding to the [M − halide]$^+$ fragment and the ^{31}P NMR spectra each contain a single resonance in the region of δ 30, the chemical shift increasing in the order Cl < Br < I; a similar trend was observed in the corresponding 5-methyl series.[12] The ^{31}P NMR spectroscopic data for complexes **32–34** are shown in Table 5. The structures of **32** and **33** have been confirmed by X-ray diffraction; the molecular structure of **32** is shown in Fig. 8. Selected bond distances and angles for complexes **32** and **33** are listed in Table 6.

Like those of $[Au_2X_2(2,2'\text{-}Ph_2P\text{-}5\text{-}MeC_6H_3C_6H_3\text{-}5\text{-}Me\text{-}PPh_2)]$ [X = Cl, Br, I],[4] and some of their arsenic analogues [X = Cl, Br, I, C_6F_5],[22] the molecular structures of **32** and **33** consist of a biphenyl backbone with two Ph_2PAuX (X = Cl, Br) substituents

Table 5 ^{31}P NMR data for the digold(I) complexes **32–34**

Compound	δ_P (C_6D_6)
$[Au_2Cl_2(2,2'\text{-}Ph_2P\text{-}5\text{-}F\text{-}C_6H_3C_6H_3\text{-}5\text{-}F\text{-}PPh_2)]$ **32**	27.2 (s)
$[Au_2Br_2(2,2'\text{-}Ph_2P\text{-}5\text{-}F\text{-}C_6H_3C_6H_3\text{-}5\text{-}F\text{-}PPh_2)]$ **33**	28.9 (s)
$[Au_2I_2(2,2'\text{-}Ph_2P\text{-}5\text{-}F\text{-}C_6H_3C_6H_3\text{-}5\text{-}F\text{-}PPh_2)]$ **34**	31.8 (s)

Table 6 Selected bond distances (Å) and angles (°) in $[Au_2X_2(2,2'\text{-}Ph_2P\text{-}5\text{-}F\text{-}C_6H_3C_6H_3\text{-}5\text{-}F\text{-}PPh_2)]$ (X = Cl **32**; Br **33**)

	32	**33**
Au(1) · · · Au(2)	3.59669(13)	3.54623(17)
Au(1)–P(1)	2.2292(6)	2.2371(7)
Au(2)–P(2)	2.2267(6)	2.2329(8)
Au(1)–X(1)	2.2908(6)	2.4060(3)
Au(2)–X(2)	2.2900(6)	2.4037(3)
P(1)–Au(1)–X(1)	175.71(2)	175.37(2)
P(2)–Au(2)–X(2)	175.06(2)	174.64(2)

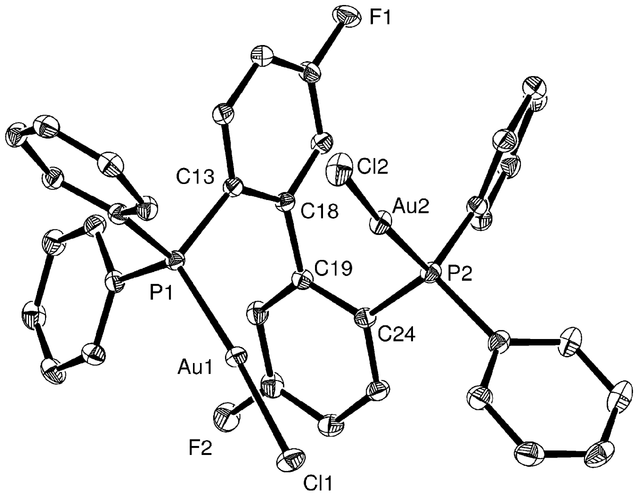


Fig. 8 Molecular structure of $[Au_2Cl_2(2,2'\text{-}Ph_2P\text{-}5\text{-}F\text{-}C_6H_3C_6H_3\text{-}5\text{-}F\text{-}PPh_2)]$ **32**. Ellipsoids show 50% probability levels and hydrogen atoms have been omitted for clarity.

in the 2 and 2′ positions. The biphenyl backbone is twisted about the central C–C bond with dihedral angles of about 80° and the gold atoms, separated by about 3.5 Å, are in a *syn*-type configuration. The unsubstituted biphenyldiyl complex $[Au_2(C_6F_5)_2(2,2'\text{-}Et_2PC_6H_4C_6H_4PEt_2)]$ shows, by contrast, an alternative *anti*-arrangement.[23] The metal–ligand distances in **32** and **33** are unexceptional.

Treatment of **25** with silver acetate, nitrate, benzoate or trifluoroacetate gave the corresponding mixed-valent complexes $[YAu(\mu\text{-}2\text{-}C_6F_4PPh_2)(\kappa^2\text{-}2\text{-}C_6F_4PPh_2)AuY]$ [Y = OAc (**35**), ONO_2 (**36**), OBz (**37**), O_2CCF_3 (**38**)] as white or pale yellow solids in 80–90% yield. The ^{31}P NMR spectroscopic data are in Table 7. The structures of complexes **35** and **36**, which have been determined by single-crystal X-ray diffraction, are similar to that of the chloro-complex **25**; selected metrical data are listed in Table 4. The Au · · · Au separations in all three compounds are in the range 3.0–3.1 Å characteristic of an aurophilic interaction. Previous efforts to isolate similar anation products in the $C_6H_3\text{-}6\text{-}Me\text{-}2\text{-}PPh_2$ series of Au(I)–Au(III) compounds had failed.[27]

Table 7 ^{31}P NMR data for the digold(I,III) complexes $[XAu(\mu\text{-}2\text{-}C_6F_4PPh_2)(\kappa^2\text{-}2\text{-}C_6F_4PPh_2)AuX]^a$

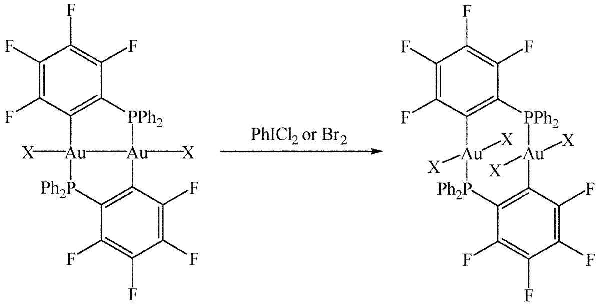
X	δ_P (C_6D_6)
Cl **25**	41.0, −58.4
Br **26**	44.3, −65.4
I **27**	46.2, −77.6
C_6F_5 **31**	50.2, −62.4[b]
OAc **35**	34.7, −49.6
ONO_2 **36**	36.0, −45.0
OBz **37**	35.5, −49.4
O_2CCF_3 **38**	34.0, −47.0

[a] Resonances are broad singlets, except where indicated. [b] Multiplet.

An attempted reaction of the bis(benzoato) complex **37** with dimethylzinc caused immediate reduction to the digold(I) complex **2**, presumably formed by rapid reductive elimination of methyl groups from a methylgold(I)–methylgold(III) intermediate. This behaviour stands in interesting contrast with the reaction of the bis(benzoato)digold(II) complex **16** with dimethylzinc to give the stable gold(I)–dimethylgold(III) derivative **19** (see above).

Reactions with an excess of halogens

Treatment of the digold(II) complexes **5** and **8** with an excess of chlorine or bromine gave the digold(III) complexes $[Au_2X_4(\mu\text{-}2\text{-}C_6F_4PPh_2)_2]$ [X = Cl **39**, Br **40**], formed by addition of a halogen atom to each gold atom (Scheme 6).



X = Cl **5**
X = Br **8**

X = Cl **39**
X = Br **40**

Scheme 6 Addition of an excess of halogen to $[Au_2X_2(\mu\text{-}2\text{-}C_6F_4PPh_2)_2]$ (X = Cl, Br).

The yellow chloride and the orange bromide are both sparingly soluble in most organic solvents. The ^{31}P NMR spectra in CH_2Cl_2–C_6D_6, which were acquired *in situ* before the solids precipitated, showed singlets at δ 9.3 and 3.2, respectively, about 11 ppm to high frequency of the resonances of their digold(II) precursors. The latter were re-formed on treatment of **39** and **40** with one equivalent of zinc powder; addition of more zinc caused reduction to **2**. The ^{31}P chemical shift of **40** is close to that of the similarly formed complex $[Au_2Br_4(\mu\text{-}2\text{-}C_6H_4PPh_2)_2]$ (δ 4.6).[3] The chlorination of **5** follows the same course as that of $[Au_2Cl_2(\mu\text{-}C_6H_3\text{-}6\text{-}Me\text{-}2\text{-}PPh_2)_2]$,[12] but the bromination of **8** differs from that of $[Au_2Br_2(\mu\text{-}C_6H_3\text{-}6\text{-}Me\text{-}2\text{-}PPh_2)_2]$. The latter reacts with bromine to give a gold(I) complex $[AuBr(Ph_2PC_6H_3\text{-}3\text{-}Me\text{-}2\text{-}Br)]$, which may be formed *via* an intermediate similar to **40** that subsequently

Table 8 Selected bond distances (Å) and angles (°) in $[X_3Au(\mu\text{-}2\text{-}C_6F_4PPh_2)(\kappa^2\text{-}2\text{-}C_6F_4PPh_2)AuX]$ (X = Cl, **41**; Br, **42**)

	X = Cl **41**	X = Br **42**
Au(1)···Au(2)	5.750	5.792
Au(1)–P(1)	2.3348(6)	2.3315(14)
Au(2)–P(2)	2.3209(6)	2.3369(14)
Au(1)–C(24)	2.077(2)	2.081(5)
Au(1)–C(6)	2.029(2)	2.046(5)
Au(1)–X(1)	2.3329(6)	2.4609(6)
Au(2)–X(2)	2.3337(7)	2.4596(6)
Au(2)–X(3)	2.2866(7)	2.4290(7)
Au(2)–X(4)	2.2804(7)	2.4198(7)
X(1)–Au(1)–C(6)	168.12(7)	167.23(15)
X(1)–Au(1)–P(1)	99.70(2)	99.03(4)
X(1)–Au(1)–C(24)	88.80(7)	89.12(15)
X(2)–Au(2)–X(3)	90.92(3)	90.24(2)
X(2)–Au(2)–P(2)	176.30(3)	175.79(4)
X(2)–Au(2)–X(4)	90.26(3)	89.58(2)
P(1)–Au(1)–C(24)	167.75(7)	167.48(15)
P(1)–Au(1)–C(6)	68.87(7)	68.91(16)
P(1)–C(1)–C(6)	100.58(16)	101.2(4)
P(2)–Au(2)–X(3)	85.38(2)	85.61(4)
P(2)–Au(2)–X(4)	93.44(2)	94.61(4)
C(24)–Au(1)–C(6)	102.01(9)	102.1(2)

undergoes electrophilic cleavage of the two metal–carbon σ-bonds. Evidently, the gold–fluoroaryl bonds are more resistant to such a process (see later).

Heating of a toluene solution of **39** to 70 °C for 7 h gave mainly the mixed-valent complex **25**, as shown by ^{31}P NMR spectroscopy, together with other unidentified products. Chlorine is probably lost initially to give **5**, which then isomerises to **25**.

Similarly, treatment of solutions of the Au(I)–Au(III) complexes **25** and **26** with an excess of halogen at room temperature gave the digold(III) complexes $[X_3Au(\mu\text{-}2\text{-}C_6F_4PPh_2)AuX(\kappa^2\text{-}2\text{-}C_6F_4PPh_2)]$ [X = Cl **41**, Br **42**]. Their ^{31}P NMR spectra show a pair of equally intense peaks at *ca.* δ 30 and −60; the highly shielded resonances confirm that the four-membered chelate rings have been retained. Selected bond distances and angles obtained from single-crystal X-ray diffraction analysis of the isomorphous complexes **41** and **42** are given in Table 8.

The molecular structure of **41** is shown in Fig. 9. In both compounds, one gold(III) atom is coordinated in a planar array by three halides and the phosphorus atom of μ-2-$C_6F_4PPh_2$, while the other gold(III) atom is bound to one halide, κ^2-$C_6F_4PPh_2$, and the σ-bonded carbon atom of μ-2-$C_6F_4PPh_2$. The gold atoms are well separated (**41**: 5.750 Å; **42**: 5.792 Å), indicating that there is no aurophilic interaction between them. The gold(III)–halide bond lengths in the AuX_3 fragments are similar to those in $[AuX_3(PPh_3)]$;[30,31] those *trans* to phosphorus are slightly longer than those *trans* to halide, consistent with the higher *trans*-influence of the P-donor. The Au–X bond lengths for X *trans* to P and *trans* to fluoroaryl carbon are identical, within experimental error, showing that the *trans*-influences of these two ligands are similar.

Attempted preparation of scrambled gold complexes

When solutions of $[Au_2(\mu\text{-}2\text{-}C_6H_4PR_2)_2]$ (R = Ph **1**, Et) are mixed, an AB quartet ($^2J_{AB}$ = 19 Hz) appears over the course of several hours in the ^{31}P NMR spectrum located about halfway between the singlets characteristic of the precursors. This can be attributed to the mixed-ligand species $[Au_2(\mu\text{-}2\text{-}C_6H_4PPh_2)(\mu\text{-}2\text{-}C_6H_4PEt_2)]$, which is in equilibrium with the precursors. It must be formed by transfer of the 2-$C_6H_4PR_2$ groups between gold atoms, However, it has not been established whether this process occurs by an initial association between dimers or by an initial dissociation of dimers to reactive mononuclear fragments $[Au(\kappa^2\text{-}2\text{-}C_6H_4PR_2)]$ and subsequent re-combination.

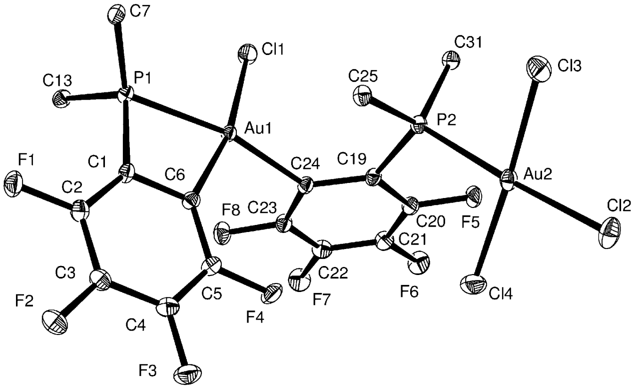


Fig. 9 Molecular structure of $[Cl_3Au(\mu\text{-}2\text{-}C_6F_4PPh_2)(\kappa^2\text{-}2\text{-}C_6F_4PPh_2)AuCl]$ **41**. Ellipsoids show 50% probability levels. Hydrogen atoms and solvent molecules have been omitted for clarity. Only the *ipso* carbons of the phenyl groups attached to the phosphorus atoms are shown.

The ^{31}P NMR pattern of a mixture of **1** and **2** is more complex. The resonances due to the precursors, at δ 36 and δ 42, are still present, but the former shows complex fine structure. A three-line pattern centred at δ 40.7 may contain the AB pattern expected for the mixed-ligand dimer $[Au_2(\mu\text{-}2\text{-}C_6F_4PPh_2)(\mu\text{-}2\text{-}C_6H_4PPh_2)]$ but there are also many less intense multiplets in the region between δ 38 and 47, suggestive of a complex mixture of species. The fact that there are resonances to such high frequency suggests the presence of higher nuclearity species (*cf.* δ_P 45.7 for the tetramer **21**), but it is not clear how these could have been formed under such mild conditions.

Discussion

The fluorine-substituted carbanions 2-$C_6F_4PPh_2$ and C_6H_3-*n*-F-2-PPh_2 (*n* = 5, 6) resemble 2-$C_6H_4PPh_2$ and its methyl-substituted derivatives in forming dinuclear gold(I) complexes $Au_2(\mu\text{-carbanion})_2$ in which each gold atom displays its usual linear coordination. They are made by reaction of the appropriate organolithium or trimethyltin-substituted reagents with $[AuBr(AsPh_3)]$. It is also possible to use the labile tetrahydrothiophene complex [AuCl(tht)] as a precursor with the fluorine-substituted carbanion, whereas this is rapidly reduced to metallic gold by 2-$LiC_6H_4PPh_2$.

We have also established the existence of tetranuclear species $Au_4(\mu\text{-carbanion})_4$ in which the carbanions bridge an approximate square of gold atoms. These compounds do not appear to be in labile equilibrium with $Au_2(\mu\text{-carbanion})_2$ and are not formed exclusively when the dimers are heated, but so far we have not found a reproducible synthesis. By contrast, in the case of palladium(II), the complex $[Pd_2Cl_2(\kappa^2\text{-}2\text{-}C_6F_4PPh_2)_2]$ dimerises cleanly to the tetramer $[Pd_4Cl_4(\mu\text{-}2\text{-}C_6F_4PPh_2)_4]$.[17] Further work is required to find out whether the presence of fluorine substituents is essential for the formation of Au_4(μ-carbanion)$_4$ complexes. In this context, we note that the pentanuclear cation [Au_5(μ-2-$C_6H_4PPh_2$)$_4$]$^+$, which was isolated from the reaction of [Au(OTf)(PPh_3)] with **1**,[32] is formally derived by the addition of Au^+ to the unknown tetramer [Au_4(μ-2-$C_6H_4PPh_2$)$_4$].

The rhomboidal Au_4 structural motif is common in gold(I) complexes of carbanions, *e.g.*, the dithioacetate, [Au_4(μ-S_2CMe)$_4$],[33,34] the 1,3-diphenyltriazido complex, [Au_4(μ-PhN_3Ph)$_4$],[35] the 1,3-diphenylformamidinato complex, [Au_4(μ-PhNCHNPh)$_4$],[36] the deprotonated ethylenethiourea derivative, [Au_4(μ-*N*,*S*-$NCH_2CH_2NH_2C{=}S$)$_4$],[37] and the deprotonated 4-methyl-1,3-thiazole-2-thione derivative, [Au_4{μ-*N*,*S*-NC(Me)CHSC=S}$_4$].[38] The Au–Au distances along the rhomboidal edges in [Au_4(μ-2-$C_6F_4PPh_2$)$_4$] **21** and [Au_4(μ-C_6F_3-5-F-2-PPh_2)$_4$] **22** (3.11–3.30 Å) are generally greater than those in the tetramers cited above (2.84–3.23 Å), and the Au–Au–Au angles in the rhombuses of **21** and **22** are generally close to 90°. In the 1,3-diarylformamidinatogold(I) system, replacement of phenyl by the more bulky 2,6-xylyl group leads to formation of a dimer, [Au_2{μ-({2,6-$Me_2C_6H_3N$}$_2$CH)$_2$}][39] instead of a tetramer, but we know of no previous example of co-existence of a dimer and a tetramer with the same anionic ligand.

The digold(I) complexes of 2-$C_6F_4PPh_2$ and C_6H_3-*n*-F-2-PPh_2 (n = 5, 6) resemble [Au_2(μ-2-$C_6H_4PPh_2$)$_2$] **1** and its methyl-substituted derivatives in undergoing two-centre, two-electron oxidative addition with halogens (X_2) to form digold(II) ($5d^9$–$5d^9$) complexes [Au_2X_2(μ-carbanion)$_2$], the axial halides of which are readily replaced by other anions. Complete replacement of hydrogen by fluorine causes a small contraction in the Au$\cdots$Au separations but there are no significant changes in the Au–P or Au–C bond lengths. In general, there are small, non-systematic changes in the Au–Au bond length in the digold(II) complexes for a given anionic ligand X with different bridging carbanions; on the other hand, there is a small but systematic lengthening, and presumably weakening, of the Au–Au bond in the series [Au_2X_2(μ-2-$C_6F_4PPh_2$)$_2$] as X is varied from X = ONO_2 to X = C_6F_5 (Table 3), *i.e.*, with increasing *trans*-influence of X. A similar effect has been noted in the corresponding C_6H_3-5-Me-2-$AsPh_2$ series[40] and is also evident from structural data for a series of digold(II) bis(ylide) complexes [Au_2X_2{μ-(CH_2)$_2PPh_2$}$_2$] (X = OAc,[41] OBz,[42] Cl,[21] Br,[43] NO_2,[44] CF_3,[24] and C_6F_5[24]).

In general, the electronegative fluorine substituents cause **2** to be chemically more robust than **1**, as shown by the greater reluctance of the Au–C bonds of **2** to undergo acid cleavage, by the failure of **2** to insert SO_2, and by the lack of reaction of **2** with methyl iodide or dibenzoyl peroxide. Correspondingly, the derived digold(II) complexes containing 2-$C_6F_4PPh_2$ are more readily reduced to gold(I) (either the dimer **2** or the tetramer **21**), particularly when the axial ligands are labile. The facile reaction of the bis(benzoato) and bis(triflato) complexes with methanol or cyclohexanol to give **2** or **21**, and the formation of **2** from the attempted preparation of a bis(trifluoroethoxide), probably proceed *via* alkoxo complexes that undergo β-elimination of the aldehyde or ketone to give hydridodigold(II) species according to a well-established sequence, which in turn eliminate HX or H_2 to give the digold(I) complex. The failure to form a bis(trifluoroethoxide) is particularly surprising, given the stability of CF_3CH_2O derivatives of gold(I)[45] and gold(III).[46]

The most obvious difference in behaviour of the 2-$C_6F_4PPh_2$ and 2-$C_6H_4PPh_2$ systems lies in the rearrangement of the digold(II) complexes [Au_2X_2(μ-2-$C_6Y_4PPh_2$)$_2$] (X = Cl, Br, I, C_6F_5; Y = H, F), specifically, in the case of Y = F, the exclusive formation of the gold(I)–gold(III) complexes without subsequent reductive elimination of the $C_6Y_4PPh_2$ groups. Moreover, the presence of just one strategically located fluorine atom, at the 6-position of the aromatic ring of the bridging ligand, is sufficient to block the reductive elimination step. The effect of four fluorine substituents or of a 6-fluorine substituent is thus similar to that of a 6-methyl substituent in the protio system, though the isomerisation from digold(II) to gold(I)–gold(III) in much faster in the latter case.

Calculations suggest that the steric effect of the 6-methyl group first causes a bending of the eight-membered Au_2(μ-carbanion)$_2$ ring in the digold(II) system that favours the transition state leading to Au(I)–Au(III), and then hinders reductive elimination from Au(III).[47] Although the van der Waals radius of F (1.35 Å) is greater than that of H (1.20 Å), it is much less than that of CH_3 (2.00 Å). We suggest, therefore, that an electronic stabilising effect of the tetrafluoro- and 6-fluoro substituents may be an important contributor to the observed behaviour, even though it is not manifest in any significant shortening of the Au–C bond lengths.

Electronically unsaturated fragments, such as [RhCp(PMe_3)], [ReCp(CO)$_2$] and [ReCp*(CO)$_2$], oxidatively add the C–H bonds of fluoroarenes *via* intermediate η^2-arene complexes, and aryl derivatives containing *ortho*-fluorine atoms, such as 2,6-$C_6H_3F_2$, are the final, thermodynamically favoured products.[48–50] It has been shown that relative bond dissociation energies (BDE) for L_nM–X [ΔD(M–X)] correlate linearly with absolute thermochemical BDE values for H–X [D(H–X)], where X is a range of C-, N- and O-based ligands.[51] For the series [ReH(Cp)(CO)$_2$($C_6H_{5-n}F_n$)] (n = 0–5), a plot of DFT-calculated D(C–H) values for the arene against DFT-calculated ΔD(Re–C) values is linear, with a slope of 2.25; it shows that the presence of *ortho*-fluorine substituents raises the Re–C bond energy, possibly owing to an increase in ionic character and Re–C back-bonding.[13] A similar effect could stabilise the gold(III)–carbon σ-bonds in the gold(I)–gold(III) complexes containing 2-$C_6F_4PPh_2$ and C_6H_3-6-F-2-PPh_2 and prevent reductive elimination.

The isomerisation of digold(II) to gold(I)–gold(III) in the μ-2-$C_6Y_4PPh_2$ (Y = H, F) systems requires transfer of one of the bridging carbanions between the gold atoms. This may occur *via* a two-electron, three-centre transition state and be preceded by reversible dissociation of one of the phosphorus atoms. Although there are many examples of stable digold(I) complexes containing bridging aryl groups, none are known for digold(II) or digold(III).[32,52,53] In the 2-$C_6H_4PPh_2$ series, the digold(II) complexes having the less polarisable axial ligands nitrate, acetate, trifluoroacetate and benzoate do not undergo C–C coupling on heating; in the 2-$C_6F_4PPh_2$ series, the digold(II) complexes containing these ligands do not rearrange to the corresponding gold(I)–gold(III) compounds, even though the latter are stable species that can be made by anation of the gold(I)–gold(III) halides. Thus, the most important factor that determines whether isomerisation occurs appears to be the strength of the Au(II)–Au(II) bond, as judged by its length; as noted above, the shortest (and presumably strongest) bonds occur for the harder anions. Another factor, which has been suggested by theoretical calculations,[47,54] may be the strengthening of aurophilic interaction in the transition state by polarisable ligands such as iodide ion.

Experimental

Most syntheses were performed under dry argon with the use of standard Schlenk techniques, although the solid gold complexes, once isolated, were air-stable. Diethyl ether was dried over sodium/benzophenone, toluene over sodium, and dichloromethane over calcium hydride.

^{1}H (300 MHz), ^{19}F (282 MHz) and ^{31}P (121 MHz) NMR spectra were recorded on a Bruker Avance 300 spectrometer in C_6D_6, unless otherwise stated. Chemical shifts (δ) are given in ppm and internally referenced to residual solvent signals (^{1}H), internal $CFCl_3$ (^{19}F) or external 85% H_3PO_4 (^{31}P). The ^{31}P NMR chemical shifts of complexes **2–18**, **20**, **25–27** and **31–38** are listed in Tables 2, 5 and 7. Elemental analyses were performed by the Microanalytical Unit of the Research School of Chemistry at the Australian National University; analytical data for all gold complexes are listed in Table S1 (ESI†). Mass spectra were recorded on a Bruker Apex 3 FTICR mass spectrometer and infrared spectra were obtained on a Perkin Elmer Spectrum 2000 FT-IR spectrometer as KBr disks (4000–400 cm^{-1}) or polyethylene disks (400–150 cm^{-1}).

Crystals suitable for single-crystal X-ray diffraction were obtained by layering a CH_2Cl_2 solution with hexane or methanol. The crystals were mounted on a glass capillary using a drop of inert oil (PARATONE) and transferred to a stream of cold nitrogen. The reflection data were collected on a Nonius Kappa CCD diffractometer equipped with a 95 mm camera and graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å), in φ- and ω-scan modes. Data integration was carried out with the DENZO software[55] and multi-scan absorption correction was performed with the SORTAV program.[56] The crystal structures were solved by direct methods using SIR92,[57] SHELXS-97,[58] or the Patterson method of SHELXS-97. Structure refinement was carried out as a full-matrix least-squares refinement on F^2 using SHELXL-97,[59] or the CRYSTALS program package.[60] Calculations were performed with use of the crystallographic software CRYSTALS.[61] Selected crystal data and details of data collection and structure refinement are listed in Table S2 (ESI†).

The compounds $[AuBr(AsPh_3)]$,[62] [AuCl(tht)],[63] 2-$BrC_6F_4PPh_2$,[64] $PhICl_2$,[65] Me_3SiPPh_2,[66] 2-bromo-4-fluoroaniline,[67] and 2-bromo-4-fluoroiodobenzene[66] were prepared by the appropriate literature procedure. 2-Bromo-3-fluoroiodobenzene was prepared following the procedure described by Heiss *et al.*, except that $BrCH_2CH_2Br$ was used as the brominating agent instead of $BrCF_2CF_2Br$.[68] All other compounds were commercially available and used as received.

The following are representative examples of the synthetic details. The complete experimental details along with Table S1 and Table S2 containing analytical data and crystal data for the gold complexes are included in ESI.†

Syntheses

Tetrafluoro-substituted digold(I) complex $[Au_2(\mu\text{-}2\text{-}C_6F_4PPh_2)_2]$ 2

A solution of 2-$BrC_6F_4PPh_2$ (1.2 mmol, 0.5 g) in ether (15 mL), cooled to −78 °C, was treated with ^{n}BuLi (1.6 M in hexanes, 0.9 mmol, 0.57 mL) over 30 min to give a pale yellow solution. To this, a cooled suspension of $[AuBr(AsPh_3)]$ (1.0 mmol, 0.58 g) in ether (10 mL) was added *via* cannula, the temperature being kept at −78 °C for 1 h. Stirring was continued for 3 h at −40 °C and then the suspension was slowly warmed to room temperature overnight. The white solid was isolated by filtration and washed successively with ether (10 mL), methanol (10 mL) and hexane (20 mL). The crude product was extracted with hot dichloromethane and filtered through Celite. Evaporation of the filtrate gave $[Au_2(\mu\text{-}2\text{-}C_6F_4PPh_2)_2]$ as a colourless solid (0.4 g, 65%). The use of [AuCl(tht)] as the gold precursor gave a yield of about 47%.

^{1}H NMR: δ 6.9–7.7 (m, 20H, aromatics). ^{19}F NMR: δ −107.1 (dd, J = 16.3, 34.8 Hz), −121.3 (m), −148.3 (ddt, J = 6.3, 20.5, 34.8 Hz), −156.4 (t, J = 21.2 Hz). ESI-MS (m/z): 1060 [M]$^+$.

Alternatively, **2** can be prepared by the reaction of [AuCl(tht)] with 2-$Me_3SnC_6F_4PPh_2$: To a stirred solution of [AuCl(tht)] (1.3 mmol, 0.4 g) in dichloromethane (20 mL) was added 2-$Me_3SnC_6F_4PPh_2$ (1.3 mmol, 0.6 g) and the mixture was refluxed for 4 h, during which time **2** precipitated out. The solvent was removed *in vacuo* and the white solid was recrystallised from dichloromethane/hexane to give $[Au_2(\mu\text{-}2\text{-}C_6F_4PPh_2)_2]$ as a colourless solid (0.56 g, 84%).

In an analogous reaction to that described above, treatment of an ether solution of 2-$BrC_6F_4PPh_2$ (1.2 mmol, 0.5 g) with ^{n}BuLi (1.6 M in hexanes, 0.9 mmol, 0.57 mL) at −78 °C, followed by the addition of an ether solution of $[AuBr(PEt_3)]$ (1.0 mmol, 0.4 g) gave a colourless solid. ^{31}P NMR: δ 23.5 (m), 38.0 (m), 42.3 (br s), 47.6 (br s).

Dihalodigold(II) complexes, $[Au_2X_2(\mu\text{-}2\text{-}C_6F_4PPh_2)_2]$ and $[Au_2X_2(\mu\text{-}C_6H_3\text{-}n\text{-}F\text{-}2\text{-}PPh_2)_2]$ (X = Cl, Br, I; *n* = 5, 6)

A stirred solution of $[Au_2(\mu\text{-}2\text{-}C_6F_4PPh_2)_2]$ or $[Au_2(\mu\text{-}C_6H_3\text{-}n\text{-}F\text{-}2\text{-}PPh_2)_2]$ (n = 5, 6) (0.1 mmol) in dichloromethane (20 mL) was cooled to −78 °C and treated dropwise with a solution of $PhICl_2$ (0.1 mmol) in CH_2Cl_2 (20 mL). After the addition was completed, the flask was shielded from light and the solution was stirred at −78 °C for 1 h, then at −40 °C for 1 h. During the work-up, the temperature was maintained below −30 °C. The volume of the solution was reduced to half under reduced pressure and hexane was added, precipitating out the product. The solvent was cannulated from the yellow solid, which was washed with hexane and dried *in vacuo.* Yields were typically 80–90%.

$[Au_2Cl_2(\mu\text{-}2\text{-}C_6F_4PPh_2)_2]$ **5**: ^{1}H NMR: δ 6.9–7.9 (m, 20H, aromatics). ^{19}F NMR: δ −112.5 (m), −127.7 (m), −144.6 (m), −154.3 (m). ESI-MS (m/z): 1095 [M – Cl]$^+$. Far-IR (ν, cm^{-1}): 288 (Au–Cl str.).

$[Au_2Cl_2(\mu\text{-}C_6H_3\text{-}5\text{-}F\text{-}2\text{-}PPh_2)_2]$ **6**: ^{1}H NMR: δ 5.6–8.1 (m, 26H, aromatics). ESI-MS (m/z): 987 [M – Cl]$^+$.

$[Au_2Cl_2(\mu\text{-}C_6H_3\text{-}6\text{-}F\text{-}2\text{-}PPh_2)_2]$ **7**: ^{1}H NMR: δ 6.2–7.5 (m, 26H, aromatics). ESI-MS (m/z): 987 [M – Cl]$^+$.

A dichloromethane solution of $[Au_2Cl_2(\mu\text{-}2\text{-}C_6F_4PPh_2)_2]$ or $[Au_2Cl_2(\mu\text{-}C_6H_3\text{-}n\text{-}F\text{-}2\text{-}PPh_2)_2]$ (n = 5, 6) (1 mmol) cooled to −30 °C was treated with a methanol solution of sodium bromide or sodium iodide (3 mmol). After the mixture had been stirred for 15 min at −30 °C, the solvents were evaporated under reduced pressure and the residue was extracted with cold dichloromethane (−30 °C). Filtration through Celite and evaporation of the solvent gave the dihalodigold(II) complexes $[Au_2X_2(\mu\text{-}2\text{-}C_6F_4PPh_2)_2]$ or

[Au$_2$X$_2$(μ-C$_6$H$_3$-*n*-F-2-PPh$_2$)$_2$] (*n* = 5, 6) as orange (X = Br) or red (X = I) solids in 75–90% yields. Complexes **8** and **11** can also be made by oxidative addition reactions of **2** with Br$_2$ or I$_2$, respectively.

[Au$_2$Br$_2$(μ-2-C$_6$F$_4$PPh$_2$)$_2$] **8**: ^{1}H NMR: δ 6.8–7.8 (m, 20H, aromatics) together with peaks at δ 0.89 and 1.24 due to hexanes. ESI-MS (*m*/*z*): 1141 [M – Br]$^+$. Far-IR (ν, cm^{-1}): 199 (Au–Br str.).

[Au$_2$I$_2$(μ-2-C$_6$F$_4$PPh$_2$)$_2$] **11**:^{1}H NMR: δ 6.9–7.8 (m, 20H, aromatics). ESI-MS (*m*/*z*): 1186 [M – I]$^+$.

[Au$_2$Br$_2$(μ-C$_6$H$_3$-5-F-2-PPh$_2$)$_2$] **9**: ^{1}H NMR: δ 6.2–7.5 (m, 26H, aromatics). ESI-MS (*m*/*z*): 1111 [M + H]$^+$.

[Au$_2$Br$_2$(μ-C$_6$H$_3$-6-F-2-PPh$_2$)$_2$] **10**: ^{1}H NMR: δ 6.2–7.5 (m, 26H, aromatics). ESI-MS (*m*/*z*): 1033 [M – Br]$^+$.

[Au$_2$I$_2$(μ-C$_6$H$_3$-5-F-2-PPh$_2$)$_2$] **12**: ^{1}H NMR: δ 6.8–8.1 (m, 26H, aromatics). ESI-MS (*m*/*z*): 1079 [M – I]$^+$.

[Au$_2$I$_2$(μ-C$_6$H$_3$-6-F-2-PPh$_2$)$_2$] **13**: ^{1}H NMR: δ 6.7–8.2 (m, 26H, aromatics). ESI-MS (*m*/*z*): 1207 [M + H]$^+$.

[Au$_2$Y$_2$(μ-2-C$_6$F$_4$PPh$_2$)$_2$] [Y = OAc (14), ONO$_2$ (15), OBz (16), O$_2$CCF$_3$ (17)]

The digold(II) dichloride complex **5** was dissolved in CH$_2$Cl$_2$ and treated with 50–100% molar excess of the appropriate silver salt. The suspension was stirred for 3 h at room temperature and shielded from light. The insoluble silver salts were removed by filtration and the volume of the solution reduced by half under reduced pressure. Addition of hexane precipitated the pale yellow products which were isolated by filtration, washed with hexane and dried. Yields were quantitative.

14: ^{1}H NMR: δ 1.64 (s, 6H, OAc), 7.0–7.6 (m, 20H, aromatics). ESI-MS (*m*/*z*): 1119 [M – OAc + H]$^+$.

15: ^{1}H NMR: δ 7.0–7.5 (m, 20H, aromatics). ESI-MS (*m*/*z*): 1059 [M – 2(NO$_3$)]$^+$.

16: ^{1}H NMR: δ 6.9–7.5 (m, 20H, aromatics), δ 8.0 (m, 10H, aromatics). ESI-MS (*m*/*z*): 1181 [M – OBz]$^+$.

17: ^{1}H NMR: δ 6.8–7.5 (m, 20H, aromatics). ESI-MS (*m*/*z*): 1173 [M – O$_2$CCF$_3$]$^-$.

[Au$_2$(C$_6$F$_5$)$_2$(μ-2-C$_6$F$_4$PPh$_2$)$_2$] 18

A solution of C$_6$F$_5$Br (0.55 mmol, 69 μL) in ether (30 mL) was cooled to –78 °C and treated dropwise with a solution of ^{n}BuLi (1.6 M in hexanes, 0.55 mmol, 350 μL). The mixture was stirred for 1 h and then treated with a solution of [Au$_2$(OBz)$_2$(μ-2-C$_6$F$_4$PPh$_2$)$_2$] (**16**) (0.25 mmol, 0.35 g) in toluene (20 mL). After being stirred at –78 °C for 30 min and then at room temperature for 3 h, the yellow solution was filtered through Celite. The filtrate was evaporated and the residue was recrystallised from dichloromethane–hexane to give **18** as a yellow solid (0.3 g, 85%).

^{1}H NMR: δ 6.7–7.4 (m, 20H, aromatics). ESI-MS (*m*/*z*): 1433 [M + K]$^+$, 1417 [M + Na]$^+$.

[Au^{I}(μ-2-C$_6$F$_4$PPh$_2$)$_2$Au^{III}(CH$_3$)$_2$] 19

A solution of complex **16** (0.15 mmol, 0.2 g) in toluene (20 mL) was cooled to –78 °C and treated dropwise with dimethylzinc (1.0 M in heptanes, 0.2 mmol, 0.2 mL). The solution was shielded from light, stirred at –78 °C for 1 h and then slowly allowed to warm to room temperature overnight. The solvent was evaporated and the residue was dissolved in dichloromethane and then filtered to remove zinc salts. Hexane was added to precipitate the product in 70–80% yield.

19: ^{1}H NMR: δ 0.56 (d, J_{PH} = 2.0 Hz, 6H, CH$_3$), 6.9–7.6 (m, 20H, aromatics). ^{31}P NMR: δ 19.8 (m), 36.1 (br s).

Tetranuclear species [Au$_4$(μ-2-C$_6$F$_4$PPh$_2$)$_4$] 21

A solution of **5** (0.1 mmol, 0.1 g) in dichloromethane (20 mL) was cooled to –30 °C and treated with silver triflate (0.5 mmol, 0.1 g). The mixture was stirred for 15 min in the dark at –30 °C and then at room temperature for 10 min. The orange solution was filtered through Celite, methanol (20 mL) was added to the filtrate and the solution left in the refrigerator for 4 days, during which time a white solid precipitated out. The solvent was evaporated and the white residue was recrystallised from dichloromethane/hexane to give **21** in 80% yield. Other preparations gave mixtures in varying proportions of the digold(I) dimer **2** and the tetramer **21**.

^{31}P NMR: δ 45.7 (br s). ESI-MS (*m*/*z*) = 2121 [M + H]$^+$.

Dihalodigold(I,III) complexes, [XAu(μ-2-C$_6$F$_4$PPh$_2$)(κ^2-2-C$_6$F$_4$PPh$_2$)AuX] or [XAu(μ-C$_6$H$_3$-6-F-2-PPh$_2$)(κ^2-C$_6$H$_3$-6-F-2-PPh$_2$)AuX] (X = Cl, Br, I). The appropriate digold(II) complex [Au$_2$X$_2$(μ-C$_6$F$_4$PPh$_2$)] or [Au$_2$X$_2$(μ-C$_6$H$_3$-6-F-2-PPh$_2$)$_2$] (X = Cl, Br, I) (1.8 mmol) was heated in toluene to 60 °C for 1–4 h, during which time the solution became almost colourless. Addition of hexane precipitated the dihalodigold(I,III) compounds which were filtered off, washed with hexane and dried *in vacuo.* Yields were 80–90%.

[ClAu(μ-2-C$_6$F$_4$PPh$_2$)(κ^2-2-C$_6$F$_4$PPh$_2$)AuCl] **25**: ^{1}H NMR: δ 7.1–8.7 (m, 20H, aromatics). ESI-MS (*m*/*z*): 1095 [M – Cl]$^+$.

[BrAu(μ-2-C$_6$F$_4$PPh$_2$)(κ^2-2-C$_6$F$_4$PPh$_2$)AuBr] **26**: ^{1}H NMR: δ 7.0–8.7 (m, 20H, aromatics). ESI-MS (*m*/*z*): 1139 [M – Br]$^+$.

[IAu(μ-2-C$_6$F$_4$PPh$_2$)(κ^2-2-C$_6$F$_4$PPh$_2$)AuI] **27**: ^{1}H NMR: δ 6.9–8.3 (m, 20H, aromatics). ESI-MS (*m*/*z*): 1187 [M – I]$^+$.

[ClAu(μ-C$_6$H$_3$-6-F-2-PPh$_2$)(κ^2-C$_6$H$_3$-6-F-2-PPh$_2$)AuCl] **28**: ^{1}H NMR: δ 6.6–8.1 (m, 20H, aromatics). ^{31}P NMR: δ –56.3 (ddd, *J* = 5.2, 13.4, 18.6 Hz), 37.7 (d, *J* = 13.4 Hz). ESI-MS (*m*/*z*): 987 [M – Cl]$^+$.

[BrAu(μ-C$_6$H$_3$-6-F-2-PPh$_2$)(κ^2-C$_6$H$_3$-6-F-2-PPh$_2$)AuBr] **29**: ^{31}P NMR (toluene/C$_6$D$_6$): δ –63.8 (ddd, *J* = 5.2, 12.6, 17.8 Hz), 39.2 (d, *J* = 13.3 Hz).

[IAu(μ-C$_6$H$_3$-6-F-2-PPh$_2$)(κ^2-C$_6$H$_3$-6-F-2-PPh$_2$)AuI] **30**: ^{31}P NMR (toluene/C$_6$D$_6$): δ –76.1 (ddd, *J* = 5.2, 12.2, 17.5 Hz), 41.4 (d, *J* = 13.4 Hz).

5-Fluoro-substituted phosphine gold(I) complexes [Au$_2$X$_2$(2,2′-Ph$_2$P-5-F-C$_6$H$_3$C$_6$H$_3$-5-F-PPh$_2$)] [X = Cl (32), Br (33), I (34)]. The yellow or orange solutions of the appropriate dihalodigold(II) complexes [Au$_2$X$_2$(μ-C$_6$H$_3$-5-F-2-PPh$_2$)$_2$] (X = Cl, Br, I) in toluene were heated to 60 °C for 3 h. The resulting colourless solutions were evaporated to small volume under reduced pressure and the carbon–carbon coupled products were precipitated almost quantitatively by the addition of hexane.

32: ^{1}H NMR: δ 5.9–8.0 (m, 26H, aromatics). ESI-MS (*m*/*z*): 987 [M – Cl]$^+$.

33: ^{1}H NMR: δ 5.9–8.1 (m, 26H, aromatics). ESI-MS (*m*/*z*): 1033 [M – Br]$^+$.

34: ^{1}H NMR: δ 5.8–8.1 (m, 26H, aromatics). ESI-MS (*m*/*z*): 1079 [M – I]$^+$.

Digold(I,III) complexes, $[XAu(\mu\text{-}2\text{-}C_6F_4PPh_2)(\kappa^2\text{-}2\text{-}C_6F_4PPh_2)AuX]$ [X = OAc (35), ONO_2 (36), OBz (37), O_2CCF_3 (38)]

Complex **25**, dissolved in CH_2Cl_2, was treated with a 10% molar excess of the appropriate silver salt and the suspension, protected from light, was stirred for several hours. The insoluble silver salts were removed by filtration and the volume of the solution was evaporated under reduced pressure to about half-volume. Hexane was added to precipitate the products, which were isolated, washed with hexane and dried *in vacuo.* Yields were 90–95%.

36: ^1H NMR: δ 7.0–8.1 (m, 20H, aromatics). ESI-MS (m/z): 1059 $[M - 2(NO_3) - H]^+$.

37: ^1H NMR: δ 6.7–8.1 (m, 30H, aromatics). ESI-MS (m/z): 1181 $[M - OBz]^+$.

38: ^1H NMR: δ 6.8–8.1 (m, 20H, aromatics). ESI-MS (m/z): 1059 $[M - 2(O_2CCF_3) - H]^+$.

Digold(III) complexes $[Au_2X_4(\mu\text{-}2\text{-}C_6F_4PPh_2)_2]$ [X = Cl (39), Br (40)]

To a solution of $[Au_2X_2(\mu\text{-}2\text{-}C_6F_4PPh_2)_2]$ [X = Cl (**5**), Br (**8**)] (0.05 mmol) in dichloromethane (10 mL) cooled to −30 °C was added a solution of $PhICl_2$ or Br_2 (0.25 mmol) in dichloromethane (10 mL). The mixture was stirred at this temperature for 30 min, warmed to room temperature and stirred for 2 h, during which time the product precipitated out. The solid was isolated by filtration, washed with hexane and dried *in vacuo.* Yields were 90–95%.

39: ^{31}P NMR (CH_2Cl_2–C_6D_6): δ 9.3 (br s). **40**: ^{31}P NMR (CH_2Cl_2–C_6D_6): δ 3.2 (br s).

Digold(III) complexes $[X_3Au(\mu\text{-}2\text{-}C_6F_4PPh_2)AuX(\kappa^2\text{-}2\text{-}C_6F_4PPh_2)]$ [X = Cl (41), Br (42)]

To a solution of $[XAu(\mu\text{-}2\text{-}C_6F_4PPh_2)(\kappa^2\text{-}2\text{-}C_6F_4PPh_2)AuX]$ [X = Cl (**25**), Br (**26**)] (0.05 mmol) in dichloromethane (10 mL) cooled to −30 °C was added a solution of $PhICl_2$ or Br_2 (0.25 mmol) in dichloromethane (10 mL). The mixture was warmed to room temperature and stirred for 2 h. Hexane was added and the solution was evaporated under reduced pressure until the product began to precipitate. The solid was isolated by filtration, washed with hexane and dried *in vacuo.* Yields were 90–95%.

41: ^{31}P NMR: δ **41** −60.7 (m), 37.7 (m). **42**: ^{31}P NMR: δ −67.6 (m), 27.6 (m).

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